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Socio-economical structure of population in Graboc të Poshtëm

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Received January 07, 2011; Accepted May 05, 2011

Abstract: This paper is aimed at researching and comparing data derived from the survey, based on factors that influenced the orientation of the population in employment by age group and certain periods of time, 50-years of them, of last century until the nowadays, as well as by analyzing the changes that have occurred between these periods. Lower Graboc has a good geographical position, located at a convenient height of 530-550m above sea level, comprising geological characteristics and major natural resources of lignite, with characteristic forms of relief that make this village very attractive and clean environment. With a favorable climate and high continental mainland and rich watermark with Drenica River which runs through the village, with fertile soil and with a rich flora and fauna world. Lower Graboc with a very good geographical position, a rich fund of forests, fields and pastures, then the position of the village near the river Drenica and joints of road and rail links, the vast resources of coal underground, and the large and new number workforce, meet the requirements for a proper economic development. Lower Graboc has about 2000 inhabitants or 4.8% of the overall population of the municipality of Fushë Kosova, with a density of 229 inhabitants in 1/km², living in the village about 200 households, averaging 6.14 member per family. Age structure of population of the village is: up to 15 years 22.1%, 15-65 years 71.4% and 6.5% over 65 years. The largest number of employees in Mining to 46%, then to other services 25%, in trade 7% etc. KEK (Kosovo Energy Corporation) plays a very important role in the recruitment of the population of Lower Graboc; this can be explained by the fact that close to the village to the East, there are layers of lignite and Surface Mining, which attracts the largest number of employees in Lower Graboc.

Key Words: Survey, Fi coefficient, Yuleu coefficient, Overvall coefficient of mutual connectivity, Agrarian structure, Mining industrial structure, Absolute and relative distance, GIS.

Introduction

The seminary work bearing the title” Socio-economical structure of population in Graboc të Poshtëm village” has the aim to research and compare the data gained from the questioner and based on factors that have impact to orient the population in employment according to age in particular period, from years of 50-ties of previus century until today, as well as analyzing the changes that have occurred between these periods. Exept employment, a look was point on physical-geographical specifics of this vicinity, starting form geographical position, geological content, landscape, climate, hydrographic as well planting and animal component.

Materials and Method

To complete this work several methods are used. The main method used in the research was the questioner method, executed through a questionere compiled along with Mentor. From 200 houses were questioned 50 households. Except the questioner method, it was used also the GIS method, where data and maps were used for physical-geographical aspects. Also another method used was history. Statistical method was used to come to different conclusion counting basic and range indexes. Also the Yueu coefficient was used regarding the general mutual link.

Geographical Position

Graboc i Poshtëm is under administration of Municipality of Fushë Kosova and together they have central position in Kosovo. They belong to the territory of Rrafshi i Kosovës. The Municipality

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of Fushë Kosova has a surface of 100 km² having around 4200 inhabitants and located 540-550m over the sea level. It is bordered with 4 Municipalities: in the east with Prishtina, in the south with Lipjan, in the west with Drenas (Gllogovc) and in the north with Kastriot.

Fushë Kosova is consisted of 7 local municipalities and 17 vicinities. It is very important industrial and communicative center, with important factories and they are Meat, Bread, and Milk Factory, etc. This Municipality is having large train station, and there are not only domestic railway connections, but also with Balkan and European Countries. The only commercial airport of Kosovo is located in this municipality.

Figure 1. Geographical Position of Fushë Kosova Municipality in regard to Kosovo.

Graboci i Poshtëm in administrative aspect belongs to the Bardh i Madh vicinity and both are under administration of Fushë Kosova Municipality. It is located 9 km in west of Fushë Kosova. It is sort of spread village and it is consisted of 7 vicinities. It is having of surface of 9.97 km² with 2000 inhabitants.

It is bordered to six villages and they are: Graboci i Epër in the north, Shipitulla, Hade, Bardhi i Madh in south east, Vasileva and Dobrashevci in south-west. Important elements that are characteristic for Graboci i Poshtëm are: in the south are large recourses of coal, then the river Drenica which flows in the middle of the village having important role for the inhabitants of the village. Also the railway Fushë Kosova- Peja which goes through the middle of the village play an important role for transport of passenger and goods. It is important to highlight that Meridian 21º crosses in the west of the village.

Physical-geographical aspects of Graboci i Poshtëm village Geological consistence

The area, where Graboci i Poshtëm is located, is having a complicated geological consistence. According to the age of rocks, this area can be divided into three groups:

- The first group is consisted from rocks which are located in lower areas, which are belong to age of Kuatenrar solids, which are represented through alluvium and diluvium;
- The second group is consisted of neogen surface represented with argil, sand, gravel, slob, conglomerates, mergele etc; and
The third group is consisted of Paleozoic slides represented through serpentines, quantize, marble, metaphorical lime, carbonic rocks, etc.

Figure 2. Introduction of Grabovc i Poshtëm in regard to Municipality of Fushë Kosova

Natural resources
The coal is the largest natural recourse. These reserves are in the east of village, where the mine is located. The consistency of the coal in this mine is around 65-85 m, and the smallest amount of coal is at 430 m, while the largest is 500-550 m. In 2001 at the Mine of Bardhi was exploited 2.171.546 m³ coal (INKOS, 2002).

The landscape and hypsometrical structure
The terrain of the village is mainly mountain and a little plain area. The mountains are created at oregene Hercine with the influence of internal factors, as tectonic movements and those external as abrasion which is noticed as a consequence of wave of the “tertiary” lake. In the plain area also are noticed fluvial forms of river Drenica as accumulative and resave terrace as well as river islands, etc. As far as hypsometrical structure is concerning, Graboci i Poshtëm is located in 615 m over the sea level, while as far as espousal of the village terrain is concerned, the following data were collected through GIS and are presented below:

- 0-2° are 9.2 % of territory;
- 2-4° are 20.1 % of territory;
- 4-6° are 33.2 % of territory;
- 6-2°1 are 37.1 % of territory and
- 12-14.5° are 0.4 % of territory

Climate
The nearest meteorological station is in Prishtina, while counting the climate data for Prishtina Region, the village Grabovc i Poshtëm is included in this region. The air temperature: Medium temperature is 9.7 ºC, while the medium temperature in the coldest month of the year January is 1.0 ºC.

- The atmospheric rainfall: The medium yearly rainfall is about 600-700 mm. The largest amount of rainfall is usually falling in autumn and in spring, while the smallest in the Summer Season.
- Winds: the most common winds are: north-east wind, which is cold wind, as well as south and test winds, which are the warmest.
- The humidity of air: the humidity of air is about 71.4%, while the largest humidity is about 84 % in the month of December, the smallest in the month of June with 63 % (Kosovo Hydrometeorology Institute).
temperatures and precipitation (1960-1980)

Figure 3. The temperature and rainfall in Prishtina region

Hydro-graphy

The main and most important element in Graboc i Poshtëm village is Drenica river. The river Drenica flows in the mountain of Caraleva and is having length of 41 km, while pool is having a surface of 447 km². The medium flux of the river is 2.4 m³/sec. As far as the water level is concerned, the biggest is in the month of March with 90 cm, while the smallest is in the month of August 38 cm (Kosovo Hydrometeorology Institute).

Flow rate and water level in the river Drenica (1960-1980)

Figure 4. Graphical show of the flux and the water level of river Drenica for the period (1960-1980)

Ground

In Graboc i Poshtëm are found three different types of ground, but the most important are three types of ground. Depending on condition and position, they are:

- Near the river are found alluvial ground and are formed with river rest (material), having the content of humus of 2%.
- Smonica ground (vertisol) is in the area near the mountains, having the content of humus of 3-5%.
- The mountains grounds (Gajnjaçe) are in the mountain area, which consist of humus of 2-5% (Dauti, 1978)

Plant World

Graboc i Poshtëm is having different types of plants, depending on natural conditions and position when they are found (in water, fields, or mountain), the most common and characteristic higher and lower plant in Graboc i Poshtëm are:

**High Plant:** In the mountain area are dominant wood plants as: Bung Tree, Bungbuti Tree, Qarr Tree, Shpardh Tree, Wild Apple, Cornel Tree, Sturgeon Tree, etc, while planted Trees are: In field are grown these types of cereal, than vegetables etc, while the plant in the mild waters are: yellow lekoi, manrose, shavar, and near the river are grown cane, willow and poplar tree.

**The lower plant:** from lower plant are grown the green alga, fungus etc.
**Animal World**

Also, the animal world is divided depending on position where animal live, we can divide them in animal that live in waters, animals that live in fields and those who live in mountain area.

- In the river Drenica live these animals: fish, birds and mouse, etc;
- In the field are live these animal: swallow, partridge, corbie, wild pigeon, etc;
- In mountain area live these animals: rabbit, fox, snake, turtle, wild pig, wolf, hawk, woodpecker, cuckoo, screech owl.
- The most important domestic animals are: cow, horse, pigeon, bee, etc.

**The history of Graboc i Poshtëm village**

Graboc i Poshtëm is for the first mentioned in cadastral map of Vëllk Villa yet in the year 1455. At that time was having 24 houses, than in Austrian map in the year 1468. As first settles of the village are considered Belega clan, for them there is no data, while first inhabitants of the village are considered Berisha clan. In the year 1878 settled one Albanian family (Sogojeva) from Toplica region. Archeological findings conducted in the year 2004 show that this settlement was inhabited since late antique time (IV-VI) and in middle ages (IX-XI), (Osmani, 2002).

**Movement and number of population**

Good geographical position of the village, good natural and conditions and society factors have impact that the population of Grabovc i Poshtëm village is growing rapidly, even though was changing in different periods of time. The following data are presented about the number of population and family economies of Graboc i Poshtëm village, since the year 1948 till 2003 (Municipal Assembly of Fushë Kosova, 2004).

**Table 1.** Table show of increase of number of population and number of family economies

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of economy families</td>
<td>82</td>
<td>86</td>
<td>89</td>
<td>137</td>
<td>170</td>
<td>224</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No of Inhabitants</td>
<td>571</td>
<td>652</td>
<td>679</td>
<td>878</td>
<td>1169</td>
<td>1213</td>
<td>1270</td>
<td>2000</td>
</tr>
</tbody>
</table>

**Economic Base**

Graboc i Poshtëm has a surface of 809.70 h or 8.970 km², from which 65% belong to agriculture land and 35% are their land. As far as overall quality of land in Graboc i Poshtëm village is concerning, the quality of land is very high. In the following table are presented data of use of land in Graboc i ultë village (Kosovo Cadastral Agency).

**Economical Development**

Graboc i Poshtëm village has a good geographical position, rich fund of agriculture land near the river Drenica, near roads and railway, being rich with coal and large number workers, which fulfills the conditions for genuine economic development. The main branches in the village are mines and agriculture, therefore only two branches are developed. The Minerals are the main industrial branch, where large number of people are employed with around 46 %;
Agriculture: The agriculture along with her branches during 90-tes was the main Brach in which the population was dealing, but with many difficulties. This was due to the reason that many Albanians were expelled from work, while after the war; the agriculture is left behind even though some signs are noticed. Below are presented the data of active members working in agriculture according to the size of property;

Table 2. Table show of use of land in Graboc i Poshtëm village

<table>
<thead>
<tr>
<th>Ordinal number</th>
<th>Categories</th>
<th>Ha</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mountain</td>
<td>342.26</td>
<td>42.4</td>
</tr>
<tr>
<td>2</td>
<td>Agriculture land</td>
<td>228.34</td>
<td>28.2</td>
</tr>
<tr>
<td>3</td>
<td>Grass field</td>
<td>37.61</td>
<td>4.6</td>
</tr>
<tr>
<td>4</td>
<td>Uncategorized roads</td>
<td>13.59</td>
<td>1.6</td>
</tr>
<tr>
<td>5</td>
<td>Pasture</td>
<td>12.80</td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>Stream</td>
<td>6.41</td>
<td>0.79</td>
</tr>
<tr>
<td>7</td>
<td>Unfertile land</td>
<td>5.59</td>
<td>0.69</td>
</tr>
<tr>
<td>8</td>
<td>Yard</td>
<td>5.25</td>
<td>0.65</td>
</tr>
<tr>
<td>9</td>
<td>Railway</td>
<td>4.30</td>
<td>0.53</td>
</tr>
<tr>
<td>10</td>
<td>Trees</td>
<td>2.54</td>
<td>0.31</td>
</tr>
<tr>
<td>11</td>
<td>Yards</td>
<td>2.12</td>
<td>0.26</td>
</tr>
<tr>
<td>12</td>
<td>Chasm</td>
<td>1.61</td>
<td>0.19</td>
</tr>
<tr>
<td>13</td>
<td>Roads</td>
<td>1.54</td>
<td>0.19</td>
</tr>
<tr>
<td>14</td>
<td>Houses</td>
<td>1.15</td>
<td>0.14</td>
</tr>
<tr>
<td>15</td>
<td>Grave yards</td>
<td>0.86</td>
<td>0.10</td>
</tr>
<tr>
<td>16</td>
<td>Private roads</td>
<td>0.49</td>
<td>0.06</td>
</tr>
<tr>
<td>17</td>
<td>Vine yards</td>
<td>0.15</td>
<td>0.01</td>
</tr>
<tr>
<td>18</td>
<td>Yaze</td>
<td>0.07</td>
<td>0.008</td>
</tr>
<tr>
<td>19</td>
<td>Schools</td>
<td>0.01</td>
<td>0.001</td>
</tr>
<tr>
<td>20</td>
<td>Water Mill</td>
<td>0.01</td>
<td>0.001</td>
</tr>
<tr>
<td>21</td>
<td>Uncategorized</td>
<td>140.96</td>
<td>17.46</td>
</tr>
<tr>
<td>22</td>
<td>Total</td>
<td>809.64</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table 3. Table show of number of active population for agriculture and size of property

<table>
<thead>
<tr>
<th>Size of property</th>
<th>Active population</th>
<th>Under 1 ha</th>
<th>Over 1 ha</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only in agriculture</td>
<td>15</td>
<td>2</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Agriculture and other activities</td>
<td>30</td>
<td>7</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>45</td>
<td>7</td>
<td>52</td>
<td></td>
</tr>
</tbody>
</table>

Counting the Yleu coefficient (Pushka 1985) in this case, it comes that the connection in this to cases is small due to the reason that the agriculture property is small.

Economic and Non-economic Objects

In the village are found 8 economic objects, six are nutritional and mixed shops, 1 is water mill and one farm. While as far as non-economic objects are concerned, it is located the elementary school “Laura Skoti”, until the 9-th class, having 15 teachers and 171 pupils. There it is also located the Ambulance building.

Economical structure of population from years of 50-ties till XX Century

- Agrar Structure: The agriculture was one of the main branches which was dealt by population on the second half of XX Century.
- The mineral-industrial structure: since the opening of Bardh Mine in the year 1968, the population of village began in majority to get employed in mine sector.
- Recent changes: In the recent 4 years, the population was oriented mainly in tertiary activities.
Structure of population in Fushë Kosova and Graboc i Poshtëm village

The Municipality of Fushë Kosova is having around 42000 inhabitants with 420 inhabitants in 1/km², around 45% is urban population, where gender structure is in favor of male with 50.8%, male 50.8% and 49.2% females (Pushka 2000).

Graboc i Poshtëm is having around 2000 inhabitants with 229 inhabitants for 1/km², with 200 family economies, having 6.14 member per family, males are 53.42, while females are 46.68%. As far as age structure is concerned, the largest contingent is active work class (15-65 years) are 71.4%, the young group (until 15 years old), 22.1% and over 65 years is only 6.5% (Pushka 2002).

Economic-Professional Structure of population in Graboc i Poshtëm village

The level of socio-economical development in Graboc i Poshtëm village is not satisfactory, where it is known that the total number of employed population is only 26%, while unemployed are 12%. As mentioned above the population of Grabovc i Poshtëm village is mainly young population, which is sign of large working class, and the largest contingent is population of active work class (15-64 years) with 71.3%.

As far as education is concerned, a large number are in high school around 88.7%, than the active population with high level of education, as HPSCH (High Pedagogic School) and Faculties with 10% and only 1.25 are attending the elementary school. Making statistical data, coefficient of general mutual link for age and educational level of active population, the link of these to aspects, comes out that a law link or weak link (0.380). In professional structure of population in Graboc i Poshtëm village several factors are important. One of the factors is absolute or relative (Bratzel 1975) affinity or distance of KEK. As mentioned above, before and the first year of war the population was employed mainly in KEK. While after the first year the population started to get employment in other activities. From the research conducted in the village, are noticed to groups of population according to profession. The population which is employed in mine and the population employed in other activities. Below are presented the table data regarding the age structure, educational and professional as well as combination between these structures.

Table 4. Table show of active population according to age and education (according to questioner)

<table>
<thead>
<tr>
<th>Age of completed education</th>
<th>Under 20 Years</th>
<th>20-245</th>
<th>2930-3940</th>
<th>4950-64</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uneducated</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Less than 8 class</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>With elementary school</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>With high school</td>
<td>1</td>
<td>14</td>
<td>10</td>
<td>18</td>
<td>22</td>
</tr>
<tr>
<td>With HPSCH and Faculties</td>
<td>5</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Total</td>
<td>1</td>
<td>19</td>
<td>11</td>
<td>18</td>
<td>23</td>
</tr>
</tbody>
</table>

Table 4. Table show of active population according to age and education (according to questioner)
Table 5. Table show of active population according to age and activities (according to questioner)

<table>
<thead>
<tr>
<th>Age Activity</th>
<th>Under 20 years</th>
<th>20-24</th>
<th>25-29</th>
<th>30-39</th>
<th>40-49</th>
<th>50-64</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Housewife</td>
<td>-</td>
<td>2</td>
<td>11</td>
<td>13</td>
<td>23</td>
<td>13</td>
<td>62</td>
</tr>
<tr>
<td>Agriculture</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mines</td>
<td>-</td>
<td>2</td>
<td>2</td>
<td>8</td>
<td>19</td>
<td>6</td>
<td>37</td>
</tr>
<tr>
<td>Industry</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Transport and relations</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Handcrafts</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Trade</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Hotel and Tourism</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Services</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Education and culture</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Health</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Administration</td>
<td>2</td>
<td>12</td>
<td>3</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
</tbody>
</table>

| Total                  | 2              | 22    | 20    | 32    | 46    | 20    | 142   |

Table 6. Table show of active population according to education level and activities (according to questioner)

<table>
<thead>
<tr>
<th>Age Activity</th>
<th>Without Education</th>
<th>Less than 8 Class</th>
<th>Elementary School</th>
<th>High School</th>
<th>HPSCH and Faculties</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agriculture</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mines</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>35</td>
<td>1</td>
<td>37</td>
</tr>
<tr>
<td>Industry</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Transport and relations</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Handcrafts</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Trade</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Hotel and Tourism</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Services</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Education and Culture</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Health</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Administration</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Other services</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>18</td>
<td>2</td>
<td>20</td>
</tr>
</tbody>
</table>

| Total                  | -                 | -                 | 1                 | 71          | 8                   | 80    |

Financial and material situation of family economies

The financial and material situation of the families is different depending on profession and financial recourses. In a better situation are families, who have one family member employed abroad, than the families employed in KEK, while worse situation have families, who have one family member employed in education sector, health and those employed in private firms.

The role of KEK in professional structure

KEK play the largest role in professional structure of the village, because of the closeness of KEK. The distance between the place of residence and working place is minimal. Therefore, expenses and time are minimal.
Table 7. Professional Structure according to age (according to questioner)

<table>
<thead>
<tr>
<th>Age Activity</th>
<th>Under 30</th>
<th>30-50</th>
<th>Over 50</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agriculture</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mines</td>
<td>4</td>
<td>27</td>
<td>6</td>
<td>37</td>
</tr>
<tr>
<td>Industry</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Transport and relations</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Handcrafts</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Trade</td>
<td>2</td>
<td>4</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Hotel and tourism</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Services</td>
<td>2</td>
<td>1</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Education and culture</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Health</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Administration</td>
<td>1</td>
<td>3</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Other services</td>
<td>17</td>
<td>3</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>Total</td>
<td>31</td>
<td>41</td>
<td>8</td>
<td>80</td>
</tr>
</tbody>
</table>

Figure 7. Graphic show of education level of population

The role of education in economic structure

Before the war, the education did not play an important role in economic structure, considering that the population was mainly employed in KEK since the beginning of mine. Furthermore, the young people were forced to leave their school and faculties in order to get employed, due to the bad financial situation. After the war the role of education was higher in economical structure and the youth understood the importance of education. Below are presented the data regarding the education structure of active members (according to the questioner).

Figure 8. Graphical show of youth involvement in education institutions

Youth and its professional orientation

Before the war, the youth was employed mainly in KEK, while after the war the youth was oriented mainly in tertiary activities, even though the conditions are very bad, noticing that a number...
of them is still unemployed. However there are positive signs, where it is known the interest for education is high and this shows the below graphics (according to questioner).

**Final analyses and perspectives**

Based on the research it can be concluded that: Graboc i Poshtëm has a very good geographical position, knowing the fact that the village is located in suitable sea level, with characteristic geological content with different rocks and the most important with large natural recourses of coal. Having characteristic landscape forms as fields, hills, and mountains makes the village an attractive and clean environment.

Having suitable climate and reach hydrographic, this place is more interesting and attractive with a flow of Drenica River in the village, with fertile land and rich plant and animal world (environment). It is still worrying law economic and social development.

Based on the research conducted, we came to conclusion that Graboc i Poshtëm village has a law economic development, leaving aside the agriculture, with the lack of investments, etc. As far as social development is concerned it is still not in the satisfactory level, not high level of education, unemployment, small number of females employed, etc.

Despite the difficulties mentioned above, after the war started some investments in infrastructure. As far as social development is concerned, even though it remains difficult, some positive signs are seen compared to the situation before the war and today. The improvements are in employment of men and female, as well as education. There is hope that the brighter days will come.

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Kosovo Hydrometeorology Institute.


Kosovo Cadastral Agency.

Different Factors of Llap as a Geographic Region

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Abstract: In this work attempts were made to express in the best possible manner the factors which differentiate the Llap as geographic region. The Llap Region is located in the north-east of Kosovo. Within the ethnic geography, the Llap area is having peripheric position, but within the Balkan Peninsula it is having a central position, while along Llap goes the Highway which connects Kosovo and Serbia. The Llap region has important natural conditions; such as very good geographic position, running and accumulative waters. Fertile surfaces of groove, meadow, pasture as well as qualitative forest. Llap is characterized with medium continental weather. The average air temperature is about 9.6 ºC. Hydrographic Network has a general length of 433 km. In this region the most important river is Llap 79.4 km long and it is as well the most important branch of Sitnica River. The settlements in Llap Region are spread into consistent and spread settlements. The consistent settlements are located in the plain area, while the spread settlements are located in hilly and mountain areas. According to estimations, in 2002 the Llap Region was having 120.00 inhabitants. The population in the area of Llap was permanently growing. The Llap Region is characterized with different economic activities, where the majority is located in the town of Besiana; as Handicrafts, Trade, and Service Shops as well as large industrial enterprises in this region. As far as industry is concerned, the Llap Region, we can say that it is not concentrated and there is no particular industrial zone. All factories which produce industrial products are build in different parts having the tendency to concentrate in peripheral parts of Podujeva.

Keywords: Llap, Besiana (Podujeva), Geographic factors, Settlements, Demographic Characteristics.

Introduction

This work reflects the factors which differentiate the Llap region as a geographic region. Within this work will be treated some physic-geographic and socio-economic factors in Llap Region, including: geographic position, geological content, climate conditions, genesis and development of settlements, demographic characteristics as well as economic development in Llap region.

Methodology of Work

To complete this study we relayed in use of historic, mathematic-statistics, chartographic, typology, comparison method as well using the geographic literature. The historic method enabled that chronologically to treat the genesys and development of settlements in Llap Region. With mathematical-statistics method attempts were made to find rules and laws regarding data which are available and table and graphic analyses were made. The chartographic method was used to present the geographic position of Llap region. Typological Method enabled to select the types of settlements according to location and number of inhabitants. By using the literature a base was established for further study and prompt achievement of the aim of the study by using the experience of other authors.

Geographic Position of Llap

The Region of Llap is located on north-east part of Kosovo. The average sea level of Llap is 825 m (Anonymos, 1995). Within the geographic contest, Llap is having peripheric position, while it is having a central position in Balkan Panninsula. As far as communication links is concerned along Llap passes the High-way which connects Kosovo and Serbia. Along Llap Region since Illyrian-Romak period passed a important Balkan Route Lissus-Naissus (Lezhë-Nish) or Via De Zenta, which

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Figure 1. Geographic Position of Llap within Kosovo

Physical-geographic characteristics in differentiating the Llap Region

**Geological Content**- Llap Region has a good geological structure around Llap River from Pollata until neck, as well as main branches as: Dumnica, Batllava, Kaçandolli, etc, which is dominant by alluvial material (Blaku R 1995). The length of alluvial plain of Llap River varies from 0.4-2 km in the hole of Llap, while after exit of Tenezhol Gizzart reaches till 5 km (Plana R, 1981). The geological compositions of Llap region is changeable, while in the lower parts in Llap Valley are present new formations, in the upper parts are mainly dominant by Palezoik formations. Broadest expansions in Llap Region have Mezozoik formations, notably those from Kretak.

**Climate Conditions**- Hydrometherological observance in Llap region are mainly from the period after the World War II. The stations of rain mass have good extension, but there is lack of data about mountain zones. The Llap Region due to geographic position, oversea level, landscape and pre-dispositions aside of air stream, it is describcd with local climate characteristics. Furthermore, Llap is characterized with medium continentak climate, but due to the morphological structure, opening from north, high over sea level, larger part of surface in mountain are, the climate of Llap eventhough it is having a characteristics of continental climate it is more cold as compser to other parts of Kosovo (Anonymus 1995).

**Air Temperature**- Is one of the main elements to determine the climate characteristics of the region. The medium air temperature is about 9.6 °C. The winters are relatively cold with -0.4°C, while the summer season os having medium temperature of 19.3°C and are relatively hot. The autumn is for 1.9 °C hotter as compared to spring.

**The Air Humidity** is closed linked to the air temperature. In the Llap area the relative air humidity varies from 72.5 % in the month of August up to 87 % in December (Bulliqi Sh, 2001).

**Claudiness and Sun Insolation**- To develop the Plant World and completing different biological processes, most important are:

Data collected by Hydromtetherological Office in Prishtina for Llap region for the period 1965-1971, which show that the sunniest months are May and June. As far as Claudiness in Llap is
concerned, they are small, and with growth of oversea level (in hilly and mountain area) they are plenty.

**Rainfall:** Also in the Llap area, the rainfall increases with oversea level. While in Llap Valley (Besiana), yearly there is 697 mm rainfall in the mountain and hilly areas, in the northern part Pollatë are 751 mm, while in the east in Orllan it is 734.7 mm. In Llap Area, the months having the heaviest rainfall are May with 77.5 mm and November with 75.4 mm, while the month with least rainfall is August with 35.5 mm (Bullqi Sh, 2001).

**Winds** show an important element of climate. From direction, force and speed depend many climate elements. The position of Llap in the middle of Kopaonik in hilly area, in the eas has determined that the winds to depend only by two directions, north and south (Çavolli R. 1997).

**Waters** - The main precondition for hidrographic characteristics of a region are mainly rainfall, the amount, pluviometrical regime as well as geological content. The amount of rainfall in Llap Valley is 679.1 mm. The distribution in time and space has had a impact that these area is characterized with relatively density water flow. The hydrographic network is having the length of 433 km. The most important River in the Llap Region is Llap with the length of 79.4 km and at the same time it is the most important branch of Sitnica. In the upper part, Llap River is typicall Mountain River with declinicity of 23.1 m/km and broadeness.

In the medium part flows through the field, taking all characteristics of Field River with declininity of 4.5 m/km, bottom of 10 meters wide and 1 m deep. Therefore, it is Quiet River.

Batllava Lake is built in Tactonic valley of Braina village. It is an artificial Lake build in 1961 with oversea level of 600m. This lake is having 50.000.000 m³ water. The Lake has a surface of 4.5 km² with length of 8 km, while the the wideness reaches up to 500 m. The Lake has clean water durin sprin. Batllava Lake is presented as a touristic attraction which distinguishes it from other parts of Kosovo Valley and the smimming begans in May until September.

**Ground in Llap Region** - In Llap region are found four types of lands: as alubial, pseudogledged, deluvial, smonic, rendzina, as well as bwon land, etc. The most important lands in Llap Valley are: Aluvial, Brown, Smonica, Deluvial, Pseudoedege and reznina ground, while in small areals are present rock and salty grounds. The Brown Grounds belong to cambric and eluvial-iluvial types (Bullqi Sh, 2001).

**Genesis and development of settlements in Llap Region**

Having good geographic and geostrategic position as well as good natural conditions made possible that Llap region was inhabited since long time ago, precicely since Neolit times. Different archelogical research and Illyrian Trace in the settlement tell us about early inhabitans of this region. So, the Illyrian- Albanian contunance is a evidence of existence of this authocton inhabitans which is relayed on archelogical, historic, language, folklore data, etc.(Drancölli J, 1994). Evidence of this contunance are following examples: Neolit Shtatore (Barileva Village), Neolit Head (Lupç Village), Venera (Afrodite) Figure former known as Vindenis (Gllamnik Village), etc.

The documents from Middleage tell us about the settlements in Llap Region. E.g. Berileva is mentioned in XIV Century and it was a property of Banjska Monestry. Vendbanimet e ndryshme që përmenden në këtë periudhë në raste të ndryshme janë: Lluzhani, Sallabaja, Sharbani, Zakuti, Dyzi, Muhazobi, Penuha etc. (Anonymus, 1995). Different settlement that are mention in this period are: Lluzhani, Sallabaja, Sharbani, Zakuti, Dyzi, Muhazobi, Penuha, etc. According to data of 1455 in Nahije (province of Ottoman period) of Llap is mentioned among others also Podujeva (today Besiana). The village was having 49 houses.

**Types of Settlements**

The settlements in Llap Region according to their expansion are known as the settlement of dense type and those of spread type. The dense settlement are located in plain area, while those spread settlement are located in mountain area.

If we take the number of inhabitans, based on number of inhabitans; we divide them in:

a) small settlements from 0-1000 inhabitans
b) medium settlements from 1000-2000 inhabitans and
c) large settlements over 2000 inhabitans, then we cane have a picture off 77 settlements that we have recorded.
From the table we can see that the small settlements are majority or 67.5 %, added by medium and large settlements.

**Table 1. Differentation of Locality in Besiana (Podujeva)**

<table>
<thead>
<tr>
<th></th>
<th>Small settlements</th>
<th>Medium settlements</th>
<th>Large settlements with over 2000 inhabitants</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-1000 inhabitans</td>
<td>52</td>
<td>21</td>
<td>4</td>
</tr>
<tr>
<td>67.5%</td>
<td>27.3%</td>
<td>5.2%</td>
<td></td>
</tr>
</tbody>
</table>

**Demographic Characteristics of Llap**

According to some estimation, in 2002 Llap was having 120.000 Inhabitans. The population in Llap is increasing permanently. The population compared to census in 1948 and 1991 was grown for 2.2, respectively near to 42.000 inhabitans. The growth of population in Llap area was lower than natural increase of this region. This difference between the growth of population and natural growth is as result of migrations inside and outside Kosovo, especially inside Kosovo after the last war, mainly the people migrated in Prishtina. Based on these migrations Llap should have less then 120.000 inhabitans (respectively 100.000-110.000 inhabitans), from them 40 % live in the Town of Besiana and 60 % in the villagea of Llap region (Pushka A, 1995).

The largest growth, the Llap region was having between censuses 1971-81, where the number of inhabitans was increasing for 15.100 inhabitans or 1508 inhabitans in year (Basha T, 1991). This large growth was motivated with low level of socio-economic development, especially this is noticed in villages. This growth was supported by improvement of conditions in health, while the mortality rate has shown tendencies of decreas.

**Table 2. Natality, Mortality and natural growth in period of 1971-80 in Llap Region**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Natality</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>37</td>
<td>33</td>
<td>27</td>
<td>34</td>
<td>35</td>
<td>35</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>Mortality</td>
<td>7</td>
<td>8</td>
<td>7</td>
<td>7</td>
<td>6</td>
<td>5</td>
<td>6</td>
<td>5</td>
<td>6</td>
<td>5</td>
<td>5.6</td>
</tr>
<tr>
<td>Natural Birth Rate</td>
<td>31</td>
<td>30</td>
<td>31</td>
<td>30</td>
<td>27</td>
<td>22</td>
<td>28</td>
<td>30</td>
<td>29</td>
<td>35</td>
<td>29</td>
</tr>
</tbody>
</table>

**Figure 2.** Natality, mortality and natural growth expressed in %‰ (promile) for the period 1971-80 in Llap Region (Çavolli, 1997).

**Economy in Llap Region**

The Llap Region is characterized with different economic activities, where the largest part are located in the Town of Besiana, as Handicraft, Trade and Service Shops as well as large industrial enterprises in this region. According to data collected from the Directory for Economy and Finance, inthe Municipality of Besiana, the number of registred companies according to devisions in the end of 2002 was 2.251 companies, while only in Besiana Town were operating 1.558 companies (enterprises).

The majority of these companies are small business (1-4 Workers). The following table composed based on collected data by the Directory for Economy and Finance in Municipality of
Besiana we will show the number of companies (enterprises) in Municipality of Besiana. From the notes mentioned above in the table, we can conclude that nearly 70% of registered Enterprises in Llap region operate in the Town of Besiana.

**Table 3. Small and Medium enterprises in Llap Region and in the town of Besiana (Business Registration Office, 2003)**

<table>
<thead>
<tr>
<th>No.</th>
<th>Types of small and medium enterprises</th>
<th>Number of enterprises in Llap region</th>
<th>Number of Enterprises in the Town of Besiana</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Import-Export</td>
<td>424</td>
<td>389</td>
</tr>
<tr>
<td>2.</td>
<td>Construction</td>
<td>226</td>
<td>102</td>
</tr>
<tr>
<td>3.</td>
<td>Transport</td>
<td>28</td>
<td>23</td>
</tr>
<tr>
<td>4.</td>
<td>Production</td>
<td>44</td>
<td>21</td>
</tr>
<tr>
<td>5.</td>
<td>Hostels</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>6.</td>
<td>Services</td>
<td>16</td>
<td>13</td>
</tr>
<tr>
<td>7.</td>
<td>Shops</td>
<td>417</td>
<td>176</td>
</tr>
<tr>
<td>8.</td>
<td>Handcrafts</td>
<td>281</td>
<td>165</td>
</tr>
<tr>
<td>9.</td>
<td>Restaurants and Bars</td>
<td>118</td>
<td>65</td>
</tr>
<tr>
<td>10.</td>
<td>Trade Enterprises</td>
<td>214</td>
<td>207</td>
</tr>
<tr>
<td>11.</td>
<td>Sellers in the street</td>
<td>118</td>
<td>101</td>
</tr>
<tr>
<td>12.</td>
<td>Taxi</td>
<td>224</td>
<td>208</td>
</tr>
<tr>
<td>13.</td>
<td>Other</td>
<td>122</td>
<td>87</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>2,251</td>
<td>1,558</td>
</tr>
</tbody>
</table>

**Industrial Development in Llap Region**

As far as Industry is concerned, in the Region of Llap we can say that there is no industrial zone. All factories that produce industrial products are build in different parts, where the larger part is outskirts of Besiana, e.g. The Factory for production of Iron Bars is build on the north-eas of the town Besiana, the factory for construction of polyester poles si constructed in south, and the factory for constructing the construction blocks is in south-east. From these examples we can conclude that Llap has no real industrial zone.

*N.SH. “Fan”, “Zahir Pajaziti”* - main activity of this factory is production of iron bars in a basic and complex form. The production capacity of this factory is 46.00 Tons per year. In this factory are employed 415 workers.

*The Block Factory “Euro Bllok”* - the production capacity of this factory is 12.00 blocs within a shift (8 hours). The primary material this factory is having near the building (about 800 metres). The number of employed people in this enterprise is about 80 workres, from them 5 workers have faculty degree, 2 High School, and 73 High School.

*N.SH. “Fapol”* - This enterprise deals the production of poliester mass, polyester poles, trapez tiles, which since the beginning of the activity faced difficultues and different problems in the process of production, because the raw material was imported. This factory was employing about 180 workers.

**Conclusion**

- During this study a large number of factors are noticed that differentiate Llap as geographic region, but the most important are:

  - **Geographic Position** - The Llap Region is located in north-east of Kosovo. The medium Oversea level of Llap is 825 m. Within the ethnical geo-extend, the Llap is having peripheric geographic position, but from the aspect of position in Balkan Penninsula is having a central position, while as far as communication likes is concerned, along Llap goes the Highway which connects Kosovo and Serbia.

  - **Geological Composition** - The Llap Region is having complex geological structure. The geological composition of Llap is changeable, while the lower parts in Llap Valley are present new formations, on the upper parts mainly dominate palezoik formations.
• **Climate Conditions**- Llap is characterized with middle continental climate. The average air temperature is about 9.6 °C. Due to the morphological structure of terrain, opening from the north, high oversea level, large extension in mountain surface, the climate of Llap eventhough is having continental climate characteristics it is colder then other parts of Kosovo.

• Also in the region of Llap, the rainfall are increasing with increas of oversea level, while in Llap Valley (Besiana) in year there is 697 mm rainfall, in the mountains or in the northern part Pollata is 751 mm rainfall, while in the eas in Orllan 734.7 mm.

• **Hydrographic Network**- The hydrographic network has a general length of 433 km. The rivers flow in Llap Valley, the source thay have outside of valley and all are drain through Llap River. Llap is having meridional flow. The most important river is Llap, with the length of 79.4 km and at the same time it is the main branch of Sitnica River. Batllava Lake was built on the tectonic valley of Braina Village. It is a artificial Lake build in 1961 in oversea level of 600 m.

• This lake is having nearly 50.000.000 m³ water; the Lake has a surface of 4.5 km². The lake is 8 km long, while the deepest part of the lake is 39 m.

• **Settlements**- Having good geographic and geostrategic position as well as good natural conditions enabled that Llap Region was inhabited since early age, preciesely since Neolit time.

• **Demographic Characteristics**- According to aosme estimations, in 2002 Llap was having 120.00 inhabitants. The population of Llap was permanently increasing.

• Growth of population in Llap Region was slower as compered to birth rate of the region. This change between the population growth and birth rate is as result of migrations in- and outside Kosovo, expecially inside Kosovo after the last war. The people mainly migrated in Prishtina.

• **Economic Development**- Llap Region is characterized with different economic activities, where the largest part are located in Besiana Town as Handicraft, Trade, Service as well as large industrial enterprises located in the region.

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Evaluation of Adsorbents for Removal of Phenol and Methylene Blue from Wastewater

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Abstract: The adsorption of phenol onto activated carbon and methylene blue dye onto Amberlite XAD4 in a fixed bed column were investigated. The effect of various influent adsorbates concentrations, flow rates, and bed depths on the performance of fixed bed was studies. Batch type experiments were carried out to study the equilibrium isotherm data, external mass transfer coefficient and interparticle diffusion coefficient by fitting the experimental data with theoretical model. The interparticle diffusion coefficient was obtained using pore diffusion model for batch adsorber by matching the experimental data with the model predicted data. The equilibrium isotherm data were fitted with five theoretical models. A mathematical model was formulated to describe the mass transfer kinetics in the fixed bed adsorbent bed’s column for both adsorbents. The results show that the mathematical model includes external mass transfer and pore diffusion using nonlinear isotherms, provides a good description of the adsorption process for phenol and methylene blue onto fixed bed adsorbent bed.

Keywords: Adsorption, fixed bed, activated carbon, Amberlite XAD4, phenol, methylene blue, mathematical model, mass transfer coefficient.

Introduction

Owing to its acute toxicity and good solubility, phenol has already been listed as one of the top priority contaminants and also the most important substructure of potentially carcinogenic pollutants discharged from fine chemical plants (Ku & Lee, 2000). Dyes are color organic compounds, these substances usually present in the effluent water of many industries, such as textiles, leather, paper, printing and cosmetics. The extensive use of dyes causes environmental problem in the ecosystem (Ozer et al., 2007). One of these dyes is methylene blue (MB).

The use of adsorption contacting systems for industrial and municipal wastewater treatment has become more prevalent during recent years (Babu & Gupata, 2004). Activated carbon and Amberlite XAD4 adsorption systems are an important unit processes that are used in the treatment of wastewaters (Yener et al., 2006).

To design and operate a fixed bed adsorption process successfully, the column dynamics must be understood; that is the breakthrough curves under specific operating conditions must be predictable. Different models for the adsorption process on fixed beds were proposed in the literature (Hsu, et al., 1997). The differences between these models arise from the different representation of the equilibrium behavior, the different expressions of the mass transfer inside and outside the adsorbent particle and from how the axial dispersion is taken into account in the material balance for the adsorbate in the fixed bed column. Several rate models have been developed that take into account an external film transfer rate step, unsteady state transport in the solid phase and nonlinear equilibrium isotherm to predict adsorption rates in batch reactor and fixed bed (Crittenden & Weber, 1978).

Under a wide range of operating conditions, the key process parameters in adsorption such as isotherm constants and mass transfer coefficients are obtained by conducting batch studies of adsorption. Langmuir, Freundlich, Radke-Prausnitz, Reddlich-Peterson, and Combination of Langmuir-Freundlich isotherms have been applied to describe the equilibrium between liquid-solid phases. The parameters that are responsible for mass transfer operation are the external mass transfer coefficient and interparticle diffusivity or surface diffusion coefficient.

The objective of this study is to investigate that the film-pore diffusion model is used to determine the breakthrough curves in fixed bed column for single component adsorption of phenol and methylene blue dye onto granular activated carbon and Amberlite XAD4 respectively and compare the
experimental results with that simulated by numerical simulation of the film-pore diffusion model, which includes film mass transfer, pore diffusion resistance, axial dispersion and non linear isotherms. To achieve these objective two sets of experimental programs were designed and performed.

**Theory**

**Fixed bed**

Fixed bed dynamics are described by the convection-diffusion equations, coupled with source term due to adsorption and diffusion inside adsorbent particles. The solution of these equations will give rise to the prediction of the needed breakthrough curves (Crittenden et. al., 1986).

General rate model refer to models containing a rate expression, or rate equation, which describe the interfacial mass transfer between the mobile phase and the stationary phase. A general rate model usually consists of two sets of differential equations, one for the bulk phase, and the other for the particle phase (Gu, 1994). The rate model considers the following: axial dispersion, external mass transfer, interparticle diffusion and nonlinear isotherm (Guiochon et. al., 1994; Ruthven, 1984).

For modeling of fixed bed adsorption the column is divided into the bulk-fluid phase and the particle phase. The model equations are based on the hypothesis of an interparticle mass transfer controlled by diffusion into macropores (pore diffusion model), and this approach considers three phases; they are: the mobile phase in the space between particles, the stagnant film of mobile phase immobilized in the macropores and the stationary phase where adsorption occurs (Ganetson & Barker, 1993; Eggers, 1989). The following basic assumptions are made in order to formulate the model (Crittenden et. al., 1986):

- Adsorption process is isothermal.
- The packing material is porous, spherical, particles of uniform size.
- The concentration gradient in the radial direction of the bed is negligible.
- Local equilibrium exists for the component between the pore surface and the stagnant fluid phase in the pores.
- The film mass transfer mechanism can be used to describe the interfacial mass transfer between the bulk-fluid and particle phase.
- The dispersion coefficient is constant.
- Surface diffusion can be ignored.

Continuity equation of the mobile phase is:

\[-D_b \frac{\partial^2 C_b}{\partial Z^2} + \nu \frac{\partial C_b}{\partial Z} + \frac{\partial C_b}{\partial t} + \rho_p \frac{1 - \varepsilon_b}{\varepsilon_b} \frac{\partial q}{\partial t} = 0\]  

Using \(C_p\), the concentration in the stagnant mobile phase and writing the expression of the interfacial flux leads to (8):

\[\rho_p \frac{\partial q}{\partial t} = \frac{3k_f}{R_p} \left(C_b - C_{p,R,R_p}\right)\]  

Substituting equation (2) in equation (1) gives:

\[-D_b \frac{\partial^2 C_b}{\partial Z^2} + \nu \frac{\partial C_b}{\partial Z} + \frac{\partial C_b}{\partial t} + \frac{3k_f(1 - \varepsilon_b)}{\varepsilon_b R_p} \left[C_b - C_{p,R,R_p}\right] = 0\]  

The particle phase continuity equation in spherical coordinates is:

\[ \left(1 - \varepsilon_p\right) \frac{\partial C_p}{\partial t} + \varepsilon_p \frac{\partial C_p}{\partial t} - \varepsilon_p D_p \left[\frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial C_p}{\partial R}\right)\right] = 0\]  

The initial and boundary conditions can be represented by the following equations:

Initial condition \((t = 0)\):

\[C_b = C_b(0, Z) = 0\]  

\[C_p = C_p(0, R, Z) = 0\]  

Boundary conditions:

\[Z = 0:\]
Z = L
R = 0
R = R_p

Defining the following dimensionless formula (8):

\[ c_b = \frac{C_b}{C_o}, \quad c_p = \frac{C_p}{C_o}, \quad c_p^* = \frac{C_p^*}{C_o}, \quad \tau = \frac{vt}{L}, \quad r = \frac{R}{R_p}, \quad z = \frac{Z}{L} \]

\[ Pe_L = \frac{vL}{D_b}, \quad Bi = \frac{k_f R_p}{\varepsilon_D P_L}, \quad \eta = \frac{\varepsilon_p D_p L}{R_p^2 \nu}, \quad \zeta = \frac{3Bi \eta(1 - \varepsilon_b)}{\varepsilon_b} \]

The model equations can be transformed into the following dimensionless equations:

\[ -\frac{1}{Pe_L} \frac{\partial^2 c_b}{\partial z^2} + \frac{\partial c_b}{\partial z} + \frac{\partial c_b}{\partial \tau} + \zeta (c_b - c_{p,r=0}) = 0 \]

\[ \frac{\partial}{\partial \tau} \left[ (1 - \varepsilon_p) c_p^* + \varepsilon_p c_p \right] - \eta \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_p}{\partial r} \right) \right] = 0 \]

The concentration \( c_p^* \) in equation (12) is the dimensionless concentration in the solid phase of the particles. It is directly linked to the isotherm, which is the extended Langmuir model:

\[ C_p^* = \frac{q_m b \rho_p c_p}{1 + b C_p} \]

The initial conditions become:

\[ \tau = 0: \]
\[ c_b = c_b(0, z) = 0 \]
\[ c_p = c_p(0, r, z) = 0 \]

And boundary conditions become:

\[ z = 0: \]
\[ z = 1: \]
\[ r = 0: \]
\[ r = 1: \]

The concentration \( c_p^* \) in dimensionless form:

\[ c_p^* = \frac{\rho_p q_m b c_p}{1 + b C_p} \]

Finite element method is used for discretization of the bulk-fluid phase partial differential equation and the orthogonal collocation method for the particle phase equation, an ordinary differential equation system is produced. The ordinary differential equation system with initial values can be readily solved using an ordinary differential equation solver such as the subroutine “ODE15S” of MATLAB which is a variable order solver based on the numerical differentiation formulas (NDFs). Optionally it uses the backward differentiation formulas (BDFs), which is also known as Gear’s method.

**Batch adsorber**

The batch model is the following:

- Mass balance in the bulk-fluid phase

\[ V_L \frac{dC_b}{dt} + \frac{3W_A}{\rho_p R_p} k_f \left( C_b - C_{p,r=R_p} \right) = 0 \]

Where \( V_L \) = volume of fluid in the batch adsorber.
\( W_A \) = mass of activated carbon in the batch adsorber.
Mass balance inside the particle

The solute diffusion inside a spherical particle is described by the following equation:

\[
\frac{\partial C_p}{\partial t} + \rho_p \frac{dq}{dt} = D_p \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_p}{\partial r} \right)
\]

The solute concentration in the pores is in local equilibrium with the concentration of solute adsorbed on the pore walls.

Initial and boundary conditions are:

\[t = 0 ; \quad C_b = C_o ; \quad C_p = 0 ; \quad q = 0\]

\[r = 0 ; \quad \frac{\partial C_p}{\partial r} = 0 ; \quad \frac{dq}{dr} = 0\]

\[r = R_p ; \quad D_p \frac{\partial C_p}{\partial r} = K_f (C_b - C_p)_{r=R_p}\]

For Langmuir isotherm model:

\[q = \frac{q_m b C_p}{1 + b C_p}\]

The external mass transfer coefficient for the solute adsorbed at certain particle size and optimum speed, can be obtained by the analytical solution (Alexander & Zayas, 1989 & Liu, et al., 2006).

\[k_f = -\frac{R_p \rho_p V_L}{3W_{at} t} \ln \left( \frac{C_i}{C_o} \right)\]

Where \(R_p\) and \(\rho_p\) the particle radius and density respectively and \(C_o\) and \(C_i\) are the solute concentration at time zero and time \(t\), respectively. Experimental concentration-time data are compared to predicted concentration-time profile for the above batch absorber model and the best statistical description used to determine the interparticle diffusion coefficient.

Materials and Methods

Set 1

Materials

Adsorbate: phenol was used as an organic pollutant; it was supplied by Sdfine-Chem limited, India. Adsorbent: granular activated carbon (GAC) was used as an adsorbent; it was supplied by Netherland Company.

Methods

The GAC was sieved into 30/35 mesh with geometric mean diameter of 0.55mm. The GAC was boiled, washed three times in distilled water and dried at 100\(^\circ\)C for 24 hours, before being used as adsorbent. The aqueous solution of phenol was prepared using reagent grades. The bulk density of the GAC used was 770 kg/m\(^3\) and its pore and bed porosity were 0.5 and 0.4 respectively and the surface area is 1000 m\(^2\)/gm. The experiments were adjusted at the initial pH of 5 for phenol (Ping & Guohua, 2001). The pH value was adjusted with 0.01 mol/l HCl.

The fixed bed experiments were carried out in Q.V.F. glass column of 50 mm (I.D) and 50 cm in height. The GAC was confined in the column by fine stainless steel screen at the bottom and glass packing at the top of the bed to ensure a uniform distribution of influent through the carbon bed. The influent solution was introduced to the column through a perforated plate fixed at the top of the column. Feed solution was prepared in Q.V.F. vessel supplied with immersed heater with a thermocouple to adjust the temperature of the solution at 30\(^\circ\)C. More details on the fixed bed experiments are given in (Ebrahim, 2008).

For the determination of adsorption isotherms, 250 ml flasks were filled with known concentration of solute and a known weight of GAC. The flasks were then placed on a shaker and agitated continuously for 30 hours at 30\(^\circ\)C. The concentration of phenol in the solution was determined by a UV-160A spectrophotometer at 270nm.

The adsorbed amount is calculated by the following equation:
The interparticle diffusion coefficient was estimated using the following steps:

- Estimating the optimum agitating speed for batch adsorber to reach the needed equilibrium concentration of phenol.
- Estimating the mass transfer coefficient in batch process at optimum agitation speed.
- Apply numerical solution of batch adsorber model to obtain the interparticle diffusion coefficient. This was done by using the pore diffusion model to best fit the experimental results.

The interparticle diffusion coefficient for phenol was obtained by 2 liter Pyrex beaker fitted with a variable speed mixer. The beaker was filled with 1 liter of known concentration solution and agitation started before adding the GAC. At time zero, the accurate weight of GAC was added. Samples were taken every 5 minutes. Different agitation speeds of 700, 800, 900, 1000 and 1100 were carried out to achieve \( \frac{C_e}{C_0} = 0.05 \).

The interparticle pore diffusion coefficient was derived from the typical concentration decay curve for the solute at optimum agitation speed and dosage of activated carbon and Amberlite by an iterative search technique predicted on the minimization of the difference between experimental and predicted data from pore diffusion model. The necessary dosage of GAC, to reach equilibrium related concentration of \( \frac{C_e}{C_0} \) equal 0.05, were calculated by using equation (25).

### Materials

**Adsorbate:** methylene blue dye was used as pollutant; it was supplied by Sigma-Aldrich Company Ltd. United Kingdom. **Adsorbent:** Amberlite XAD4 was used as an adsorbent; it was supplied by Sigma-Aldrich Company Ltd. United Kingdom.

### Methods

The Amberlite XAD4 was sieved into 28/32 mesh with geometric mean diameter of 0.5mm. For pre-treatment, the resin was washed with distilled water then cleaned by extraction using methanol as a solvent, for the removal of residual monomer, after that all particles were washed with distilled water then dried at 100°C for 24 hours before being used as adsorbent. The aqueous solution of methylene blue was prepared using reagent grades.

The bulk density of the Amberlite XAD4 used was 700 kg/m³ and its pore and bed porosity were 0.52 and 0.36 respectively and the surface area was 750 m²/gm. The fixed bed experiments were carried out in acrylic column of 30cm height, 7.5cm (I.D). The Amberlite bed was supported in the column by a fine porous stone; the influent solution was introduced to the column through a perforated plate, fixed at the top of the column. Feed solution was prepared in polyethylene square tank. The system temperature was 20°C. More details on the fixed bed experiments are given in (Ebrahim, 2008). For determination of adsorption isotherms and the interparticle diffusion coefficient, the same procedure was used as in set (1) except that the methylene blue concentration in the solution was determined by using GC technique.

### Results and Discussions

#### Adsorption isotherm

The equilibrium isotherms display a nonlinear dependence on the equilibrium concentration. The adsorption data for both systems were fitted by Langmuir model (Lucas & Cocero, 2004), Freundlich model (Weber & Walter, 1972), Radke-Prausnitz model (Radke & Prausnitz, 1972), Reddlich-Peterson (Jossens et. al, 1978) and Combination of Langmuir-Freundlich isotherm model (Sips, 1984). The determination coefficients are shown in table (1 and 2) for the phenol and methylene blue systems. Table (1 and 2) indicates that Langmuir model provides the best fit as judged by its correlation coefficient. Langmuir model was therefore selected to be introduced in the fixed bed model:

\[
q_e = \frac{q_m b C_e}{1 + b C_e}
\]
The equilibrium isotherms for phenol and methylene blue onto GAC and Amberlite XAD4 are presented in Figures 1 and 2.

**Table 1. Parameters of isotherm for phenol and correlation coefficient for various models**

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q_e = \frac{q_m b C_e}{1 + b C_e} )</td>
<td>( q_m, ) b, m³/kg Correlation coefficient 0.999</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( q_e = KC_e^{1/n} )</td>
<td>( K, n, ) Correlation coefficient 0.999</td>
</tr>
<tr>
<td>Radk-Prausnitz</td>
<td>( q_e = \frac{K_{RP} C_e}{1 + \left( \frac{K_{RP}}{F_{RP}} \right) C_e^{4-n_{RP}}} )</td>
<td>( K_{RP}, F_{RP}, N_{RP}, ) Correlation coefficient 0.994</td>
</tr>
<tr>
<td>Reddlich-Peterson</td>
<td>( q_e = \frac{A_R C_e}{1 + B_R C_e^{m_R}} )</td>
<td>( A_R, B_R, m_R, ) Correlation coefficient 0.988</td>
</tr>
<tr>
<td>Combination of Langmuir-Freundlich</td>
<td>( q_e = \frac{b q_m C_e^{1/n}}{1 + b C_e^{1/n}} )</td>
<td>( q_m, b, n, ) Correlation coefficient 0.998</td>
</tr>
</tbody>
</table>

**Table 2. Parameters of isotherm for MB and correlation coefficient for various models**

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Methylene Blue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q_e = \frac{q_m b C_e}{1 + b C_e} )</td>
<td>( q_m, b, ) Correlation coefficient 0.99</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( q_e = KC_e^{1/n} )</td>
<td>( K, n, ) Correlation coefficient 0.952</td>
</tr>
<tr>
<td>Radk-Prausnitz</td>
<td>( q_e = \frac{K_{RP} C_e}{1 + \left( \frac{K_{RP}}{F_{RP}} \right) C_e^{4-n_{RP}}} )</td>
<td>( K_{RP}, F_{RP}, N_{RP}, ) Correlation coefficient 0.971</td>
</tr>
<tr>
<td>Reddlich-Peterson</td>
<td>( q_e = \frac{A_R C_e}{1 + B_R C_e^{m_R}} )</td>
<td>( A_R, B_R, m_R, ) Correlation coefficient 0.569</td>
</tr>
<tr>
<td>Combination of Langmuir-Freundlich</td>
<td>( q_e = \frac{b q_m C_e^{1/n}}{1 + b C_e^{1/n}} )</td>
<td>( q_m, b, n, ) Correlation coefficient 0.986</td>
</tr>
</tbody>
</table>
The amounts of activated carbon and Amberlite XAD 4 used for phenol and methylene blue were calculated for final equilibrium related concentration of $C_e/C_0=0.05$. Using equation (26) with mass balance in one liter of solution, the initial concentrations were 0.2 Kg/m$^3$ for each solute with the doses of activated carbon of $2.2 \times 10^{-3}$Kg and $24 \times 10^{-3}$Kg of Amberlite XAD4.

The optimum agitation speed needed to achieve $C_e/C_0=0.05$ was found to be 1000 rpm. It is clear that, if the speed is above 1000 rpm, the equilibrium relative concentration is less than 0.05; this is due to pulverization of activated carbon and Amberlite XAD4 at high speed agitation.

There were a good matching between batch experimental results and predicted data using pore diffusion model for batch operation as shown in Figures 3& 4.

The pore diffusion coefficient for each solute are evaluated from the batch experiments to be $D_{p,\text{phenol}} = 5.25 \times 10^{-8}$ m$^2$/sec, $D_{p,\text{methylene blue}} = 2.6 \times 10^{-10}$ m$^2$/sec.

The external mass transfer coefficients in packed bed model for each solute were evaluated by the correlation of Wilson and Geankoplis (Ping & Guohua, 2001).
Figure 3. Comparison of the measured concentration-time data with that predicted by pore diffusion model in batch adsorber for phenol system

Figure 4. Comparison of the measured concentration-time data with that predicted by pore diffusion model in batch adsorber for MB system

\[
\frac{Sh}{\epsilon_b} = \frac{1.09}{Sc^{1/3}} \frac{Re^{1/3}}{Re=0.0015-55}
\]

Where: 
\[
Sh = \frac{K_f d_v}{D_m}, \quad Sc = \frac{\mu_w}{\rho u D_m} \quad \text{and} \quad Re = \frac{\rho u d_v}{\mu_w}.
\]

In which the molecular diffusion coefficient \(D_m\) of phenol and methylene blue in aqueous solution are \(9.6 \times 10^{-9}\) m\(^2\)/sec and \(3.6 \times 10^{-10}\) m\(^2\)/sec respectively (Hawley, 1981; MERCK, 2005). These values substituted in equation (23) to evaluate the mass transfer coefficient \(K_f\) in m/sec at different interstitial velocity in the mathematical model. The axial dispersion coefficient \(D_b\) in m\(^2\)/sec was calculated from Chung and Wen equation (24):
Breakthrough curves
- The effect of varying phenol and methylene blue initial concentrations were investigated, the experimental and predicted breakthrough curves are presented in Figures 5 & 6. The change in initial concentration will have a significant effect on the breakthrough curves. An increase in the initial concentration of both adsorbates (phenol and MB) makes the breakthrough curves much steeper, which would be anticipated with the basis of increases driving force for mass transfer with the increase of concentration of adsorbate in the solution (25). A high adsorbates concentration may saturate the adsorbent more quickly, thereby decreasing the breakthrough time. The same conclusion was obtained by (Gupta, 2001; Lin & Wang, 2001; Sulaymon & Ahmed, 2007; Sulaymon et. al., 2009).

\[
\frac{D_w \rho_w}{\mu_w} = \frac{Re}{0.2 + 0.011Re^{0.48}}
\]

Figure 5. Experimental and predicted breakthrough curves for phenol adsorption onto activated carbon at different initial concentration

Figure 6. Experimental and predicted breakthrough curves for MB adsorption onto amberlite XAD4 at different initial concentration

- Figures 7 & 8 show the experimental and predicted breakthrough curves for phenol and methylene blue at different flow rates. An increase in the adsorbates flow rate decreases the breakthrough time.
due to the decrease in the contact time between the adsorbate and the adsorbent along the adsorption bed. Increasing the flow rate may be expected to make reduction of the surface film thickness. Therefore, this will decrease the resistance to mass transfer and increase the mass transfer rate. Also, because the reduction in the surface film thickness is due to the disturbance created when the flow of the feed increased resulting of easy passage of the adsorbate molecules through the particles and entering easily to the pores. This will decrease contact time between the adsorbate and the adsorbent. An increase in the flow rate will increase Bi number and with slight increase Pe number as listed in Table 3. Biot number is defined as the ratio of the external mass transfer to intraparticle mass transfer. While, Peclet number is the ratio of axial convection rate to axial dispersion rate. When the Biot number is high the time of breakthrough point will appear early. These results agree with that obtained by (Babu & Gupta, 2004; Gupta, et. al., 2001; Lin & Wang, 2002; Sulaymon & Ahmed, 2007).

**Figure 7.** Experimental and predicted breakthrough curves for phenol adsorption onto activated carbon at different bed depths

**Figure 8.** Experimental and predicted breakthrough curves for MB adsorption onto amberlite XAD4 at different bed depths
Table 3. Values of Pe and Bi numbers for different flow rates of phenol and MB systems

<table>
<thead>
<tr>
<th>Flow rate (m3/sec)</th>
<th>Phenol system</th>
<th>Flow rate (m3/sec)</th>
<th>Methylen blue system</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Pe Bi</td>
<td></td>
<td>Pe Bi</td>
</tr>
<tr>
<td>1.39×10^-6</td>
<td>19.3 147.6</td>
<td>2.2×10^-6</td>
<td>41.8 49.2</td>
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<tr>
<td>2.78×10^-6</td>
<td>19.7 185.9</td>
<td>2.78×10^-6</td>
<td>42.0 53.0</td>
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<tr>
<td>4.17×10^-6</td>
<td>20.0 212.8</td>
<td>3.33×10^-6</td>
<td>42.2 56.3</td>
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<tr>
<td>8.33×10^-6</td>
<td>20.7 268.0</td>
<td>4.17×10^-6</td>
<td>42.5 60.7</td>
</tr>
</tbody>
</table>

- The experimental and predicted breakthrough curves for phenol adsorption onto activated carbon and methylene blue adsorption onto Amberlite XAD4 at different bed height shown in Figures 9 & 10. Hence, the internal and external resistances are confirmed to be the main parameters that control the adsorption kinetics with the increase of bed depth. An increase in the bed depth of the two types of adsorbent (activated carbon and Amberlite XAD4) will increases the breakthrough time and the residence time of both adsorbate in the column. The increase in the bed depth will increase Pe number with constant Bi number. Table 4 shows the values of Pe and Bi numbers for different bed depth of activated carbon and Amberlite XAD4 at constant flow rate and initial concentration for both adsorbates. These results also agree with results obtained by (Gupta et al., 2001, Sulaymon & Ahmed, 2007, Sulaymon et al., 2009; Malkoc & Nuhoglu, 2006). The breakpoint was related to the flow rate, bed depth and initial concentration, i.e. the time required to reach breakpoint decreases with the increases of flow rate, decreases of bed depth, and increases of solute initial concentration.

Table 4. Values of Pe and Bi numbers for different bed depth for phenol and MB systems

<table>
<thead>
<tr>
<th>Bed depth (m)</th>
<th>Phenol system</th>
<th>Methylene blue system</th>
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<tbody>
<tr>
<td></td>
<td>Pe Bi</td>
<td>Pe Bi</td>
</tr>
<tr>
<td>0.05</td>
<td>33.8 56.5</td>
<td>19.7 185.9</td>
</tr>
<tr>
<td>0.08</td>
<td>- -</td>
<td>31.5 185.9</td>
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<tr>
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<td>42.2 56.5</td>
<td>39.4 185.9</td>
</tr>
<tr>
<td>0.15</td>
<td>63.3 56.5</td>
<td>59.4 185.9</td>
</tr>
</tbody>
</table>

Figure 9. Experimental and predicted breakthrough curves for phenol adsorption onto activated carbon at different flow rates.
Conclusions

1. The granular activated carbon was found to be suitable adsorbent for the removal of organic materials because of its high surface area compared with Amberlite XAD4 which has a lower surface area.

2. The equilibrium isotherm for each solute (phenol and MB) is of favourable type. The obtained data of phenol and MB were correlated with five models. Langmuir models give the best fit for the experimental data.

3. The batch experiments for both solutes were helpful in estimating the isotherm model constants such as isotherm model constants, external mass transfer coefficient and interparticle diffusion coefficient. There was a good matching between experimental and predicted data in batch experiment by using pore diffusion model for all solutes. Hence the transfer of solutes within the activated carbon and Amberlite XAD4 are controlled by pore diffusion.

4. A general rate model which includes axial dispersion, film mass transfer, pore diffusion resistance and non-linear isotherms provides a good description of the adsorption process for both solutes (phenol and MB) in fixed bed adsorber. Fixed bed studies indicates that the time of the breakthrough point decreases with the increases in the flow rate, increases in the initial adsorbates concentration and decreases in the bed height. These results improve the understanding of adsorption phenomena with reference to pore diffusion and are very useful in the design of adsorption column.

Acknowledgment: We would like to express our sincere thanks and deep gratitude to Prof. Hawel Thomas and Dr. Talib Mahdi from the School of Engineering, Cardiff University, Wales, United Kingdom, for experimental supporting and the valuable advices during the work.

Notation

Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR</td>
<td>Reddich-Peterson model parameter</td>
</tr>
<tr>
<td>B</td>
<td>Langmuir constant, l/mg</td>
</tr>
<tr>
<td>Bi</td>
<td>Biot number $\left( \frac{k_f R_p}{e_p D_p} \right)$</td>
</tr>
<tr>
<td>BR</td>
<td>Reddich-Peterson model parameter</td>
</tr>
<tr>
<td>C</td>
<td>Concentration in fluid, kg/m$^3$</td>
</tr>
<tr>
<td>C_o</td>
<td>Initial concentration, kg/m$^3$</td>
</tr>
<tr>
<td>C_e</td>
<td>Concentration of solute at equilibrium, kg/m$^3$</td>
</tr>
<tr>
<td>D_a</td>
<td>Axial dispersion coefficient, m$^2$/sec</td>
</tr>
<tr>
<td>D_m</td>
<td>Molecular diffusion coefficient, m$^2$/sec</td>
</tr>
<tr>
<td>D_p</td>
<td>Pore diffusion coefficient, m$^2$/sec</td>
</tr>
<tr>
<td>d_p</td>
<td>Particle diameter, m</td>
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<tr>
<td>F_RP</td>
<td>Radke-Prausnitz model parameter</td>
</tr>
<tr>
<td>K</td>
<td>Freundlich empirical constant</td>
</tr>
<tr>
<td>k_f</td>
<td>Fluid to particle mass transfer coefficient, m/sec</td>
</tr>
<tr>
<td>K_RP</td>
<td>Radke-Prausnitz model parameter</td>
</tr>
</tbody>
</table>


**Greek symbols**

- \( \varepsilon_b \) Bed porosity
- \( \varepsilon_p \) Porosity of adsorbent
- \( \mu_w \) Viscosity of water
- \( \rho_w \) Density of water, kg/m\(^3\)
- \( \rho_p \) Bulk density of adsorbent, kg/m\(^3\)

**References**


Kinetic Model of the Sorption of Cu$^{2+}$ and Pb$^{2+}$ From Aqueous Solution Using Carbonized Trecilia Africana Husk as Biomass

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$^{1}$Department of Chemistry, Delta State University, Abraka, Nigeria; $^{2}$Chemistry Department, Nnamdi Azikiwe University, Awka; $^{3}$Delta State Polytechnic, Ogwashi-Uku

Received February 22, 2011; Accepted June 29, 2011

Abstract: The sorption kinetics of model (Cu$^{2+}$ and Pb$^{2+}$) from aqueous solution using carbonized Africana brad fruit (Trecilia Africana) husk was investigated. The effect of contact time, variation in mass and particle size of adsorbent and adsorption isotherms were studied. The time-dependent experiment showed rapid sorption between 15-30 minutes with maximum sorption at 30mins, after which the rate of adsorption became almost constant. The sorption capacity is dependent on its particle size. A particle size of 150μm, recorded 88.0% and 88.9% sorption capacity for Cu and Pb respectively. While, 84.7% and 80.9% sorption capacity was observed for a particle size of 300μm for Cu and Pb respectively. Adsorption decreased with increase in mass of biomass. The linear isotherm parameters ($q_m$, $K_l$ and $S_f$) for Langmuir model showed that Trecilia Africana husk has a high adsorption capacity for Pb than Cu, with $q_m$ value of 0.067 and 0.062 respectively. The adsorption coefficient $(K_l)$ was observed as 49.75 and 40.32 for Pb and Cu respectively. The $S_f$ value was obtained as 0.002 and 0.0025 respectively. The separation parameters $(S_f)$ for the two metals are less than unity indicating that the biomass is a very good adsorbent for the metals. The Freundich sorption isotherm constant observed $K_f$ value of Pb as 1.05, greater than 1.02 of Cu obtained and $(1/n)$ adsorption intensity as 0.23 for Pb and 0.20 for Cu, indicating preferential sorption of Pb, by the biomass. The sorption process is not obeying the pseudo-first and second order models for both metals.

Keywords: Heavy metal sorption process, Adsorption isotherms and pseudo-order models

Introduction

The rate of influx of heavy metals into our ecosystem especially our aquatic environment is on the increase. This is due to the geometric increase in the use of heavy metals over the past few decades and little care taken to remove the waste product (Mombershora, Osinbany and Afayi 1983). It is well known that environmental pollution is a product of urbanization, technology and other attendant factors of population density, industrialization and mechanization that serves the necessities of the population and through food chain (Velseky, 2003).

Many heavy metals are toxic at low concentration. However, some heavy metals such as copper and zinc are also essential elements. Concentrations of essential elements in organisms are normally thermostatically controlled with uptake from environment, regulated according to the nutritional demand (Carson, Ellis a Mcatin, 1986). The effects on organisms are manifest when this regulation mechanism breaks down as a result of either insufficient (deficiency) or excess (toxicity) metal (Loe, 2005).

Whether the sources of heavy metal are natural or anthropogenic the concentration in terrestrial and aquatic organisms is determined by the size of the source and adsorption/precipitation in soils and sediments (Nriagu and Pacyan, 1988). The extent of adsorption, depends on the metal, the adsorbent the characteristic of the environment (e.g pH, Waterharches and redox Potential) and the concentration of metals and complex chemicals present in the soil, water, rivers or lake (Ford 1981). The concentration of metals in bioavailable form is not necessarily proportional to the total concentration of the metal (Wesley, 2000).

However, the increasing awareness about eco-toxicological effects of metals has resulted in more stringent legal requirement for reduction in industrial emissions. This therefore necessitates research and development in the area of wastewater treatment. Some of the conventional methods

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which have been used for metal removal include granular activated carbon and reverse osmosis. They are often ineffective or extremely expensive when the initial heavy metal concentrations are in the range of 100-mg/l and when the discharge concentrations are required to be less than 1mg/l (Al-Asheh and Durylak, 1999). These process are however not economically feasible for small scale industries prevalent in developing countries due to large capital investment (Horsfall and Spiff, 2004). Biosorption processes using biomaterials have been developed to decrease the concentrations of hazardous metals in wastewater to acceptable level before being discharged into the environment (Addon Bellocine, Bouldes and Caneau, parus and Maneri 1999).

Industrial wastewater in Nigeria undergoes little or no treatment before being discharged into receiving water bodies or is too expensive. There is therefore the need to explore ways of treating waste using locally available materials such as crop residues. Other researchers have used several indigenous crop residues for wastewater treatment. Cassava waste biomass (Horsfall and Abia 2003), wild cocoyam biomass Horsfall and Spiff 2004. Brewery biomass Tse-young et al 2005 Rhizopus nigricans biomass (Sudha and Abraham 2001) bakers yeast biomass (Mahamdadi and Torto 2007) among others.

The present study evaluates the potentials of Treculia Africana husk biomass as a useful adsorbent for the sorption of some metals. Assess effect of some factors (conditions) in the sorption process. Above all, to examine the adsorption isotherms and kinetic process in the sorption process so as to determine design conditions to operate the process.

Materials and Methods

This research work was aimed at determining the extent and design conditions for the adsorption of heavy metal ions of copper and lead using inactivated carbonized Treculia Africana husk while varying particle size, dosage of adsorbent and contact time.

Collection of sample

The adsorbent was collected from a trader in Eke Akwa market in Awka South Local government Area, Anambra State of Nigeria.

Preparation of stock solutions

The concentration of the stock solution prepared and used was 1000mg/l of copper Nitrate and (1 g/l) lead Nitrate. The copper nitrate was prepared weighing 1000mg of copper Nitrate into a Reagent Bottle dissolving it using 0.5L of Distilled Water and then making it up to 1L, while lead nitrate was prepared by weighing 1000mg of lead Nitrate into a reagent Bottle, dissolving it using 0.5L of Distilled water and then making it up to 1L.

Procedure of adsorption and analysis

Varying particle size of 150μm and 300μm and weighing out 1 g, 2 g, 3 g of the adsorbent, a simple adsorption column was built using a burette set on its stand by packing the adsorbents properly with the tap of the burette locked with a lip. This was done using each weight of each of the particle size. Exactly 10ml of the stock solution measured using a measuring cylinder and emptied into the burette and allowed to stay a contact time of 15, 30, 45, 60 minutes respectively. The effluent containing the unabsorbed metal was ran off after the contact time, collected in a small bottle and analyzed or assayed for Cu and Pb using atomic absorption spectrophotometer, to determine the percentage adsorption (Horsfall and Spiff 2004). The eluted solutions, including the stock solution were analyzed for metal ion of Cu and Pb using atomic absorption spectrophotometer with acetelyn flame of 260°C.

Data evaluation

Calculation of the amount of metal ion removed. The amount of Cu$^{2+}$ and Pb$^{2+}$ ions removed by the biomass during the series of study were determined using a mass balance equation as in equation 1 below.

$$q_e = \frac{V}{M} (C_{o} - C_{e}) \tag{1}$$

Where $q_e$ metal ion concentration on the biomass in mg/g biomass at equilibrium.
Ce = metal ion concentration in solution (mg/l) equilibrium
Coe = Initial metal ion concentration in solution (mg/l)
V = volume of initial metal ions solution used (L)
M = mass of biomass used (g) (Horsfall and Spiff 2004 and Gad and Rome 1988)

**Equilibrium isotherm**

Sorption equilibrium provide fundamental physico-chemical data for evaluating the applicability of phytosorption process as a unit operation usually described by isotherm models whose parameters express the surface properties and affinity of the sorbent. Two adsorption models were used to fit the experimental data. The Longmuir and maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface and expressed by equation 2.

\[
q_e = \frac{q_m KL C_e}{1 + KL C_e}
\]  

(2)

Where KL = Longmuir isotherm constant (LG\(^{-1}\)) qm = Longmuir monolayer adsorption capacity (mg g\(^{-1}\)) the linear form of the above equation after arrangement is given in equation 3.

\[
\frac{C_e}{q_e} = \frac{1}{q_m KL} + \frac{C_e}{q_m}
\]  

(3)

The experimental data were fitted into equation e by plotting C\(_e\)/q\(_e\) against C\(_e\) Freundlich (f) model was chosen to estimate the adsorption intensity of the sorbent towards the biomass and is represented in equation 4.

\[
q_e = Kf(C_e)^{1/n}
\]  

(4)

Where q\(_e\) = the adsorption density (mg of metal ion adsorbed qg biomass), C\(_e\) = the concentration of metal ion in solution at equilibrium (mg/l)
Kf and n are freundlich constant

The value of indicates that the affinity of the sorbent towards the biomass equation is conveniently used in Luker form by taking the natural Logarithm of both sides.

\[
\ln q_e = \ln kf + \frac{1}{n} \ln C_e
\]  

(5)

A plot of ln\(_q_e\) that yields a straight line indicating the confirmation of the Freundlich adsorption isotherm. The constants 1/n and lnkf can be determined from the slope and indicate respectively (Gad & Rome, 1988).

**Kinetic treatment of experimental data**

In order to study the mechanism of adsorption, some equations were applied to the experimental data. The mechanisms employed in the pseudo-first mechanism. The kinetics of sorption by biological materials which have been described previously by the pseudo first order expression given by Langergreen was adopted. The linear form of Langergreen pseudo-first order model is given by the equation below (Gad and Rome, 1988).

\[
\ln (q_e - q_t) = \ln q_e - k t
\]  

(6)

Where q\(_e\) = Mass of metal adsorbed at equilibrium (mg/l)
K = Equilibrium rate constant
A linear plot of \((q_e-q_t)\) versus t confirms the model

The pseudo-second order equation developed by Ho et al for the sorption systems of divalent metal ions using sphagnum moss plant was adopted. The linear form of Ho’s pseudo-second order model is generally expressed as follows:

\[
\frac{1}{q_t} = \frac{1}{h_o q_e^2} + \frac{t}{q_e}
\]  

(7)
Where $q_t$ = the amount of divalent metal ion on the biomass surface (mg/g) as any time $t$, $q_e$ – amount of divalent metal ion sorbed at equilibrium $h_0$ = the initial sorption capacity (mg/gmin).

The initial sorption $h_0$ is shown in equation 8

$$h_0 = k_2 q_e^2$$  \hspace{1cm} (8)

Where; $k_2$ is the pseudo-second order rate constant (g/mgmin)

A linear plot of $t/q_t$ against $t$ confirms the models.

**Results and Discussion**

The result below obtained after analyzing the filtrate gotten after experimental work (i.e after adsorption) for Cu$^{2+}$ and Pb$^{2+}$ using atomic absorption spectrophotometer.

**Table 1. The concentration of unadsorbed metal ion of copper and lead**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Particle size (μm)</th>
<th>Mass (gr)</th>
<th>Time (min)</th>
<th>Copper (Cu$^{2+}$)</th>
<th>Lead (Pb$^{2+}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150</td>
<td>1</td>
<td>15</td>
<td>1.20</td>
<td>1.11</td>
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<td></td>
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<td>3</td>
<td>15</td>
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<td>4.05</td>
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<tr>
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<td></td>
<td>1</td>
<td>30</td>
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<td></td>
<td>3</td>
<td>60</td>
<td>3.42</td>
<td>6.30</td>
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</table>

**Table 2. Cu Adsorption (%)**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Particle size (μm)</th>
<th>Mass (gr)</th>
<th>Time (min)</th>
<th>Copper II (Cu$^{2+}$)</th>
<th>Lead II (Pb$^{2+}$)</th>
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<tr>
<td></td>
<td>150</td>
<td>1</td>
<td>15</td>
<td>88.0</td>
<td>88.90</td>
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<td>15</td>
<td>72.4</td>
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<td>76.0</td>
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<td>55.6</td>
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<td>72.0</td>
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<td>60</td>
<td>65.8</td>
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<td>2</td>
<td>60</td>
<td>47.2</td>
<td>71.8</td>
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<td></td>
<td></td>
<td>3</td>
<td>60</td>
<td>36.1</td>
<td>62.3</td>
</tr>
</tbody>
</table>

**Effect of particle size**

Preliminary adsorption studies of metal ions of copper II and lead II by Africa brad fruit (Treculia Africana) husk indicated the sorption capacity is dependent on its particle size. The sample with 150μm exhibits maximum adsorption efficiency when compared to the sample with 30μm. for example, when considering/comparing the adsorption capacity fo 1g of sample for 15 minutes, 150μm and 30μm of sample adsorbed 88.00% and 84.4% of copper respectively (Table 1a & 2a), while 150μm and 300μm of adsorbent sample adsorbed 88.90 and 80.90 of lead respectively (table 1b and 2b). The same trend was shown by other parameters considered. This increase in adsorption with decrease in particle size may be attributed to the larger surface area of the adsorbent materials (Osei, 2002). Diffusion resistance to mass transport in the case of adsorbent with larger particle sizes is higher and most of the internal surface of these particles may not be utilized for adsorption. Consequently, the amount of metal ions adsorbed is less in such cases (Wase & Hosler, 1996).

**Effect of contact time**

Contact time required for the maximum removal of metal ions of copper II and lead II ions by Treculia Africana husk according to above experimental results showed a step increase in the adsorption in the initial stages of the reaction between 15-30 minute (Table 2a and 2b). maximum adsorption occurred at the 30th minute after which the adsorption remained almost uniform representing the attainment of equilibrium. The could be seen from table 2a and 2b, showing
percentage adsorption of copper II and lead II ions when considering 1g of adsorbent of particle size 150μm at various times of 30, 45 and 6 minutes optimum adsorption took place between 15-30 minute with 73.00% and 76.00% of copper and lead adsorbed respectively. This trend was observed in other parameters. This behaviour indicates the formation of monolayer coverage on the outer interface of the adsorbent. The effect of contact time on adsorption of Cu and Pb is further represented in fig 1 and 2 below.

Figure 1. Effect of contact time on copper. 

Figure 2. Effect of contact time on lead 

Effect of increase in mass (effect of dosages) 

Results of the adsorption experiments using three different masses (dosages), Viz 1g, 2g and 3g of Trecuila Africana husk (carbonized). 10mg/l of copper and 10mg/l of lead (table 1a-2b) showed a decrease in adsorption with increase in mass. This decrease of adsorption with increase in mass of adsorbent may been attributed to the high mass of adsorbent not allowing effective contact between the adsorbent and the metal ions. It is observed when considering different mass of adsorbent (1g, 2g, and 3g) at 15 minutes and 150 pm that 88.00, 72.40, 59.50 of copper was adsorbed respectively and 88.90, 77.40, 74.00 of lead was adsorbed respectively.

Evaluation of bio-sorption efficiency 

Sequestering of metallic specie by biomass has been traced mainly into the cell wall forthe biomass. The cell wall is not necessarily the only site where the sequestered metal might be situation. They may also be found within the cell. Coupled with various organic parts or any crystallized in the cytoplasm. The drying and grinding of bio adsorbent until sites where metal ion could be sequestered, increasing the probability of encountering metal at such site. The biosorption data for the removal of PblI and Cull were evaluated with Longmuir and Freundlich model.

Longmuir Isotherm 

The Longmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to monolayer coverage on the biomass surface. The plots specific sorption ce/qe against the equilibrium concentration Ce for Pb II and Cu II are show in figure e and table 3.

Table 3. Longmuir parameter of Cu

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Ce(mg/l)</th>
<th>qe =V/m (Co-Ce)(mg/l)</th>
<th>Ce/qe(g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.2000</td>
<td>0.0880</td>
<td>13.6364</td>
</tr>
<tr>
<td>30</td>
<td>2.7000</td>
<td>0.0730</td>
<td>36.9863</td>
</tr>
<tr>
<td>45</td>
<td>2.7600</td>
<td>0.0724</td>
<td>38.1215</td>
</tr>
<tr>
<td>60</td>
<td>2.8200</td>
<td>0.0718</td>
<td>39.2758</td>
</tr>
</tbody>
</table>
Table 4. Langmuir parameter for lead

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>C_e (mg/l)</th>
<th>q_e = V/m (C_e - C_m) (mg/l)</th>
<th>C_e/q_e (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.1100</td>
<td>0.0889</td>
<td>12.4859</td>
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<tr>
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<td>2.400</td>
<td>0.0760</td>
<td>31.5789</td>
</tr>
<tr>
<td>45</td>
<td>2.4200</td>
<td>0.0758</td>
<td>31.6623</td>
</tr>
<tr>
<td>60</td>
<td>2.42</td>
<td>0.0757</td>
<td>32.1004</td>
</tr>
</tbody>
</table>

The longmuir

Linear isotherm parameters q_m and K_L are presented in the table 5 below;

Table 5. Presentation of linear isotherm parameters q_m and K_L

<table>
<thead>
<tr>
<th></th>
<th>Copper</th>
<th>Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>q_m</td>
<td>0.062</td>
<td>0.067</td>
</tr>
<tr>
<td>K_L</td>
<td>40.32</td>
<td>49.75</td>
</tr>
<tr>
<td>S_f</td>
<td>0.0025</td>
<td>0.0020</td>
</tr>
</tbody>
</table>

The sorption q_m which is a mass measure of maximum adsorption capacity corresponding to complete monolayer coverage showed that African bread fruit husk has a high adsorption capacity for Pb than Cu which had q_m value of 0.067 and 0.062 respectively the adsorption coefficient K_L which is relate to the apparent energy of (49.75) was greater than that of Cu (40.32).

Further, the favourability of adsorption of the 2 metal ion on the African bread fruit husk biomass using the essential feature of the Langmuir isotherm model expressed in terms of dimensionless constant called separation factor (s_f) (x) the separation factor is defined by the following relationship.

\[ S_f = \frac{1}{1 + \frac{K_L}{C_0}} \]

Where K_L = langmuir isotherm constant, C_0 = initiation concentration of 10mg/l of Cu and 10mg/l of Pb respectively.

The s_f value of Cu is 0.0025 and that of Pb is 0.0020

The parameter indicate the shape of the isotherm as follow;

S_f > 1 unfavorable isotherm
S_f = 0 irreversible isotherm
0 < S_f < 1 favorable isotherm

The separation parameters for the two metals are less than unity indicating that African bread fruit waste biomass is very good adsorbent for the two metal ions. The s_f value of Cu is greater than...
that of \( \text{Pb}^{2+} \) ion. Indicating that in a mixed ion system, \( \text{Cu} \) will adsorb faster than \( \text{Pb}^{+} \) ion. This observed separation factor indicates that high concentration of \( \text{Cu} \) and \( \text{Pb} \) ions in an effluent will not be a limiting factor in the ability of \( \text{Treculia African} \) husk to adsorb metal ions.

**Freundlich isotherm**

The freundlich model was chosen to estimate the adsorption capacity of the adsorbate on the sorbent surface. The linear freundlich isotherm for the sorption of the 2 divalent metal onto \( \text{African bread fruit husk biomass} \) are presented in figure 5 below. Examination of the plot revealed that freundlich isotherm is also an appropriate model for sorption study of \( \text{Cu} \) and \( \text{Pb} \) ion.

![Freundlich Isotherm for Copper](image1)

**Figure 3. Freundlich isotherm for Cu**

![Freundlich Isotherm for Lead](image2)

**Figure 4: Freundlich isotherm for Pb**

Freundlich sorption isotherm constant

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>( i/n )</th>
<th>( K_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.23</td>
<td>1.05</td>
</tr>
<tr>
<td>Cu</td>
<td>0.20</td>
<td>1.02</td>
</tr>
</tbody>
</table>

The \( K_f \) value of \( \text{Pb} \) which is 1.05 is greater than that of \( \text{Cu} \) which is 1.02 suggesting that \( \text{Pb} \) has a greater adsorption tendency towards \( \text{African bread fruit husk biomass} \) than the \( \text{Pb} \). The freundlich equation parameters (\( i/n \)) which is a measure of adsorption intensity \( \text{Pb} \) (0.23) is higher than \( \text{Cu} \) (0.20) indicating a preferential sorption of \( \text{Cu} \) by \( \text{African bread husk biomass} \).

**Kinetic of sorption**

The kinetics of sorption is probably the most important factor in predicting the rate at which sorption takes place for a given system and also very essential in understanding sorber design with sorbate residence time and reactor dimension. However, sorption kinetics shoes a large dependence on the physical and/or chemical characteristics of the adsorbent material, which also influences the sorption process and the mechanism.

**Pseudo-first order model**

A plot of \( \ln (q_e - q_t) \) against \( t \) gave the pseudo first order kinetic from the plot in figure below. It was observed that the relationship between metal ion diffusivity, \( \ln (q_e - q_t) \) and time is non-linear, indicating that the diffusivity metal was onto tequila \( \text{Africana husk biomass} \) surface is film-diffusion controlled. The non-linearity of the diffusivity plot showed that the pseudo-first border equation proposed was not adequate in describing the reaction of two divalent metal ions on the \( \text{Treculia Africana} \) husk biomass. It was found that the larngergreen equation is not a good description for the sorption of the two divalent metals.
PSEUDO-FIRST ORDER REACTION FOR COPPER

![Graph showing pseudo-first order reaction for copper](image1)

**Figure 5:** Pseudo-First order reaction for Cu.  **Figure 6:** Pseudo-First order reaction for Pb

**Table 6:** Pseudo-first order model for Cu;

<table>
<thead>
<tr>
<th>Time (t)</th>
<th>q_e</th>
<th>q_t</th>
<th>q_e-q_t</th>
<th>In(q_e-q_t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.2</td>
<td>0.0880</td>
<td>-1.1120</td>
<td>-0.1062</td>
</tr>
<tr>
<td>30</td>
<td>2.70</td>
<td>0.0730</td>
<td>-2.627</td>
<td>-0.09658</td>
</tr>
<tr>
<td>45</td>
<td>2.76</td>
<td>0.0724</td>
<td>-2.6876</td>
<td>-0.9886</td>
</tr>
<tr>
<td>60</td>
<td>2.82</td>
<td>0.0718</td>
<td>-2.7482</td>
<td>-1.0109</td>
</tr>
</tbody>
</table>

**Table 7.** Pseudo-first order model for Pb

<table>
<thead>
<tr>
<th>Time (t)</th>
<th>q_e</th>
<th>q_t</th>
<th>q_e-q_t</th>
<th>In(q_e-q_t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.11</td>
<td>0.0889</td>
<td>-1.0211</td>
<td>-0.209</td>
</tr>
<tr>
<td>30</td>
<td>2.40</td>
<td>0.0760</td>
<td>-2.324</td>
<td>-0.08433</td>
</tr>
<tr>
<td>45</td>
<td>2.42</td>
<td>0.0758</td>
<td>-2.3442</td>
<td>-0.8519</td>
</tr>
<tr>
<td>60</td>
<td>2.45</td>
<td>0.0757</td>
<td>-2.3543</td>
<td>-1.8557</td>
</tr>
</tbody>
</table>

**Pseudo-first order model**

A plot of t/q_t against t are presented in table below

**Figure 7.** Pseudo- second order for Cu .  **Figure 7.** Pseudo- second order for Pb

The non-linearity of the graph showed that the pseudo-second equation is not a good model for describing the adsorption of Cu^{2+} and Pb^{2+} from aqueous solution using African bread fruit husk.

**Conclusion**

Optimal conclusion for Cu^{2+} and Pb^{2+} uptake by 0 carbonized Treculia Africana husk has been determined. Results indicated that the adsorption increased at early stage between 15-30 minutes and became constant with further increase in time. Increase in the mass of the adsorbent reduced the rate of adsorption. While decreased in the particle size of the adsorption. The equilibrium data fitted very well
into Langmuir and Freundlich isotherms the separation factor or equilibrium parameter obtained from langmuir isotherm, showed adsorption of Cu$^{2+}$ and Pb$^{2+}$ onto Treculia Africana husk is favourable. The data could not fit well into the first and second pseudo-order model indicating that it is not a good model for describing the sorption process. Therefore, Treculia African husk is a good adsorbent for the removal of heavy/or toxic metal in igneous solution. It is hereby recommended to small and medium-scale industries, because it is a cheap and affordable technology and above all environmentally friendly.

Reference
Mombershora C, Osiobany O, Ajayi BO, (1983) Pollution studies on Nigerian river, the onset of lead pollution of surface water. Itactan Emoron Int. 9, 81-84
Experimental Study of Catalytic Activities of Natural and Activated Bentonites of Kosova on $\text{H}_2\text{O}_2$ Dissociation

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Abstract: The result of an experimental study of catalytic activities of Kosova bentonites on $\text{H}_2\text{O}_2$ dissociation is presented. Despite the fact that the specific surface of bentonite researched grow up to a certain degree of activated acid with case catalytic ability should be increased, the results from table 1 show that activation with hydrochloric acid 10% and 20% causes decrease in catalytic activity of Gushica bentonite. Among natural bentonites, the best results have shown bentonites of Kabash and Gushicë localities, while despite the fact that bentonite of Karâçevë locality contains more montmorillonite than bentonites of the other two localities its catalytic activity was less intensive. Additional studies with bentonites activated with HCl as well as complementary studies with X-ray diffraction and ESR spectroscopy have shown that catalytic activity of natural bentonites of Gushicë and Kabash is linked not only with montmorillonite but also with Mn$^{2+}$ present in calcite and dolomite minerals contained in these bentonites. The bentonite of Gushicë locality activated with 3% Na$_2$CO$_3$ have shown the best catalytic activity, partially due to the alkalinity of the solution formed by dissolution of this bentonite in water.

Keywords: bentonit, montmorillonite, $\text{H}_2\text{O}_2$, catalyst, complementary research.

Introduction

Kosova possesses large bentonite resources. Geologic explorations show that the locations of these deposits are concentrated in two main regions: in Kamenica (Dardana) and in Vitia. The main deposit in the region of Kamenica is that of Karâçevë, and the most important deposits in Vitia are those of Gushica, Sadovinës of Jerlive and Kabash.

The exploration of different chemical-physical characteristics of bentonites in Kosova is of double importance. On one hand, bentonites serve for many purposes in different fields of industry, and on the other hand, they are abundant in Kosova and they can be used for the economic development in Kosova. Among the most important characteristics of bentonites are also their catalytic abilities, thus, as part of large explorations related to the physical-chemical characteristics of bentonites in Kosova were also explored their catalytic abilities, which are the focus of this study (Pula-Beqiri, 2006). Based on data from the literature, the catalytic abilities of bentonites increase with their acidic activation, therefore, besides the natural samples of deposits in Gushica, Kabash and Karâçevë were also explored the activated samples of bentonite in Gushica, where the largest number of resources is found (Grim, 1967). Explorations were carried out in the natural samples. The activation was made with different concentrations of chlorhydric acid (10%, 20% and 30%) and with sodium carbonate (3%). The exploration of catalytic abilities was done against the dissolution of hydrogen peroxide ($\text{H}_2\text{O}_2$).

In order to acquire extensive knowledge, besides the research of the kinetics of hydrogen peroxide, complementary explorations of the structure of bentonites were also conducted (Pula-Beqiri, 2006).

Material and Methods

In order to determine the catalytic abilities of bentonites in Kosovo against the dissolution of $\text{H}_2\text{O}_2$ the gasimetric method was used (Kola, 1986). The essence of the method consists in the time monitoring of the volume of oxygen emitted upon the dissolution of hydrogen peroxide in certain temperature:

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Given the small constant of the speed of hydrogen peroxide dissolution at room temperature, the measurements of catalytic activity of bentonite argils were taken at temperature 50°C, through uninterrupted stirring of the mixture and keeping constant reaction temperature. The emitted volume of oxygen was measured on the basis of the compressed volume of water located in scaled U-tube, a wing of which was subjected to atmospheric pressure, and the other wing was connected to hermetically sealed space, in which the reaction of peroxide dissolution takes place.

\[ 2H_2O_2 \rightarrow 2H_2O + O_2 \]

The scaled tube is kept at constant room temperature. The apparatus used for measuring the catalytic activity of hydrogen peroxide dissolution was assembled by standard laboratory devices, whereas the apparatus scheme is presented in figure 1. The measurements were taken in the following conditions: The temperature of surrounding air \( T_a = 295K \), reaction temperature \( T_r = 323K \), air pressure \( p_a = 102,057kPa \), normal air pressure \( p_0 = 101,324kPa \), water steam pressure (20°C) \( p_{sw} = 5,32kPa \), volume of solution 1,33% \( \text{H}_2\text{O}_2 \) \( V_o = 40ml \), volume of emitted oxygen during the full dissolution of 40 ml of the solution, 1.33% of \( \text{H}_2\text{O}_2 \) in normal conditions \( V_k = 175 \cdot 10^{-6} m^3 \).

The preliminary processing of acquired experimental data showed that the reaction of hydrogen peroxide dissolution can be approximated with the chemical reaction of first class, meaning that the time dependence of the volume of emitted oxygen can be presented by way of equation:

\[
\ln \left( \frac{V_k}{V_k - V} \right) = V \cdot k \cdot t \quad \text{(1)}
\]

\[
V = \frac{y}{0.00014514x} \quad \text{y = 0.00014514x}
\]

\[
V = \frac{y}{0.0001314x} \quad \text{y = 0.0001314x}
\]

\[
V = \frac{y}{0.00005813x} \quad \text{y = 0.00005813x}
\]
Including:

\( V_k \) - the volume of oxygen made up during the full dissolution of \( \text{H}_2\text{O}_2 \) present in the solution (\( \text{m}^3 \)), \( V \) - volume of emitted oxygen (\( \text{m}^3 \) normal), \( t \) - time (s), \( k \) - reaction constant (s\(^{-1}\)).

The results of the measurements for the natural bentonites of Gushica, Kabash and Karaçeva were graphically presented in the figure 2. The respective values of constants for the dissolution of hydrogen peroxide in the presence of natural bentonites of Gushica, Kabash and Karaçeva, acquired through the statistical processing of data, are presented in the table 1.

<table>
<thead>
<tr>
<th></th>
<th>( k (\text{s}^{-1}) )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral water solution</td>
<td>0.0000030</td>
<td>0.995</td>
</tr>
<tr>
<td>0.1N NaOH</td>
<td>0.0000423</td>
<td>0.985</td>
</tr>
<tr>
<td>Karaçeva bentonite</td>
<td>0.0000581</td>
<td>0.996</td>
</tr>
<tr>
<td>Kabash bentonite</td>
<td>0.0001451</td>
<td>0.989</td>
</tr>
<tr>
<td>Gushica bentonite</td>
<td>0.0001131</td>
<td>0.995</td>
</tr>
<tr>
<td>Gushica bentonite activated with 10% HCl</td>
<td>0.0000337</td>
<td>0.991</td>
</tr>
<tr>
<td>Gushica bentonite activated with 20% HCl</td>
<td>0.0000318</td>
<td>0.997</td>
</tr>
<tr>
<td>Gushica bentonite activated with 3% Na(_2)CO(_3)</td>
<td>0.0002119</td>
<td>0.995</td>
</tr>
</tbody>
</table>

Discussion of Results and Conclusion

The results of the research of hydrogen peroxide dissolution with or without the presence of natural bentonites show that the bentonites of Kosova possess certain catalytic abilities for the development of this reaction, since the respective constants of the reaction are much higher than the constant of the reaction of respective dissolution in neutral water solution and slightly higher than the constant of the reaction of dissolution in alkaline water solution. Of natural bentonites, the highest catalytic activity against the dissolution was showed by the bentonite of Kabash, followed by that of Gushica, and the smallest activity was showed by the bentonite of Karaçeva. This data is not in concordance with the results of defractometric measurements taken as part of this study (figure 3), since the natural bentonite of Karaçeva in itself contains more montmorillonite than the bentonite of other two deposits, its catalytic activity against the dissolution of hydrogen peroxide is not in concordance with this data. (Grim, 1967; Skarchenko, 1963)

![Rentgenograms of natural bentonites of Kosova](image)
Table 2. Classical chemical analyse of main components bentonites of Kosova (%)

<table>
<thead>
<tr>
<th>Samples</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>Losses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Gushica</td>
<td>54.58</td>
<td>14.51</td>
<td>6.38</td>
<td>6.19</td>
<td>3.48</td>
<td>2.43</td>
<td>0.38</td>
<td>11.43</td>
</tr>
<tr>
<td>2-Kabash</td>
<td>41.96</td>
<td>12.61</td>
<td>5.98</td>
<td>13.15</td>
<td>3.75</td>
<td>2.85</td>
<td>0.41</td>
<td>19.09</td>
</tr>
<tr>
<td>3-Karaçeva</td>
<td>52.42</td>
<td>18.24</td>
<td>3.99</td>
<td>2.56</td>
<td>3.58</td>
<td>0.75</td>
<td>0.43</td>
<td>15.52</td>
</tr>
</tbody>
</table>

The explanation of this discordance was possible only through the complementary defractometric study, ESR-spectroscopic and chemical, on grounds of the experimental data of the dissolution of hydrogen peroxide in the presence of activated bentonites. Despite the fact that specific surface of explored bentonites is increased to a certain extent of acid activation, which would result in the increase of catalytic ability (Grim, 1967; Kola, 1986), the results from table 1 show that the activation with chlorhydric acid 10% and 20% results in the decrease of catalytic activity of the bentonite of Gushica.

ESR-spectroscopic research under this study show that the presence of ions Mn²⁺ is expressed in both, bentonite of Gushica and that of Kabash, and much less in the bentonite of Karaçeva, and that through acidic activation of bentonite of Gushica and Kabash these ions practically disappear (figure 4). On the other hand, defractograms of the samples of Gushica and Kabash activated by chlorhydric acid show that during this activation calcite and dolomite are washed off bentonites.

Given these circumstances, it is reasonable to claim that one part of catalytic activity of natural bentonites of Kosovo is related to the presence of ions of manganese in the minerals of calcite and dolomite found in natural bentonites. Such claim is also confirmed by figure 5, which describes the dependence of the constant of hydrogen peroxide dissolution on the contents of calcium and magnesium oxides in natural bentonites, which are determined by the classical chemical analysis.

As presented in table 1, after the removal of greatest part of calcite and dolomite from the natural bentonite of Gushica through acidic activation, its catalytic activity falls under the catalytic abilities of natural bentonite of Karaçeva (see figure 3). This data is in concordance with the fact that catalytic abilities of bentonites in general depend on the quantity of montmorillonite present in bentonites.

Figure 4. ESR-Spectrograms of natural and activated bentonites of Kosova
Of all explored samples, bentonite of Gushica with 3% Na$_2$CO$_3$ showed the best catalytic abilities against the hydrogen peroxide dissolution. This data is explained by the fact that the created water environment of this bentonite is alkali, in which environment the dissolution of hydrogen peroxide is much more expressed than in the neutral water environment—see table 1.

![Dependence of reaction constant of hydrogen peroxide dissolution on the content of CaO and MgO in the bentonites of Kosova](image)

**Figure 5.** Dependence of the constant of reaction of hydrogen peroxide dissolution on the content of CaO and MgO in the bentonites of Kosova

Given the large resources of bentonite that Kosova possesses, the exploration of their chemical-physical characteristics is in the interest of economic development of municipalities that possess these resources, but also of Kosova in general.

The gasimetric, rentgenographic and ESR spectrometric research of H$_2$O$_2$ dissolution in the presence of bentonite has showed that:

- Of natural bentonites, the best catalytic characteristics against the reaction of hydrogen peroxide dissolution were manifested by the bentonites of deposits in Kabash and Gushica, whereas the bentonite of the deposit in Karaçeva was less active, despite the fact that it contains more montmorillonite than the bentonites of other two deposits.
- Given that the catalytic activity of bentonites derives from the quantity of montmorillonite present in them, this deviation showed the need for additional experimental research not only in natural bentonites but also in the activated ones.
- The additional exploration of bentonites activated with chlorhydric acid as complementary roentgenographic and spectroscopic research showed that the catalytic activity of natural bentonites of Gushica and Kabash derives not only from montmorillonite but also from the ions of manganese contained in the minerals of calcite and dolomite of these bentonites.

This was determined that different chemical-physical characteristics of bentonites require complementary complex research and good scientific explanation in order to avoid wrong and ambiguous conclusions.

**References**


Study of Pesticide-Induced Changes in Anabaena fertilissima, Aulosira fertilissima and Westiellopsis prolifica

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Abstract: The biotransformation of four pesticides to different functional groups on four days interval was studied using biomass of three different cyanobacterial species- Anabaena fertilissima Rao, Aulosira fertilissima Ghose and Westiellopsis prolifica Janet by Fourier Transform Infrared (FT-IR) Spectroscopy. This study demonstrated different absorption peaks associated with phenols and alcohols, aromatic amines, aromatics, carboxylic acids, 1°, 2° amines, alyknes, alkyl halides and nitro compounds generated by different concentration treatments of pesticides on Anabaena fertilissima. In 2,4-D and pencycuron treated Aulosira fertilissima the peaks of nitro compounds, 1°, 2° amines, aromatics, aromatic amines, carboxylic acids, 1°amines and aliphatic amines were involved in pesticide-bioma ss interaction. Moreover, the IR bands of Tebuconazole treated Aulosira fertilissima suggested unique functionalities, i.e., 1°, 2° amines and 1°amines, whereas no new peaks were recorded in Endosulfan treatments as compared to the untreated cultures. With respect to untreated biomass of Westiellopsis prolifica, differences in the peak patterns of four selected pesticide treated cultures were attributable to the presence of aromatic amines, aliphatic amines, carboxylic acids, aromatics, alkenes and 1°amines. Several other such changes were also evident and revealed that FT-IR technique proves to be an efficient tool for detecting structural and compositional changes in functional groups and probable binding sites induced by the presence of a pesticide contamination.

Keywords: Cyanobacterial species, Endosulfan, Fourier Transform InfraRed (FT-IR) spectroscopy, Pencycuron, Tebuconazole, 2,4-D

Introduction

Fourier Transform Infrared (FT-IR) spectroscopy analysis not only allows the identification of inorganic and organic functional groups but also elemental composition (Kögel-Knaber, 2000). The composition and structure of molecular functional groups can be determined by analyzing the position, width, and intensity of infrared light absorption (Yee et al., 2004). According to Davis et al., (2003), the ability of algae to adsorb and accumulate xenobiotics mainly depends upon its chemical composition and the algal samples were studied using FT-IR technique. During the last decade, FT-IR spectroscopy has proven and accepted to be a powerful tool for the study of functional groups in biological samples (Dumas and Miller, 2003). The primary reason for this is that common biomolecules such as nucleic acids, lipids and carbohydrates, have characteristic functional groups having unique molecular vibrational modes (vibrational fingerprints) corresponding to specific infrared light frequencies (Griffiths and de Haseth, 1986).

Cyanobacteria (also known as blue-green algae) are the largest and most diverse group of photosynthetic prokaryotes. Their habitats vary from fresh and marine water to terrestrial environments. They are oxygen-evolving organisms that respond to stress conditions such as light deprivation (Borbely et al., 1990.). These cells have developed natural methods of responding to metals such as copper, lead, and cadmium through passive accumulation in cells and through surface binding to various functional groups. The mats have also been shown to degrade many organic compounds including trinitrotoluene, chrysene, naphthalene, hexadecane, phenanthrene, polychlorinated biphenyl, trichloroethylene, and the pesticides chlordane, carbofuran, and paraquat (Kuritz & Wolk, 1994). Perchloroethylene (PCE) and trichloroethylene (TCE) are common xenobiotic

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contaminants that are recalcitrant to degradation. Recent experiments have demonstrated a significant potential for microbial mats to assimilate and transform the organic compound PCE and TCE in aqueous media (O’Neill et al., 1998). The aim of this study was to carryout FT-IR spectroscopic technique to study in vivo changes in diverse functional groups induced by four different pesticides in three cyanobacterial species and to detect the biotransformation by 2,4-D ethyl ester, Pencycuron, Endosulfan and Tebuconazole on living cyanobacterial cells.

Materials and Methods
Incubation and maintenance of culture
Anabaena fertilissima, Aulosira fertilissima, Ghose and Westiellopsis prolifica, Janet were obtained from Centre for conservation and utilization of Blue-Green Algae, IARI, New Delhi, India and was cultured in BG-11 medium (Rippka, 1979) and maintained at room temperature (25±2°C), illuminated by 2500-3000 lux light for 14:10 h light/dark periods.

Axenic cultures were grown in nitrogen-free BG11 medium for heterocystous, nitrogen fixing forms. All the experiments were carried out in replicates. Samples were thoroughly homogenized and drawn during exponential phase of growth for further analysis. 2,4-D (38% EC 2,4-D ethyl ester), Monceren (22.9% SC Pencycuron), Endocel (35%, Endosulfan) and Folicur (25.9%, Tebucoazole) were procured from Northern minerals limited, Haryana, Bayer Crop Science limited, Mumbai, Excel Crop Care, Gujarat and Bayer Crop Science, Mumbai respectively (Table 1).

<table>
<thead>
<tr>
<th>Xenobiotic compound</th>
<th>Class of compound</th>
<th>Structure</th>
<th>IUPAC name</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-D</td>
<td>Herbicide</td>
<td><img src="image" alt="Structure" /></td>
<td>Ethyl Ester of 2,4-Dichloro Phenoxy Acetic Acid</td>
</tr>
<tr>
<td>Pencycuron</td>
<td>Fungicide</td>
<td><img src="image" alt="Structure" /></td>
<td>N-[(4-chlorophenyl)methyl]-N-cyclopentyl-N'-phenylurea</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>Organochin insecticide</td>
<td><img src="image" alt="Structure" /></td>
<td>6,7,8,9,10,10 hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine-3-oxide</td>
</tr>
<tr>
<td>Tebuconazole</td>
<td>Triazole fungicide</td>
<td><img src="image" alt="Structure" /></td>
<td>1-(4-Chlorophenyl)-4,4-dimethyl-3-(1,2,4-triazol-1-ylmethyl)pentan-3-ol</td>
</tr>
</tbody>
</table>

LC₅₀ values of the organisms for 2,4-D, Pencycuron, Endosulfan and Tebuconazole were determined in terms of quantitative estimation of chlorophyll-a and accordingly, various concentrations of the pesticides were used in all further experiments (Table: 2). Sterile cultures and conditions are maintained throughout the experimental period. Stock solution of both the pesticides were prepared in sterilized double-distilled water and added aseptically to the culture medium to the final concentrations indicated for each treatment. Samples (Control and treated) were taken after every four days, dried and powdered for further analysis using Fourier Transform Infrared Spectroscopy (FT-IR).
Table 2. The pesticide treatments of the test organisms for 2,4-D ethyl ester, Pencycuron, Endosulfan and Tebuconazole based on their LC$_{50}$ values

<table>
<thead>
<tr>
<th>Xenobiotic compound</th>
<th>Class of compound</th>
<th>Organisms selected for study</th>
<th>Treatments decided based upon LC$_{50}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anabaena fertilissima</td>
<td>Herbicide</td>
<td>Aulosira fertilissima</td>
<td>15, 30, 60, 20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Westiellopsis prolifica</td>
<td>40, 80, 30, 60</td>
</tr>
<tr>
<td></td>
<td>Pencycuron</td>
<td>Aulosira fertilissima</td>
<td>3, 6, 12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Westiellopsis prolifica</td>
<td>10, 20</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>Insecticide</td>
<td>Aulosira fertilissima</td>
<td>7.5, 15, 30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Westiellopsis prolifica</td>
<td>15, 30</td>
</tr>
<tr>
<td>Tebuconazole</td>
<td>Fungicide</td>
<td>Aulosira fertilissima</td>
<td>30, 60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Westiellopsis prolifica</td>
<td>30, 60</td>
</tr>
</tbody>
</table>

Sample Preparation for Fourier Transform Infrared Spectroscopy (FT-IR)
Sample preparation was carried out as described by Naumann et al., (1991). Known weight of algal samples (1 mg), dried after four days was taken in a smooth agate mortar and mixed thoroughly with 2.5 mg of dry potassium bromide (KBr) using a pestle. The powder was filled in the micro-cup of 2 mm internal diameter to obtain the diffuse reflectance infrared spectrum for replicate samples. All IR spectra were recorded at room temperature (26 °C ± 1 °C) in the mid infrared range (4000–400 cm$^{-1}$) using Perkin-Elmer FT-IR Spectrophotometer (Perkin Elmer Model No. 337).

Results and Discussion
The FT-IR spectrums of four pesticide treated Anabaena fertilissima, Aulosira fertilissima and Westiellopsis prolifica at their highest concentrations are depicted in Figures 1, 2 and 3.

FT-IR analysis of Anabaena fertilissima exposed to four different pesticides
FT-IR spectrum of the 2,4-D ethyl ester adsorbed biomass of A. fertilissima showed many changes of band over the herbicide-free biomass. Although different treatments of 2,4-D on A. fertilissima reflected a consistent absence of 1703 cm$^{-1}$ which attributed to C=O of $\alpha$, $\beta$ unsaturated aldehydes, ketones and 1321 cm$^{-1}$ to C-N stretch of aromatic amines, and newer peaks of 3511 cm$^{-1}$ indicating O-H of phenols & alcohols were detected in all the treatments. The region 3700–3300 cm$^{-1}$ is characteristic
for O-H and N-H stretching vibrations (Guo and Zhang, 2004). However, the only peak of 869 cm\(^{-1}\) representing C-H of aromatics was recorded at the highest concentration (60 ppm) after 4 days of herbicide exposure.

Each treatment of endosulfan on \(A. \text{fertilissima}\) indicated the nonexistence of C-O stretch falling in the wavelength of 1238 cm\(^{-1}\) and 1113cm\(^{-1}\) (alcohols, carboxylic acids, esters and ethers), C-N stretch having a wavelength of 1037 cm\(^{-1}\) (aliphatic amines). The shift of peak from 1030-1110 cm\(^{-1}\) could be due to involvement of the C-O of polysaccharide in the biosorption process (Han et al., 2007). A common functional group of aromatics (C-C stretch (in-ring)) of a wavelength 1410cm\(^{-1}\) was noted in 3 ppm and 6 ppm treatments. Moreover, all the treatments also induced new functional group of alkyl halides C-Br stretch in the wavelength of 515-690 cm\(^{-1}\).

*Figure 1* The FT-IR Spectrum pattern of (A) untreated (B) 30 ppm 2,4-D treated (C) 12 ppm Endosulfan treated (D) 30 ppm Pencycuron treated (E) 30ppm Tebuconazole treated \(Anabaena \text{ fertilissima}\) after 4 days of exposure.
The IR spectrum of pencycuron treated biomass showed the omission of a single peak, (1703 cm\(^{-1}\)). The absorption wavelength at 1703 cm\(^{-1}\) could be assigned to the C=O stretching vibration of \(\alpha,\beta\) unsaturated aldehydes, ketones. Comparing the IR spectrum of three Pencycuron treatments, addition of aromatic amines (C-N stretch) at 30ppm, while carboxylic acids (O-H stretch) and 1\(^o\), 2\(^o\) amines (N-H wag) at 60ppm of the absorption wavelengths of 1313, 3109 and 870 cm\(^{-1}\) respectively were observed. The O–H group stretch can also occur from carboxylic acids (COOH) and is extremely broad, ranging from 3400 to 2400 cm\(^{-1}\) which often interferes with C–H absorptions (Pavia et al., 1979).

\textbf{Figure 2} The FT-IR Spectrum pattern of (A) untreated (B) 80 ppm 2,4-D treated (C) 30 ppm Pencycuron treated (D) 60 ppm Endosulfan treated (E) 60 ppm Tebuconazole treated \textit{Aulosira fertilissima} after 4 days of exposure.

\textit{A.fertilissima} treated with tebuconazole led to the stimulation of newer functional groups such as nitro and aromatic compounds indicated by N-O symmetric stretch and C-C stretch (in ring) at wavelengths of 1549cm\(^{-1}\) and 1415 cm\(^{-1}\) as well as elimination of aromatic amines ((C-N stretch) at 1321cm\(^{-1}\).
**FT-IR analysis of Aulosira fertilissima exposed to four different pesticides**

An induction of new functional groups such as nitro compounds (N-O symmetric stretch at 1339-1342 cm\(^{-1}\)), 1°, 2° amines (N-H wag at 869 cm\(^{-1}\)), aromatic amines (C-N stretch at 1285 cm\(^{-1}\)) and aromatics (C-C stretch (in-ring) at 1425 cm\(^{-1}\)) were observed solely at the highest concentration (80 ppm) of 2,4-D treated *Aul. fertilissima* after 4 days of exposure.

Endosulfan treatment did not stimulate any significant changes in the functional groups of the organism. A similar fashion of peak arrangement was also noted in Tebuconazole treatments after 4 days of exposure. A major change observed was the development of new functional groups of 1°, 2° amines (N-H wag at 779 cm\(^{-1}\)).

Moreover, pencycuron incubation induced nitro compounds (N-O symmetric stretch) of 1348 cm\(^{-1}\) at 15 ppm, alcohols, carboxylic acids, esters, ethers of 1313-1244 cm\(^{-1}\) (C-O stretch) at 30 and 60 ppm and an exceptional presence of carboxylic acids (O-H bend) of 929 cm\(^{-1}\) at 60 ppm.

**Figure 3** The FT-IR Spectrum pattern of (A) untreated (B) 120 ppm 2,4-D treated (C) 200 ppm Pencycuron treated (D) 40 ppm Endosulfan treated (E) 60 ppm Tebuconazole treated *Westiellopsis prolifica* after 4 days of exposure.
FT-IR analysis of Westiellopsis prolifica exposed to four different pesticides

As compared to the control, the spectra of all the treatments of 2,4-D on *W. prolifica* biomass resulted in the occurrence of one common functional group, aromatic amines (C-N stretch) with a wavelength of 1288 cm\(^{-1}\). While exposure of pencycuron generated new peaks with wavelengths of 1597 cm\(^{-1}\) and 1245 cm\(^{-1}\) representing aromatics (C-C stretch (in-ring)) and aliphatic amines (C-N stretch) respectively when compared to control. An initial treatment of endosulfan to *W. prolifica* resulted in the development of alkenes (-C\(=\)C-) falling in the wavelength of 1652 cm\(^{-1}\). Tebuconazole incited a new functional group of alkenes (-C\(=\)C-) of wavelength 1651 cm\(^{-1}\), whereas 1° amines (N-H bend) of 1647 cm\(^{-1}\) were documented. Functional groups present on the cell surface can be detected by FT-IR as each group has an unique absorption band (Majumdar et al., 2008). The metal absorption is dependent on factors such as quantity of sites, their accessibility, chemical state and affinity between site and metals (Khambhaty et al., 2009). Several other researchers have also used FT-IR technique for studying changes in the chemical composition in higher plants and algae (Sheng et al., 2004).

The differences in the peak pattern observed in the functional groups of each treated organism when compared to the control may be a result of the metabolic changes occurring after pesticidal exposure (Nirmal Kumar et al., 2010).

**Conclusion**

FT-IR is a reliable and efficient tool for studying stress-induced changes in cyanobacterial species-*Anabaena fertilissima*, *Aulosira fertilissima* and *Westiellopsis prolifica* under pesticide contamination. This technique is sensitive and is particularly important when a large number of samples need to be analyzed in a short period of time as it involves minimum sample preparation steps and requires very small quantity (≤2 mg) of sample to yield IR spectrum. Based on this technique, it can be inferred that the order of pesticide tolerance of each organism towards 2,4-D and Pencycuron can be described as *Westiellopsis prolifica* > *Aulosira fertilissima* > *Anabaena fertilissima*, whereas for endosulfan and tebuconazole, it can be expressed as *Anabaena fertilissima* > *Westiellopsis prolifica* > *Aulosira fertilissima*. Hence, it is possible to identify the transformation of broad chemical composition of biological samples using FT-IR which uses a non-invasive extraction-less method.

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**References**


and Surfaces B: Biointerfaces 63, 138–145.


The Management of Thermal Quantity and Carbon Monoxide during Lignite Combustion

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1,2Faculty of Mining and Metallurgy, UP Mitrovica, Kosovo; 3American University in Kosovo, Prishtina, Kosovo

Abstract The impact of gases from the lignite combustion in the production of electrical power is a current crucial factor for planning and development of thermo-energetic companies. Furthermore, it is a sensitive area of study that has an influence in the overall environmental issues. The paper’s objective is to analyze the issue of effective management of thermal quantity during lignite combustion and emissions of gases that are product of full and non-full combustion of lignite in the furnace. Thus, the losses of thermal quantity at ignition and during combustion of lignite directly depend on the diameter of lignite pieces intended for combustion. Paper contains the analyses of the thermal value, the composition of combustible and non-combustible materials of Kosova’s lignite. The research on theoretical and practical field of management of thermal quantity of lignite is based and verified by DIN 1942, 1952, 1956 standards which describe effective thermal quantity and losses of thermal quantity during the process of lignite combustion in furnaces.

Key words: Combustion, boilers, lignite, carbon, and carbon monoxide.

Introduction

Boilers and combustion of lignite in "The Corporation of Energy in Kosovo " are basic processes for economic and environmental sustainability of the Energy Corporation. The paper analyses the process of combustion of lignite in the oxidizing zone by minimizing the burning of carbon that is related to hydrogen, the hydrogen combustion, the sulfur combustion, the melting area and the grace area. The paper also examines the chemical composition, the power and the thermal value of lignite which depends on the percentage of carbon, hydrogen, sulfur, moisture and sterile parts.

In particular, the thermal balance of quantity of lignite in Kosovo will be analyzed for full combustion of lignite where we have as a product the carbon dioxide and a good use of the thermal quantity of lignite. It is also analyzed the balance of thermal quantity for incomplete combustion of lignite, where as a product we have the carbon monoxide and also losses of the thermal quantity of lignite in the process of combustion in boilers. Also, we have rich gases with carbon monoxide, which release the thermal quantities in the environment, also pollute the environment and reduce the economic sustainability in the technological process in the energy corporations.

Energy resources

There are many energy resources that are being used while some resources are very little used, the main pillars of energy resources are:

- Capital resources of energy and
- Flowing resources of energy.

Capital resources of energy are the energies of natural and artificial burning substances that are limited. Capital resources of energy are also considered the nuclear energies. Capital resources of energy of artificial burning substances are considered as commercial energies that cover the consumption of energy approximately 75% worldwide while 25% of energy consumption is covered by liquid energy resources. Table 1 shows the energy consumption at world level.

The world energy reserves according to global convention are approximately 1500 billion tons of stone lignite which have caloric value of 29 260 kJ / kg while nuclear reserves of energy substances are 37 500 billion tons of high thermal value and with limited quantity. Resources of flowing energy

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are e.g. sun energy, wind energy, energy of gasses that are considered with economic and environmental sustainability.

Table 1. The energy consumption at world level.

<table>
<thead>
<tr>
<th>Type of energy</th>
<th>Energy consumption in percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial resources of energy</td>
<td>75%</td>
</tr>
<tr>
<td>Resources of flowing energy</td>
<td>25%</td>
</tr>
</tbody>
</table>

Figure 1. The energy consumption at world level is graphically presented.

Fuels

Fuels are substances that during the oxidation (combustion) release thermal quantity which are practically consumed in different branches of the economy. In order to be considered a fuel a substance has to meet some criteria:

- It must have certain speed of combustion, meaning the oxidation should be done quickly by releasing thermal quantity,
- It should have good thermal value,
- It should not be expensive,
- It should be easily transported and stored,
- It should be stable in certain range of temperature,
- It should not release toxic gases during the oxidation (burning) to the environment

Composition of fuel

The main components of fuel are carbon, hydrogen, sulfur, moisture and heterogeneous composition of oxygen, nitrogen and ash.

Determinant of quality fuel is moisture and ash which reduce the quality of fuel. Analytical composition of the fuel-Kosovo lignite is as follows:

\[
C+H+O+N+S+W+A=100
\]

Thus, based on laboratory analysis has this proportion of the elements.

C 27%, H 2.20%, O 13.63%, N 0.0100%, 0.63% S, W 40.7%, A 14.8%.

Only fuels and combustible materials consist of non-combustible materials mentioned above and presented in Figure 2.

Figure 2. Graphically presents the composition of fuel.
Sulfur, sulfate, ash, and moisture in the fuels are substances without good thermal value. Carbon in fuel is found detached and as such determines the heating value of fuel, and is also associated with hydrogen as methane, ethane, propane, etc.

**Lignite combustion**

The lignite combustion is a complex process and involves four areas: heating area, the area of reduction, oxidation zone and the area of ashes. The oxidation - burning zone is the object of study in the paper. Products of complete combustion of lignite are $\text{CO}_2$ and $\text{H}_2\text{O}$ and the incomplete combustion of lignite are $\text{CO}$ and $\text{H}_2$.

**The carbon combustion**

The full combustion of carbon is done according to the below expression:

$$\text{C} + \text{O}_2 = \text{CO}_2 \quad \Delta H = 33910 \text{ kJ}$$

In order to find absolute enthalpy of a kilogram of carbon we use the expression

$$\Delta H_c = 33910 \times 100\% / \text{PMC} \text{ kJ/ kg}$$

$100\%$ represents the percentage of carbon that binds with oxygen (combustion of carbon).

$\text{PMC}$ represents the molecular weight of carbon.

$$\Delta H_c = 33910 \times 100\% / \text{PMC} = 33910 \times 1 / 12 = 2825.8 \text{ kJ/kg}$$

**Alternative I** with relative combustion, or $50\%$ of carbon is attached with oxygen, then the enthalpy is:

$$\Delta H'_{c} = 33910 \times 50\% / \text{PMC} = 1412.9 \text{ kJ/kg}$$

**Alternative II** with weak combustion, or $50\%$ of carbon is related with oxygen, then the enthalpy is:

$$\Delta H''_{c} = 33910 \times 50\% / \text{PMC} = 1412.9 \text{ kJ/kg}$$

In order to find the thermal quantity acquired with carbon combustion we use the expression:

$$Q = m \times \Delta H \text{ kJ/h}$$

$m$ – the carbon weight,

$\Delta H$ – enthalpy

With $100\%$ carbon combustion the thermal quantity acquired is:

$$Q = 100\% \times \Delta H_c = 2825.8 \text{ kJ/h}$$

**Alternative I** with $80\%$ carbon combustion the thermal quantity acquired is:

$$Q' = 80\% \times \Delta H'_{c} = 1808.4 \text{ kJ/h}$$

**Alternative II** with $50\%$ carbon combustion the thermal quantity acquired is:

$$Q'' = 50\% \times \Delta H''_{c} = 706.4 \text{ kJ/h}$$

In table 2 is represented the thermal quantity acquired according to the percentage combustion of carbon.

![Figure 3](image)

**Figure 3.** Presents the thermal quantity acquired carbon combustion.
Table 2. Presents the thermal quantity acquired with carbon combustion.

<table>
<thead>
<tr>
<th>The percentage of carbon combustion (%)</th>
<th>The carbon weight (kg)</th>
<th>Enthalpy (kJ/kg)</th>
<th>The acquired thermal quantity (kJ/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1</td>
<td>2825.8</td>
<td>2825.8</td>
</tr>
<tr>
<td>80</td>
<td>0.8</td>
<td>2260.6</td>
<td>1808.4</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>1412.9</td>
<td>706.4</td>
</tr>
</tbody>
</table>

The combustion of carbon monoxide

The carbon monoxide is the product of non-complete combustion of lignite and to have a complete combustion of carbon we must input additional quantity of air in the combustion process.

The combustion of carbon monoxide is done according to the expression:
\[ CO + \frac{1}{2}O_2 = CO_2 \quad \Delta H = 12700 \text{kJ} \]

In order to find the enthalpy for absolute combustion of a kilogram carbon monoxide we use the expression:
\[ \Delta H_{\text{CO}} = \frac{12700 \times 100\%}{\text{MWCO}} \text{kJ/kg} \]

100% - represents the percentage of carbon monoxide with is attached with oxygen (the combustion of carbon monoxide).

MWCO – presents the molecular weight of carbon monoxide.

In order to find the enthalpy for absolute combustion of a kilogram carbon monoxide we use the expression:
\[ \Delta H_{\text{CO}} = \frac{12700 \times 100\%}{\text{MWCO}} = \frac{12700 \times 1}{28} = 453.5 \text{kJ/kg} \]

Alternative I with relative combustion or 80% of carbon monoxide which is attached with oxygen, then the enthalpy is:
\[ \Delta H'_{\text{CO}} = \frac{12700 \times 80\%}{\text{MWCO}} = 362.8 \text{kJ/kg} \]

Alternative II with weak combustion or 50% of carbon monoxide which is attached with oxygen, then the enthalpy is:
\[ \Delta H''_{\text{CO}} = \frac{12700 \times 50\%}{\text{MWCO}} = 226.7 \text{kJ/kg} \]

In order to find the acquired thermal quantity with the combustion of carbon monoxide we use the expression:
\[ Q = m \times \Delta H_{\text{CO}} \text{kJ/h} \]

m – the weight of carbon monoxide,
\[ \Delta H_{\text{CO}} \] – enthalpy,

With 100% combustion of carbon monoxide the acquired thermal quantity is:
\[ Q = 100\% \times \Delta H_{\text{CO}} = 453.5 \text{kJ/h} \]

Alternative I with 80% combustion of carbon monoxide the acquired thermal quantity is:
\[ Q' = 80\% \times \Delta H'_{\text{CO}} = 290.2 \text{kJ/h} \]

Alternative II with 50% combustion of carbon monoxide the acquired thermal quantity is:
\[ Q'' = 50\% \times \Delta H''_{\text{CO}} = 113.3 \text{kJ/h} \]

In table 3 is represented the thermal quantity according to the percentage of carbon monoxide combustion.

![Figure 4](image-url). Presents the acquired thermal quantity with full combustion of carbon monoxide.
Table 3. Presents the thermal quantity acquired with complete combustion of carbon monoxide.

<table>
<thead>
<tr>
<th>The percentage combustion of carbon monoxide (%)</th>
<th>The weight of carbon monoxide (kg)</th>
<th>Enthalpy (kJ/kg)</th>
<th>The acquired thermal quantity (kJ/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1</td>
<td>453.5</td>
<td>453.5</td>
</tr>
<tr>
<td>80</td>
<td>0.8</td>
<td>362.8</td>
<td>290.2</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>226.7</td>
<td>113.3</td>
</tr>
</tbody>
</table>

The balance of thermal quantity

The graphical and analytical analyses done for carbon and carbon monoxide combustion in the zone of oxidation analyze the management of the combustion process of lignite in the zone of boilers. Also, it analyses in detail the thermal quantity acquired with combustion of carbon and carbon monoxide and proved that have different values. This change of thermal quantity has a potential for loss or bad management of thermal quantity in the process of lignite in the boilers. In table 4 is represented the thermal quantity acquired with carbon and monoxide carbon combustion.

Table 4. Presents the thermal quantity acquired with carbon and carbon monoxide combustion.

<table>
<thead>
<tr>
<th>The weight of carbon and carbon monoxide (kg)</th>
<th>The thermal quantity acquired with carbon combustion (kJ/h)</th>
<th>The thermal quantity acquired with monoxide carbon combustion (kJ/h)</th>
<th>Change in thermal quantity (kJ/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2825.8</td>
<td>453.5</td>
<td>2372.3</td>
</tr>
<tr>
<td>0.8</td>
<td>1808.4</td>
<td>290.2</td>
<td>1518.2</td>
</tr>
<tr>
<td>0.5</td>
<td>706.4</td>
<td>113.3</td>
<td>593.1</td>
</tr>
</tbody>
</table>

Figure 5. Presents the thermal quantity acquired with carbon and monoxide carbon combustion.

Based on the analysis of carbon and monoxide carbon combustion and thermal value acquired from their combustion and the thermal value of lignite of Kosova paddle is treated in statistical manner the thermal quantity acquired with full combustion and non-full combustion of lignite. Also, it has been treated the remaining of thermal quantity which if left unused during the technological process of lignite combustion in oxidative zone and can be potentially a loss and environmental pollution.

In the table 5 is represented the thermal value of lignite and the remaining of thermal value of lignite unused during the carbon combustion.

Table 5. Represents the thermal value of lignite and the remaining of thermal value of lignite unused during the carbon combustion.

<table>
<thead>
<tr>
<th>The weight of lignite (kg)</th>
<th>The thermal value of lignite (kJ/kg)</th>
<th>The percentage of carbon in lignite (%)</th>
<th>The percentage of carbon combustion (%)</th>
<th>The weight of carbon (kg)</th>
<th>Enthalpy (kJ/kg)</th>
<th>The remaining of thermal value of lignite (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11063</td>
<td>27</td>
<td>100</td>
<td>1</td>
<td>2825.8</td>
<td>8237.2</td>
</tr>
<tr>
<td>1</td>
<td>11063</td>
<td>27</td>
<td>80</td>
<td>0.8</td>
<td>2260.6</td>
<td>8802.4</td>
</tr>
<tr>
<td>1</td>
<td>11063</td>
<td>27</td>
<td>50</td>
<td>0.5</td>
<td>1412.9</td>
<td>9650.1</td>
</tr>
</tbody>
</table>
The weight of lignite (kg)
The thermal value of lignite (kJ/kg)
The percentage of carbon in lignite (%)
The percentage of carbon combustion
The weight of carbon (kg)
Enthalpy (kJ/kg)
The remaining of thermal value of lignite (kJ/kg)

Figure 6. Presents the thermal value of lignite and remaining of thermal value unused during the carbon monoxide combustion.

In table 6 is represented the thermal value of lignite and the remaining of thermal value of lignite unused during the monoxide carbon combustion.

<table>
<thead>
<tr>
<th>The weight of lignite (kg)</th>
<th>The thermal value of lignite (kJ/kg)</th>
<th>The percentage of carbon monoxide combustion (%)</th>
<th>The weight of carbon monoxide (kg)</th>
<th>Enthalpy (kJ/kg)</th>
<th>The remaining of thermal value of lignite (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11063</td>
<td>100</td>
<td>1</td>
<td>453.5</td>
<td>10609.5</td>
</tr>
<tr>
<td>1</td>
<td>11063</td>
<td>80</td>
<td>0.8</td>
<td>290.2</td>
<td>10772.8</td>
</tr>
<tr>
<td>1</td>
<td>11063</td>
<td>50</td>
<td>0.5</td>
<td>113.3</td>
<td>10949.7</td>
</tr>
</tbody>
</table>

Conclusions
The paper analyses the thermal energy and quality of fuel and the spot and future situation of thermal energy based on the lignite reserves. Also, the paper analyses the effective thermal value which depends on the percentage of combustible matter and the quantity of air infused in the technological process of lignite combustion. In particular we have analysed the thermal quantity acquired from full combustion and non-full combustion of lignite and their products during the technological process in the oxidative zone. Based on the acquired results we recommend as below:

With the full combustion of carbon we acquire thermal quantity of 2825.8 kJ/kg.
With the full combustion of carbon monoxide we acquire the thermal quantity of 453.3 kJ/kg.
Based on the thermal value of lignite and its usage during the carbon combustion and monoxide carbon combustion and the results acquired it is recommended as below:
With full combustion of carbon the usage of thermal value of lignite is more complete and has an average value of 19.5%.
With full combustion of carbon monoxide and the usage of thermal value of lignite is weak and has an average value of 1.632%.

We emphasize that with full combustion of carbon we have a good usage of the thermal quantity of lignite in the combustion process in boilers. The paper is based on DIN 1942, 1952, 1956 standards and positively reflects the usage of thermal quantity of lignite in the oxidative zone of boilers with positive effects in environmental and economic sustainability.

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Evaluation of Agricultural Water Management in Water – Starved Konya Basin, Turkey

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Abstract: In this study, water resources uses and irrigation water management were evaluated for Konya closed Basin Agriculture. The basin is fourth biggest water basin of Turkey. In this respect, general characteristics of basin, water resources and their allocation in agriculture, irrigation areas, crop pattern in irrigated lands and crop water requirements with irrigation organizations were described first and then analyzed with detail. The data about water resources of basin and their allocation amount in agriculture, irrigation areas opened with plan and irrigation organizations were obtained from General Directorate of State Hydraulic Works and General Directorate of Rural Services. The records about irrigation land sizes opened by uncontrolled and crop pattern were taken from General Directorate of State Hydraulic Works as well as Turkish Statistical Institute. The results of study showed that water resources have been used inefficient and irrigation water management is poor. The basin has 11% of total arable land potential of Turkey and all can be irrigated. However, basin has only 2.5% of available water potential of Turkey. Farmers tend to intensive uses of water resources so 1.5 billion m³ over water extraction is present from unregistered wells. By considering water use in the exception of allocated amount and irrigation areas opened without plan, it can be estimated that about 612,000 hectares lands have opened for irrigation. On the other hand, allocated water potential is not enough to meet all irrigation water requirement of current crop pattern. Thus, water resources uses and their management are very poor. To irrigate the whole areas opened to irrigation by allocated water amount and some regulations preventing over extraction of water resources are necessarily prerequisites.

Key Words: Agricultural water management, Crop pattern, Irrigation water requirement, Irrigation organizations, Konya basin

Introduction

Although the total amount of water made available by the hydrologic cycle is enough to provide the world’s current population with adequate freshwater, most of this water is concentrated in specific regions, leaving other areas water-deficient (Pimentel et al. 1999; Qadir et al. 2003). Because of the uneven distribution of water resources and population densities worldwide, water demands already exceed supplies in near 80 countries with more than 40% population of the world (Bennett, 2000). The minimum average annual amount of water required per capita for food production is 0.4x10⁶ L (Postel, 1996). Similarly, the minimum daily per capita water requirement is of 50 L for human health, including drinking water (Gleick, 1996).

Agriculture commands more than any other activity on this planet. Agriculture is the largest single user of water with 65-75% of fresh water being currently used for irrigation (Bennett, 2000; Prathapar, 2000). In some cases, it draws as much as 90% of the total water (Allan, 1997).

Konya basin is a region of water scarcity because of low precipitation. The total annual water resources available in region are 3.09 billion m³. With a population of 2.96 million, the available water per capita water is approximate 1000 m³, one seven the world average.

With its population, Turkey cannot maintain food security without irrigation. Total arable land potential of Konya basin accounts of 12 % of total arable land of Turkey with wheat production of 15%. In Konya basin of Turkey where natural rainfall does not match the needs of crops in both quantity and temporal distribution, supplementary irrigation is used to increase yields and provide the food needs of the nation. Available water potential of basin is highly scant and accounts of only 2.5% (2.76 billion m³) of the total Turkey (Topak et al. 2008). However, excessive-use of groundwater has caused severe environmental problems. For instance, lakes with fresh water have been dried or water levels of those have reduced. In Konya basin where groundwater is the primary source of water for

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irrigation, the groundwater level has declined rapidly since about 2000 year. Flood irrigation and drip irrigation is negligible and irrigation systems such as sprinklers is predominant in basin. Therefore, irrigation efficiency is high as about 70% (Topak et al. 2008). The main cause of excess water consumption in basin is poor management of water resources.

The main condition in opening the irrigation areas is availability of water supplies. It is necessary to be applied well designed water management for sustainable water uses in irrigated areas. To overcome this, irrigation areas should be kept by considering the allocated water amount for agriculture in current crop pattern conditions. In this study, agricultural water management for Konya Basin was analyzed with detail and necessary evaluations were made.

General characteristics of Konya basin

Climate and farming systems in Konya basin

The Konya basin is located south of Ankara in the heart of Turkey and covers an area of 53,850 km² (Figure 1). Konya Closed Basin is 4th biggest basin of Turkey according to its precipitation area. Uneven rainfall has observed in basin general and reaches up to 600 mm in small areas of South and South-West parts and about 300 mm in large areas of North and East parts of basin (Figure 2). The 70% of annual rainfall has recorded in winter and spring seasons. In basin, low rainfall is present in large plain areas.

![Figure 1. Location of Konya basin in Turkey](image1)

![Figure 2. Konya basin’s long-term mean annual precipitation distribution](image2)
Cereals are the most important crop and about 15% of total wheat production of Turkey has obtained from this basin. Winter wheat and barley, important two crops, have produced in large areas both in rain fed and irrigation conditions in basin. In irrigated lands, winter wheat and sugar beet are the most common crops. The 40% of sugar beet production area of Turkey is within Konya basin. Winter wheat is usually planted in early October and harvested in early July. Sugar beet is planted in April and harvested in October and November. The annual rainfall is not enough to support sugar beet crop and therefore irrigation is applied during summer and occasionally also to the winter wheat if early spring rainfall is deficient.

**Water Potential and Availability**

Basin has one of the largest areas in accordance of groundwater potential in Turkey. Annual water potential of basin is almost 7.95 billion m³ but, only 38% of this can be used. The arable land potential is 2.75 million hectares (ha) and all such areas have exposed to agricultural drought. The scarcity of water potential for irrigation of large agricultural lands have resulted difficulty in efficient water management. Some information about total available and available water potential in agriculture for Konya basin were presented in Table 1 (Anonymous, 2007, 2011a,b).

<table>
<thead>
<tr>
<th>Water Resources</th>
<th>Annual Potential</th>
<th>Available Water Potential</th>
<th>Basin Resources</th>
<th>Open for Usage from Basin Resources</th>
<th>Basin + Goksu River Final Available</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>General Basin</td>
<td>Agriculture Residential</td>
<td>Agriculture Residential Residential</td>
</tr>
<tr>
<td>Surface(SW)</td>
<td>5.949</td>
<td></td>
<td>1.025</td>
<td>0.064</td>
<td>0.900</td>
</tr>
<tr>
<td>Groundwater (GW)</td>
<td>1.998</td>
<td></td>
<td>1.735</td>
<td>0.263</td>
<td>1.735</td>
</tr>
<tr>
<td>Total</td>
<td>7.947</td>
<td></td>
<td>2.760</td>
<td>0.327</td>
<td>2.635</td>
</tr>
</tbody>
</table>

According to last population records of 2010 year, it has reached up to the 2.96 million in basin. As seen from Table 1, available water potential of basin is 3.09 billion m³. By evaluating this, annual available water potential per person is 1040 m³. This shows that basin is characterized as water scant region according to the international standard. In standard, water scant can be defined as annual available water potential per capita is lower than the 1000 m³.

**Irrigation in Konya basin**

**Characteristics related to irrigation area sizes**

The most important condition of efficient water resources uses is to use only allocated amount of water for agriculture. The size of the irrigation area should be designed in respect to water supply and it should not be adapted to the size of the area. To overcome this, opening the new areas for irrigation with plan is necessarily prerequisites. General Directorate of State Hydraulic Works (GDSHW) has the responsibilities of planning water resources as well as opening the areas for irrigation in Turkey. Some information obtained from Konya 4th GDSHW about irrigation areas were given in Table 2.

<table>
<thead>
<tr>
<th>Ways of opening irrigation</th>
<th>Land size opened to irrigation (ha)</th>
<th>Water supply</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDSHW</td>
<td>167,000</td>
<td>Surface(SW)</td>
</tr>
<tr>
<td>General Directorate of Rural Services (GDRS)</td>
<td>60,190</td>
<td>Surface(SW)</td>
</tr>
<tr>
<td>Irrigation cooperatives</td>
<td>197,500</td>
<td>Ground(GW)</td>
</tr>
<tr>
<td>Public irrigation (permitted)</td>
<td>94,508</td>
<td>Surface(SW)</td>
</tr>
<tr>
<td>Public irrigation by deep wells (permitted)</td>
<td>unknown</td>
<td>Ground(GW)</td>
</tr>
<tr>
<td>Public irrigation by deep wells(unpermitted)</td>
<td>unknown</td>
<td>Ground(GW)</td>
</tr>
<tr>
<td>Basin General</td>
<td>518,198 ha + unknown area</td>
<td></td>
</tr>
</tbody>
</table>
As seen from Table 2, agricultural lands have opened to irrigation by different ways. The areas managed by GDSHW and General Directorate of Rural Services (GDRS) were opened by considering the surface water resources and is obtained by both dam and small dams (Anonymous, 2011a). Those areas managed by cooperatives were opened to irrigation by the leader of the GDSHW and irrigation water has obtained from groundwater resources. In public irrigation, farmers have used some water resources by permission of GDSHW (Anonymous, 2011a). In Table 2, 95000 ha areas have been irrigated by public irrigation from surface water resources but, the surface water supply is not available. In the other way, this size area can not be irrigated. In the exception of this, there are two different public irrigations in basin as well. The first is the wells constructed by the permission of legislation but the land size irrigated by this way can not be known in basin. The other is construction wells on the own areas of farmers by without any permission and land size irrigated by this way also can not be known. There are plenty of wells in basin constructed by this way and those wells have the negative effects on sustainable groundwater resources of basin.

By considering information mentioned above, agricultural lands have not opened to irrigation by monopoly as well as plan in basin. Therefore, land size opened to irrigation has not known correctly in basin. By evaluation the data obtained from this study, agricultural lands for open irrigation has estimated (Table 3).

**Table 3. Estimated values of irrigation land size for open to irrigation in basin general**

<table>
<thead>
<tr>
<th>Ways of opening irrigation</th>
<th>Land size opened to irrigation (ha)</th>
<th>Water supply</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDSHW</td>
<td>167000</td>
<td>SW</td>
</tr>
<tr>
<td>GDRS</td>
<td>20000 (60190)*</td>
<td>SW</td>
</tr>
<tr>
<td>Public irrigation (permitted)</td>
<td>00 0000 (94508)**</td>
<td>SW</td>
</tr>
<tr>
<td>Irrigation cooperatives</td>
<td>197500</td>
<td>GW</td>
</tr>
<tr>
<td>Public irrigation (permitted)</td>
<td>80700***</td>
<td>GW</td>
</tr>
<tr>
<td>Public irrigation (unpermitted)</td>
<td>146600*** (+64000a +16000b)</td>
<td>GW</td>
</tr>
<tr>
<td>Total irrigated area by groundwater</td>
<td>505000</td>
<td></td>
</tr>
<tr>
<td>Basin General</td>
<td>611800</td>
<td></td>
</tr>
</tbody>
</table>

*: Irrigation area has determined as 20000 ha from GDRS records ; **: There in no surface water supply to meet this. Even small size water resources has not considered within planned surface water resources of basin.
***: According to 2001 year farm number records, estimation was done by considering plot size distributions.
a: We have estimated that at least 40% of unregistered wells (64000) have been in planned irrigation areas.
b: 16000 ha of planned irrigation areas has been irrigated by GDSHW- supplement wells.

In Table 3, agricultural land size opened irrigation in basin has estimated about 612000 ha. Of this, about 187000 ha area has opened irrigation with plan by surface water resources but, nowadays water requirement of this area has not met due to scarcity of rainfall. Thus, some of unregistered wells have opened in such areas and according to our estimation about 64000 ha of this area has irrigated by groundwater resources. In addition, 16000 ha of this area has irrigated by GDSHW supplemental wells. In addition, it can be concluded that about 505000 ha agricultural land of basin has irrigated irrigation by groundwater resources. The rest 107000 ha area has irrigated by only surface water resources.

**Sustainable crop pattern in basin**

The main important subject in irrigation projects is to determine the crop patterns that are suitable for country need and regions in respect to the available water potential. In briefly, crop pattern determination is very important. Irrigation water management is performed according to the crop pattern. There is no regulation or control mechanism to force the crop pattern consideration in Turkey as well as Konya basin. The main reason of this is that there is not production plan in Turkey general. Thus, crop pattern has varied every year and high water consuming crops are in favour. Table 4 shows suggested and current crop patterns in Çumra irrigation project. The crop pattern of Çumra irrigation project area is a sample model for basin.

As seen Table 4, current crop pattern of basin is quite different from the Çumra irrigation area crop pattern. In crop pattern, cereals have reduced as 50% while sugar beet has increased as four folds. In result, the share of the cereals and high water consuming crops should be 80% and 20%, but
nowadays, they are 44.5% and 45.5%, respectively. This shows that target crop pattern has not been considered in basin irrigation areas. It is impossible to say that water resources have used with plan and well management of irrigation water. By considering irrigation area and crop pattern in basin, irrigation water amounts applied for some major crops have estimated and are presented in Table 5.

**Table 4. Current crop pattern in Konya basin**

<table>
<thead>
<tr>
<th>Crops</th>
<th>Suggested*</th>
<th>Current status in basin**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Production area (ha)</td>
<td>Crop pattern (%)</td>
</tr>
<tr>
<td>Cereals</td>
<td>28640</td>
<td>80</td>
</tr>
<tr>
<td>Leguminous</td>
<td>1070</td>
<td>3</td>
</tr>
<tr>
<td>Water melon and melon</td>
<td>2148</td>
<td>6</td>
</tr>
<tr>
<td>Sugar beet</td>
<td>1790</td>
<td>5</td>
</tr>
<tr>
<td>Alfalfa</td>
<td>1432</td>
<td>4</td>
</tr>
<tr>
<td>Fruit</td>
<td>716</td>
<td>2</td>
</tr>
<tr>
<td>Vegetables + carrot + water melon and melon</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Maize</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Potato</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sunflower</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*: Suggested crop pattern for Çumra irrigation project (Çakmak, 1994).
**: Estimated crop pattern in basin

**Table 5. Irrigation water amounts applied to major crops in irrigated areas**

<table>
<thead>
<tr>
<th>Crops</th>
<th>Cereals</th>
<th>Sugar beet</th>
<th>Potato</th>
<th>Leguminous</th>
<th>Maize</th>
<th>Vegetable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water applied to crops (mm)*</td>
<td>400</td>
<td>1050</td>
<td>700</td>
<td>750</td>
<td>800</td>
<td>900</td>
</tr>
<tr>
<td>Consumed water from supply (billion m³)</td>
<td>1.1</td>
<td>1.26</td>
<td>0.245</td>
<td>0.242</td>
<td>0.276</td>
<td>0.33</td>
</tr>
</tbody>
</table>

*Topak et al. (2008).

In Table 5, the highest water use has observed in sugar beet and in cereals planted areas. The cereal production area is 2.5 times greater than the sugar beet production area but, sugar beet is the highest water user in basin. As known that sugar beet has consumed more water 900 – 1200 mm (Dunham, 1993; Hills et al. 1990) and production area should be limited in arid and semi-arid regions (Fabeiro et al. 2003). Under this evaluation, average 1050 mm irrigation water has applied for sugar beet in basin and this is not excess or normal amount. Since, in some previous studies net irrigation water requirement of sugar beet was determined as 750 – 850 mm (Ertaş, 1976; Ertaş, 1984; Poçan, 2008; Topak et al. 2011). Thus, excess water uses in agriculture has not resulted from the over irrigation and has caused from expansion of high water consuming cropped lands. In basin sugar beet production areas has increased as 2 folds in last 4 – 5 years. The reason is that there is not crop pattern with plan in basin. On the other hand, more water than required has applied for winter cereals. Irrigation water requirement of wheat was determined as 180 – 200 mm in Konya basin (Ertaş, 1980). However, up to 400 mm water has applied during the vegetation period of wheat crop. This is almost equal to 2 folds of water consumption in winter cereals. The reason is that irrigation organizations have the poor capabilities of irrigation program. Since, there is no need to irrigate wheat crops within definite intervals. This crop can be irrigated in the stages of stem-extension or grain formation even in both stages.

**Agricultural water management organizations in basin**

The water resources of Konya basin have managed two different types. The first one is irrigation organizations under legal authority, and second is management by public irrigation. Irrigation organizations cover water user associations (WUA), irrigation cooperatives and local management irrigation organization (LIO). LIO are very few and have responsibility from small amount of irrigation areas. Therefore, they were evaluated within the irrigation cooperatives. Individual irrigation cooperatives have the great share in basin and have used only groundwater. These cooperatives are met within two different types. The first one is registered while the others
unregistered wells. The structural properties of irrigation water managers in basin are presented in Table 6.

Table 6. Information about water management organizations in basin

<table>
<thead>
<tr>
<th>Properties</th>
<th>WUA* (Wells)</th>
<th>LIO (Wells)</th>
<th>Irrigation cooperatives* (Wells)</th>
<th>Registered Well</th>
<th>Unregistered Well</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>17</td>
<td>-</td>
<td>4176</td>
<td>18913*</td>
<td>53873*</td>
</tr>
<tr>
<td>Irrigation area (ha)</td>
<td>167000</td>
<td>20000</td>
<td>197500</td>
<td>80700</td>
<td>146600**</td>
</tr>
<tr>
<td>Water supply</td>
<td>SW+GW</td>
<td>SW+GW</td>
<td>GW</td>
<td>GW</td>
<td>GW</td>
</tr>
</tbody>
</table>

*: Anonymous, 2011b.; **: Our projections according to the estimation.

In Table 6, irrigation water management of surface water resources in opened to irrigation with plan has transferred to the WUA while management of groundwater resources has transferred to irrigation cooperatives as well as to the farmers. There are 17 WUA for management of irrigation in 167000 ha irrigation areas. Almost all irrigation cooperatives have the status of groundwater irrigation cooperatives (GWIC). The number of groundwater wells managed by cooperatives is 4176. In addition, there are about 72786 (18913 registered and 53873 unregistered) farmer wells in basin (Anonymous, 2011b). In examine Table 6, about 70% of the irrigation areas in basin have irrigated by groundwater resources. This is our evaluation by considering analysis of data in above. Irrigation areas irrigated by surface water resources is 187000 ha but, they can not always be irrigated due to none water present in canals. In this period, serious problems have observed. Some farmers have solved those problems by constructions of wells within their fields. Thus, the areas for irrigation by surface water resources also have irrigated by groundwater resources. Therefore, the area irrigated by groundwater resources is higher than the 70% in basin.

Irrigation water management capacities of irrigation organizations

To use water resources efficiently and sustainably, safely available water potential should be well planned and water requirement in irrigation should be used or at least limited by consideration of safely available water potential. This should be performed and evaluated for each production year. This plan should be made by use of both surface and groundwater resources. Irrigation organizations are made irrigation plans with alternatively in accordance of allocated safely water amount. Those organizations may limit the production areas of crops that are not growth without irrigation or irrigation numbers. They should be announced for the farmers about which farmers produces what types of crops and what is the sizes of production areas.

As seen from this information, to use water resources as an environmental friendship, irrigation organizations should work very hard and make plans. The designs of available water potential and irrigation areas and management are technical issues and needs experiences.

Irrigated agriculture in basin is not based on the compulsory production plan and is not controlled. It can be obviously seen that water resources have used without permission and groundwater resources have used excessively therefore, groundwater levels have reduced dramatically. Groundwater resources have used in irrigation randomly and present status and regulations of irrigation organizations have some deficiencies in water management.

The 70-80% of irrigation organizations of basin is in Konya plain. Almost all organizations in basin have similar characteristics. They are not responsible from agricultural water management and applications. They don’t have the responsibility of employing technical person that are very important in preparing of technical plans and performing water management program. Therefore, none irrigation organizations have the specialist agriculture engineers in basin. Thus, the current statuses of irrigation organizations in basin don’t contribute the efficient water resources uses. They do not have the capacity of planning of irrigation water requirement and evaluation of the situations.

There are 72786 farmer wells that are out of the management of irrigation organizations. The 53873 of this is unregistered and opened without permission and unplanned. There is not compulsory crop pattern in organizations that have those wells. There is no water allocation and they don’t have the compulsory irrigation program. In basin, only number of the wells was determined and none information was obtained about size of the area irrigated by public or farmer wells, amount of the
water extracted from those wells, the areas opened to irrigation with or without project. This has resulted in some difficulties in projection of size of the irrigation areas and as well as crop water uses.

The areas opened to irrigation irrigated by surface water resources with project is about 187000 ha (Anonymous, 2011b). However, especially low rainfall amount in recently has not met the project discharges. Most farmers observed this situation have opened to their own wells by their own budget and they have solved their irrigation water problems by this way. In fact, public wells have opened like this but heir numbers are not really known. Similarly, some producers or farmers within the Irrigation cooperatives areas have also constructed their wells with getting permission. They wanted to have those wells with freedom. Since, there has not been a control mechanism about new well constructions. In basin, the size of the area irrigated by GWIC is about 197500 ha (Anonymous, 2011b).

In basin, it is possible to say that about half of the unregistered wells have opened within the irrigation areas of farms. Under this situation, about 32325 unregistered wells have resulted new areas opened to irrigation. It is certain that 18913 registered wells also let to some new areas opening to irrigation. This issue has considered in registration of wells. In the exception of irrigation areas by project in basin, registered and unregistered 51238 wells have caused formation of new irrigation areas open.

New irrigation areas opened by public wells have been unregistered or unknown in basin. In our research, average farm size in basin is 13.3 ha with 3 divisions (Anonymous, 2011c). It shows that average plot size is 4.4 ha. By considering this and each well has served for one plot, it was estimated that additional area opened to irrigation is 225448 ha (51238x4.4 ha = 225448 ha). By adding this to the calculation, total area opened to irrigation is about 610 000 ha (187000+197500+225500=610000), but this projection is still far from the real irrigated land size.

**Evaluation of Agricultural Water Management**

The estimation of basin irrigation area size, current crop pattern and irrigation water applied were presented in Table 7. In Table 7, projection obtained from estimated data showed that water use in agriculture is higher than the safely available water resources in basin. Total water requirement of irrigation area 3.97 billion m$^3$. This consumption has resulted about 1.535 billion m$^3$ over water extraction from the groundwater resources of basin. This is an indicator that there is a poor or none irrigation water management strategies in basin. The most important reason of this is that irrigation water has obtained from the wells that are without project and unregistered. The uses of groundwater resources in irrigation without project or unplanned shows that water resources are without conservation or in great danger.

<table>
<thead>
<tr>
<th>Estimated irrigation area in basin (ha)</th>
<th>Irrigation water applied* (m$^3$ ha$^{-1}$)</th>
<th>Total irrigation water used for irrigation area (billion m$^3$)</th>
<th>Available water potential in agriculture (billion m$^3$)**</th>
<th>Over extracted water amount (billion m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>610000</td>
<td>6500</td>
<td>3.97</td>
<td>2.435</td>
<td>1.535</td>
</tr>
</tbody>
</table>

* Revised from Topak et al. 2008.; **: Anonymous 2011b

The shares of irrigation organizations and public activities on irrigation water use in basin are presented in Table 8. In such table, the 18.0 % and 82.0% of water use from the basin resources were obtained from surface water resources managed by WUA and LIO and groundwater resources managed by WUA, irrigation cooperatives and farmers. In present, the area opened irrigation by surface water resources is about 187000 ha and available surface water potential is 0.7 billion m$^3$. In examine the crop patterns of basin, water consumption in this area is 1.21 billion m$^3$. There is only 0.7 billion m$^3$ surface water potential allocation, but how can be used 1.21 billion m$^3$ from not allocation from surface water resources? This situation shows that the records of land sizes opened irrigation are not reliable or incorrect. In reality, assuming 187000 ha arable lands have irrigated in basin, in addition to current 0.7 billion m$^3$ surface water resources uses, 0.520 billion m$^3$ irrigation water also has extracted from groundwater reservoir in basin. Since, by considering the current crop pattern of basin, only 107000 ha areas can be irrigated by 0.7 billion m$^3$ water.
Table 8. Water consumption by both organizations and farmers

<table>
<thead>
<tr>
<th>Properties</th>
<th>WUA+LIO (GDSHW-wells)</th>
<th>WUA (GDSHW-wells)</th>
<th>Irrigation cooperatives</th>
<th>Registered public wells</th>
<th>Unregistered public wells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irrigation area (ha)</td>
<td>107,000</td>
<td>16,000</td>
<td>197,500</td>
<td>80,700</td>
<td>146,600+64,000 (210,600 ha)</td>
</tr>
<tr>
<td>Water consumption (billion m³)</td>
<td>0.70</td>
<td>0.104</td>
<td>1.28</td>
<td>0.525</td>
<td>1.37</td>
</tr>
<tr>
<td>Consumption ratio (%)</td>
<td>17.6</td>
<td>2.6</td>
<td>32.2</td>
<td>13.2</td>
<td>34.5</td>
</tr>
<tr>
<td>Water resources</td>
<td>SW</td>
<td>GW</td>
<td>GW</td>
<td>GW</td>
<td>GW</td>
</tr>
</tbody>
</table>

By examine Table 7, it is obviously seen that water extraction from basin groundwater resources is 3.27 billion m³. The 1.5 billion m³ of this is unpermitted or over extraction. The 58% of basin groundwater resources has managed by public (42% from unregistered and 16% from registered wells). The rest 42% part has managed by irrigation organizations.

Conclusion
The information about irrigation areas, crop pattern, irrigation cooperatives and 73000 public wells are not certain and safe for Konya Closed Basin of Turkey. Anonymous (2007) showed that groundwater levels have been continuously decreased every year. The main reason is that current irrigated agriculture has resulted in over extraction of groundwater resources. Improper data has resulted in difficulties in annual excess water consumption. This issue has expanded the senseless in conservation and development of water resources as well as stress in water resources. In conclusion, well plan and proper management are not available especially in use of groundwater resources. Thus, it is impossible to say that water management in agricultural by conservation of environment, reliable and safe are present.

References


Geological Characteristics of the Prusačka River Catchment Area in Bosnia and Herzegovina

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Abstract Territory of Bosnia and Herzegovina is characterized by complex geological structure and heterogeneous flora and fauna, what also characterize the city of Prusac and the environment. The region of Prusac lies in the central Bosnia, southwest of Donji Vakuf. Field access is possible from the direction of Donji Vakuf, and then by the road along the Prusačka River. The paper presents geomorphologic, geological, hydrogeological, engineering-geological and seismological characteristics of the terrain in the Prusačka River catchment area. According to published data, this area has been poorly researched and is rich in occurrences and deposits of various minerals, some of which are used as technical-building stone. The aim of this paper is to present basic engineering-geological conditions and the possibility of constructing hydraulic structures that enable better building design and subsequent construction in accordance with the legal norms that regulate this matter. This paper presents data on the geological composition, thickness of proluvial and alluvial sediment, surface cover, especially debris eluvial clay blanket, and information about the state of rock mass that are essential for defining the basic conditions for defining basic engineering-geological conditions for building these objects.

Key words: Prusačka River, Bosnia, flora and fauna, hydraulic structures

Introduction

Bosnia and Herzegovina is characterized by complex geological structure and heterogeneous flora and fauna, and these are also the qualities of Prusac with its environment. The old city of Prusac-Biograd has been built by the Romans. In the year of 1463 the Turks conquered it and called Akhisar, which means The White City, and under the name of Biograd was mentioned in 1503. Prusac City is located near the crossroads of Bugojno-Jajce-Travnik, 3-4 km south of Donji Vakuf. The town is situated at the foot of the mountain Šuljaga below which is the Ajvatovica spring, which is the center of cultural and religious event "Days of Ajvatovica".

The area between Donji Vakuf and Jajce is rich in occurrences and deposits of various minerals. Valuable geological data for this area gave John (1880) and Rucker (1896), then Mojsisovics, et al. (1880) and Katzer (1903, 1906, 1921, 1924, 1925). The first data of the optical and chemical tests on melapfyes gave Čutura M. (1918). Recent data on the geology, stratigraphy, and tectonics of the area gave Jovanović (1957), Pamić and Jurić (1962), Herak (1962, 1969, 1971 and) Maksimčev and Jurić (1964) and Jurić (1968, 1971). They dismembered the Paleozoic and Triassic formations and gave more realistic interpretation of the tectonic relations. Geological and mineralogical-petrological characteristics of the middle Triassic volcanic rocks in the valley of the Vrbas gave Trubelja Šibenik-Studen (1965) and Šibenik-Studen and Trubelja (1967), and Pamić with associates (Pamić et al. 1976). The first data on the occurrence of gypsum in the vicinity of Donji Vakuf, we have found in the works of Katzer (1924 and 1926) and Podubski (1957, 1965 and 1976). Katzer mentioned so-called salt springs that were related to deposits of anhydrite and gypsum.

The area of Prusac determined for research was poorly researched in the last hundred years, according to published data. For the great majority of the mentioned area published data related to geology are based on data of Katzer (1903, 1904, 1906, 1924 and 1926) and the basic geological map of R 1: 100 000 (Vujnović et al. 1967-1975). The first researches yet with a small volume of research works were performed on the left side of the Prusačka creek during the 1979 for enterprises "Komar"

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and "Geotechnical Engineering" from Zagreb. Those researches were performed in order to determine reserves of limestone, and technical construction stone and the development of project and laboratory documentation necessary to open a quarry. More detailed researches of the Prusac region and its wider environment haven’t been done even in the postwar period when the exploitation was intensified on the aforementioned quarry.

The task of the research whose results have been presented in this work was consisted in obtaining necessary information about the geological composition, thickness of proluvial and alluvial sediment, surface cover, especially clay debris eluvial covers. In that way, the necessary information on the state of rock mass in the base of future hydropower facilities was obtained. All these information and research results should enable defining the basic conditions for building Geotechnical Engineering hydraulic structures.

Collecting and processing data from literature and graphic materials (topographic and geologic map) were done in the first phase. In the second phase was carried out geological reconnaissance of the terrain, and detailed geological mapping of the Prusac River catchment area.

Graphical reports and statements have been accomplished in the cabinet business. In order to obtain necessary data for making the main construction project of Prusac River hydropower, it is necessary to give the conditions on foundation and construction (water intake, sedimentation tanks, pressure pipeline and the operator) to perform geological researches, or make a project of detailed geological investigations.

It is necessary by this project to predict all research works and field testing to define the geological, geological engineering and geotechnical conditions of the terrain on which to build hydroelectric facilities. This project includes all research works with extents and types that should meet project demands.

The geographical position of the field

Prusac region lies in the central Bosnia, southwest of Donji Vakuf. Field access is possible from the direction of Donji Vakuf, and then by the road along the Prusac River. The Old town and the City of Prusac are situated on the right side of the Prusac River which general direction is southwest-northeast. Hypsometrically observed, the terrain lies at an approximate height of 941 m. Valley sides rise up to 1197 m on the left bank and up to 1100 m on the right bank. Vegetation cover is highly developed. It is predominantly coniferous forest, and sporadically mottled with deciduous forest.

Geomorphological features of the Prusac River valley

Prusac River is characterized by expressed decrease of the longitudinal gradient profiles which is approximately 191 m in the observed area. Cross-section of the valley in the subject area has stretched V-shape.

In the area of the intake structures, operators and sedimentation of MHE Mujada, Prusac River is located in the enlarged left and right side valley. Lateral parts of the valley are dissected by grooves smaller tributaries which are roughly perpendicular to the main stream. These side streams are generally of permanent or temporary character.

In the area of planned hydro buildings, the Prusac River Valley was made of geological formations of heterogeneous composition, largely impermeable rock masses, and the river drift does not exceed a thickness of 2.5 m.

Erosion and stability of the terrain

Rock masses in the considered valley belong to different categories of rocks resistant to the effects of erosion and denudation. For example, limestone and dolomite rock masses are dependent to processes of decay along the tectonic brakes as cracks and faults. In the cover zones they are eluvial weakened and very supple on the effects of erosion. Can be considered that the zone of surface and subsurface degradation and division of rocks of the geological substrate covers the whole terrain, not exceeding a thickness of 1-2 m, but locally more (with more cracks and faults in the spring, hissing zones or leaks and wetting). On the other hand, vegetation cover in the form of forest vegetation seems adequate protection against erosion. The effect of erosion is expressed in the bed of the stream and the occasional side-streams, as well as in the existing road cuts.
Erodibility of the cover mass is in direct function of rainfall and humidity. This applies to all considered flow. Host is that much greater if hydrological conditions are unfavorable and if rainfalls are plenitudinous and short-lived. Side slope’s stability during the construction of facilities shall not disturb the excavations because excavations are not of great depths. Geomechanical properties of rock masses can meet the conditions of static bearing capacity and allowable loads. Excavation may be done without any special restrictions to the depth of 2-3 m.

It is characteristic that the cover materials in dry season can be quite solid and even hold the vertical cuts, while in wet season, the artificial opening and to memory, due to the presence of side streams and debris material source rocks, which cover Padinska hand, (especially in the part of the future pipeline route), can cause the collapse in the same trench. In these zones during the excavation of more than 2-3 m, there must be taken measures of precaution to avoid caving. All the activity at opening of the excavation and indentation must take place in a dry season.

Geological structure and tectonic fabric of the terrain

The terrain provided for research lies in central Bosnia, southwest of Donji Vakuf. Field access is possible from the direction of Donji Vakuf, and then by the road along the Prusačka river. On the left side of the river there is a limestone quarry that is used as a technical-building stone and as aggregate for concrete construction tampons layers, as well as aggregates for bituminous mixtures, for supporting the pavement and the various types of mortar. In the geological structure of the wider environment of Prusac participate the following lithological members:
- Aleurolites and breccias permianotriassic age
- Calcareous shales, and alverolite sandstones Lower Triassic
- Middle Triassic carbonate sediments (anizika)
- Ladinian magmatic rocks and
- Upper Triassic carbonate rocks

**Sediments of permianotriassic age** spread northeast of Donji Vakuf Oboračke River valley. Featured are generally alevrolites, green sandstone known as "Travnik series."

**Mesozoic sediments**
Mesozoic sediments are represented by Lower Triassic sediments middle Triassic and Upper Triassic.

**Lower Triassic sediments** ($T_1$) are presented in the north of Prusac west from Kutanja and on the area of Novo Selo. These sediments are identified as calcareous shales, and sandstones aleurolites. Continuously exceed the Anisian limestone and breccia. The colors are red and purple. The most common are type feldspathic sandstone, greywacke and feldspathic subgreywacke. Mentioned sediments are found as erosion remnants or portions of a sheet and their thicknesses are not determined.

**Middle Triassic sediments** ($T_2$) are represented by limestone, limestone breccias, marble and dolomite. Carbonate sediments are massive and layered. Their course is northwest-southeast. Limestone quarries in the area "Prusac" are light gray, banked and less layered. In addition to limestone there are also limestone breccias, marble and dolomite. Limestone layer surfaces are difficult to observe because of the large tectonic damage.

Limestones are separated by a fault which extends along the Prusăčka River valley and fault zone towards Dolomites. On quarry were found two faults. One is in the western part of the reservoir and extends NW-SE, and the other is on the east side of the direction of ZI. Yet there has been no disruption of continuity of calcareous mass in the quarry. With the upper Triassic sediments they are in tectonic relation and towards lower Triassic sediments are continuous except in the disturbed parts of the terrain. The estimated thickness of these layers is about 400 m.

**Upper Triassic sediments** ($T_3$) are built by dolomite and limestone that stretch along the right side of the Prusăčka River i.e. the western part of the map. The most common are striped and layered and rarely come banked and a massive gray and light gray dolomites. In the dolomite are observed smaller calcareous inserts and in the lower parts come laminated, gray and dark gray limestone dolomites. Upper Triassic carbonate rocks are the youngest sediments record Gorica, Ljuša, Bugojno. The estimated thickness of dolomite package is about 800 m.

Within middle Triassic magmatic, in the wider area of diabases occur and dolerites (BB) then spilites and keratophyres (n Rbab).

However, the most common igneous rocks are spilites and keratophyres which often cannot be separated from each other. This volcanic mass extends from the northwest towards the southeast to the town of Prusac. Their mineralogical composition is as follows: albite, augite, amphibole, followed by chlorite, epidote, calcite, ankerite, celadonite and various accessory minerals. It was noted that the feldspar is almost always filled with these secondary minerals. In some specimens of volcanic rocks was determined also potassium-feldspar sanidine. It is characteristic that spilites and keratophyres contain greater amounts of almonds, which are filled with calcite, chlorite and quartz. Spilites and keratophyres have porphyry, holocrystallyne structure, and less hypocrystallyne intersertal. Ophite varieties are subordinate. During the earlier study was not carried out the separation of spilites and keratophyres, because greater number of chemical analysis had not been done. In fact, the researchers have shown dominant role of spilites.

**Cenozoic sediments** ($M_3$ and Pl, Q)

These sediments are built of clay, marl with coal, limestone, conglomerates, sandstones and sands and clays (Pl, Q). Cenozoic sediments are present on the left bank of the river to Prusăčka Kutanja and Donji Vakuf.
Quaternary sediments are made by eluvial, colluvial blankets or screes material as well as river, alluvial and prolluvial deposits. They are represented by different varieties of clay up to the transition to clay inwards. Eluvial-deluvial covers are of debris to sandy clay. In the steep slope sides there are screes, debris materials in the form of colluvial accumulation. In the bed of the Prusačka River and close to the bed there are sand and gravel, then fragments of source rocks in the form of fluvial-prolluvial and alluvial deposits. In the field of mining quarries these products are mainly removed. These are disintegrating rocks whose final product is the red soil which fills breccias with tufa as binder, as well as it fills unconsolidated inwards and limestone blocks.

Tufa occurs like erosion rest of the great mass of tufa made close to waterfalls on the creek just above his mouth. Since the open pit limestones “Prusac” tufa occurs in small amounts but with developed mining operations, it will be removed.

In connection with the tectonic features of the wider Prusac area can be emphasized the dominant tectonic structures, means cover that stretches from northwest to southeast. Specifically it is about launching middle Triassic sediments on the Upper Triassic dolomite. Besides the covers, there are numerous faults which can be generally grouped into two main directions of as follows: The east-west and northwest-southeast. Northeast-southwest faults laid out watercourses of Prusačka stream and Semišnica, and other smaller waterways. The faults of northwest-southeast course cross the upper Triassic sediments and other lithologic members.

**Figure 2.** Geological Survey map of the wider environment of Prusac (the list of Bugojno-Basic Geological SFRJ 1:100 000; Vujnović L. et al. 1967-1975 year.)

Hydrogeological features of the terrain

In building this terrain there are involved rocks of various hydro geological characteristics and functions. This way can be extracted:

**Crack-cavernous porosity rocks** are made by solid and laminated limestone and dolomites ($T_2$ and $T_3$). They are characterized by crack porosity, good permeability and cavernous. In hydrogeological sense they make aquifers or collectors.

**Intergranular porosity rocks** are made by alluvial and terrace drifts, as well as eluvial, colluvial and deluvial covers. They are characterized by various water permeability and porosity. It is performed through them the infiltration and percolation of surface water and flowing water. Basically they perform collectors. Permeability of the rock mass depends on granulometric composition and the
presence of clay particles. If they are debris or sandy-gravel composition, then they have locally water permeability and are very permeable. Generally speaking they are poor aquifers because they are thin (maximum 1-3 m). But even so with regard to their filtering characteristics they are important for local construction conditions (rapid flow of rainwater to emphasizing the infiltration of water through them, and particularly along the contact with the geological substrate). The complex of these rocks is made from covers, alluvial and proluvial deposits and river terraces.

Concerning the position of the Prusačka River flow and hydrogeological characteristics of the rock masses the flow is intagliated in, then the appearance of sources of varying character and capacities (permanent, casual, seep and seepage springs), we may say about the terrain the followings:

- Abundance fluctuation of sources is seasonal, which applies to surface water bodies,
- Climatic characteristics and phenomena associated with them cause wet and dry period when there were expressed differences in rainfall quantities, source capacities and the amount of flow
- Geologically complex of hydrogeological collectors and insulators with the above characteristics provides a continuity of Prusačke River flow.
- Hydro-geological properties of rock masses which are mostly treated area streams are good aquifers and as such they are accumulative for underground streams.

**Catchment area**

The Prusačka River is the left tributary of the river Vrbas. The basin has an elongated elliptical shape, and adjoins Kupreška River catchment on north-west and with the Milač River on south-west. The region of the Prusačka River together with neighbour basins is a regional entity, which by its hydrogeological characteristics generally can be considered as unambiguous. Accordingly, the catchment boundary is orographic with established underground watershed of the south and covers an area of 27.50 km² with average flow Qₘᵢₐᵩ = 0.64 m³/s (up to intake seats).

The Prusačka River Basin belongs to the basin of the river Vrbas. Hydrographic network within the watershed is highly developed.

It flows by general direction from southwest to northeast. On the left side it receives the larger streams Arapka and Široki Do, and from the right – number of smaller streams.

**Geological engineering terrain features**

In the geological structure of the terrain in which hydroelectric facilities are to be built, participate: well petrified related carbonate rocks, the group of unpetritified grained clayey rocks and unrelated coarse and fine grain poorly-composed to lose carbonate rock mass.

**Related petrified carbonate rocks** are lime stones and dolomites of the Middle and Upper Triassic. Tectonic are very broken and the surface divided decay small block size of gravel. They are characterized by a strong bond between the grains, the crystalline structure cryptocrystalline and good physical and mechanical properties. The textures are layered to massive. Basically build a stable terrain.

Basic physical and mechanical properties of dolomite and limestone are:

For dolomite:

- Compressive strength in dry condition $\sigma_p = 21.20$ to $29.23$ kN/cm²
- Compressive strength of the state water permeation $\sigma_s = 22.05$ to $25.60$ kN/cm²
- Compressive strength after freezing $\sigma_m = 20.22$ to $27.60$ kN/cm²
- Volumetric weight $g = 27.5$ kN/m³
- Specific gravity $g_s = 28$ kN/m³
- Wear $a = 21.3-29.60$ cm² cm²/50cm²
- Water absorption $u= 0.367\%$
- Static elastic modulus $E_s = 2690-5710$ kN/cm²
- The dynamic elastic modulus $E_d = 830-2120$ kN/cm²
- Velocity of longitudinal elastic waves $V_l = 1.90-2.97$ km/s
- Velocity of transverse elastic waves $V_t = 1.31-2.05$ km/s

For the limestone:
Half bounded rocks with calcareous clay binder cover are eluvial and deluvial origin. They are characterized by plastic ties between the grain and the different structural and textural and physical-mechanical properties. They mostly build mild slope sides and bays in wider area of the river. They have variable potency ranging and mainly covering basic rock formations.

Unbound coarse and fine grain weak complex to lose rocks are represented by local deposits and accumulations of sand and gravel alluvial type, paragraphs and blocks of source rocks, proluvian type and screes applied. They mostly build bottom of riverbeds and alluvial terraces. So these are applied in thickness, ranging from 0.5 to 2 m. These materials are very heterogeneous and variable particle size distribution and uniform physical and mechanical properties. In the slope areas there are also presented colluvial deposits of limestone and dolomite debris that occur in the form of talus materials.

Seismological features of the terrain

Seismological features of the terrain are mostly dependent on the structural-tectonic and lithostratigraphic complex terrain structure. To determine the seismic activity in the Prusacka River catchment area and areas to build hydropower facilities, Seismological Map of Yugoslavia scale of 1:1 000 000 published by the Association for Seismology of the former Yugoslavia in 1987 temporarily have used.

On this map, the Prusacka River catchment is located within the isolines 5th MCS scale return period of 50 years, while the period of 100, 200 years this area has been under isoline 6th-7th MCS. For a return period of 500 and 1000 years, this space is isolines 7-8th MCS.

Concluding Remarks

- The Prusac City is a place rich in natural beauty, with lots of monuments, legends and all that we classify in the natural and historical-cultural heritage.
- The Prusacka River catchment area lies in the ground which was built from the creation of the Middle and Upper Triassic (T₂ and T₃) and Quaternary age. The watershed is defined orographic.
- Bearing in mind the increase in seismic activity in the building budgets, it should be taken the adequate value of 8th MCS.
- The Prusacka River Valley in the area of planned hydraulic structures are formed in the main geological formations of heterogeneous composition, largely impermeable rock masses, and the river drift does not exceed a thickness of 2.5 m.
- The terrain in the zone of buildings is slight-erodibilited and appears stable in its natural condition.
- Excavations in the area objects should be done in good geotechnical properties of rocks and by GN 200 to the IV-V category for the basic rock mass and II and Category III for blankets and applied.

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Behaviour of Naturally Occurring Radionuclides in Perennial Plants

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Abstract: Much of our food directly or indirectly originates from plant material, thus detailed studies on plant contamination processes are an essential part of international environmental research. This overview attempts to identify and describe the behavior of natural radionuclide transfer to plants. Knowledge of this behavior can help to assess and prevent radiological exposure of humans. This knowledge can also help to guide researches and modelling related to transfer of radionuclides to food chain. A comprehensive study was conducted to determine the soil to plant transfer factor (TFs–P) of $^{232}$Th, $^{238}$U, $^{40}$K and $^{137}$Cs in perennial plants using high-resolution $\gamma$ spectrometry. A total of 40 soil and 60 plant samples were collected from different locations in the nearby area from nuclear research centre (NRC) of Egypt (about 30 km radius) at Inshas area.

Keywords: Transfer factor [TFs–P], $^{232}$Th, $^{238}$U, $^{40}$K and $^{137}$Cs.

Introduction

Radioactivity in the soil due to anthropogenic radionuclide is indicative of the distribution and accumulation of radioactivity in the environment due to nuclear facilities whereas the natural radionuclide in the soil is a true representation of rock material beneath the surface soil (Zararsiz et al., 1997). Measurement of radioactivity content in the terrestrial environment is useful for the evaluation of the extent of direct and indirect exposure to human. The specific levels of terrestrial environmental radiation is related to the geological composition of each lithologically separated area and to the content of thorium (Th), uranium (U) and potassium (K) of the rock from which the soil originate in each area. (Hamby, 2002; Tzortzis et al., 2003). The soil-to-plant transfer factor (TFs–P) of radionuclide, which accounts for the transfer of the nuclides uptake via the root system, varies enormously. Moreover, the term transfer factor implies a constant value but in reality uptake is a function of the plant development stage. Determination of (TFs–P) in case of perennial plant is an important tool for understanding the impact of local geo-chemical environment on the uptake of radionuclide from soil. The soil to plant transfer factor (TFs–P) has a strong dependence on geochemical environment prevailing around the plants and the metabolic processes of the plants. Generally, soil characteristics such as pH, clay content, organic matter, and cation exchange capacity have great influence on the radionuclide uptake from the soil while some chemical analogues further influence the uptakes (Bergeiik et al, 1992). In this category, potassium content determines the capacity for $^{137}$Cs sorption by soils. In cases of seasonal crops, a large number of studies are available compared to perennial plants. Although many researches evaluated the soil to plants uptake factors for wide range of radionuclides, both under actual environmental conditions as well as by simulated experiments in the laboratory (Abu Khadra, 2009) limited data are available for the perennial plants.

Perennial plants are those (Latin per, "through", annum, “year”) that live for more than two years and are commonly divided into two large groups (woody and herbaceous). All woody plants are perennial since they form woody tissue that persists from one year to the next. Woody perennials develop a woody base or root system from which the foliage and flower stems grow year after year while the plant is alive. Surveillance of woody perennial plants provides the vital information on uptake of natural and long lived ($^{40}$K, $^{232}$Th and $^{238}$U) and anthropogenic radionuclide ($^{137}$Cs). These plants can also serve as a reference for dose assessment due to abundant natural $^{40}$K, $^{232}$Th and $^{238}$U and anthropogenic ($^{137}$Cs) radionuclide in the soil.

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Materials and Methods
Sampling and Preparation:

40 surface soil samples and Leaves of 60 perennial plants collected from different locations in the nearby area from nuclear research centre (NRC) of Egypt at Inshas area. This area has many industrial factories such as phosphoric acid and phosphate fertilizer, which produce some of gaseous or volatile radioactive waste (Baestle, 1994). A representative surface soil samples (0–15 cm) taken after mixing the surface soils of four locations around the tree and each locations were separated by 500 cm from each other. Soil samples were cleaned by removing the stones, decaying the plants leaves and then dried and grinded. The prepared soil samples were put in plastic jars (300 ml volume) weighed, sealed and analyzed for gamma emitting radionuclides after keeping aside for 30 days allowing secular equilibrium to be attained between $^{238}$U, $^{232}$Th and their daughter products. Leaves thoroughly washed, air-dried and kept in oven at 110°C. The dried leaves were grinded in a mixer and sieved through a mesh size of 2,000 $\mu$m. Also the prepared leaves samples were put in plastic jars (300 ml volume) weighed, and analyzed directly for gamma emitting radionuclides. (Fig. 1) shows the sampling sites.

Gamma Spectrometry

The radioactivity measurements were performed by a high-resolution gamma spectroscopic system employing a high purity germanium crystal (HPGe) coupled with multichannel analyzer (TENNELEC); it is a p-type co-axial detector. Radioactivity concentration of each sample measured for about 20 hours .The activity concentration of the background also measured. Sample preparation and both of energy and efficiency calibration were mentioned in other publications (Abu Khadra, 1998). The naturally occurring radionuclides considered in the present analysis of the measured γ ray spectra are $^{212}$Pb (239 keV and a gamma yield of 43.1%), $^{214}$Pb (352 keV, 37.1%), $^{214}$Bi (609 keV, 46.1%), $^{228}$Ac (911 keV, 29 %), and $^{40}$K (1460 keV, 10.7 %). Under the assumption that secular equilibrium has been attained between $^{232}$Th / $^{238}$U and their daughter products, the concentration of $^{232}$Th was determined from the average concentrations of $^{212}$Pb and $^{228}$Ac in the samples, and that of $^{238}$U was determined from the average concentrations of the $^{212}$Pb and $^{214}$Bi (Hamby, 2002 ,Tzortzis et
al., 2003). A direct measurement of $^{40}$K and $^{137}$Cs concentrations was determined from (1460 keV and 662 keV) $\gamma$-energy respectively.

**Results and Discussion**

The uptake values of a specific radionuclide by the perennial plants are dependent on the physical and chemical characteristics of the soil, which in themselves do not necessarily remain constant over a long time because the soil is a dynamic system (Abbazov et al., 1978). Because of its dependence on many soil properties, the value of the transfer factor for a specific radionuclide in soil can range over several orders of magnitude (Salbu, 1995). Thus, it is very essential to study the physicochemical characteristics of soil over a time. Table 1 shows the mean values of various physicochemical characteristics of the surface soils under study.

**Table 1. Physical and Chemical Characteristics of Soils of Egypt**

<table>
<thead>
<tr>
<th>Physico-chemical parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand %</td>
<td>7.6 - 94</td>
</tr>
<tr>
<td>Silt %</td>
<td>4.5 - 42.8</td>
</tr>
<tr>
<td>Clay %</td>
<td>2.0 - 49.6</td>
</tr>
<tr>
<td>Bulk density ( g cm$^{-3}$)</td>
<td>1.56 - 1.85</td>
</tr>
<tr>
<td>Field capacity (cm$^3$water cm$^-3$soil)</td>
<td>0.1 - 0.55</td>
</tr>
<tr>
<td>pH</td>
<td>7.5 - 8.0</td>
</tr>
<tr>
<td>CaCO$_3$ %</td>
<td>1.78 - 3.57</td>
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<tr>
<td>O.M %</td>
<td>0.07 - 1.79</td>
</tr>
<tr>
<td>Cations (mg kg$^{-1}$):</td>
<td></td>
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<tr>
<td>Na$^+$</td>
<td>2600 - 3100</td>
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<tr>
<td>K$^+$</td>
<td>9300 - 15900</td>
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<tr>
<td>Ca$^{2+}$</td>
<td>23900 - 38100</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>11400 - 12800</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>21 - 33.3</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>19.2 - 27.6</td>
</tr>
</tbody>
</table>

**Radioactivity Concentration of $^{137}$Cs, $^{40}$K, $^{232}$Th, and $^{238}$U in Soil and Perennial Plant Leaves**

Tables 2 and 3 give the activity concentrations (Bq kg$^{-1}$) in both surface soil and leaves of perennial plants respectively. The mean activity concentrations of different radionuclides were quantified on dry weight basis for soil and the measured concentrations of $^{137}$Cs, $^{40}$K, $^{232}$Th, and $^{238}$U in soil samples were ranging from (1.0-3.0), (44.5-163.2), (6.7-19.5) and (6.7-27.7) Bq kg$^{-1}$ respectively. Whereas in case of leaves of perennial plants the activity concentrations of $^{137}$Cs, $^{40}$K, $^{232}$Th, and $^{238}$U were ranging from (1.6 - 4.5), (93.7 - 286), (8 -23.3) and (10 -18.3) Bq kg$^{-1}$ (wet bases) respectively. From the measurements, it is noticed that the mean activity ratio of $^{232}$Th / $^{238}$U in plants was 1.1, while in soil the ratio was 1.2. In soil samples, it can be noted that, the average concentrations of the same isotope differ from site to the other. The ranges of the concentrations of $^{232}$Th are slightly higher than those of $^{238}$U for most soil samples (with few exceptions as that of Guava and Grape trees) .While $^{137}$Cs exhibits the lowest values and $^{40}$K shows the highest values, which is normally expected due to the difference in the soil nature, taking into consideration the nature of the Egyptian soil. These results are in good agreement with those obtained previously for the same sites of Egypt (Abu Khadra, 2009). In leaves of perennial plants , it should be noted that the average concentration values of $^{137}$Cs, $^{40}$K in all plants in the present study are higher than those obtained for their corresponding soils( except for Guava which has a lower concentration than that of the soil) .The average concentration values of $^{232}$Th in most plants in the present study are higher than those obtained for their corresponding soils (except for Pear, cypress, plum and Guava which have lower concentrations than that of their soils). The average concentration values of $^{238}$U in most perennial plants are higher than those obtained for their corresponding soils (except for Guava which has the lowest concentration than that of the soil). From these results, it can be noticed that leaves of Guava trees have nearly the lowest concentration.
values of $^{137}$Cs, $^{40}$K, $^{232}$Th, and $^{238}$U. This phenomenon can be explained on the basis that, there is a wide variability in the bioaccumulation of trace elements among plant species (Saric et al., 1995).

### Transfer factor of $^{137}$Cs, $^{40}$K, $^{232}$Th, and $^{238}$U from soil to different perennial plants

Table 4 gives the transfer factors of $^{137}$Cs, $^{40}$K, $^{232}$Th, and $^{238}$U for different plants. The soil to plant transfer factors for $^{137}$Cs, $^{40}$K, $^{232}$Th, and $^{238}$U were found to range from (1.4-2.0), (0.9-2.4), (0.5-9.7) and (0.4-7.2) respectively. It is obvious that the Guava trees have the lowest transfer factor for all radionuclides; Olive trees showed the highest transfer factor for $^{232}$Th, and $^{238}$U, while Alvix trees showed the highest transfer factor for $^{137}$Cs and $^{40}$K. The average values of transfer factors for $^{137}$Cs, $^{40}$K, $^{232}$Th, and $^{238}$U were found to be 1.56, 1.63, 1.38, 1.50 respectively, and hence the sequence of uptake factor from least to greatest for radionuclide in perennial plants was found to be $^{232}$Th < $^{238}$U < $^{137}$Cs < $^{40}$K.

### Table 2. Mean concentration of $^{137}$Cs, $^{40}$K, $^{232}$Th, and $^{238}$U, in soil samples collected, around various types of perennial plants

<table>
<thead>
<tr>
<th>Perennial plants</th>
<th>Number of Soil samples</th>
<th>Activity concentrations(surface soil) Bq kg$^{-1}$(dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Olive trees</td>
<td>3</td>
<td>$^{137}$Cs: 44.45, $^{40}$K: 12.4, $^{232}$Th: 12.4, $^{238}$U: 1.0</td>
</tr>
<tr>
<td>2-Mango trees</td>
<td>3</td>
<td>$^{137}$Cs: 1.2, $^{40}$K: 97.7, $^{232}$Th: 9.9, $^{238}$U: 7.5</td>
</tr>
<tr>
<td>3-Prickly pear</td>
<td>4</td>
<td>$^{137}$Cs: 1.0, $^{40}$K: 117, $^{232}$Th: 11.6, $^{238}$U: 9.7</td>
</tr>
<tr>
<td>4-Alvix trees</td>
<td>4</td>
<td>$^{137}$Cs: 1.7, $^{40}$K: 69.5, $^{232}$Th: 6.7, $^{238}$U: 6.7</td>
</tr>
<tr>
<td>5-Castor-pear trees</td>
<td>4</td>
<td>$^{137}$Cs: -, $^{40}$K: 109, $^{232}$Th: 9.9, $^{238}$U: 8.3</td>
</tr>
<tr>
<td>6-Towia trees</td>
<td>3</td>
<td>$^{137}$Cs: -, $^{40}$K: 100, $^{232}$Th: 14.1, $^{238}$U: 8.7</td>
</tr>
<tr>
<td>7-Camphor</td>
<td>4</td>
<td>$^{137}$Cs: 3.0, $^{40}$K: 98.2, $^{232}$Th: 10.6, $^{238}$U: 8.3</td>
</tr>
<tr>
<td>8-Pear trees</td>
<td>3</td>
<td>$^{137}$Cs: 1.4, $^{40}$K: 156, $^{232}$Th: 19.5, $^{238}$U: 12.5</td>
</tr>
<tr>
<td>9-Cypress</td>
<td>3</td>
<td>$^{137}$Cs: 1.6, $^{40}$K: 163.2, $^{232}$Th: 15.6, $^{238}$U: 10.1</td>
</tr>
<tr>
<td>10-Grape</td>
<td>3</td>
<td>$^{137}$Cs: 1.2, $^{40}$K: 100.3, $^{232}$Th: 9.6, $^{238}$U: 13.1</td>
</tr>
<tr>
<td>11-plum</td>
<td>3</td>
<td>$^{137}$Cs: 1.3, $^{40}$K: 98.5, $^{232}$Th: 13.5, $^{238}$U: 11.4</td>
</tr>
<tr>
<td>12-Guava</td>
<td>3</td>
<td>$^{137}$Cs: 1.2, $^{40}$K: 112, $^{232}$Th: 17.4, $^{238}$U: 27.7</td>
</tr>
</tbody>
</table>

### Behaviour of $^{137}$Cs and $^{40}$K in soil–plant environment

$^{40}$K, a natural radioactive element having a half-life of $1.3 \times 10^9$ years is an integral part of stable potassium (i.e.$^{39}$K) with isotopic abundance of 0.018 %. The observed concentration of potassium in surface soil samples around Inshas region ranged from 9300 – 15900 ppm against the global range of 80–37,000 ppm (Bowen, 1979). In soil solution, potassium is generally present as $K^+$, and is the most mobile element in plants and does not occur as part of any stable organic compound. Therefore, $^{40}$K along with stable potassium ($^{39}$K) transport from the roots of the plants to the leaves, where it serves two important purposes: (1) It is an important osmotic constituent of cell sap and is an activator/cofactor of many enzymes including adenosine triphosphates. (2) It is important in growth and accumulates to high concentrations since turgid required for cell enlargement (Cline, 1960).

$^{137}$Cs which is one of major fission products originating from the thermal fission of $^{235}$U, spread globally due to atmospheric weapon testing, and some of the major nuclear accidents, and have a concentration in the surface soil of 0.8 - 10 Bq kg$^{-1}$, with a few exception of high value regions around Chernobyl (Antonopoulos et al., 1997). Due to chemical similarity (alkali metals), the uptake of Cs and K from soil by perennial plants can be compared. Though $^{40}$K and $^{137}$Cs have similar chemical behavior, the lower ratio for $^{137}$Cs is due to the higher concentration of $^{40}$K in soil, which suppresses the uptake of $^{137}$Cs by the plant.
Table 3. Mean concentration of $^{137}$Cs, $^{40}$K, $^{232}$Th, and $^{238}$U in leaves of different perennial plants

<table>
<thead>
<tr>
<th>Perennial plants</th>
<th>Number of plant samples</th>
<th>Activity concentrations (plants) Bq kg$^{-1}$Bq kg$^{-1}$(wet)</th>
<th>$^{137}$Cs</th>
<th>$^{40}$K</th>
<th>$^{232}$Th</th>
<th>$^{238}$U</th>
<th>$^{232}$Th/$^{238}$U</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Olive trees</td>
<td>5</td>
<td></td>
<td>93.7</td>
<td>23.3</td>
<td>16.4</td>
<td>13.2</td>
<td>1.4</td>
</tr>
<tr>
<td>2-Mango trees</td>
<td>5</td>
<td></td>
<td>1.63</td>
<td>135.2</td>
<td>16.4</td>
<td>13.2</td>
<td>1.2</td>
</tr>
<tr>
<td>3-Prickly pear</td>
<td>6</td>
<td></td>
<td>1.8</td>
<td>158.4</td>
<td>14.2</td>
<td>13.3</td>
<td>1.1</td>
</tr>
<tr>
<td>4-Alvix trees</td>
<td>5</td>
<td></td>
<td>3.3</td>
<td>164.1</td>
<td>20.6</td>
<td>17.7</td>
<td>1.2</td>
</tr>
<tr>
<td>5-Castor-pear trees</td>
<td>5</td>
<td></td>
<td>-</td>
<td>135.7</td>
<td>18.7</td>
<td>15.8</td>
<td>1.2</td>
</tr>
<tr>
<td>6-Towia trees</td>
<td>5</td>
<td></td>
<td>-</td>
<td>164.6</td>
<td>21.6</td>
<td>14.2</td>
<td>1.5</td>
</tr>
<tr>
<td>7-Camphor</td>
<td>5</td>
<td></td>
<td>4.5</td>
<td>163.6</td>
<td>21.1</td>
<td>18.3</td>
<td>1.2</td>
</tr>
<tr>
<td>8-Pear trees</td>
<td>5</td>
<td></td>
<td>2.0</td>
<td>165</td>
<td>13.3</td>
<td>14.5</td>
<td>0.9</td>
</tr>
<tr>
<td>9-Cypress</td>
<td>5</td>
<td></td>
<td>3.0</td>
<td>286</td>
<td>8.0</td>
<td>10</td>
<td>0.8</td>
</tr>
<tr>
<td>10-Grape</td>
<td>4</td>
<td></td>
<td>1.9</td>
<td>175</td>
<td>11.5</td>
<td>13.5</td>
<td>0.9</td>
</tr>
<tr>
<td>11-plum</td>
<td>5</td>
<td></td>
<td>2.2</td>
<td>158</td>
<td>10.2</td>
<td>11.9</td>
<td>0.9</td>
</tr>
<tr>
<td>12-Guava</td>
<td>5</td>
<td></td>
<td>1.7</td>
<td>98.5</td>
<td>9.8</td>
<td>10.4</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table 4. Transfer factor for $^{137}$Cs, $^{40}$K, $^{232}$Th, and $^{238}$U from soil to leaves of different perennial plants

<table>
<thead>
<tr>
<th>Perennial plants</th>
<th>Transfer factor</th>
<th>$^{137}$Cs$<em>{plant}$/ $^{137}$Cs$</em>{soil}$</th>
<th>$^{40}$K$<em>{plant}$/ $^{40}$K$</em>{soil}$</th>
<th>$^{232}$Th$<em>{plant}$/ $^{232}$Th$</em>{soil}$</th>
<th>$^{238}$U$<em>{plant}$/ $^{238}$U$</em>{soil}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Olive trees</td>
<td></td>
<td>2.1</td>
<td>9.7</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>2-Mango trees</td>
<td></td>
<td>1.4</td>
<td>1.4</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>3-Prickly pear</td>
<td></td>
<td>1.8</td>
<td>1.4</td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>4-Alvix trees</td>
<td></td>
<td>2.0</td>
<td>2.4</td>
<td>3.1</td>
<td>2.7</td>
</tr>
<tr>
<td>5-Castor-pear trees</td>
<td></td>
<td>-</td>
<td>1.2</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>6-Towia trees</td>
<td></td>
<td>-</td>
<td>1.7</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>7-Camphor</td>
<td></td>
<td>1.5</td>
<td>1.7</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>8-Pear trees</td>
<td></td>
<td>1.4</td>
<td>1.1</td>
<td>0.7</td>
<td>1.2</td>
</tr>
<tr>
<td>9-Cypress</td>
<td></td>
<td>1.9</td>
<td>1.8</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>10-Grape</td>
<td></td>
<td>1.6</td>
<td>1.7</td>
<td>1.2</td>
<td>1.0</td>
</tr>
<tr>
<td>11-plum</td>
<td></td>
<td>1.7</td>
<td>1.6</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>12-Guava</td>
<td></td>
<td>1.4</td>
<td>0.9</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Average values of TF$_{p}$</td>
<td></td>
<td><strong>1.56</strong></td>
<td><strong>1.63</strong></td>
<td><strong>1.38</strong></td>
<td><strong>1.50</strong></td>
</tr>
</tbody>
</table>

Behaviour of natural occurring thorium and uranium in soil–plant environment:

Uranium and thorium not considered essential for plant growth. Plant uptake of U is limited and affected by soil pH. Typical concentration factor of uranium is usually in the range of $10^{-2}$ to $10^{-4}$ (IAEA, 1994). Under acidic conditions of soil, UO$_2^{2+}$ is the predominant uranium species in the soil whereas Th has only one stable oxidation state i.e. IV under all redox conditions in soil and is extremely particle reactive having Kd value of the order of $10^6$ (Saric et al. 1995; Zararsiz et al. 1997). Hence, higher transfer factor from soil to plant observed in case of uranium compared to
thorium (Table 4). $^{232}$Th concentrations were slightly higher in plant than $^{238}$U concentrations. Therefore, U and Th movement through plant limited by adsorption and controlled by discrimination mechanisms. The tetravalent forms of U and Th considered as highly particle reactive, immobile and insoluble in aqueous environment. Although UO$_2^{2+}$, which is a hexavalent form of uranium, is highly soluble, as per the study work carried out by (Saric et al., 1995), it is found tightly bounded to the cell wall of the plant. However, transfer factor (TF$_{s-p}$) of $^{232}$Th is lower than that of $^{238}$U, which indicates that Th is immobile and has lower solubility compared to U. This is also indicated by the ratio of $^{232}$Th/$^{238}$U in soil, which is 1.1 times higher than the ratio in plant.

Regression analysis of the Data:

Figure 2 shows linear regression analysis of the observed values of $^{232}$Th and $^{238}$U in soil and plant. To establish a correlation between U and Th in soil and plants, a linear correlation coefficient was used. For Th concentration, a linear correlation showed a coefficient of $R^2 = 0.23$ with intercept = 24.4 and slope = -0.69. Similarly, U concentration showed a correlation coefficient of $R^2 = 0.26$ with the intercept = 16.9 and slope = -0.25. In both cases, a poor degree of correlation observed indicating that concentration of U and Th in plants not influenced too much by their concentration in soil. Due to long-term effect, they would have migrated through soil and slowly taken up by the plant. Thus, it can be concluded that Th and U concentrations in plants are not linearly related to their concentrations in soil. However, uptake of U with Th showed a high degree of correlation (coefficient of $R^2 = 0.83$, intercept = -0.21 and slope = 1.11) indicating that uptake of U and Th in plants was linearly related to each other. This result is in good agreement with that obtained by (Ajay, 2008).

Similarly, Figure 3 shows a correlation between $^{137}$Cs and $^{40}$K, in soil and plants studied using linear coefficients. Regression analysis of $^{137}$Cs in soil and plants shows a high degree of linear correlation (coefficient of $R^2 = 0.88$ with the intercept = +0.15 and slope = +1.53), indicating that the concentration of $^{137}$Cs in plant is influenced by its concentration in soil and to some extent they are linearly dependent on each other. $^{40}$K concentration showed a moderate degree of linear correlation (coefficient of $R^2 = 0.42$ with the intercept = +55.6 and slope = +0.97) indicating that activity concentration of $^{40}$K in plant is not influenced too much by its concentration in soil. Nevertheless, uptake of $^{137}$Cs with $^{40}$K showed a moderate degree of correlation (coefficient of $R^2 = 0.53$ with the
intercept = 3.84 and slope = -3.70) indicating that uptake of $^{137}$Cs is proportional to some extent to the uptake of $^{40}$K in plants (Bergeiik et al., 1992; Ajay, 2008).

Figure 3. Linear regression analysis of the observed values of $^{137}$Cs and $^{40}$K in soil and plant

Conclusion
Radionuclide migration and redistribution in the ecosystem is a result of various physicochemical and biological processes. Therefore, studying them for perennial plants is of special importance due to their long life. The activity concentration values for $^{40}$K, $^{137}$Cs, $^{232}$Th and $^{238}$U in soil were ranging from (44.5-163.2), (1.0-2.97), (2.4-17.4) and (2.4-27.7) Bq kg$^{-1}$ respectively. In case of plants, the activity concentration values were ranging from (93.7-286), (1.6-4.8), (8-23.3) and (10-18.3) Bq/kg respectively. The activity ratio of $^{232}$Th / $^{238}$U in plants is ranging from (0.8-1.5) while in soil the ratio is ranging from (0.6-1.62). The soil to plant transfer factor (TF$_{S-P}$) calculated for $^{40}$K, $^{137}$Cs, $^{232}$Th and $^{238}$U are ranging from (0.8-2.4),(1.3-3.7),(0.5-9.7) and (0.4-7.2) respectively. Uranium and thorium concentrations in plants were not linearly related to their concentrations in the soil. Thus, a single value for use as a conservative concentration ratio for a soil type could not be determined. On the other hand the uptake of U and Th in plants was linearly related to each other. The concentration of $^{137}$Cs in plant is influenced by its concentration in soil and to some extent they are linearly dependent on each other. The activity concentration of $^{40}$K in plant is not influenced too much by its concentration in soil, while the uptake of $^{137}$Cs is proportional to some extent to the uptake of $^{40}$K in plants.

References


Formation of Disinfection By-products (DBPs) and Strategies to Reduce Their Concentration in the Water Treatment Plant in Përlepnica – Gjiolan, Kosovo

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Abstract Chlorine is the most widely used disinfection agent in drinking water industry in the world. Chlorine is a strong oxidant, and has the ability to kill or inactivate most pathogenic microorganisms commonly found in water. As such, chlorine used for disinfection of drinking water reacts with natural organic matter (NOM) contained in raw water, and forms the so called disinfection by-products (DBPs), of which trihalomethanes (THMs) and halo acetic acids (HAAs) are the two main groups of DBPs. It is confirmed that the exposure to aforementioned DBPs has various negative health effects in humans, therefore agencies dealing with public health have set rules for maximum concentration levels (MCL) for the THMs and for the HAAs, which are enforceable for each public water supply company. It has been documented that concentrations of THMs and HAAs and other halogenated substances can be reduced at the treatment plant, by utilizing following available alternatives such are: using an alternate disinfection agent, reduce the free-chlorine contact time, reduce the concentration of total organic carbon (TOC) from the water before chlorine is added, remove bromide before chlorine addition and change the pH of the water during chlorination. In this paper are presented the dependencies of concentration of total organic carbon (TOC), concentration of residual chlorine and bromine ion in water vs. level of concentration of DBPs in the drinking water.

Key words: chlorine, chlorinated disinfection by-products, trihalomethanes, halo acetic acids and natural organic matter.

Introduction

The primary role of disinfection process in the water treatment is to kill or achieve the necessary microbial inactivation and to maintain the disinfection residual through the distribution system. Chlorine has many attractive features that contribute to its wide use in the drinking water industry, such:

• effectively inactivates a wide range of pathogens commonly found in water;
• leaves a residual in the water that is easily measured and controlled;
• it is economical; and
• has an extensive track record of successful use in improving water treatment operations.

However, there are, some health related concerns regarding chlorine usage that directly impacts its use, as listed below:

• chlorine reacts with many naturally occurring organic and inorganic compounds in water to produce undesirable DBPs;
• hazards associated with using chlorine, specifically chlorine gas, require special treatment and response programs; and
• high chlorine doses can cause taste and odour problems.

In the water industry in Kosovo, chlorine, due to his very strong oxidation properties and low cost, is most widely used disinfection agent. Chlorine is utilized in the liquid form (as calcium hypochlorite or sodium hypochlorite solution) or as gas chlorine.

Water Supply System of Gjiolan

The town of Gjiolan receives the major portion of its drinking water supply from water treatment plant located at Përlepnica (North-East of Gjiolan). The water treatment plant in Përlepnica, as shown in the figure 1, receives raw water from accumulation lake with capacity of 120 – 180 l/s and from the thermal groundwater source Guri i Hoxhës with capacity of 50 – 70 l/s.

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Treatment chain in Përlepnica plant was selected to address conventional and non-conventional contaminants, such as: turbidity, prevent algae growth, remove taste and odours, removal of manganese and iron. Water from Guri i Hoxhës is of very good quality, water quality tests indicate that the chemical parameters of Guri i Hoxhës spring are within the WHO limits, and is blended with treated water exiting the filtration plant just before the disinfection point, see figure 1. Gas and liquid chlorine are used for disinfection purposes.

Figure 1. Treatment scheme of the WTP Përlepnica

Methods and Equipment
For determination and quantification of physical-chemical parameters, particularly the DBPs (THMs and HAAs) that are the key focus of this study, following equipments have been used:
- Gas chromatograph
- Mass Spectrometer
- Spectrophotometer UV/ VIS HACH DR 5000
- Spectrophotometer UV 254 nm
- JAR Testing Bench
- Pocket Colorimeter™ HACH
- Turbidimeter HACH 2100

Methods used for identification and quantification of chemical parameters are listed in the table 1.

Table 1. Methods used for water quality tests

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Method used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total organic Carbon (TOC) tests are done in SGS Institute Fresenius, Taunusstein, Germany</td>
<td>ISO EN 1484 and SUVA at 254 nm</td>
</tr>
<tr>
<td>Trihalomethanes (THM) tests are done in SGS Institute Fresenius, Taunusstein, Germany</td>
<td>DIN EN ISO 10301</td>
</tr>
<tr>
<td>Haloceticacids (HAA) tests are done in SGS Institute Fresenius, Taunusstein, Germany</td>
<td>DIN EN ISO 23631</td>
</tr>
<tr>
<td>Turbidity</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>Residual Chlorine</td>
<td>Colorometry</td>
</tr>
<tr>
<td>Bromide ion</td>
<td>Colorometry</td>
</tr>
</tbody>
</table>
Results and Discussions

Strategies to control formation of disinfection by-products

Halogenated organic by-products are formed when natural organic matter (NOM) reacts with free chlorine or free bromine. Free bromine results from the oxidation of the bromide ion in source water, when adding the chlorine. Other important factors which have impact on formation of halogenated DBPs are: 1) concentration of natural organic matter in the source water, measured as TOC; 2) disinfectant type and dosage rate; 3) contact time of water with the disinfectant; 4) bromide ion concentration; 5) pH value of water; and 6) temperature. In this paper is evaluated the impact of TOC concentration, concentration of bromide ion and chlorine concentration in formation of DBPs.

Reducing the DBP precursors

It has been documented that the concentration of DBPs produced during water treatment strongly depends on the concentration of NOM contained in source water and measured as total organic carbon (TOC). Therefore, reducing the concentration TOC, before the water is coming in contact with disinfection agent will result in lowering the total concentration of DBPs. In the table 2 are summarized the results how the concentration of TOC is reduced after coagulation and filtration as per daily operation regime of the treatment plant in WTP Përlepnica. Other key water quality parameters are also presented in the table, considering their importance and impact for TOC removal efficiency and their potential for producing the DBPs.

Table 2. TOC concentration of raw water from both sources, TOC concentration after coagulation & filtration processes and of blended water

<table>
<thead>
<tr>
<th>Date (Method used)</th>
<th>Other key parameters</th>
<th>Concentration of total organic carbon – TOC (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Values</td>
<td>Raw water</td>
</tr>
<tr>
<td>Oct. 7th, 2009 (EN 1484)</td>
<td>pH</td>
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</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>14.9</td>
</tr>
<tr>
<td></td>
<td>Residual chlorine (mg/l)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Bromide Br⁻ (mg/l)</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>Al-sulphate dose (g/m³)</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Flow (m³/h)</td>
<td>430</td>
</tr>
<tr>
<td>Dec. 22nd, 2009 (EN 1484)</td>
<td>pH</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Residual chlorine (mg/l)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Bromide Br⁻ (mg/l)</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>Al-sulphate dose (g/m³)</td>
<td>25.8</td>
</tr>
<tr>
<td></td>
<td>Flow (m³/h)</td>
<td>350</td>
</tr>
<tr>
<td>Jan. 16th, 2010 (SUVA at 254 nm)</td>
<td>pH</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>Residual chlorine (mg/l)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Bromide Br⁻ (mg/l)</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>Al-sulphate dose (g/m³)</td>
<td>25.8</td>
</tr>
<tr>
<td></td>
<td>Flow (m³/h)</td>
<td>320</td>
</tr>
<tr>
<td>Apr 20th, 2010 (EN 1484)</td>
<td>pH</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>Residual chlorine (mg/l)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Bromide Br⁻ (mg/l)</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>Al-sulphate dose (g/m³)</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Flow (m³/h)</td>
<td>369</td>
</tr>
<tr>
<td>Sep. 14th, 2010 (EN 1484)</td>
<td>pH</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Residual chlorine (mg/l)</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>Bromide Br⁻ (mg/l)</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>Al-sulphate dose (g/m³)</td>
<td>400</td>
</tr>
</tbody>
</table>
Results obtained from WTP Përlepnica shows that the TOC removal after coagulation & filtration processes, under normal operational conditions, is not quite sufficient, the TOC concentration remains above 2 mg/l in all cases. There is no regulation specifying the TOC concentration level in water, however, the TOC concentration exceeding 2 mg/l (MWH Global Water Treatment Principles and Design 2005, John Wiley & Sons, Second Edition, U.S.) is defined as high potential for producing DBPs. Water exiting the filtration plant is blended with the water from Guri i Hoxhës spring, which has very low TOC concentration (see table above – under column Guri i Hoxhës spring) and it dilutes the overall concentration of the TOC considerable, see column of blended water. It has to be emphasized that the dosage of aluminium sulphate (used as coagulant) has significant impact on removal efficiency of TOC. The better the dose of coagulant is adjusted the better the TOC removal efficiency is achieved, see the results presented in the table 3.

Table 3. Removal efficiency of TOC

<table>
<thead>
<tr>
<th>Dosage of al-sulphate (g/m³)</th>
<th>Raw water (mg/l)</th>
<th>Removal (%)</th>
<th>After coagulation and filtration</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.6</td>
<td>44.4</td>
<td>2</td>
</tr>
<tr>
<td>25.8</td>
<td>3.9</td>
<td>17.9</td>
<td>3.2</td>
</tr>
<tr>
<td>25.8</td>
<td>4.6</td>
<td>28.6</td>
<td>3.1</td>
</tr>
<tr>
<td>35</td>
<td>2.9</td>
<td>13.7</td>
<td>2.5</td>
</tr>
<tr>
<td>11.76</td>
<td>3.1</td>
<td>9.7</td>
<td>2.8</td>
</tr>
</tbody>
</table>

The type and the dosage rate of disinfectant

Now it is known that all chemical disinfectants and oxidants used in water treatment form chemical by-products, out of them chlorine produces the most known DBPs. There are different alternative disinfection strategies which can be used to control formation of DBPs.

1. Use an alternative disinfectant and/or oxidant to chlorine:
   a. Substitute chlorine as disinfectant with chloramines, chlorine dioxide or. At the moment this is not an option due to high investment costs.
   b. Substitute the chlorine as pre-chlorination reagent with other chemicals, such potassium permanganate to reduce the contact time. This is possible to apply.

2. Optimizing the chlorine dosage can have big impact in the total amount of DBPs produced. As shown in the figure 2, by increasing the disinfectant (chlorine) dose, the total amount of DBPs produced is increased significantly.

3. Reduction of free-chlorine contact time can reduce significantly the DBP formation. The contact time of free chlorine can be reduced by moving the chlorine addition to the end of the treatment chain.

Figure 2. Total DBP formation and dependence on residual chlorine concentration
Bromide ion concentration

Free chlorine oxidizes bromide ion to free bromine, which in contact with water produces hypobromous acid. Hypobromous acid, same as hypochlorous acid, forms brominated organic by-products, the higher the bromide ion concentration, increases the brominated species, see the table 6. Therefore, removal of the bromide via enhanced coagulation can reduce the overall concentration of DBPs.

### Table 4. Percentage of chlorinated, brominated and mixed (chlorinated + brominated) species

<table>
<thead>
<tr>
<th>Total DBP concentration (μg/l)</th>
<th>Brominated substances (μg/l)</th>
<th>Percentage brominated substances (%)</th>
<th>Chlorinated substances (μg/l)</th>
<th>Percentage chlorinated substances (%)</th>
<th>Mixed substances (μg/l)</th>
<th>Percentage of mixed substances (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.7</td>
<td>0</td>
<td>0</td>
<td>44</td>
<td>86.8</td>
<td>6.7</td>
<td>13.2</td>
</tr>
<tr>
<td>44.9</td>
<td>0</td>
<td>0</td>
<td>40</td>
<td>89.1</td>
<td>4.9</td>
<td>10.9</td>
</tr>
<tr>
<td>51.5</td>
<td>0</td>
<td>0</td>
<td>47</td>
<td>91.2</td>
<td>4.5</td>
<td>8.8</td>
</tr>
<tr>
<td>34.9</td>
<td>0</td>
<td>0</td>
<td>28</td>
<td>80.2</td>
<td>6.9</td>
<td>19.8</td>
</tr>
</tbody>
</table>

Formation of Disinfection By-Products in WTP Përlepnica

In the table 5 are summarized data obtained for DBP formation, based on the 1 year tests. Tests have been conducted quarterly to cover one whole year period, including the seasonal changes of the raw water quality and different operational conditions. In the table 5 are indicated the concentration of the two main groups of DBPs, trihalomethanes THM and haloacetic acids HAA. Other chlorinated substances, such: 1,1,1–trichloroethan; trichloroethen; tetrachloroethen; cis-1, 2–dichloroethen; trans-1, 2–dichloroethen; 1, 2–dichloropropan; 1, 3–dichloropropan; and 1, 1, 2–trichloroethan have been also tested, but their concentrations were well below the detection limits.

### Table 7 Summary of DBPs (TTHMs and THAAs) concentrations found in WTP Përlepnica*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method of detection</th>
<th>Lower detection limit (μg/l)</th>
<th>Max. Conc. Level (MCL)</th>
<th>Concentration (μg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethan</td>
<td>/</td>
<td>5</td>
<td>/</td>
<td>&lt; 5.0</td>
</tr>
<tr>
<td>Trichloromethan</td>
<td>/</td>
<td>0.5</td>
<td>/</td>
<td>22</td>
</tr>
<tr>
<td>Tetrachloromethan</td>
<td>DIN EN ISO 10301</td>
<td>0.1</td>
<td>/</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Dibromochloromethan</td>
<td>0.1</td>
<td>/</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>Tribromomethan</td>
<td>0.1</td>
<td>/</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Bromodichloromethan</td>
<td>0.1</td>
<td>/</td>
<td>3.9</td>
<td>3.3</td>
</tr>
<tr>
<td>Total Trihalomethanes (TTHMs)</td>
<td>/</td>
<td>80</td>
<td>26.7</td>
<td>17.6</td>
</tr>
<tr>
<td>Bromochloroacetic acid</td>
<td>1.0</td>
<td>/</td>
<td>2</td>
<td>1.3</td>
</tr>
<tr>
<td>Monobromoacetic acid</td>
<td>1.0</td>
<td>/</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Monochloroacetic acid</td>
<td>DIN EN ISO 23631</td>
<td>1.0</td>
<td>/</td>
<td>1</td>
</tr>
<tr>
<td>Dichloroacetic acid</td>
<td>1.0</td>
<td>/</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td>1.0</td>
<td>/</td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td>Dibromoacetic acid</td>
<td>1.0</td>
<td>/</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Total Haloacetic Acids (THAAs)</td>
<td>/</td>
<td>60</td>
<td>24</td>
<td>27.3</td>
</tr>
</tbody>
</table>

*Tests have been conducted in the SGS Institute Fresenius, Taunusstein, Germany

Conclusions

Based on what was presented in this paper, the following conclusions can be drawn:

1. As it was clearly indicated and documented in this paper, concentration of DBPs is strongly dependent on the concentration of TOC in source water.
a. So one of the best strategies to avoid producing the DBPs is to choose the best working coagulant and/or coagulant aids and adjust properly their dose via JAR tests.

b. The situation is serious in WTP Përlepniça (where the surface water is being used). Concentration of TOC after coagulation/filtration is exceeding the limit of 2 mg/l, but after the water is blended with Guri i Hoxhës spring, TOC reduces close to or below 2 mg/l in all cases. Higher attention shall be paid when the capacity of Guri i Hoxhës spring is reduced during dry summer periods.

2. The amount of produced DBPs is strongly dependent on the disinfection reagent used
   a. Reducing the dosage of chlorine leads to formation of fewer amounts of DBPs.
   b. The chlorine is added at the end of the treatment train, which reduces the contact time between chlorine and water.
   c. Usage of chlorine for oxidation (pre-chlorination) purpose shall be restricted. Actually the usage of any alternative disinfectants is not possible due to financial and operational implicated costs.

3. Higher bromide concentration in the source water results in higher concentrations of DBPs (THM and HAA). Therefore, removal of bromide, by utilizing coagulant and adjusting appropriately the dosage, before adding the disinfection reagent is very important.

4. Actual concentration of produced DBPs at the treatment plant in Përlepniça is below the maximum concentration levels. However, considering the health effects of these substances, it is recommended to follow their concentration at least quarterly.

References
Research on Cheese from Cows and Sheep's Milk /2:1/ Produced in Kosovo


1Ministry of Education, Science and Technology, Kosovo; 2 University of Prishtina, Kosovo; 3, 4, 6Secondary School, Kosovo

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Abstract: The possibility of producing cheese Kačkaval with a combination types of milk, in recent times has encountered trouble in the manufacturing and industrial interest for such cheese market with the possibility of a combination of types of milk. Milk processing in Kačkavall cheese takes very important place in productivity of dairy, in the same time takes very important roll in domestic economy as well as nutritive for humankind. This study is done to research the technology for production of Kačkaval cheese, (This types of cheese is classified to hard group of cheeses) with a little milk to produce 1kg cheese (Until now we need 10 liters of milk to produce 1 kg. of this kind of cheese), after research and analyses of physical-chemical peculiar feature of milk, research of technological process to forming the coagulum, curd forming, storage, preparation for drying of curd and additives that we need for this technologic process of production line. We have followed the processes from drying of cheese until preparing it for market, physical-chemical peculiar feature: pH, 0SH, percentage fat, percentage of proteins in general, percentage of sec matter, and percentage of solids for daily fresh cheese, 15 to 30 days maturing. Organo-leptic peculiar feature, its storage in suitable temperatures. There were made near 100-s of analyses to searching better production method. Peculiar future of organic tasting (organo-leptic) for estimation of cheese kačkavall from combinations milk (Between Cow’s & sheep milk 2:1 in favor of cows milk) with 3.6% of fat, with Traditional technology – industrial could be produced, production with desirous organic tasting (organo-leptic) for consumer and market.

Key Words: Milk, coagulum, whey, curd, cheese, Kačkavall, Kosova.

Introduction

Cheese is a fermented food derived from the milk of various mammals. Cheese is a generic term for a diverse group of milk-based food products. Cheese is produced throughout the world in wide-ranging flavors, textures, and forms. Cheese consists of proteins and fat from milk, usually the milk of cows, buffalo, goats, or sheep. It is produced by coagulation of the milk protein casein. Typically, the milk is acidified and addition of the enzyme rennet causes coagulation. The solids are separated and pressed into final form. Some cheeses have molds on the rind or throughout. Most cheeses melt at cooking temperature.

The possibility of producing cheese Kačkaval with a combination types of milk, in recent times has encountered trouble in the manufacturing and industrial interest for such cheese market with the possibility of a combination of types of milk. The interest in Kačkaval cheese production in Kosovo has been grounded on searching for this cheese variety in worldwide scale; moreover it can be produced from different milk varieties (between cows and sheep milk 2:1 in favors of cows milk) with 3.6% of fat, with Traditional technology – industrial could be produced, production with desirous organic tasting (organo-leptic) for consumer and market.

Corresponding: E-mail: shumax4@hotmail.com, Tel: +377 44 14 84 34, +381 38 231 613, +381 38 545 88.
leptic) for estimation of cheese Kazkaval from combinations milk, with Traditional technology – industrial could be produced, production with desirous organic tasting (organo-leptic) for consumer and market [Coralba G, (1982), Dimitrije S, (1996), Maxhuni Sh, (2009), and Pravilnik (1983)].

Materials and Methods

It’s used fresh milk to produce cheese of Kacaval - unpasteurized cows and sheep’s with these parameters. For physical-chemical peculiar feature of milk and Kacaval samples were used these methods: Organo-leptic of cheese (Group, 1980).

Soxhelt-Henkels method were used to define sour taste $^{6}$SH, For definition of pH value were used the pH-meter, Miskra, Kranj, Type MA 5730, For definition of milk density g/cm$^3$ were used Laktodezimetre, For definition of fat percentage % were use the method of Gerber, For definition of dry matters until drying up of constant mass, Dry quantity of mass without fat has been done in calculated way, Percentage of fat at dry mass has been done in calculated way, Water quantity has been done in calculated way, For definition of general Nitrogen (N), were used the Kjeldahs method, For definition of saline’s (NaCl) were done according to the IDF standards, Beside, equipments and devices which are provided with regulations to define the physical-chemical peculiar feature of milk and cheese were used as well the below mentioned, Technological line for production of Kacaval cheese, consist from: two fold bath with capacity of 5000 l (Nederland’s bath equipped with equipment for benefit ion of coagulant-dough mass-curd), Coagulant baking line – “Maxhar” Budapest, Hungarian, Frames, Shelves.

In our research work we have used international standard methods (IDF) for analyzing the parameters of combinations milk to production cheese kacaval, with methods mentioned above. In this work research we have made three experiments were done with 5000l by combinations milk (between Cows and sheep milk 2:1) fresh non-pasteurized milk (with 3.6% fat) (Luqeut, 1990, Pravilnik, 1983).

Results and Discussion

For the first time a survey is done in such Kosovo for this type of cheese production with a combination of types of milk, trying to produce a kind of cheese that requires market.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>$^{6}$SH</th>
<th>Density g/m$^3$</th>
<th>Fat %</th>
<th>Mat. sec %</th>
<th>Mat. sec without fat %</th>
<th>Waqter %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.86</td>
<td>11</td>
<td>1.025</td>
<td>3.5</td>
<td>10.5</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.35</td>
<td>8</td>
<td>1.027</td>
<td>3.6</td>
<td>10.5</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5.83</td>
<td>12</td>
<td>1.028</td>
<td>3.7</td>
<td>9.88</td>
<td>6.18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.01</td>
<td>10.83</td>
<td>1.0266</td>
<td>3.6</td>
<td>10.29</td>
<td>6.69</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. The physical – chemical analysis results of Cows & sheep’s milk

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>$^{6}$SH</th>
<th>Fat %</th>
<th>Mat. sec</th>
<th>Mat. sec without fat (NaCl)</th>
<th>Solids N</th>
<th>Prot. gene</th>
<th>Water gene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.78</td>
<td>60</td>
<td>20</td>
<td>53.7</td>
<td>33.7</td>
<td>1.17</td>
<td>3.87</td>
<td>24.18</td>
</tr>
<tr>
<td>2</td>
<td>4.8</td>
<td>60</td>
<td>20.05</td>
<td>54.07</td>
<td>34.02</td>
<td>1.31</td>
<td>4.33</td>
<td>27.06</td>
</tr>
<tr>
<td>3</td>
<td>4.73</td>
<td>56</td>
<td>23.05</td>
<td>58.76</td>
<td>35.71</td>
<td>1.75</td>
<td>3.42</td>
<td>21.37</td>
</tr>
</tbody>
</table>

As for the production of cheese kacaval, we have used the traditional method for producing this type of cheese in Kosovo. In the fact for this product is that has found nice place in milk industries in Kosova. Peculiar future of organic tasting (oregano – leptic) for estimation of cheese kazkaval from
cows and sheep’s milk, with traditional technology – industrial could be produced, production with desirous organic tasting (organo – leptic) for consumer and market. The samples of chemical-physical analysis have been done from fresh milk (Table.1 and Fig.1).

Diagram 1. Processing diagram of kačkaval cheese
Table 3. The results of physical – chemical peculiarity of kaçkaval cheese produced cows & sheep milk during 15 days baking

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>%SH</th>
<th>Fat %</th>
<th>Mat. sec %</th>
<th>Mat. sec without % fat</th>
<th>Solids (NaCl) %</th>
<th>N gene %</th>
<th>Prot. gene %</th>
<th>Water %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.95</td>
<td>58</td>
<td>20</td>
<td>53.7</td>
<td>33.7</td>
<td>1.6</td>
<td>4.27</td>
<td>26.68</td>
<td>46.3</td>
</tr>
<tr>
<td>2</td>
<td>4.85</td>
<td>56</td>
<td>20.05</td>
<td>54.07</td>
<td>34.02</td>
<td>1.95</td>
<td>4.49</td>
<td>28.06</td>
<td>45.93</td>
</tr>
<tr>
<td>3</td>
<td>4.8</td>
<td>54</td>
<td>23.05</td>
<td>58.76</td>
<td>35.71</td>
<td>2.2</td>
<td>4.71</td>
<td>29.43</td>
<td>41.22</td>
</tr>
<tr>
<td>X</td>
<td>4.86</td>
<td>56</td>
<td>21.03</td>
<td>55.51</td>
<td>34.48</td>
<td>1.91</td>
<td>4.49</td>
<td>28.06</td>
<td>44.49</td>
</tr>
</tbody>
</table>

Table 4. The results of physical – chemical peculiarity of kaçkaval cheese produced by cows & sheep milk during thirty days baking

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>%SH</th>
<th>Fat %</th>
<th>Mat. sec%</th>
<th>Mat. sec without % fat</th>
<th>Solids (NaCl) %</th>
<th>N General %</th>
<th>Prot. gene%</th>
<th>Water %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.01</td>
<td>56</td>
<td>20</td>
<td>53.7</td>
<td>33.7</td>
<td>2.1</td>
<td>4.95</td>
<td>30.93</td>
<td>46.3</td>
</tr>
<tr>
<td>2</td>
<td>4.95</td>
<td>55</td>
<td>20.05</td>
<td>54.07</td>
<td>34.02</td>
<td>2.1</td>
<td>4.92</td>
<td>30.75</td>
<td>42.93</td>
</tr>
<tr>
<td>3</td>
<td>4.95</td>
<td>50</td>
<td>23.05</td>
<td>58.76</td>
<td>35.71</td>
<td>2.34</td>
<td>4.35</td>
<td>27.18</td>
<td>41.24</td>
</tr>
<tr>
<td>X</td>
<td>4.97</td>
<td>53.6</td>
<td>21.03</td>
<td>55.51</td>
<td>34.48</td>
<td>2.18</td>
<td>4.74</td>
<td>29.62</td>
<td>44.49</td>
</tr>
</tbody>
</table>

Three experiments were done with 5000l by combinations milk (between Cows and sheep milk 2:1) fresh non-pasteurized milk (with 3.6% fat). The samples of milk and cheese produced in industrial way by traditional technology were taken to be analyzed from combinations milk; the chemical-physical peculiar analysis has been done for fresh milk and fresh cheese lasting from one day, fifteen day and thirty days.

In addition, the analyses were taken for Saline percentage % (NaCl), total percentage of Nitrogen, and total percentage of proteins in cheese. The samples of every seven roundel have taken to analyze. More than 100 analyses were done to research the best method to produce this kind of cheese. In the table 1, we can see the chemical-physical results of combinations milk (between Cows and sheep milk 2:1): pH = 6.01, %SH = 10.83, density = 1.0266 kg/m². Fat = 3.6%, matter sec = 10.29%, matter sec without fat = 6.69, water = 89.71%. The samples of cheese produced in industrial way by traditional technology were taken to be analyzed the chemical-physical analysis has been done for fresh milk and fresh cheese lasting from one day, fifteen day and thirty days (Table 2 to 4 and Fig. 2 to 4).

Table 5. Organo-leptik results for evaluation of cheese produced by cows & sheep milk after thirty days.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Average number of points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Externals</td>
<td>3</td>
</tr>
<tr>
<td>Color</td>
<td>2.5</td>
</tr>
<tr>
<td>Consistency</td>
<td>2.5</td>
</tr>
<tr>
<td>Cutting</td>
<td>3</td>
</tr>
<tr>
<td>Smell</td>
<td>2.5</td>
</tr>
<tr>
<td>Taste</td>
<td>7.5</td>
</tr>
<tr>
<td>Total number of points</td>
<td>21</td>
</tr>
</tbody>
</table>

The cheese is baked for thirty days in temperature up to 20°C to 25°C, as well as on moisture up to 85%. The cheese is moistened in the store (the cheese is whirl about, salted and cleaned). Chemical-physical results of cow’s milk produced and stored cheese kaçkaval per one day are: pH = 4.77, %SH = 58.66, fat = 21.03%, matter sec = 55.51, matter sec without fat = 34.48%, saline (NaCl) = 1.41%, total nitrogen(N) = 3.87%, total proteins = 24.18%, water = 44.49%.
Chemical-physical results of fifteen days are: pH = 4.86, o SH = 56.00, fat = 21.03%, matter sec = 55.51, matter sec without fat = 34.48%, saline (NaCl) = 1.91%, total nitrogen = 4.49%, total protein = 28.06%, water = 44.49%. Chemical-physical results of thirty days are: pH = 4.97, o SH = 53.60, fat = 21.03%, matter sec = 55.51, matter sec without fat = 34.48%, saline (NaCl) = 2.18%, total nitrogen = 4.74%, total protein = 29.62%, water = 44.49%.

All parameters are of world standards, but mode and technology of this cheese makes possible less expense than needed liters to one liter milk. During the production of cheese, very important role takes the sort and the quality of milk. It is ascertained that during baking-drying of cheese in the store, from the first day until the thirtieth day the physical-chemical parameters are raising, such as raising percentage of total nitrogen (N), saline (NaCl), total protein. With traditional technology and with good quality of milk we can have a good product of this kind of cheese, with very good organo-leptik peculiarity: nice smell, good taste and strong cheese.

Production of this kind of cheese has nutritious value for the population and good economic value for milk industry considering profit of 1 kg cheese In normal standards is needed 10 litres of milk to produce 1 kg cheese of this kind. By means of this method, for 1 kg Kaçkaval, the economic parameters are improved. This kind of cheese can hold out in surroundings temperature up to 25°C. Furthermore, the gained results of such good production with good quality of cheese are showing that it has good economic importance for milk processing industry having in consideration the market interest for this kind of cheese with such peculiarity, because we have prepared for the market this kind of cheese for 30 days.

Organo-leptik valuation of kaçkaval after thirty days it was ascertained it has achieved the peculiarity of smell, taste, Consistency becouse in general it has achieved very good estimation (Table 5, Fig 5). Valuation of organo-leptik experimental cheese samples were don according to Regulation for evaluation of milk and milks products, Novi Sad 1980. The evaluation he’s been done by fifth members and samples were valuated with points. Good taste, texture, quality, and safety are all very important in the food industry. Food science technicians test and catalog the physical and chemical properties of food to help ensure these aspects.

Conclusions
More than 100 analyses were done to research the best method to produce this kind of cheese.
All parameters are of world standards, but mode and technology of this cheese makes possible less expense than needed liters to one liter milk.
During the production of cheese, very important role takes the sort and the quality of milk. As percentage of fat in milk changes so the percentage of fat in cheese changes also in matter sec, proteins, saline and water are changes too.
There are opportunities for technological and industrial production cheese combined with milk, to meet the needs of the market.
With this type of combination of milk, consumers would be Ken possibility of consuming types of cheese combined with a joint production.
It is ascertained that during baking-drying of cheese in the store, from the first day until the thirtieth day the physical-chemical parameters are raising, such as raising percentage of matter sec, total nitrogen (N), saline (NaCl) and in very small percentage the percentage quantity of fat.
Organo-leptik valuation of kaçkaval after thirty days it was ascertained it has achieved the peculiarity of smell, taste, Consistency be souse in general it has achieved very good estimation.
With traditional technology and with good quality of milk we can have a good product of this kind of cheese with very good organo-leptik peculiarity: nice smell, good taste and strong cheese.
Production of this kind of cheese has nutritious value for the population and good economic value for milk industry considering profit of one kg cheese. The economic parameters are improved.
This kind of cheese can hold out in surroundings temperature to 25°C, as well as on moisture up to 85%.
Normally for this cheese we must wait forty days for market. But with this processing diagram of kaçkaval cheese, we can give this kind of cheese for market for days.
Furthermore, the gained results of such good production with good quality of cheese are showing that it has good economic importance for milk processing industry having in consideration of the market interest for this kind of cheese with such peculiarity.
In the future

- A prospective dairy from combinations milk, the producer must take into account a number of potential difficulties and challenges.
- First of all, any dairy operation requires a high degree of management skill.
- Raising dairy industry involves the combination of two production systems - animals and milk.
- For people who haven’t done either one, there will be a period of time spent learning each of cheese systems.
- In the future manufacturing milk should devote special attention to milk production of cheese combined with EU standards.

Acknowledgment: Thanking all the friends, who have they helping in this work research.

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Engineering geological mapping for the seismic microzoning of Saranda town, Albania

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Abstract: This paper is a summary of engineering geology mapping on scale 1: 10000 carried out in the Saranda town, for seismic for urban development and microzoning purposes. The studied area is located in southwest of Albania. Lithologically, it’s built by the limestones, flysch, sands and silty clay deposits. Whereas, from geomorphological point of view, the urban area is represented from flat geomorphological and hills units. On the other hand, from the hydrological investigation results that underground water tab le in flat area is shallow and hills area is deep, as well as, it’s good chemical properties. According to geotechnical properties, the studied area is built from hard rocks-limestones, soft rocks – flyschs, combination of claystones and sands, silty clays soils. The engineering geology mapping is based on several criteria as lithology, morphology, hydrogeology, geodynamic phenomena and physical-mechanical properties. So, base on these criteria, the urban area is classified in five engineering geological zones and fourteen engineering geological sites. In the end are given conclusion.

Keywords: sands, limestones, flyschs, engineering geological zoning.

Introduction

As we known, the engineering geological zoning maps, being a special type of geological maps, presents generalization of all those components of the geological environment which are necessary for purposes of land-use planning, design, construction, utilization various structures and for microzoning purposes. The Saranda town is located in southwestern part of Albania along of Ionian Sea side (Figure 1). It’s the most beautiful town in Albania; because of there are several wonderful beaches. In Saranda region and Albania too, the current time is characterized by rapid economic and social changes, which are closely related to accelerated urban development, as well as, the environmental problems have involved the increasing interest in the rational use of landscape of geo-environment. The Saranda urban area currently is occupied by residence. That is why, during 2004-2006 year an engineering geological mapping on scale 1: 10000 for the seismic microzoning purpose in urban area of Saranda town is carried out (Muceku 2006). For this work are carried out in the oriented profile on scale 1:10000 a surface engineering geological investigation, excavation of many pits with depth 3.0-5.0m, boreholes with depth range from 10.0m up to 20.0m. Besides of them in different level of the lithological profile in pits and boreholes during fields works are taken soils and rocks samples to analyses in laboratory for physical-mechanical properties. The purpose of this study was to give base information according to characteristics of the territory for planning, land use and engineering structures and microzoning, as well. In recent years information about ground conditions of urban environment as we above mentioned, has assumed increasing importance in Albania, confirmed by problems resulting from unfavorable engineering geological conditions (landslides, collapsible soils, etc).

Materials and Methods

The studied area is located in southwest of Albania (Figure 1) and it is 14.0 km². The following criteria have been used (Muceku 2006) for discrimination of engineering geological mapping units:

- Lithology, geometry-thickness of the different soils, spatial relation between the strata, etc.
- Geomorphology.
- Hydrogeology.
- Geodynamics phenomena.

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Physical and mechanical properties of rocks and soil.

Figure 1. Location of studied area

![Location of studied area](image)

Figure 2. Litological and geohazard map of studied region (Shkupi 2000)

1. Quaternary deposits, gravels, silts and sands, 2. Upper Cretaceous (Cr₂) deposits, limestones rocks, 3. Lower-Upper Oligocene (Pg₁ - Pg₃) deposits, flysch rocks-siltstones, claystones and sandstones, 4. active faults, 5. sea erosion, 6. landslides, 7. earthquake, 8. national border

Based on above criteria the engineering geological map of Saranda town on scale 1: 10 000 is worked in several phases as:
1. Data gathering-desk study;
2. Reconnaissance survey and field mapping;
3. Laboratory analysis;
4. Interpretation and correlation of the date obtained from field-laboratories works and preparation of the engineering geological map together with engineering geological study. Preliminary data concerning geology, engineering geology of Saranda urban area were taken from other authors (Gjovreku 2004). After that, we have worked on the oriented profile on scale 1:10 000 (Muceku 2006) for documentation of earth’s surface. The first step has been the mapping of landforms (alluvial terraces, alluvial fans, hills and hills slopes etc.), weathering crust, karstic process, rock structure and discontinuities, resulting active erosions, hydrogeological features (underground water table and
aggressive), tectonics and seismic activity, mass movements on slopes, vegetation cover, stabilization and potential for mass movement. In the second step, for each landform are done a lot of drillings and pits, where are recorded the nature and lithologic characteristics of soils and rocks up to 30.0m deep. Hence in the studied area are carried out 160 trial pits with depth 2.5-5.0m and 22 drilling with depth 15.0-20.0m up to 30.0m, where in different level are taken 107 soils and rocks samples (77 undisturbed and 30 disturbed) to analyze in laboratory for determination of mechanical and physical properties. They are the soils grain size distribution, bulk density, Atterberg’s limits, moisture content, specific density, dry density, porosity, porosity coefficient, shear strength, oedometer modules and uniaxial compressive strength test etc. The data were processed and analyzed in terms of quality, which were generally good for the geotechnical investigations. The borehole logs have been compiled in detail. These required simplifications: 8 dominant lithological deposits were identified (inorganic clays, sand-clay mixtures, sand-silt mixtures, organic silts, gravel-sand-silt mixtures, claystones, sandstones, limestones). Based on these lithological data of the boreholes and trial pits, laboratories tests results, terrain surface records, geomorphology characteristics, geodynamics phenomena and water condition was compiled the engineering geological map on scale 1:10 000. Several engineering geological zone and sites were thus identified as being homogeneous from a lithological, geomorphological, hydrogeological, geodynamics phenomena and geotechnical point of view.

**Results**

A detailed study at a scale of 1:10 000 was completed on the Saranda urban area for the seismic microzoning purpose. For compilation of engineering geological zoning map are used the above mentioned criterions, as well as are carried out a lot of works from which are taken many data related to these topics, which we treat here.

**Lithology**

Basing on field works done in the studied area are determined three lithological types as alluvial deposits-sands, deluvial deposits mixtures of rubles with silts, and limestones rocks (Figure 2).

*Alluvial deposits* extend on southern part of the studied area and construct the delta of the Bistrica River. These are represented by middle-course sands with thickness 2.5-5.0m and soft silty clay soils are10.0m-20.0m thick. They are situated on the limestones deposits.

*Diluvial deposits* are found along the lower-middle part of the hills slopes and in the major part of the torrent joining the main water course, which are developed on hills slope. They are composed by silts with mixture of rubbles-stones of limestones rocks with irregular shape. These deposit formed a thickness range from 1.0-2.0m up to 3.0-3.5m. Generally they are of heterogeneous character.

*Flysch deposits* belonging to the Lower-Upper Oligocene (Pg13- Pg13) are found in eastern part of the study area. These deposits build a syncline structure that extends from north-west to south-east (Figure 3). The western flunk underlie of limestone rocks with tectonic boundary (Figure 3). They are comprised by combination thin strata of claystone-siltstone with sandstones. In upper part of lithological profile this formation are highly weathered.

![Figure 3. Lithological profile from west to east in Saranda urban area (Muceku 2006)](image)

1. Limestones deposits, 2. Flyschs deposits, 3. Soils deposits, sands, silts with mixture of rubbles-stones of limestones, 4. tectonics fault

*The Limestone’s* rocks belong in Upper Cretaceous (Cr3) age. Mostly of urban area of the Saranda town is constructed by limestones rocks. They build an asymmetric anticline structure with northwest to southeast extension (Figure 3). The eastern flank of anticline has a dip angle 26-30° to northeast, whereas the western flank dip to southwest with angle 10-15°. The eastern flank of anticline
in the east direction is separated and moved down by active faults (Figure 2, 3). These rocks in some places are covered from diluvium deposits represented by silts with mixture of rubble-stones and alluvium deposits represented by sands, silts and clayey soils. Better parts of construction activities in the town have taken place in these rocks. The limestones rocks consist of thin strata with light beige and grey colors, compact, dense and with low porosity as well. They are micrite’s and biomicrite’s types. In general the upper part of these limestones are cracked and fissured.

Geomorphology

The geomorphology of the studied area is closely related to the geology. Geomorphologically, two units were identified, which are flat geomorphology unit and hills geomorphology unit. The flat geomorphology unit is located in southern part of the studied area representing by delta of Bistrica River. It’s composed by the river beds and first terrace of Bistrica River morphological subunits, which respectively consists of sands and silts and mixtures of sands, gravels and silts. Whereas, the hills geomorphology unit is built by limestones and flyschs rocks with above sea level varies from 150-250m up to 350-400m. Along of this zone many torrents have established its valleys on this morphological unit. They have the valleys like “V” shape with width varies from 5-10m up to 20-25m. From our observation (Muceku 2006) result that hills slope angle ranges from 6°-15° up to 25°-30°. In upper of the lithological profile (2.5-4.0m deep from surface), limestones and flysch rocks are weathered. In several places from manmade works the terrain has an escalating shape.

Hydrogeology

According to hydrogeology in the studied area are found three complexes are complex of limestones rocks, flysch rocks and sands-gravels. The limestones rocks regarding to the water-keeping form a rich aquifer where the underground waters are related to the karst and formations contact. So, in this complex the underground waters are discharged in rivers valley and sea. From hydrogeological exploration (Gelaj 2004) the underground water in these complex are found in deep level various from 20-25m. From these formations generates several water springs with discharge 2.5-4.0m³/sec up to 12.0-20.0m³/sec in Ionian Sea in north of the studied area. According to chemical composition the underground waters this complex are $Na^+ + K^+ = 21.85$mg/l, $Ca^{2+} = 96.19$mg/l, $Mg^{2+} = 11.55$mg/l, $Fe^{2+3+} = 0.15$mg/l, $NH_4^+ = 0.0$ mg/l, $HCO_3^- = 201.3$mg/l, $CO_3^{2-} = 0.0$mg/l, $Cl^- = 46.15$mg/l, $SO_4^{2-} = 99.9$mg/l, $NO_3^-= 1.2$mg/l, $NO_2^-=0.0$ mg/l, PH =7.37. The flysch rocks are characterized of poor water bearing capacity. Generally, the eventual waters are related to sandstones and conglomerates. Several water sources crop out in the northern part, but their yielding is low and it is varying from 0.05l/sec to 0.2 l/sec. In this complex the underground water level is below 15.0 m. The chemical composition of flysch waters are $Na^+ + K^+ = 63.83$mg/l, $Ca^{2+} = 119.23$mg/l, $Mg^{2+} = 44.99$mg/l, $Fe^{2+3+} = 0.02$mg/l, $NH_4^+ = 0.0$mg/l, $HCO_3^- = 469.70$mg/l, $CO_3^{2-} = 0.0$mg/l, $Cl^- = 72.78$mg/l, $SO_4^{2-} = 120.98$mg/l, $NO_3^- = 7.2$mg/l, $NO_2^-=0.04$ mg/l, PH =7.39. The others complex represent by sands-gravels formation extend on east and southeast of the studied area and is spread principally in the Bistrica River valley. From our investigation this complex is found from 0.7-7.5m up to 22.0m deep. They compose rich horizons with underground waters which are principally feed by the above mentioned river. This complex is situated on the limestones and flysch rocks. The underground waters table in this sands-gravels complex range from 1.0m to 1.8m. The concentrations of chemical constituents in water of this complex are $Na^+ + K^+ = 12.19$, $Ca^{2+} = 110.22$mg/l, $Mg^{2+} = 18.24$ mg/l, $Fe^{2+3+} = 0.08$ mg/l, $NH_4^+ = 0.0$mg/l, $HCO_3^- = 280.6$mg/l, $CO_3^{2-} = 0.0$ mg/l, $Cl^- = 21.3$mg/l, $SO_4^{2-} = 111.93$mg/l, $NO_3^- = trace$, $NO_2^- = 0.04$mg/l, PH = 7.18. As it shown, the underground waters of three complexes related to chemical composition are characterized by good chemical properties, that mean these waters are not aggressive towards concrete, but on the contrary they are very good to use for domestic purposes.

Geodynamics phenomena

Debris slides

In north of studied area as result of the geodynamics phenomena development are weathering crust, karst and erosions is formed a trough, which during precipitation period collect the surface water and together debris material discharge down to hill slope. The flow
material is consisting of mixtures of rubles, broken stones and cobbles with sands and silts. Most of these debris flow occurrence, during heavy rain periods are moving down slope.

**Erosion**

The Ionian Sea coast in the Saranda’s area is built by limestones rocks. From sea wave’s activity, it is under sea erosion effect. So, during calm’s weather period, wave action is at a minimum. Whereas, during storm’s weather period the impact of sea waves against the coast is not too small. Each breaking wave hurls thousands of tons of water against the land causing a damage and instability of the coast even though it is built by limestones rocks. In addition, the erosion is favored by limestones type-thin strata limestones and geological weakness-fractures, cracks and tectonics line. So, erosion phenomenon causes the rocks to break off in fragments and transport along sea side. It is very important to emphases that from erosion activity in this region are formed the Saranda’s Bay and many small bays in north and south of it, as well as several beaches.

**Neotectonic setting**

According to Albanian geotectonic classification the studied area takes part in the Ionian geotectonic zone and includes in external area of Alpine folding. The main structural characteristic of this geotectonic zone is the presence of a series of anticlines and synclinal belt, both extending parallel and sub-parallel through almost the entire length of the zone in sub-meridional position. It is strongly affected by tectonics movement are mainly extended from Northwest to Southeast and comprises thrust and back thrust active faults expressing a pure extensional tectonic regime (Aliaj Sh 2000). Also, it is very important to emphases the Saranda region is part of the Ionian-Adriatic longitudinal fault zone locating in the south of it. From the recent studies are identified three main longitudinal active faults and some small transversal active faults (Figure 2). First one is located in east of Saranda town and marks the boundary between the Saranda anticline and Finiqi syncline. It extends from Northwest to Southeast and represents by active fault. It has moved down the eastern flank of the Saranda anticline (Figure 3). Two others are located in east and south of Saranda town and mark the boundary between the Saranda anticline and Lukova syncline, as well as Finiqi anticline. They extend from North to South and represent by active faults. As is shown in Fig. 2, from development of these active faults, are formed the Bistrica valley River. In addition, the Saranda zone is recognized as seismically active regions due to several of active faults have been identified within the region. Here are lists briefly some of strong earthquakes occurred in Saranda and surrounding area from 58 B.C until now a days (Alija Sh 2000), as follow: 358 Ms=6.6; 1153 Ms=6.6; April 16, 1601 Ms=6.6; January 1, 1674 Ms=6.6; April 5, 1701 Ms=6.6; February 20, 1743 Ms=7.0; December 10, 1813 Ms=6.6; June 19, 1823 Ms=6.6; January 19, 1833 Ms=6.6; October 12, 1851 Ms=6.6; January 2, 1866 Ms=6.6; December 4, 1866 Ms=6.6; February 11, 1872 Ms=6.6; June 14, 1893 Ms=6.6; November 26, 1920 Ms=6.4. Whereas, from recent instrumental seismology studies, from 1964 up to 2008 are registered 1103 earthquakes with M > 2.0, in and around of Saranda region.

**Physical mechanical properties**

From fields works (Muceku 2006) in the studied are taken 107 soils and rocks samples (77 undisturbed and 30 disturbed) to analyze in laboratory. The laboratory rocks and soils analysis in existing rocks and soils conditions include the mechanical and physical properties, as soils grain size distribution, bulk density, Atterberg’s limits, moisture content, specific density, dry density, porosity, porosity coefficient, shear strength, oedometer modules and uniaxial compressive strength test etc. In the Tables 1, 2 and 3 are shown the main of laboratories results of soils and rocks samples taken in the studied area.

**Engineering Geological Mapping**

The study, described in this paper, attempts to divide the basin area of the Saranda town into engineering geology zones (Figure 4).
Figure 4. Engineering geological zoning map of central part of Saranda urban area on scale 1:10000 (Muceku, 2006)

It is done basing on criteria’s as lithological characteristics, geomorphological and hydrogeological conditions, geodynamics phenomena and physical and mechanical properties of rocks and soils. So, on basis of these criteria’s is determined the engineering geology zoning, the Saranda urban area according to geomorphologic criteria is divided in two major units:

a. Flat geomorphology unit

b. Hills geomorphology unit

d. First engineering geology zone “I” is the bed deposits of Bistrica River.
eg. Second engineering geology zone “II” is the first terrace of Bistrica River.

“I”-first engineering geology zone-bed deposits of Bistrica River. It is composed by layer nr. 2 and nr. 8 (Figure 5). The soils of layer 2 consist of sand-clay mixtures and sand-silts mixtures “SC-SM” type is grey color. The soils of this layer are in loose condition state, saturated, 2.5-3.0m thick
and underground water table is 0.5-0.7m deep. This site is situated on limestones rocks. The physical-mechanical of this soil is given in Tables 1 and 2.

"II"-second engineering geology zone, represented by first terrace of Bistrica River. According to rocks basement where the soils are situated this zone is divided in two engineering geology subzones “II$^a_2$ and II$^b_2$” (Figures 4 & 5), where “a” letter shows the rocks basement type are limestones and “b” letter shows the flyschs rocks basement type. Whereas, in relation to soils thickness each engineering geology subzone is divided in two engineering geology sites are “II$^{a, b}_2$-1, II$^{a, b}_2$-2”. The engineering geology sites “II$^{a, b}_2$-1, II$^{a, b}_2$-2” have soils thickness from 5.0-7.0m to 10.0m and II$^{b}_2$-2, II$^{a}_2$-2” have soils thickness from 10.0m to 20.0-30.0m. So, the engineering geology site “II$^b_2$-1” with soils thickness 5.0-10.0m, underground water table 1.0-1.5m is built by layer 1, 3, 4, 6 and 8 (Figures 5). The layer 1 is vegetal soils. The layer 3 represent by inorganic clays of low to medium plasticity-“CL” type (USCS), beige-brown color, in stiff-medium condition, ranging from 0.8m to 7.5m deep and are saturated. Below this layer we have the layer nr. 4 consist of gravelly clays and sandy clays -“CL” type (USCS), beige-gray, grey color, in medium condition, ranging from 7.5m to 11.0m deep, saturated. The layer 6 lies below of layer nr.4 and over layer 8. It is inorganic clays of low to medium plasticity-“CL” type (USCS), beige-grey.

**Figure 5.** The engineering geology models of sites “I” and “II” (Muceku 2006)
color, in hard condition. In lower part of lithological profile is situated the layer 8, which are flyschs rocks-combination of thin layers of sandstones and claystones-siltstones, including in the low uniaxial compressive strength rocks group (ISRM, 1981).

The engineering geology of site “II’$_{b,2}$” with soils thickness 10.0-30.0m, underground water table 1.0-1.5m is built by layers 1, 3, 4, 5, 6 and 8 (Figures 5). Since all geotechnical layers are described here we analyses the layer nr.5, which is situated in lower part of soils lithological profile from 10.0-24.5 up to 30.0m. It is represented by poorly-graded gravels with little fines -“GP” type (USCS) are in dense condition.

The engineering geology sites “II’$_{b,1}$” has soils thickness varies from 7.0 up to10.0m, underground water table 0.9-1.2m. From top to lower part this site is built by layers 1, 3, 4 and 9 are analyzed beside of layer 9, consist of hard rocks are limestones and dolomites rocks.

The engineering geology sites “II’$_{b,2}$” is built by soils is 10.0 up to20.0m thick. In this site the underground water table is 0.9-1.2m. It is composed by layers 1, 3, 4, 5 and 9 are described in above sites. The physical-mechanical of the engineering geological unit each site is given in Tables 1 and 2.

b. Hills geomorphology unit according to criteria’s as lithological composition, thickness of soils, inclination of hills slopes, as well as soils and rocks physical-mechanical properties, is divided in three engineering geology zones (Figures 4 & 6) are:

b. 1. Third engineering geology zone “III”, diluvium deposits of hills slope.

b. 1. Fourth engineering geology zone “IV”, hard rocks are limestones and dolomites rocks.

b. 1. Fifth engineering geology zone “V”, soft rocks, flysch deposits are combination thin strata of claystones-siltstones with sandstones and sandstones with claystones-siltstones.

“III”-third engineering geology zone- deluvial cover of hills slope.
It is built by four of engineering geology site of “III” with soils thickness 1.5-2.9m, hills slope inclination angle 3.0-5.0°, “III’” with soils thickness 1.5-2.5m and hills slope inclination angle 6.0-10.0°, “III” , with soils thickness 1.2-2.2m, hills slope inclination angle 11.0-15.0° and “III’” soils thickness 0.8-1.7m, hills slope inclination angle over 16.0°-20.0°,without underground water table.
The engineering geology sites as “III$_{1}$ and III$_{2}$” consist of a layer nr. 1/1 is composed by gravelly clays and sandy clays soils type (Fig. 6) -“CL”, brown color, in very stiff-hard condition.

The engineering geology sites as “III$_{3}$ and III$_{4}$” consist of a layer nr. 1/2 is sand-clay mixtures soils type-“SC” (USCS), brown color, in medium condition. The physical-mechanical of the engineering geological unit each site is given in Tables 1 and 2.

“IV”-fourth engineering geology zone-hard rocks, limestones and dolomites rocks.
This engineering geology zone is built by three of engineering geology site as “IV$_{1}$”, with hills slope inclination angle 10.0-15.0°, underground water table below 15.0m and “IV$_{2}$” with hills slope inclination angle 16.0-20.0°, underground water table below 15.0m, as well as “IV$_{3}$” hard rocks, limestones and dolomites rocks with hills slope inclination angle 21.0-30.0°, underground water table below 15.0m (Fig. 4, 6). The engineering geology sites are “IV$_{1}$, IV$_{2}$ and IV$_{3}$” consist of geotechnical layer nr. 9, where in several places is covered by layer 1/3. The layer 9 is represented by thin-medium strata limestones with light beige, white and grey in color, with fissures randomly oriented, filled by clays sediments and cemented with calcite. According to geotechnical properties this layer is included in high uniaxial compressive strength rocks group (ISRM, 1981). The layer 1/3 is extended in many places on this zone and is composed by sand-clay mixtures and gravelly-clays mixtures soils types (Figure 6) “-SC and GP”, brown color, in medium condition. The physical-mechanical of the engineering geological unit each site is given in Tables 1 and 2.

“V”-fifth engineering geology zone-soft rocks, flysch’s rocks-combination of thin layers of sandstones with claystones-siltstones and claystones-siltstones with sandstones.
The engineering geology zone of “V” is built by tow of engineering geology site as “V$_{1}$”, with hills slope inclination angle 10.0-15.0°, underground water table below 15.0m and “V$_{2}$” with hills slope inclination angle 16.0-20.0° (Fig. 4, 6), underground water table below 15.0m.
The engineering geology sites are “V$_{1}$ and IV$_{1}$”, and composed by geotechnical layer 6, 7 and layer 1/4 (Fig. 6), which covers it in several parts. The layers 7 consist of flyschs rocks, are combination of thin layers of claystones-siltstones with sandstones and includes in low uniaxial compressive strength group (ISRM, 1981). The layer 1/4 is sand-clay mixtures and sandy clays soils types-“CL and SC”
The geological layer 6 is well described in above sites. The physical-mechanical of the engineering geological unit each site is given in Tables 1 and 2.

**Figure 6.** The engineering geology models of sites “III”, “IV” and “V” (Muceku, 2006)

**Table 1.** Physical properties of engineering geology units of soils

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Layer</th>
<th>Gravel</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>WL %</th>
<th>WP %</th>
<th>Soils type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>nr.1/1</td>
<td>20.5</td>
<td>23.6</td>
<td>51.7</td>
<td>4.2</td>
<td>36.3</td>
<td>19.5</td>
<td>CL</td>
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<tr>
<td>2</td>
<td>nr.1/2</td>
<td>47.8</td>
<td>23.9</td>
<td>24.8</td>
<td>3.5</td>
<td>32.1</td>
<td>18.8</td>
<td>SC</td>
</tr>
<tr>
<td>3</td>
<td>nr.1/3</td>
<td>47.8-60.5</td>
<td>22.9-23.9</td>
<td>14.6-24.8</td>
<td>2.0-3.5</td>
<td>32.1</td>
<td>18.8</td>
<td>SC</td>
</tr>
<tr>
<td>4</td>
<td>nr.1/4</td>
<td>16.8-21.5</td>
<td>25.3-29.6</td>
<td>44.4-50.1</td>
<td>7.8-9.5</td>
<td>36.7-38.6</td>
<td>19.8-21.2</td>
<td>CL</td>
</tr>
<tr>
<td>5</td>
<td>nr.2</td>
<td>15.2-22.7</td>
<td>47.8-73.0</td>
<td>3.4-24.5</td>
<td>0.9-13.3</td>
<td>-</td>
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<td>SC</td>
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<tr>
<td>6</td>
<td>nr.3</td>
<td>3.5-5.3</td>
<td>28.5-30.7</td>
<td>54.8-60.3</td>
<td>12.7-18.2</td>
<td>40.4-42.6</td>
<td>22.9-24.2</td>
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<tr>
<td>7</td>
<td>nr.4</td>
<td>13.8-17.6</td>
<td>27.3-33.2</td>
<td>35.6-38.3</td>
<td>14.7-15.4</td>
<td>36.5-38.7</td>
<td>20.6-23.6</td>
<td>CL</td>
</tr>
<tr>
<td>8</td>
<td>nr.5</td>
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<td>22.9</td>
<td>14.6</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>GP</td>
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<tr>
<td>9</td>
<td>nr.6</td>
<td>0.0</td>
<td>37.1</td>
<td>51.4</td>
<td>11.5</td>
<td>36.4</td>
<td>22.1</td>
<td>CL</td>
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</table>

nr.1 Top soils, vegetal soils

WL - Liquid limits, WP - Plastic limit
Table 2. Physical and mechanical properties of engineering geology units of soils

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Layer</th>
<th>Wn (%)</th>
<th>γ (%)</th>
<th>γo (%)</th>
<th>φ (°)</th>
<th>c (kPa)</th>
<th>E (kPa x 10^4)</th>
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</thead>
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<tr>
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<td>21.2</td>
<td>19.4-19.8</td>
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<tr>
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<td>nr. 1/2</td>
<td>18.2</td>
<td>19.6-19.8</td>
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<td>44</td>
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<td>4.00</td>
</tr>
<tr>
<td>3</td>
<td>nr. 1/3</td>
<td>18.8-19.7</td>
<td>19.2-19.4</td>
<td>24.0-26.3</td>
<td>29-44</td>
<td>0.00</td>
<td>1.00-4.00</td>
</tr>
<tr>
<td>4</td>
<td>nr. 1/4</td>
<td>24.8-25.3</td>
<td>18.7-18.9</td>
<td>25.8-26.0</td>
<td>24-30</td>
<td>14-16</td>
<td>0.40-0.50</td>
</tr>
<tr>
<td>5</td>
<td>nr.2</td>
<td>29.5-35.1</td>
<td>19.4-19.6</td>
<td>26.4-26.50</td>
<td>28-32</td>
<td>5.0</td>
<td>0.90-2.26</td>
</tr>
<tr>
<td>6</td>
<td>nr.3</td>
<td>30.5-34.6</td>
<td>18.6-18.8</td>
<td>27.0-27.10</td>
<td>14-16</td>
<td>10-12</td>
<td>0.36-0.52</td>
</tr>
<tr>
<td>7</td>
<td>nr.4</td>
<td>28.2-32.9</td>
<td>18.6-18.8</td>
<td>26.35-26.5</td>
<td>28-32</td>
<td>10-14</td>
<td>0.54-0.80</td>
</tr>
<tr>
<td>8</td>
<td>nr.5</td>
<td>35.7</td>
<td>19.9-21.0</td>
<td>26.42-26.5</td>
<td>42-44</td>
<td>0.00</td>
<td>3.5-4.0</td>
</tr>
<tr>
<td>9</td>
<td>nr.6</td>
<td>19.3</td>
<td>19.8-20.0</td>
<td>2.67</td>
<td>26</td>
<td>35-55</td>
<td>3.0-3.5</td>
</tr>
</tbody>
</table>

*Wn* - Natural water content, γ - Bulk density, γo - Specific density, φ - Internal friction angle, c - Cohesion, E - Eodometric module.

Table 3. Physical and mechanical properties of engineering geology units of rocks

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Layer</th>
<th>Wn (%)</th>
<th>γ (%)</th>
<th>γd (%)</th>
<th>γo (%)</th>
<th>n (%)</th>
<th>τc (kPa x 10^4)</th>
<th>Rock type</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>nr.7</td>
<td>2.7-3.9</td>
<td>24.76-24.76</td>
<td>24.11-24.11</td>
<td>25.35-25.35</td>
<td>3.84</td>
<td>0.33-3.84</td>
<td>Flysch-claystones and sandstone</td>
</tr>
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<td>2</td>
<td>nr.8</td>
<td>2.5-3.4</td>
<td>25.21-25.21</td>
<td>24.75</td>
<td>25.94</td>
<td>4.76</td>
<td>0.68-4.76</td>
<td>Flysch-sandstones</td>
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<tr>
<td>3</td>
<td>nr.9</td>
<td>0.11-0.14</td>
<td>26.7-26.7-26.7</td>
<td>26.7-26.7-26.7</td>
<td>26.7-26.7</td>
<td>1.86-1.86</td>
<td>9.1-9.94</td>
<td>Limestones</td>
</tr>
</tbody>
</table>

*Wn* - Natural water content, γ - Bulk density, γd - Dry density, γo - Specific density, n - porosity, τc - uniaxial compressive strength in natural condition.

Conclusions and Recommendations

In the studied area are determined three lithological types as alluvial deposits-sands, deluvial deposits mixtures of rubles with silts, and limestones rocks.

- The Saranda region in Albania is part of the Ionian-Adriatic longitudinal fault zone locating in the southern part.
- In Saranda region are identified three main longitudinal active faults and some small transversal active faults, which mark the boundary between the Saranda anticline and Finiqi syncline.
- The studied area is built by three complexes are complex of limestones rocks, flysch rocks and sands-gravels.
- Basing on the criteria’s that determine the engineering geology zoning, the Saranda urban area according to geomorphologic criteria is divided in two major units as flat geomorphology and hills geomorphology units.
- Flat geomorphology unit according to criteria’s as hydrogeological conditions, lithological characteristics, soils and rocks physical-mechanical properties, as well as thickness of soils is divided in two as engineering geology zone of bed deposits of Bistrica River and engineering geology zone of the first terrace of Bistrica River.
- Hills geomorphology unit according to criteria’s as lithological composition, thickness of soils, inclination of hills slopes, as well as soils and rocks physical-mechanical properties, is divided in three engineering geology zones are engineering geology zone of diluvium deposits of hills slope, hard rocks are limestones and dolomites rocks and soft rocks, flysch deposits are combination thin strata of claystones-siltstones with sandstones and sandstones with claystones-siltstones.
- Based on data of lithology characteristics, geomorphology and hydrogeological conditions, geodynamics phenomena and physical and mechanical properties of rocks and soils the Saranda urban area was divided into fifth engineering geology zones and 14 engineering geology sites.
- The engineering geology map on scale 1: 10 000 is base information for seismic microzoning purpose of the Saranda town.
From engineering geology zoning results that, Saranda town have to develop in third engineering geology zone “III”- deluvial cover of hills slope at engineering geology site of “III_1”, “III_2”, “III_3” and “III_4”, in fourth engineering geology zone “IV”- hard rocks, limestones and dolomites rocks at engineering geology site as “IV_1”, “IV_2” and “IV_3” and fifth engineering geology zone “V”- soft rocks, flysch’s rocks-combination of thin layers of sandstones with claystones-siltstones and claystones-siltstones with sandstones at engineering geology site “V_1” and “V_2”.

References
Water Pollution of the River Ibër with Heavy Metals from the Landfill Located in the Village Kelmend of Mitrovica

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1Faculty of Mining and Metallurgy, University of Prishtina, Mitrovica, Kosovo; 2Department of Chemistry and Biology, Faculty of Education, University of Prishtina, Kosovo; 3Diakonie Training Center, Mitrovica, Kosovo

Abstract: As a consequence of the existence and functioning units of departments “Trepça” in the past, environmental situation in Mitrovica and surrounding area is of concern, although these units of this plant since 2000 are not in function, the consequences of their presence are still present. Industrial Complex units “Trepça” who located in the north and south of Mitrovica, together with the Stari Trgu mine and flotation which is located on the first tunnel, have been permanent environmental pollutants in the city of Mitrovica and surrounding area. Exploitation, preparation and processing of lead and zinc ore, have affected the chain in order to release harmful substances, heavy metals, toxic gases and at the same time as the deposit of industrial waste into the environment. The drafting of this paper, consists in making analysis and benefit the results of these sources of pollution, regarding the impact of industrial waste landfill Kelmendi, located 2-3 km in the north-eastern part of Mitrovica, and the impact of heavy metals in pollution of water in river Ibër. This paper reflects the results of analysis regarding the presence of heavy metals: Pb, Cu, Cd, Zn, Mn, Fe, Cr, Ni in the waters of the river Ibër, due to the existence of the landfill that is located in the village Kelmend of Mitrovica.

Key words: landfill, physico-chemical analysis, heavy metals, pollution, water, river Ibër

Introduction

According to some research performed, Trepça, during the years 1967-1985, was the largest producer of Pb, Zn, Ag and Au in Europe. As part of this plant have existed and operated 20 units with about 25000 workers. In that period Trepça within a year has produced the 120000 t Pb concentrate, 100000 t Pb refined, 100 t Ag, 80000 t Zn electrolytic, etc. Rentabile production of Trepça, during that period, impacted positively on economic development of Mitrovica with surrounding, Kosovo and former Yugoslavia, but had a negative impact on the environment, including waters under and over land, air and land.

Exploiting Pb-Zn ore from the mine of Stari Trgu and its processing in first tunnel flotation, since 1967 the transport of Lead concentrates in Zvecan smelter, while transporting Concentrate of Zinc in the units of Metallurgy of Zinc in Mitrovica. Industrial wastes from the first tunnel flotation through the pipes, were transported to landfill Kelmend, who considered a source of pollution of river Ibër with heavy metals.

Heavy metals penetrate in the hydrosphere from natural and anthropogenic sources. Some of anthropogenic sources are: industry with industrial waste, the existence of mining, smelting of ores, and the existence of different landfills (Dauwalter and Rognerud, 2001). Heavy metals dissolve in water quickly, then deposition in the end of the river bed as carbonate, sulfate and sulfide, which are less soluble (Goletić Š.,2005).

The impact of the Kelmendi landfill in water pollution into the river Ibër

Urban environmental degradation in Mitrovica and surrounding area has continued even after cessation of work in units Trepça, because the exploitation of mineral by the Stari Tërgu mine and processing it in the First Tunnel flotation, has continued with placement of industrial waste in Kelmendi.

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landfill, causing air pollution, groundwater and surface water, land. In Figure 1 are presented location of the landfill through topographic mapping. As we noted above, Kelmendi landfill located 2-3 km, in the space between two hills, in the north-eastern part of Mitrovica.

On the western side of the landfill, at bottom, is a torrent that topographic maps known through his Zharkov Potok and through his polluting substances discharged into the river Ibër. This landfill, formed in 1975 in self contained industrial waste leaving from the first tunnel flotation. This landfill is still active and able to deposit 8.2 million cubic meters of industrial waste.

![Figure 1. Location of landfill](image)

Industrial waste from flotation to the lake of Kelmendi landfill carried by pipes, but due to the serious political situation, the war that occurred in Kosovo during 1990-2000, in no case is made reclamation of landfill, so that the surface of dam has a white appearance under the influence of wind raised dust, cloud which covers Mitrovica and some villages located in its vicinity. For transfer of water caused by heavy weather, there are two channels constructed of concrete, located 100-200 meters from the circle of the dam which prevent the infiltration of water towards the dam, interrupted by the potential erosion of the dam screen.

Composition of waste disposed changes, while the clear water which carries with it heavy metals, from lake of landfill through the collector and the stream flows into the waters of the river Ibër. There are years that nobody cares about the revitalization of the landfill and as such, it presents potential risk to groundwater pollution and surface pollution. Heavy metals, due to the high toxicity, may pass into drinking water sources and food products and thus cause serious consequences to human health and therefore it is imperative that their presence kept under control (Çullaj A., 2005).

Results and Discussion

In the month deadline from February to December of 2010 water samples were taken immediately after the spill of water from the landfill Kelmendi into the river Ibër, while another sample is taken also in the Ibër River where the railroad bridge located.

This is the method which we have applied during this research to obtain water samples. In this way, twice per year, has followed the concentration of heavy metals Pb, Cu, Cd, Zn, Fe, Mn, Cr and Ni and continuously the presence of physical and chemical parameters that characterize the water quality.
Table 1 The water of the river Ibër in Kelmend

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<td>II</td>
<td>III</td>
<td>IV</td>
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266
Table 2 The water of the river Ibar in Mitrovica

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<td>III</td>
<td>IV</td>
<td>V</td>
<td>VI</td>
<td>VII</td>
<td>VIII</td>
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**Chemical Parameters**

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**Heavy metals**

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For determining the concentration of heavy metals in water, we have taken samples and treated with the method of absorption atomic spectrofotometry (AAS) until the evidence of the presence of other physical and chemical parameters are given with photometric, volumetric, comparative and visual methods, using manual instruments simultaneously. Review the content of heavy metals and physical-chemical components, is presented in Table 1 and 2.

**Chart 1.1.** The concentration of heavy metals in the waters of the river Iber in the downstream landfill Kelmendi.

**Chart 2.1.** The concentration of heavy metals in the waters of the river Ibar near the neighborhood of the Bosnians.

On the basis of physico-chemical parameters shows that the waters of the river Iber belong third class (III) based on water quality standards for overhead, while it is known that by 1965, according to quality, these waters belong to the second class (II). The results obtained for some heavy metals, which are defined in the water of Iber river do not comply with the criteria and standards of the EU 2000/60 (UNECE, 1966 Guidelines). The results obtained show that Pb, Cd and Mn values exceed the maximum
allowed. Field situation obliges us to conclude that landfill occurred in Kelmend, which is still active, it remains one of the potential sources of pollution of the river Ibrë.

Water pollution is carried out in several ways: Setting uncontrolled industrial waste, which directly attacks the quality of water and destroys flora and fauna of the river Ibrë. Waters located on lake of landfill itself contain heavy metals, and then through aqueous solutions penetrate in the Ibrë river flows. The distribution of dust through the winds and storage of materials in soil, water, etc..

Based on the results obtained with experimental methods and relevant scientific literature (Dudka, and Adriano, 1997) recommend: That at present be revitalization of the landfill based on criteria set by the EU. In our opinion, acting in this way, somehow, will decrease the level of water pollution with heavy metals, but because of continuing contamination, not achieved their full elimination

Conclusions
Existing landfill is located in the village Kelmend has been and is a source of heavy metal pollution of the river Ibar. As such, this landfill has remained a heavy burden of inheritance for future generations, which will be forced to continuously commit to its repair.

With the development of modern technology and the application of advanced methods of maximum exploitation and production to the heavy metals by ore, and the establishment of industrial waste in places where it is exploited in galleries of mines, and utilization of waste industrial construction will significantly affect the reduction of industrial waste and heavy metals in the environment. These efforts should consist, in particular, the design of projects dealing with a permanent monitoring of water for the purpose of preserving and improving water quality of the Ibrë River, which for now is contaminated with heavy metals.

Reference
Çullaj.A, (2005) ;Kimia e mjedisit, Tiranë
Goletić Š, (2005) ; Teški metali u okolišu,Univerzitet u Zenici, Mašinski fakultet u Zenici, Zenica.
The Quality of Drinking Water in Some Rural Areas of the Region of Mitrovica

Sadija Kadriu1,∗, Besnik Hoxha2, Fatmire Azemi-Myftiu3, Lavdim Zeqiri4, Mehush Aliu1

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Abstract: This paper aims to assess the drinking water of some rural areas of municipalities Mitrovicë, Vushtrri and Skende raj. In the absence of urban sewage network, in most villages of the three municipalities, many families have been forced to make temporary solution to wastewater, building just a few meters away from their home septic tanks. However, the opening of these septic tanks and the continued existence of natural fertilizers and the impossibility of installing a sewage system in accordance with urban standards, has caused contamination of drinking water in wells of different families. In our research were followed organo-leptic, microbiological, physico-chemical parameters, the presence of undesirable substances and other parameters that affect in the quality of drinking water for residents of these rural areas. Samples were taken in a period of time and taking into consideration the time of stay allowed in the incubator. As a result of non compliance with standard values, microbiological parameters and undesirable substances, in general the water in rural areas of these municipalities is considered non potable.

Keywords: wastewaters, spill, physico chemical analysis, rural areas, pollutant

Introduction

It is known that water is one of the most important factors of life on our planet, because as such it is necessary for the development of all vital processes in the biosphere. The role of water is indispensable for the human organism, although only a small amount of water used for drinking, until its importance is vital character content. According to some scientific data validated in anatomical way the 2/3 of human body is composed of water, so water considered as essential factor for life. It is known the fact that in rural areas usually use underground water (wells) for drinking.

Except that water used for drinking, for the maintenance of individual and general hygiene, for producing food products and other needs in agriculture and farming, water also carries several infectious diseases.

The quality of drinking water in rural areas

According to a research report made by the OSCE (OSCE study, 2005), in Kosovo, in the context of environmental analysis, 28% of families which living in rural areas have not arranged even nearly flow system of wastewaters. Communities that have less than 5000 residents are not obliged by law to themselves to build systems of sewage purification and cleaning of the environment where are located the remains of natural fertilizers farmers, so as such, these sources pollution pose a serious problem for residents of these areas which have remained in a serious situation requiring choice, or otherwise remains constant source of various infectious diseases.

The main criterion about the quality of water for public use is that they should be clean and healthy to use (Çullaj, 2005). After the recent war in Kosovo, in Mitrovica region, were built several local water supply in rural areas. These water supply are built with the help of some NGOs that have operated in this region, such as: Oxfam, Act, Mersy Corps and with the help of the contribution of municipalities and communities that have participated with their own tools and physical work.

The construction of local water supply in municipalities and rural areas resulted as follows:
1. Mitrovica (Zubin Potok), Qabër
2. Vushtrria: Skromë, Sllakovc, Strofc, Brusnik, Bukosh, Grace and Beqiq.

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Unplanned construction of the septic tanks, then the presence of natural fertilizers near drinking water sources, presence of wastewaters that penetrate in these resources as result of poor installation of the network of pipes in and around their homes, lack of systems to clean wastewater and simultaneously disregard of standards allowed distance between wells and potential sources of pollution in them, highlight the major problems for families of these rural areas and for the environment in general.

Although a special importance to the residents of these rural areas, for these objects does not care one for their maintenance, except in some villages, where residents themselves are those who voluntarily care for their maintenance.

Special problems are presented, especially in the local water supply, which carry water through pumps, who because of frequent interruptions electricity have suffered serious technical breach.

Local water supply, of these rural areas, who were left without anyone's care, denote permanent risk of infection for residents who use this water.

**Results and Discussion**

In some countries of the world are set rate the quality of drinking water in accordance with the recommendations of the World Health Organization (WHO), because the standards for drinking water quality are very strict. Quality of water for public use specified by chemical, physical and microbiological analysis. In this paper were treated the samples of drinking water of wells in rural areas and are defined organoleptic, physico-chemical and microbiological parameters, undesirable substances and other parameters. In this paper are applied:

- Volumetric (titration) methods: consumption of KMnO₄, chloride, sulfate, hardness
- Photometric methods: ammonia, nitrites, nitrates
- Bacteriological determining method of water with vacuum filters
- Visual and comparative method: the smell, taste, color, residual chlorine
- Manual instruments: pH, temperature, turbidity, electrical conductivity

The results are given in form of table and chart as follows: Tabular and graphical presentation of physical-chemical analysis of local water supply facilities

**Table 1. Physical-chemical analysis of water in local water supply facilities**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Standard reference value</th>
<th>Date: 13.05.2010</th>
<th>Date: 22.02.2010</th>
<th>Date: 25.09.2009</th>
<th>Date: 29.08.2009</th>
<th>Date: 16.05.2009</th>
<th>Date: 09.05.2009</th>
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<tbody>
<tr>
<td>Temperature</td>
<td>281.16-285 K/0C</td>
<td>17.5</td>
<td>8.7</td>
<td>13.1</td>
<td>16.5</td>
<td>16</td>
<td>15.2</td>
</tr>
<tr>
<td>Odor</td>
<td>Without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
</tr>
<tr>
<td>Taste</td>
<td>Without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
</tr>
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<td>0.0</td>
<td>0.41</td>
<td>0.0</td>
<td>0.0</td>
<td>0.64</td>
</tr>
<tr>
<td>Color</td>
<td>10-20 ShkCo-Pt</td>
<td>4.309</td>
<td>3.119</td>
<td>3.89</td>
<td>4.34</td>
<td>7.15</td>
<td>5.652</td>
</tr>
<tr>
<td>pH value</td>
<td>6.8-8.5/6.5-9.5</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
</tr>
<tr>
<td>KMnO₄ consumption</td>
<td>8-12 mg/l O₂</td>
<td>7.45</td>
<td>7.79</td>
<td>7.85</td>
<td>7.77</td>
<td>7.71</td>
<td>7.66</td>
</tr>
<tr>
<td>Residual chlorine</td>
<td>0.2-0.5mg/l Cl₂</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
</tr>
<tr>
<td>Chloride</td>
<td>200 mg/l Cl⁻</td>
<td>35</td>
<td>17</td>
<td>12</td>
<td>16</td>
<td>50</td>
<td>12</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.1mg/l NH₄⁺</td>
<td>0.038</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Nitrates</td>
<td>0.005mg/l NO₂⁺</td>
<td>0.004</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.007</td>
<td>0.003</td>
</tr>
<tr>
<td>Nitrates</td>
<td>10 mg/l NO₃⁻</td>
<td>2.2</td>
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<td>0.2</td>
<td>1.1</td>
<td>6.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Electrical cond.</td>
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<td>847</td>
<td>628</td>
<td>308</td>
<td>430</td>
<td>965</td>
<td>471</td>
</tr>
<tr>
<td>Sulphates</td>
<td>200 mg/l</td>
<td>28.26</td>
<td>12.7</td>
<td>6.14</td>
<td>6.14</td>
<td>56.38</td>
<td>6.14</td>
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<tr>
<td>Hardness</td>
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<td>5.936</td>
<td>18.01</td>
<td>6.27</td>
<td>9.75</td>
<td>21.62</td>
<td>6.384</td>
</tr>
</tbody>
</table>
Figure 1. The graphical presentation of temperature, pH and spending of KMnO₄.

Figure 2. The graphical presentation of concentration of ammonia and nitrites.

Figure 3. The graphical presentation of the hardness and concentration of chlorides and sulphates.
Figure 4. Graphical presentation of turbidity and concentration of nitrates.

Figure 5. Graphical presentation of electrical conductivity

Table 2. Physical-chemical analysis of water in local water supply facilities

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
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<td>281.16-285 (8-12)K/°C</td>
<td>15.1</td>
<td>10.1</td>
<td>20.9</td>
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<td>Without</td>
<td>without</td>
<td>Without</td>
<td>without</td>
<td>without</td>
</tr>
<tr>
<td>Taste</td>
<td>Without</td>
<td>Without</td>
<td>Without</td>
<td>Without</td>
<td>Without</td>
<td>Without</td>
<td>without</td>
<td>without</td>
</tr>
<tr>
<td>Turbidity</td>
<td>1.2-2.4 NTU</td>
<td>0.08</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.96</td>
<td>1.72</td>
<td>1.72</td>
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<td>pH value</td>
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<td>Without</td>
<td>Without</td>
<td>Without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
</tr>
<tr>
<td>KMnO₄ consump.</td>
<td>8-12 mg/l O₂</td>
<td>6.342</td>
<td>2.28</td>
<td>2.52</td>
<td>3.87</td>
<td>4.25</td>
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<td>10.02</td>
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<tr>
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<td>Without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
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<tr>
<td>Chlorides</td>
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<td>60</td>
<td>13</td>
<td>14.5</td>
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<td>15</td>
<td>273</td>
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<tr>
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<td>0.02</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
<td>0.0</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Nitrates</td>
<td>0.005mg/LNO₂⁻</td>
<td>0.011</td>
<td>0.003</td>
<td>0.004</td>
<td>1.785</td>
<td>0.004</td>
<td>0.007</td>
<td>0.007</td>
</tr>
<tr>
<td>Nitrates</td>
<td>10 mg/l NO₃⁻</td>
<td>0.6</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Electrical cond.</td>
<td>1500 µs</td>
<td>1040</td>
<td>730</td>
<td>772</td>
<td>1217</td>
<td>557</td>
<td>1824</td>
<td>1824</td>
</tr>
<tr>
<td>Sulphates</td>
<td>200 mg/l</td>
<td>25.34</td>
<td>21.18</td>
<td>6.496</td>
<td>/</td>
<td>9.02</td>
<td>37.82</td>
<td>37.82</td>
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<td>Hardness</td>
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<td>29.56</td>
<td>7.504</td>
<td>21.28</td>
<td>21.28</td>
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</table>
Figure 6. The graphical presentation of temperature, pH and spending of KMnO₄

Figure 7. The graphical presentation of concentration of ammonia and nitrites

Table 3. Physical-chemical analysis of water in local water supply facilities

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>281.16-285 (8-12)K/°C</td>
<td>9.0</td>
<td>10</td>
<td>16.5</td>
<td>13</td>
<td>19</td>
</tr>
<tr>
<td>Odor</td>
<td>Without Land</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
</tr>
<tr>
<td>Taste</td>
<td>Without</td>
<td>Land</td>
<td>Land</td>
<td>Land</td>
<td>Land</td>
<td>Land</td>
</tr>
<tr>
<td>Turbidity</td>
<td>1.2-2.4 NTU</td>
<td>276</td>
<td>0.03</td>
<td>0.0</td>
<td>0.81</td>
<td>2.19</td>
</tr>
<tr>
<td>Color</td>
<td>10-20 ShkCo-Pt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH value</td>
<td>6.8-8.5/6.5-95</td>
<td>7.8</td>
<td>7.0</td>
<td>7.77</td>
<td>8.0</td>
<td>7.1</td>
</tr>
<tr>
<td>KMnO₄ consumption</td>
<td>8 -12 mg/l O₂</td>
<td>17.738</td>
<td>5.16</td>
<td>4.34</td>
<td>6.54</td>
<td>1.905</td>
</tr>
<tr>
<td>Residual chlorine.</td>
<td>0.2-0.5mg/l Cl₂</td>
<td>Without</td>
<td>without</td>
<td>without</td>
<td>without</td>
<td>without</td>
</tr>
<tr>
<td>Chlorides</td>
<td>200 mg/l Cl⁻</td>
<td>14</td>
<td>20</td>
<td>16</td>
<td>18</td>
<td>22.5</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.1mg/LNH₄⁺</td>
<td>0.49</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.08</td>
</tr>
<tr>
<td>Nitrites</td>
<td>0.005mg/LNO₂⁻</td>
<td>0.316</td>
<td>0.006</td>
<td>0.003</td>
<td>0.008</td>
<td>0.006</td>
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<td>10 mg/l NO₃⁻</td>
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<td>0.1</td>
<td>1.1</td>
<td>16.54</td>
<td>0.8</td>
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<tr>
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<td>617</td>
<td>430</td>
<td>914</td>
<td>765</td>
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<td>Sulphates</td>
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<td>/</td>
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</table>
Figure 8. The graphical presentation of the hardness and concentration of chlorides and sulphates.

Figure 9. Graphical presentation of turbidity and concentration of nitrates.

Figure 10. Graphical presentation of electrical conductivity.
Figure 11. The graphical presentation of temperature, pH and spending of KMnO₄

Figure 12. The graphical presentation of concentration of ammonia and nitrites.

Figure 13. The graphical presentation of the hardness and concentration of chlorides and sulphates
Figure 14. Graphical presentation of turbidity and concentration of nitrates.

Figure 15. Graphical presentation of electrical conductivity.

Table 4. Physico-chemical and bacteriological analysis of water to local water supplies

<table>
<thead>
<tr>
<th>Municipality</th>
<th>Village with local objects of water</th>
<th>Chemical analysis</th>
<th>Bacteriological analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mitrovicë</td>
<td>loc. ob. vill. Qabër</td>
<td>potable</td>
<td>potable</td>
</tr>
<tr>
<td>Skenderaj</td>
<td>loc. ob. vill. Burojë</td>
<td>potable</td>
<td>non potable Enterobacter</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Runik</td>
<td>potable</td>
<td>non potable Citrobacter</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Baks</td>
<td>potable</td>
<td>non potable E.coli,Tot.colif.</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Marinë</td>
<td>non potable NO(^2)(1.785)</td>
<td>non potable Enterobacter-Tot.colif.E.coli.</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Llaushe</td>
<td>non potable NO(^2)(0.006)</td>
<td>non potable Providentia.Redgeri .Total.colif.</td>
</tr>
<tr>
<td></td>
<td>Ob.loc.likovic</td>
<td>non potable NO(^2)(0.006)</td>
<td>non potable Citrobacter.Tot.colif.</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Tërnovë</td>
<td>non potable NO(^2)(0.016), NH(^3)(0.19)</td>
<td>non potable E.coli-Tot.colif.</td>
</tr>
<tr>
<td>Vushtri</td>
<td>loc. ob. vill. Bukosh</td>
<td>potable</td>
<td>non potable Eribero bacter.</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Strovc</td>
<td>potable</td>
<td>non potable Citrobacter.Tot.colif.</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Bivolak</td>
<td>non potable NO(^2)(0.007)</td>
<td>non potable Acinetobacter</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Gracë</td>
<td>non potable - NO(^2)(0.011)</td>
<td>non potable B.Agrestis</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Bruznik</td>
<td>potable</td>
<td>non potable -E.coli-Tot.colif.</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Ceceli</td>
<td>potable</td>
<td>non potable Enterobacter,Tot.colif.</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Vilanc</td>
<td>non potable -NO(^2) (0.007)El.cond(1824)</td>
<td>non potable -Enterobacter,B.gj.12kllostridie</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Slakovc</td>
<td>non potable NO(^2)(0.316) NH(^4)(^+) (0.49)Tur (276)</td>
<td>non potable -Enterobacter,Tot.colifB.gj.</td>
</tr>
<tr>
<td></td>
<td>loc. ob. vill. Beqiq</td>
<td>non potable NO(^2)(0.008)</td>
<td>non potable E.coli-Tot.colif.</td>
</tr>
</tbody>
</table>
According to results presented in the table shows that water used for drinking in the village Qabër of Mitrovica is potable. In rural areas of Skenderaj, as in villages Burojë, Runik, Baks and Mikushnicë by chemical analysis water is potable, but on the basis of bacteriological analysis shows that water is not potable. In rural areas of Vushtrri, as in villages Bukosh, Strovc, Brusnik and Ceceli by chemical analysis water is potable, but on the basis of bacteriological analysis shows that water is not potable.

While, in the villages Bivolak, Grace, Vilanc, Sllakovc and Beqiq based on chemical and bacteriological analysis, water is not potable. Taking into account the results of chemical and bacteriological analysis, made in the laboratory of the Regional Public Health Institute located in Mitrovica, found that in addition Qabër village of Mitrovica, in all other villages in the municipality of Skenderaj and Vucitrn, where tests are done, water can not be used for drinking due to the enormous presence of various bacteria that cause infectious diseases to these rural communities.

Conclusions
Nowadays, the cleaning of wastewater is multidimensional problem that requires major investments without reservation, that we have at our disposal always clean drinking water. Therefore, residents of these areas is recommended:
until a more convenient choice.
Installation of a network of sewage spilling into the house and its surrounding.
Become installing modern plumbing for transferring wastewater from residential homes and farms, at an allowed distance, based on criteria and standards.
Opening, concreting and isolation of septic tanks, always taking into consideration the allowed standards.
Municipal governments urgently need to plan the installation of sewage network in these rural areas considering the criteria of the World Health Organization (WHO).

Reference
Çullaj.A, (2005), Kimia e mjedisit, Tiranë.
OSCE study (2008),The roots of poverty in Kosovo, Prishtina.
Pravilnik o ispuštanju otpadnih voda, 42/02, Beograd.
The Influence of Maternal Nutritional Status on the Growth of Neonates of Saudi Women

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Abstract: This study was undertaken to investigate the effects of maternal nutritional status on the growth of neonates. One hundred Saudi Arabia pregnant women were chosen at delivery with their full term newborns. Anthropometric measurements and serum albumin, prealbumin, retinol binding protein, transferrin and fibronectin were determined in pregnant women at delivery and in the cord blood of their corresponding offsprings. The data showed the presence of statistical significant correlation coefficient between the most maternal anthropometric measurements and the neonatal measurements. The mean serum albumin level in mothers was lower, while the mean levels of maternal serum prealbumin, retinol binding protein, transferrin and fibronectin were significantly higher than their corresponding level in the cord blood prealbumin, retinol binding protein, transferrin and fibronectin. None of these prealbumin, retinol binding protein, transferrin and fibronectinoteins were correlated to the birth weight. The mean serum albumin, retinol binding protein and fibronectin levels measured for mothers and in cord blood was correlated.

Key words: Anthropometric measurements, serum albumin, prealbumin, retinol binding protein, transferrin and fibronectin.

Introduction

Nutrition is the science of food and its relationship to health. Nutritional status is one of the key indicators of health. Although there is evidence of the importance of maternal nutrition as a determinant of the outcome of pregnancy (Tyler et al., 1990).

On the basis of data from animal studies and cross country comparisons, poor maternal nutrition has been implicated as one of the key “adverse environmental influences in utero,” which could lead to compromised fetal and placental growth and adverse long term consequences (Barker, 1992; Barker et al., 1993). Their observational studies of British women also suggest that maternal diet is an important determinant of infant and placental size (Campbell et al., 1996; Fraser and Cresswell 1997). The “Barker hypothesis” has led to calls for improvements in maternal diet, which have generated some concern among obstetricians (Godfrey et al., 1997). The data of Han et al., (2010) demonstrate the risk of nutritional deficiency in the newborn even with uneventful pregnancies in an economically favoured population. Their data confirmed the utility of biochemical analysis in a longitudinal study in order to assess the risk of nutritional deficiencies.

Although there is widespread recognition of the importance of adequate maternal nutrition during pregnancy in developing countries, there is considerable uncertainty about its role in industrialized countries, where profound malnutrition is uncommon.

Even near starvation, such as occurred during the Dutch “Hunger winter”, reduced mean birth weight (Mathews et. al., 1999). The evidence from adequately nourished population is conflicting. Observational studies have found only weak and inconsistent associations between intake of macronutrients and infant size (Haste et al., 1991) and few data are available for micronutrients (Mathews, 1996). In supplementation trials, micronutrients have not shown to have important impact on mean birth or placental weights (Mahomed, 1993a,b). Protein and energy supplementation have produced both increases and decreases in birth weight, with high-density protein supplements seem to reduce birth weight (Kramer, 1994). The results of such trials are difficult to generalize, however, as

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intakes are often increased well beyond normal levels. In addition, trials are usually designed to detect changes in adverse outcomes of pregnancy rather than in birth weights within the normal range.

This study aims to assess mother’s weight, height and body mass index as well as maternal and cord blood prealbumin, albumin, retinol binding protein, transferrin and fibronectin and their impact on fetal growth in Saudi Arabia women.

Material and Methods
The study included 100 pregnant women at delivery with their corresponding full term newborns delivered in the Saudi German Hospital and Al Thager Hospital. They were chosen to be free of any medical or obstetric problems that may interfere with intrauterine growth and development. All newborn infants were full term and born by normal vaginal delivery with gestational age between 37-42 weeks.

Blood sampling
5ml of venous blood was withdrawn from the mothers before delivery and the same amounts of mixed arterio-venous cord blood from each corresponding newborn infants at birth. The separated serum was preserved at -20°C until used.

Maternal anthropometric Measurements
Weight, height and body mass index (BMI) were determined. BMI was calculated by dividing weight (kg)/height² (m). Mid-arm circumference measurement, taken on the left arm midway and thigh circumference was measured (Guthrie, 1989)

Newborn anthropometric measurements
Newborn body weight, length, head circumference, arm circumference, chest circumference and Ponderal Index (PI = weight in grams/length in cm²) were recorded as described by Martorell et al., (1975); Landicho et al., (1985) and Hendricks (1990).

Biochemical tests
Serum albumin was determined using spectrophotometer method described by Doumas et al., 1971). Serum prealbumin, retinol binding protein, transferrin and fibronectin in maternal and cord blood were evaluated using radial immunodiffusion kits (purchased from Sigma) and applying the method of Mancini et al.(1965).

Statistical analysis:
Statistical analysis using SPSS program of personal computers version 10 and employed the student for comparison of the mean values the simple correlations. Pearson correlation was calculated to evaluate the relationship between the variables and values <0.05 were considered statistically significant.

Results
Our study group consisted of 100 pregnant mothers at delivery and their corresponding newborns. The collected data shows the anthropometric characteristics (Table 1) and the biochemical measurements (Table 2) of neonates and mothers. Mother weight after delivery ranged from 42-115 kg with mean of 61.67 kg. Mother height ranged from 142-180 cm; with mean value of 160 cm. Arm and thigh circumference of mother were 17-40 and 32-70 cm, respectively. Body mass index of mother ranged from 1558.17-4275.73 kg/cm² with a mean of 2381.26 kg/cm². Weight of neonates after birth ranged from 2200-4200 g with a mean of 3207 g. Their length was ranged from 45 to 55cm with mean value of 50 cm. The mean values of head, chest and arm circumference were 33.16, 10.93 and 2.5 cm, respectively. Ponderal index ranged from 1.77-3.17 g/m² with mean value of 2.5 g/m²

The mean value of maternal serum albumin, prealbumin, retinol binding protein, transferrin and fibronectin were 3.61 ± 0.43, 20.56 ± 6.29, 2.54 ± 1.16, 4.38 ± 1.63, and 14.2 ± 11.69 mgdL⁻¹, respectively (table 2). The mean values of the tested nutritional biochemical parameters (serum albumin, prealbumin, retinol binding protein, transferrin and fibronectin) in cord blood of neonates were 3.96 ± 0.41, 14.66 ± 3.87, 1.61 ± 0.84, 2.59 ± 2.92 and 4.96 ± 4.69 mgdL⁻¹, respectively.
Table 1. Anthropometric characteristics (mean value ± SD) of 100 pregnant women at delivery and their corresponding newborns

<table>
<thead>
<tr>
<th>Character</th>
<th>Range</th>
<th>mean± SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maternal weight (kg)</td>
<td>42-115</td>
<td>61.67±1.29</td>
</tr>
<tr>
<td>Maternal height (cm)</td>
<td>142-180</td>
<td>160.53±0.69</td>
</tr>
<tr>
<td>Maternal Arm circumference (cm)</td>
<td>17-40</td>
<td>25.88±0.37</td>
</tr>
<tr>
<td>Maternal thigh circumference (cm)</td>
<td>32-70</td>
<td>46.98±0.59</td>
</tr>
<tr>
<td>Body mass index (w/ht)(kg/m²)</td>
<td>1558-4275</td>
<td>3281.26±40.88</td>
</tr>
<tr>
<td>Neonatal weight (g)</td>
<td>2200-4200</td>
<td>3207.95±46.00</td>
</tr>
<tr>
<td>Neonatal length (cm)</td>
<td>45-55</td>
<td>50.43±0.20</td>
</tr>
<tr>
<td>Head circumference of neonates (cm)</td>
<td>29-36</td>
<td>33.20±0.14</td>
</tr>
<tr>
<td>Chest circumference of neonates (cm)</td>
<td>28-37</td>
<td>33.16±0.13</td>
</tr>
<tr>
<td>Arm circumference of neonates (cm)</td>
<td>8-14</td>
<td>10.93±0.10</td>
</tr>
<tr>
<td>Ponderal index on neonates</td>
<td>1.77-3.17</td>
<td>2.5±0.03</td>
</tr>
</tbody>
</table>

Table 2. Maternal and cord biochemical characters of 100 pregnant women at delivery and their corresponding newborns

<table>
<thead>
<tr>
<th>Character</th>
<th>Maternal venous</th>
<th>Cord blood</th>
<th>t-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Serum albumin</td>
<td>3.61±0.43</td>
<td>3.96±0.41</td>
<td>5.94</td>
</tr>
<tr>
<td>Prealbumin</td>
<td>20.56±6.29</td>
<td>14.66±3.87</td>
<td>8.02</td>
</tr>
<tr>
<td>Retinol binding protein</td>
<td>2.54±1.16</td>
<td>1.61±0.84</td>
<td>6.54</td>
</tr>
<tr>
<td>Transferrin</td>
<td>4.38±1.63</td>
<td>2.59±2.92</td>
<td>9.58</td>
</tr>
<tr>
<td>Fibronectin</td>
<td>14.2±11.69</td>
<td>4.96±4.69</td>
<td>7.19</td>
</tr>
</tbody>
</table>

The results shows that the maternal weight positively correlates with each of the neonatal body weight, ponderal index, cord blood fibronectin, and negatively correlates with each of neonatal length and circumferences of head, chest and arm (Table 3). Further, maternal height correlates with neonatal weight, length and ponderal index. Maternal arm circumference indicates significant correlation with neonatal weight, length, head circumference, chest circumference, arm circumference, ponderal index and fibronectin. Maternal thigh circumference shows significant correlation with neonatal weight, head circumference, chest circumference, and ponderal index. BMI positively correlates with the neonatal ponderal index. Maternal albumin shows significant correlation with neonatal arm circumference, ponderal index and albumin. Maternal prealbumin correlates with neonatal Retinol binding protein. Maternal Retinol binding protein shows correlation with neonatal prealbumin and Retinol binding protein. There were also correlations between maternal transferrin with neonates head circumference and maternal fibronectin with neonatal transferrin and fibronectin.

Table 3. Correlation matrix between different maternal and neonatal anthropometric and biochemical parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>weight</th>
<th>height</th>
<th>Arm circ</th>
<th>Thigh circ</th>
<th>BMI</th>
<th>Albumin</th>
<th>Prea.</th>
<th>RBP</th>
<th>Trans.</th>
<th>Fibr</th>
</tr>
</thead>
<tbody>
<tr>
<td>weight</td>
<td>0.36**</td>
<td>0.51**</td>
<td>0.38**</td>
<td>0.32**</td>
<td>0.18</td>
<td>0.11</td>
<td>0.02</td>
<td>-0.006</td>
<td>0.08</td>
<td>-0.006</td>
</tr>
<tr>
<td>length</td>
<td>0.09</td>
<td>0.26**</td>
<td>0.19*</td>
<td>0.14</td>
<td>-0.02</td>
<td>-0.06</td>
<td>0.08</td>
<td>0.11</td>
<td>0.13</td>
<td>-0.11</td>
</tr>
<tr>
<td>Head circ</td>
<td>0.17</td>
<td>0.14</td>
<td>0.20*</td>
<td>0.27**</td>
<td>0.13</td>
<td>0.13</td>
<td>0.02</td>
<td>0.02</td>
<td>0.20*</td>
<td>-0.04</td>
</tr>
<tr>
<td>Chest circ</td>
<td>0.14</td>
<td>0.18</td>
<td>0.22*</td>
<td>0.28**</td>
<td>0.07</td>
<td>-0.01</td>
<td>0.11</td>
<td>0.01</td>
<td>0.19</td>
<td>0.09</td>
</tr>
<tr>
<td>Arm circ</td>
<td>0.12</td>
<td>0.18</td>
<td>0.34**</td>
<td>0.19</td>
<td>0.14</td>
<td>0.23*</td>
<td>-0.001</td>
<td>0.15</td>
<td>0.03</td>
<td>-0.11</td>
</tr>
<tr>
<td>PI</td>
<td>0.31**</td>
<td>0.33**</td>
<td>0.25*</td>
<td>0.25*</td>
<td>0.21*</td>
<td>0.20*</td>
<td>-0.06</td>
<td>-0.11</td>
<td>-0.05</td>
<td>0.12</td>
</tr>
<tr>
<td>Albumin</td>
<td>0.09</td>
<td>0.16</td>
<td>0.00</td>
<td>0.02</td>
<td>-0.06</td>
<td>0.28*</td>
<td>-0.07</td>
<td>0.13</td>
<td>-0.03</td>
<td>-0.11</td>
</tr>
<tr>
<td>Prealbumin</td>
<td>0.07</td>
<td>0.17</td>
<td>-0.05</td>
<td>-0.04</td>
<td>-0.01</td>
<td>0.001</td>
<td>0.15</td>
<td>0.25*</td>
<td>-0.11</td>
<td>-0.10</td>
</tr>
<tr>
<td>RBP</td>
<td>0.18</td>
<td>0.12</td>
<td>0.13</td>
<td>0.07</td>
<td>0.15</td>
<td>0.08</td>
<td>-0.23*</td>
<td>0.26*</td>
<td>-0.02</td>
<td>0.08</td>
</tr>
<tr>
<td>Transferring</td>
<td>-0.02</td>
<td>0.07</td>
<td>0.01</td>
<td>-0.07</td>
<td>-0.05</td>
<td>0.12</td>
<td>0.13</td>
<td>0.05</td>
<td>-0.08</td>
<td>-0.21*</td>
</tr>
<tr>
<td>Fibronectin</td>
<td>0.19*</td>
<td>0.11</td>
<td>0.32**</td>
<td>0.16</td>
<td>0.17</td>
<td>0.18</td>
<td>0.13</td>
<td>-0.08</td>
<td>0.19</td>
<td>0.28*</td>
</tr>
</tbody>
</table>

*Significant correlation at the 0.05 level; **Significant correlation at the 0.01 level. Prea.: Prealbumin Trans: Transferring, Fibr.: Fibronectin
Discussion

The traditional state that anthropometric measurements of pregnant mothers assess their nutritional status (Bissenden et al., 1981). Body mass index (BMI) is an average dependent index for nutritional status evolution (Guthrie, 1989). Although there is evidence of the importance of maternal nutrition as a determinant of the outcome of pregnancy (Tyler et al., 1990, Jonxis, 1991), studies showed that intrauterine malnutrition have more consequences that are serious for children than postnatal malnutrition. It is difficult to find a direct correlation between maternal nutrition and the health of the newborn (Neel and Alvarez, 1990), especially in a population without marked economic deprivation. The birth weight, often used as the only indicator of nutritional status, is clearly not very useful under these conditions (Shah and Rajalakshmi, 1988 and Han et al., 2010).

Kulkarni et al., (2006) reported that maternal lean body mass was found to be the most important determinant of birth weight. Thame et al., (2004) found that maternal weight and weight gain was directly related to fetal anthropology through influencing the placental volume and the rate of placental growth. Neonatal nutrition status is measurable using weight and length versus gestational age (Graicer et al., 1981). The ponderal index is used to calculate the relative amount of soft tissue present in an infant (Miller and Hassanein, 1971). Hendricks (1990) stated that ponderal index is the accurate indicator of body built and nutritional status. The neonate arm and chest circumference measures are simple, quick, easy and cheap indicator for birth weight. Arm circumference reflects skeleton muscle protein and fat stores (Raubenstein et al., 1990). Arm circumference measures less than 9cm when birth weight is less than 2500g. Neonatal mortality was shown to have an inverse relation with arm circumference (Ahmed et al., 2000). Naik et al., (2003) reported that chest circumference had the maximum sensitivity of detected low birth weight in newborn. While, the current proves a positive correlation between mother weight and BMI on one side and newborn weight and ponderal index on the other side. The correlation between mother weight and BMI on one side and neonatal mid arm and chest circumference on the other side was negative.

Many authors reported the relationship between birth weight and maternal prealbumin, transferrin and retinol binding protein (Jain et al., 1995). Others proved the use of serum level of some selected nutrients as nutritional indicators is method of choice, namely in an attempt to correlate their levels in maternal venous and cord blood at birth (Charlton, 1991). Physiological changes associated with pregnancy including plasma volume expansion and pregnancy related effects on protein biosynthesis in the liver were theoretically attributed as factors behind negative relations. A significant correlation between birth weight and cord blood transferrin was obtained. Wu et al., (2004) obtained similar correlation. The maternal serum albumin detected in this study was similar to that obtained by Olufemi et al., (1991). On contrast, Hasin et al., (1996) reported that from one hundred and fifty one poor pregnant woman of Dhaka, Bangladesh, about 49% had subnormal serum albumin. The mean cord blood albumin level detected in this study was higher than that obtained by Dong et al., (1990).

In the present work, correlation matrix between different maternal and neonatal anthropometric and biochemical parameters showed a relationship between maternal serum albumin and cord blood albumin. Analysis of variance and correlation coefficient for the two albumins confirmed the above relationship. Conversely, lack a correlation between maternal serum albumin and neonatal weight. Vudhivai et al., (1990) reported similar observation. On contrast, Hasin et al., (1996) suggested that maternal serum albumin levels were found to have significant independent effect on birth weight.

Mohsen and Wafay (2007) using 54 Egyptians pregnant women at delivery with their corresponding full term newborns found that maternal underweight and low BMI reduce newborn weight, length, head, chest, and arm circumferences. This maternal under weight also lead to maternal hypo-albuminemia. They further added that low fibronectin reduces newborn body length and ponderal index, low prealbumin, retinol binding protein and transferrin have no influence on fetal growth.

In conclusion, mother weight and BMI affect newborn weight. Hypo-albuminemia has negative effect on newborn length, head, chest and arm circumferences. Low fibronectin reduces newborn body length and ponderal index while low prealbumin, retinol binding protein and transferrin have no effect on growth. Thus, we conclude that nutritional surveillance during pregnancy must remain an important part of preventive health care. Further large epidemiological studies will assist in assessing the diet and anthropometric measurements of pregnant women and its relationship to maternal weight, weight
gain, low birth weight and biochemical nutritional indicators in countries with a considerable prevalence of maternal undernutrition and maternal overweight/obesity.

References


Rehabilitation of Empty Areas from Exploration of Kosovo Lignite

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Abstract: Energy production is a key to economic development of the country. Environmentally friendly behavior by legal regulation, conventions and EU directives, is necessary. Environment in the area of KEK is influenced by the past wild use of lignite for energy production and current activities. Areas assessed as “hot spots’ in this paper are: pit remaining from existing mines (Mirash & Bardh) and existing ash dumps of TC “Kosovo A and B”. The influenced environmental mediums are: air, water and soil. It’s a priority for environment the rehabilitation of the remaining pit holes from existing mines and existing ash dumps. Rehabilitation should include: storage of fresh ash in existing mines pits, using of technologic water for the creation of ash-water pulps and its transfer, non-creation of new ash hills (dumps), prevention the coal self-burning, stopping of air pollution, restoring the soil in the primary function and regulation of landscape. Positive example to mention until now for the environment is at KEK project started: ”Return of the fresh ash from Kosovo B Thermal Power Plant (TPP) in empty pit-holes of Mirash open pits. Objectives to be achieved with the realization of these priorities to the environmental rehabilitation (remaining pits of existing mines and ash dumps) are: closing of the industrial cycle of lignite exploration and its using for energy production.

Keywords: environment, pollution, mine, ash dump, energetic.

Introduction

Energy production for Kosovo is the key to restructuring of all its economy. Rehabilitation of surfaces, degraded areas, stabilization of lignite production and increasing of energetic production capacities, especially the renewed energy, also bring improvements on the environment and increasing also the living standard.

The complete view of Kosovo basin (KEK area) is the result of mining activities from the time of the commencement of the exploration of lignite (1922). Existing mines of lignite (Bardh and Mirash) operating since 1963/64. Nowadays, these two mines supply two power plants with approximately 7 million tons annually of lignite. According to recently evaluations, existing mines will be fully exhausted by the years 2010/2011, which depends on the energy production compared to the lignite reserves in existing mines. Initiative and the proposal of expanding the open pits from Kosovo Basin in open pit of Sibovc, presents plan to respond to the growth of electricity production in Kosovo as well as improving the quality of the lignite that for both mines Mirash and Bardh occasion from durability and other technical geological barriers is falling and represents the first step to renewal efforts for production processes after the war in Kosovo.

From previous studies the field of Sibovc has been identified as a source of lignite. This open pit is given priority from the other sources in the Kosovo Basin, so plans were made for use with the start of the planning modernization and expansion of production capacities of electricity, which mainly depends on activating the work in the mines. For this purpose in the near future planned construction of a new TPP (Kosovo C) who thought it would replace the existing TPP "Kosovo A".

Environmental issues

From the environmentalist view KEK doesn’t present a good example of mining resources (lignite) by considering only the production of electricity, without any supplement activity - to the environment. This is the controversy with: the closure of the industrial cycle from the source, the
processing to returning again to resource; the returning of lands in the primary function; protection of water; air protection and sustainable economic development, etc.

In the countries where legal regulation, conventions and EU directives applied, this is not allowed.

As environmental “hot spots” separated from all other environmental problems at KEK, mentioned in this paper are: remaining pit of existing mines and existing of ash dumps of TPP "Kosovo A and B".

The mediums which are affected at KEK and the areas impacted from it are: water, air and soil.

**Water**

The impact of activities from the exploitation of lignite and creating of ash dumps in water pollution are very evident as:

- The emission of large quantities of contaminated water, the ratio 1:10 (ash: water) hydraulic dumps,
- The storage of hazardous materials (especially a phenol waters that represent a big issue)
- The atmospheric rainfalls – bland.

These factors generate pollution. Tests had shown an obvious contamination with excess of the maximum allowable limits in certain parameters such as: pH basic, the suspended matter, organic matter, phenol, and the lack of dissolved oxygen. BOD5 showed the second or third class pollution of surface waters.

**Open pits Mirash and Bardh**

Open pits of lignite "Kosovo" (Mirash and Bardh) are potential water pollutants. In areas of coal exploration accumulate surface waters, waters from atmospheric rainfalls, and spring waters from own mines which by pumps, without any prior treatment discharge at recipient - Sitnica River.

It is important that from the mining non-level (below level of Sitnica River) is evident infiltration of water from the river in the mine, which contaminated surface waters lies through contaminated surfaces and collected as polluted and return into the river. The exceeded of pollution are evident in some parameters, even for several tens of times in some cases.

We recommend protecting the mine from infiltration of surface water from the outside in the River Sitnica. In this way would create less waste waters from mines. To build basins for physical treatment of collected waters and other measures for their decontamination with plants before being discharge in rivers, as the necessary measure.

**Ash dumps of TPP "Kosovo A & B"**

Ash dumps present potential contaminant in both qualitative and quantitative terms (about 150 ha of land usurped). Pollution is particularly evident in periods of time with major atmospheric rainfalls, while waters joining with polluted materials deposited at dumps and by leaching passing this contamination in the ground waters. Frequently we have high alkaline medium, high concentrations of phenol and other parameters that exceed the allowed limit values.

We recommend preventive measures as priority because it is a matter that affects all three environmental mediums: water, air and soil. Ash dumps have a temporary character, thought in its returning to the empty pits of coal mines.

Permanent and definitive solution of this issue is the returning of ash in the empty pits of coal mines. This should be accomplished under the project which has begun: "Returning of the fresh ash from TPP Kosovo B in empty pits of Mirash" (et.al. Institute “INKOS” Environmental report: Environmental Impact Assessment for project folding of fresh ash from TPP "Kosovo B" in empty areas of open pit Mirash, Pristina, February 2005) according to the principle of creating pulps ash: water in ratio 1:1.5 and under pressure transporting in destination place, and then becomes biological re-cultivation of the land surfaces. Temporary and partial solution can be done with re-cultivation of the dumps surfaces in the current place:

- by classical method of re-cultivation – placing the humus above dumps prepared prior in terms of visual appearance and greenness.
- re-cultivation with hydro-sowing called as method of hydro-semi, by which can be done greenness the dumps areas even without the adding humus.

The biological re-cultivation of dumps reduces the possibility of the ash bland from surface waters by reducing the degree of its pollution. As determining the consumption of KMnO4 which serve as the control parameter for measuring the pollution of organic character of waters, the level of pollution in
the KEK area is different in different locations of this area. Especially has enormous pollution from effluent waters discharged from the mines and ash dumps. Figure 1 presents the consumption of KMnO₄ with high values in M1 (open pit of Bardh), M2 & M3 (open pit of Mirash), and M4 (ash dump of TPP A).

![Graph](image)

**Figure 1.** Consumption of KMnO₄ with high values in M1

**Impact on the air – self combustion of lignite**

Fires as a result of spontaneous combustion of lignite occurs in slope of open pits mines Mirash and Bardh, and rarely, in excavation fronts and on the dumping places of lignite. Lignite seems as self-combust as a result of the combustible sulfur oxidation, which in contact with atmospheric oxygen produce the heating energy which is needed for self-combustion. Common methods to prevent and fight of fires coal are:

- The coverage of the lignite fires with soil or any other material overloaded to reduce the supply of oxygen;
- Excavation and isolating of the involved material by fire;
- Injection of chemical vapors or other mixtures in fractures to extinguish fire of lignite by "stoppage" the supply of oxygen;
- Fighting the fire by water.

In mines of KEK, several isolated measures were taken in order to stop the frequent fires, such as coverage with soil or injection of bentonite. However, till now no action plan to combat the problem.

The main environmental effects from the spontaneous combustion of lignite are:

- The emission of "greenhouse" gases (CO₂, CH₄, NOx, etc.).
- The emission of toxic gases and their spreading in the region (CO, N₂O, SOx, etc.)
- The destabilization of mining slopes.

Estimates that about 2.5 million tons of lignite burned every year with influence at close area about 1 km², are supposed values for this study, that cause economical losses and damage to the environment. There is no monitoring of the emission in the mines, so the authors have calculated the respective emission of air for year 2005.

Air pollution from these emissions has only local impact. However, it should be taken into account that the "greenhouse" effect of methane is approximately 21 times higher than of carbon dioxide, and annual emission of methane from self-combustion of coal is 6.4 times lower than the total methane emission in Germany (et.al. European Agency for Reconstruction: Environmental impact assessment and action plan for TPP Kosovo A and B and coal mines. EIA, Pristina, May 2003).

The negative effects on the environment are health risks to workers and local residents living near the mines as a result of air pollution. During the winter, smoke combined with microclimatic conditions creates a dense fog, which causes problems in view aspect. Other potential effects of coal fires can be even slipped and land slide in affected areas. Currently there is no investigation about the size of the coal fires and their influence on slippages reported and the risk of subsidence in deposition areas.
Emission of gases from self-combustion of coal

Burning of about 2.5 million tons of lignite at mines produce about 1743000 tons of CO₂, 423000 tons of CH₄ (greenhouse gases) and 886000 tons of CO. The reason for the emission of SO₂ is the presence of sulfur in lignite. However, a natural desulphurization happen after lignite contains large CaO (CaO/S ratio over 5). Self-combustion of lignite in mines produce about 10 000 tons of SO₂. The emission of nitrogen oxides comes as a result of the content of nitrogen in lignite. Production of nitrogen oxides by self-combustion of lignite is not such important as the result of low temperature of combustion.

The institute of “INKOS” monitoring the air quality in the measurement points Mirash and Bardh and founded values indicate the presence of pollution in the extension areas of mines and the area impacted from them. Values for dust exceed the limits by the EU directives as SO₂ has assets that are much lower than the maximum limit values (et.al. Source: Institute “INKOS”, Environmental department).

Common pollution that comes from power plants, mines and ash dumps exceeds the area of KEK, and depending on atmospheric conditions and other environmental factors, spreading of pollutants reaches several tens of kilometers, while the most affected region is the SW direction from 20 - 40 km, the last of the concentration levels are only 10% of the levels calculated in location.

Distance from mining activity for the concentration of measured pollutants is calculated from 0 to 5 km from the location. However, the authors of this study may conclude that KEK has a big problem with dust in the surrounding area and particularly in the SW of site.

Emission of dust

Dust (fly ash) from self-caused fires in mines remain in these burning locations and not indicate any important source of pollution. However, this is a local environmental problem. It is estimated that both two open pit mines produce about 1000 tons of dust, while the storage and manipulation create about 19000 ton of dust. Large dust particles tend to settle down within 500 meters from the source. However, particulates brought by air-suspended (PM10) can be transported to large distances from 5000 to 10000 km, depending on atmospheric conditions. Thus, dust emissions are contributing to significant in total air pollution and not only locally.

The dust from erosion (outside ash dumps) in slope of open pit mines is another serious environmental and health issues, especially during the dry seasons. Furthermore, the development of the new open pit (Sibovc) in the near future will increase the emission of dust in this area, if appropriate measures are not implemented.

Ash, use and impact on the environment

During the self-combustion process of the coal created unknown quantity of ash which remains in combustion place and is covered with soil. Environmental effects are not known. Analysis of ash and its composition is presented in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Fly ash, %</th>
<th>Bottom ash, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>26.96</td>
<td>59.76</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.28</td>
<td>20.38</td>
</tr>
<tr>
<td>CaO</td>
<td>38.64</td>
<td>3.79</td>
</tr>
<tr>
<td>MgO</td>
<td>5.17</td>
<td>0.93</td>
</tr>
<tr>
<td>SO₃</td>
<td>12.58</td>
<td>2.36</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.24</td>
<td>0.86</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.78</td>
<td>2.42</td>
</tr>
<tr>
<td>TiO</td>
<td>0.48</td>
<td>0.28</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.44</td>
<td>8.01</td>
</tr>
<tr>
<td>Total</td>
<td>98.57</td>
<td>98.79</td>
</tr>
</tbody>
</table>

This is the composition of ash; its components through surface water and groundwater pollute rivers and land. Content of trace elements is not known, although in environmental terms are most significant. Until nowadays researches is ascertain that ash can be used in the cement industry,
construction and as a tampon for the construction of roads, etc. So far there is no movement in this direction except for a symbolic amount which uses by cement industry in the Han Elez. Ash contain salts and trace elements by which an amount, when comes in contact with water, early or late will be released and will pollute groundwater and surface waters.

Lands

Land occupied by KEK in one or different way have changed their destination and are transformed into industrial land with about 5000 hectares. This area belongs to the territory of municipalities: Pristina, Kastriot, Drenas, Vushtrri and Lypjan. These lands have been damaged by mines, TPP "Kosova A & B" with Separation and respective ash dumps and other old industrial objects which are in this area (Chemistry and Energy, Heating, Dryer). Existing ash dumps are created in the vicinity of rural residences, and any eventual sliding of the stored material presents a risk to local residents. Most risks villages are: Dardhishta and Aneslumi (former Plemetin). From this it results that the damage of lands in this area belongs to a serious degree damages that can defined as:

- Physical damage of land, and
- Chemical contamination of land.

Contaminated land in this way from the water surface rinse generate contaminated waters, the phenomenon is especially evident near ash dumps, in the time period with high level of atmospheric rainfalls.

Conclusions

The dump site of ash from TPP "Kosovo B" is virtually filled and would not be rational expansion across the river Sitnica. The new place is provided in a part of the empty area of open pit "Mirash". The dump site is designed to inability infiltration of drain waters into ground waters. Starting from the actual situation (of ash dumps) required urgent commitment and approach to resolving the problem of rehabilitation - return of this industrial tailings in areas from aforetime lignite is used (dig) to produce electric energy.

This would be the best solution to the problem of ash dumps and rehabilitation of degraded areas of land by use of actual and far future of Kosovo lignite. Recommended that the other empty areas of the mines Mirash and Bardh to be used for ash storage from the old existing dumps and fresh ash also. With this project will be achieved the minimization, eliminating the problems collected historically (started a few last decades) and in the same time fade solution of the problem of storage of fresh ash.

References


Group of authors (2005) KEK, Institute "INKOS", Office for Environmental Protection, Environmental Impact Assessment for project folding of fresh ash from TPP "Kosovo B" in empty areas of open pit Mirash, Pristine.


Enterobacteria Carried by *Muska domestica* in the Western Region of Saudi Arabia

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**Abstract:** The incidence of enterobacteria carried by *Muska domestica* (house fly) was investigated. A total of 148 house flies were collected from three cities of the western region (Jeddah, Makkah and Taif), Saudi Arabia. Areas of high and low socio-economic level in addition to a poultry farm in Taif City were included. Twenty-eight bacterial isolates representing different species and strains belonging to the target family *Enterobacteriaceae* were recovered from the flies. The most prevalent isolates encountered were: *Klebsiella pneumoniae* (23.64%), *Proteus mirabilis* (16.1%), *Enterobacter cloacae* (14.8%), *Serratia marcescens* (13.51%). However, *Escherichia coli*, *Esch. vulneris*, *Esch. hermanii*, *Enterobacter agglomerans*, *Providencia spp*, *Klebsiella oxytoca*, *Providencia alcalifaciens*, *Enterobacter cloacae* and *Enterobacter agglomerans* were isolated in different percentages. Antibiotic sensitivity pattern of some isolates were tested and the following species were resistant to Penicillin G: 30 isolates of *Klebsiella pneumoniae*, 11 isolates of *Enterobacter cloacae*, 8 of *Esch. coli*, 7 of *Serratia marcescens*, 7 of *Klebsiella oxytoca* and 4 of *Proteus mirabilis*. The results obtained emphasize the important role of house flies in transmitting pathogens and/or opportunistic pathogens to different environments especially hospitals, restaurants and schools. Control of house flies should therefore be mandatory.

**Keywords**: House fly, Enterobacteria, Incidence, Muska domestica

**Introduction**

Adult house flies (*Musca domestica*) are important agents in the dissemination of numerous infectious diseases. The flies get onto and into almost everything of human's food or drink and visit every conceivable form of excreta and other filth (West, 1951). It has been claimed that although house flies are rarely the dominant transmitting agent in any epidemic disease, they represent a considerable hazard to health wherever they have access to both faeces and human food (Fotedar et al., 1992a). Moreover, hibernating or reared flies from infected larvae, and dead ones may also harbor pathogens (Kluth et al., 2002). Essentially, four different ways in which house flies may transmit pathogenic microorganisms: on the hairs and surface of its body, on the glandular hairs on its feet, by regurgitation of vomits (http://www.articlesbase.com/health-articles). Faecal deposits of the house fly may later transmit a multiplicity of these organisms to the food or man (Adeyemi and Dipeolu, 1984, Umeche and Mandah, 1989, Cohen et al., 1991). Hence, either the fly may function as a temporary mechanical vector, or the pathogen concerned may survive for a longer period within the fly's body, in many instances with no adverse effect upon the carrier host (Graczky et al., 2001). This latter possibility provides an opportunity for multiplication of the pathogen (Nayduch, 2010).

Flies are known to become contaminated with more than 100 species of pathogenic organisms, thereby are able to transmit bacterial diseases such as typhoid fever, shigellosis, salmonellosis, amoebic dysentery, cholera, anthrax, leprosy, tetanus, diphtheria, syphilis, trachoma, and the viruses of poliomyelitis, infectious hepatitis and in addition to conjunctivitis, streptococcal and staphylococcal infections (Harwood & Prelino, 1978, Butler et al., 2010). Interestingly, it is well known that during wars, housefly-associated typhoid fever had killed more soldiers than the enemy bullets (Cirillo, 2006).

The number of organisms associated with house flies are in hundreds (Greenberg 1971; Olsen 1998; Nmoris et al. 2007) and commonly include *Bacillus* spp., *Staphylococcus* spp, *Enterococcus* spp.
spp, *Campylobacter*, *Bacillus anthracis*, *Chlamydia* sp., *Corynebacterium* spp, and other bacteria belonging to family Enterobacteriaceae. The present study was concerned with the incidence and carriage rate of different members of the family Enterobacteriaceae carried by the house fly in the Western Region of Saudi Arabia, especially those incriminated in diseases and nosocomial infections.

**Materials and Methods**

148 adult house flies were collected from three cities of the Western Region of Saudi Arabia, namely Jeddah, Makkah, and Taif. The flies were collected during 12 months; they were randomly selected as follows: 77 flies from Jeddah, 35 from Makkah, and 36 from Taif. In addition, 13 flies were collected from a poultry farm near Taif city. Flies collection was based on several factors including economic level.

According to the previous factor, specimens were collected from the following areas: Low socio-economic areas which was characterized by high population density and poor Sewage disposal (Gholail, Al-Hindaweiah, Al-Gourayat districts; Al-Hindaweiah, Al-Kakeiah districts; Al-Sharquiea district) and high socio-economic areas (Al-Hamra, Al-Jamea'h districts; Al-Awali district; Al-Salama district). Captured flies were around garbage in open spaces and indoors of a hospital, University cafeteria and houses.

**Collection of house flies:**

*Musca domestica* were captured from different areas by fresh shrimp baited flytrap according to Borror *et al.* (1976). The collected flies were transferred to a sterile 250 ml flask and each fly was then transferred to a sterile test tube (15 ml) by placing the open end of the tube against the flask.

**Sampling method**

2 ml of 0.5% Tween 80 pH 7.9 was pipetted into each tube containing a fly. The tubes were mechanically agitated for one minute on a Rotamixer. A known volume representing the sample was then taken from this suspension and streaked evenly all over the surface of each growth suitable media namely; Nutrient agar (N.A), Cystine Lactose Electrolyte Deficient medium (C.L.E.D), and Salmonella Shigella agar (S.S agar).

**Choice of surfactant and inoculum size**

For washing off the bacteria from the house flies, quarter strength Ringer's solution pH 7, Saline (Fluka), and 0.5% Tween 80 pH 7.9 (Fluka) were tested as surfactant. Fifteen flies were studied, five flies for each solution. Each fly was washed separately and serial dilutions were made from the original suspension. One drop of $10^{-2}$ dilution was taken from each different suspension and pipetted on nutrient agar. A Pasteur pipette was used in which each drop equals 0.05 ml. The plates were then incubated aerobically at 37°C for 24 hours and viable counts as CFU/ml were determined for each surfactant (Collee *et al.*, 1989).

To determine the suitable inoculum size, serial dilutions ($10^{-1} - 10^{-6}$) of 5 flies shaken in 0.5% Tween 80 were prepared. Using Pasteur pipette, one drop of each dilution was spread evenly on nutrient agar plates and the plates were incubated aerobically at 37° C for 24 hours.

**Antibiotic susceptibility tests**

Antibiotic susceptibility was carried out as described by Koneman *et al.*, (1983).

**Identification of the isolated Enterobacteriaceae**

Identification was carried out according to Koneman *et al.*, (1983) in which API 20E kits (Analytab product, Planview, NY) were used.

**Statistical analysis**

Data were analyzed to detect the significant differences between the rates of microbial isolation according to socio economic levels by the chi-square test of independence (Snedicor and Cochran, 1967). The analysis was carried out with SPSS/PC+ (Norusis, 1986) and differences were considered significant if the $p <0.05$. 

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Results

Choice of surfactants and inoculum size

Viable counts of members of Enterobacteriaceae that were obtained by washing and suspending flies in 0.5% Tween 80, quarter strength Ringer's solution, and Saline were listed in Table 1. Tween 80 was chosen for subsequent use since it gave higher yield of bacterial isolates (7.5x10^4 CFU) followed by Quarter Strength Ringer's solution (1.4x10^4 CFU) and saline solution (0.9 x10^2 CFU). 16 different species were recovered from five flies when 0.5% Tween 80 was used including Enterobacter cloacae, capsulated and non-lactose fermenter strains of Escherichia coli I (Esch. coli), non-capsulated and lactose fermenter strains of Esch. coli 1, Enterobacter agglomerans, Klebsiella pneumoniae ssp pneumoniae, Kleb. pneumoniae ssp. rhinoscleromatis, Proteus mirabilis, Serratia marcescens, Providencia rettgeri. The species recovered from five flies when quarter strength Ringer's solution was used were Ent. cloacae, Proteus mirabilis, Serratia marcescens, Kleb. Pneumoniae. Whereas, Serratia marcescens, Proteus mirabilis and Kleb. Pneumoniae were isolated when using saline solution.

### Table 1. A comparison of viable counts of enterobacteria obtained by washing and suspending flies in three different solutions

<table>
<thead>
<tr>
<th>House fly Number</th>
<th>0.5 % Tween 80</th>
<th>Quarter Strength Ringer’s Solution</th>
<th>Saline solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly1</td>
<td>1.0 X 10^4</td>
<td>5.0 X 10^4</td>
<td>0.9x10^2</td>
</tr>
<tr>
<td>Fly2</td>
<td>15 X 10^4</td>
<td>1.0 X 10^4</td>
<td>10^3</td>
</tr>
<tr>
<td>Fly3</td>
<td>3.05 X 10^4</td>
<td>0.1 X 10^4</td>
<td>0.7x10^2</td>
</tr>
<tr>
<td>Fly4</td>
<td>2.5 X 10^4</td>
<td>0.02 X 10^4</td>
<td>0.9x10^2</td>
</tr>
<tr>
<td>Fly5</td>
<td>1.6 X 10^4</td>
<td>1.0 X 10^4</td>
<td>10^2</td>
</tr>
<tr>
<td>Mean</td>
<td>7.5X10^4</td>
<td>1.42X10^4</td>
<td>0.9x10^2</td>
</tr>
</tbody>
</table>

In respect to inoculum size results were as follows: 10^-1 dilution gave a confluent bacterial growth which made it difficult to obtain discrete colonies, 10^-2 dilution gave 4x10^5 CFU /ml, 10^-3 gave 3x10^4 CFU /ml whereas, 10^-4 gave 1x10^3 CFU /ml. On the other hand, no growth was obtained from 10^-5 and 10^-6 dilutions. Thus, 10^-2 dilution was used, streaked on different suitable media and incubated aerobically at 37°C for 24-48 hours.

The Incidence of different bacteria belonging to the family Enterobacteriaceae isolated from 148 house flies collected from low and high socio-economic areas from the Western Region (Saudi Arabia) was shown in Table 2. Klebsiella pneumoniae ssp pneumoniae showed an incidence of 23.6%, whereas Enterobacter cloacae, and Serratia marcescens showed an incidence of 14.8% and 13.51% respectively. Providencia rettgeri showed an incidence of 8.78%, whereas the percentage of Klebsiella oxytoca was 6.75%. However, the carriage rates of different isolates of Esch. coli was 20.2%. The following organisms Klebsiella oxytoca, was in a small percentages 3.37% whereas capsulated and lactose fermenter strains of Escherichia coli 1 (Esch. coli), Enterobacter agglomerans 4, Serratia liquefaciens, Providencia alcalifaciens, Providencia stuartii, were found in a smaller and almost similar percentages (2.70%) as shown in Table 2. Capsulated and non-lactose fermenter strains of Esch. coli 1, Klebsiella pneumoniae ssp rhinoscleromatis, Serratia rubidaea were found at the same percentage 2.02. In contrast the isolation rate of non-capsulated and non-lactose fermenter strains of Esch. coli 1, Enterobacter agglomerans 1, Enterobacter agglomerans 2, capsulated and lactose fermenter strain of Esch. hermanii, non-caopsulated strain of Morganella morganii, Klyuvera sp., Cedecea spp. were in small percentages of 1.35%.

Effect of socio-economic level on the incidence of enterobacteria isolated from 135 house flies collected from the Western Region

The percentages of different enterobacteria isolated from 135 house flies collected from high and low socio-economic areas in Western Region were presented in Table 2. Significant difference was noted among the following bacteria: Klebsiella pneumoniae ssp pneumoniae, Klebsiella oxytoca 1, Proteus mirabilis, Providencia rettgeri, and Esch. vulneris. On the other hand, 11 different species were isolated at a lower percentages 0.67-4.8 % from high socio-economic area and were not
recovered from low socio-economic areas. Furthermore, a number of species were not recovered from the high socio-economic area but were isolated from the low socio-economic area such as, non-capsulated and non-lactose fermenting isolates of *Esch. coli*, *Enterobacter agglomerans*, *Klebsiella oxytoca*, *Cedecea* spp. which were found at a lower percentages 1.9-9.6%. *Serratia marcescens* was found to be higher among flies captured from high socio-economic area with incidence rate of 18.3% while *Klebsiella pneumoniae* ssp pneumoniae was a common isolate in both high and low socio-economic area with incidence rate of 16.9% and 40% respectively. On the other hand, the most common isolates in low socio-economic area were *Klebsiella pneumoniae* ssp pneumoniae, *Enterobacter cloacae*, *Proteus mirabilis* and *Esch. coli*

Table 2. Incidence of different enterobacteria isolated from 148 houseflies collected from the Western Region (S.A.)

<table>
<thead>
<tr>
<th>Microorganisms isolated</th>
<th>Incidence of isolation (148 flies)</th>
<th>Incidence of isolation from different habitats</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No.</td>
<td>%</td>
</tr>
<tr>
<td><em>Cedecea</em> spp.</td>
<td>1</td>
<td>0.67</td>
</tr>
<tr>
<td>Enterobacter aerogenes</td>
<td>2</td>
<td>1.35</td>
</tr>
<tr>
<td>Enterobacter agglomerans 1</td>
<td>1</td>
<td>0.67</td>
</tr>
<tr>
<td>Enterobacter agglomerans 2</td>
<td>1</td>
<td>0.67</td>
</tr>
<tr>
<td>Enterobacter agglomerans 4</td>
<td>4</td>
<td>2.7</td>
</tr>
<tr>
<td>Total Enterobacter agglomerans</td>
<td>6</td>
<td>4.05</td>
</tr>
<tr>
<td><em>Enterobacter cloacae</em></td>
<td>21</td>
<td>14.8</td>
</tr>
<tr>
<td><em>Esch. coli</em> (cap.&amp; N.L.F)</td>
<td>3</td>
<td>2.02</td>
</tr>
<tr>
<td><em>Esch. coli</em> (cap.&amp; L.F.)</td>
<td>4</td>
<td>2.7</td>
</tr>
<tr>
<td><em>Esch. coli</em> 1(non-cap.&amp; N.L.F)</td>
<td>1</td>
<td>0.675</td>
</tr>
<tr>
<td><em>Esch. coli</em> 1(non-cap &amp; L.F)</td>
<td>6</td>
<td>4.05</td>
</tr>
<tr>
<td><em>Esch. coli</em> 1(cap &amp; L.F)</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td><em>Esch. coli</em> 2(cap.&amp;L.F)</td>
<td>4</td>
<td>2.7</td>
</tr>
<tr>
<td>Total <em>Esch. coli</em></td>
<td>30</td>
<td>20.2</td>
</tr>
<tr>
<td><em>Klebsiella oxytoca</em> ssp. pneumoniae</td>
<td>5</td>
<td>3.3</td>
</tr>
<tr>
<td><em>Klebsiella oxytoca</em> 11</td>
<td>10</td>
<td>6.7</td>
</tr>
<tr>
<td><em>Klebsiella pneumonia</em> ssp rhinoscleromatis</td>
<td>35</td>
<td>23.64</td>
</tr>
<tr>
<td><em>Kluyvera</em> sp.</td>
<td>1</td>
<td>0.675</td>
</tr>
<tr>
<td><em>Morganella morgani</em> (cap)</td>
<td>2</td>
<td>1.35</td>
</tr>
<tr>
<td><em>Morganella morgani</em> (non cap)</td>
<td>1</td>
<td>0.675</td>
</tr>
<tr>
<td><em>Proteus mirabilis</em> 11</td>
<td>24</td>
<td>16.1</td>
</tr>
<tr>
<td><em>Proteus vulgaris</em></td>
<td>2</td>
<td>1.35</td>
</tr>
<tr>
<td><em>Providencia alcalifiaciens</em></td>
<td>4</td>
<td>2.7</td>
</tr>
<tr>
<td><em>Providencia retgeri</em> 11</td>
<td>13</td>
<td>8.7</td>
</tr>
<tr>
<td><em>Providencia stuartii</em></td>
<td>4</td>
<td>2.7</td>
</tr>
<tr>
<td><em>Serratia liquefaciens</em></td>
<td>4</td>
<td>2.7</td>
</tr>
<tr>
<td><em>Serratia marcescens</em></td>
<td>20</td>
<td>13.51</td>
</tr>
<tr>
<td><em>Serratia rubidae</em></td>
<td>3</td>
<td>2.02</td>
</tr>
</tbody>
</table>

Incidence of enterobacteria isolated from 13 house flies collected from a poultry farm

In the case of poultry farm, *Klebsiella oxytoca* 11 was the main common isolate (38%), followed by *Providencia alcalifiaciens* (15.5%), *Enterobacter cloacae* and *Enterobacter agglomerans* 4, with the same percentages (7.7%) as shown in Table 2. The antibiotic sensitivity pattern of members of the isolated enterobacteria were shown in Table 3. Most of the members were sensitive to amikacin, tobramycin, gentamicin, nalidixic acid, tetracycline and trimethoprim sulphamethoxide. Whereas, 30 isolates of *Klebsiella pneumoniae*, 11 isolates of *Enterobacter cloacae*, 8 of *Esch. coli*, 7 of *Serratia marcescens*, 7 of *Klebsiella oxytoca* and 4 of *Proteus mirabilis* were resistant to Penicillin G.
Table 3. Number of resistant isolates of some members belonging to family Enterobacteriaceae to different antibiotics

<table>
<thead>
<tr>
<th>Antibiotic used</th>
<th>E. cloacae</th>
<th>E. coli2</th>
<th>E. coli1</th>
<th>K. oxytoca</th>
<th>K. pneumoniae</th>
<th>Klyvera sp</th>
<th>Alchifaciens</th>
<th>Pr. mirabilis</th>
<th>P. liquifaciens</th>
<th>S. marcescens</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG10</td>
<td>11</td>
<td>4</td>
<td>8</td>
<td>7</td>
<td>30</td>
<td>0.0</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>AMP10</td>
<td>0.0</td>
<td>0.0</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td>0.0</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CAR100</td>
<td>11</td>
<td>3</td>
<td>10</td>
<td>5</td>
<td>13</td>
<td>0.0</td>
<td>1</td>
<td>11</td>
<td>1</td>
<td>8.0</td>
</tr>
<tr>
<td>OB5</td>
<td>11</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CTX30</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>AK30</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>TOB30</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>GN10</td>
<td>0.0</td>
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Discussion

Houseflies are much more than a nuisance since they pose serious health risks as vectors for disease transmission, and obviously, fly control is still an important public health measure in the 21st century (Cirillo, 2006).

At the present study, different members of the family Enterobacteriaceae were isolated and identified from 148 houseflies collected from the Western region of Saudi Arabia. The method developed in this study for enumerating the enterobacteria carried by the house fly was found to be reproducible and gave relatively representative high yield of bacteria compared to the results obtained by other authors using different methods (Merdan et al., 1982; Fotedar, 2001). For the collection of houseflies, the fresh shrimp baited trap method (Peefly & Labrecque, 1956) was used since it attracted more numbers of flies in a shorter time. Agitation of the specimens was employed for dispersing the majority of microorganisms carried on the body surface of the fly that enabled the recovery of different bacterial isolates. This is in agreement with Milyani and Selwyn (1976) who mentioned that agitation had led to the breakdown of bacterial aggregates resulting in high quantitative numbers of bacteria.

Choice of surfactant is another factor that allowed a higher yield in this study. Among three different solutions tested for washing house flies, tween 80 allowed the recovery of sixteen different bacterial species on contrast to the two other solutions which allowed lower numbers of isolates. Similarly, Neelgound et al. (1982) obtained only seven species out of 100 flies when using peptone broth for washing. Graham et. al. (2009) suggested that an external wash of the flies must be carried out by using 0.1% Tween 80. Moreover, Tween 80 was also used in studying the human skin flora, and proved to be effective and non-toxic (Milyani, 2001; Jayakumar et al., 2011). In addition to the previous factors, the variety of media used in this study allowed the isolation of varies species.

The habitual movement of house fly from filthy substrata such as human faeces, animal excreta, carcasses, garbage, etc. makes them ideal candidates for disease transmission when settling on food. Therefore, the present study investigated the incidence of different enterobacteria carried on the body surface of houseflies from various locations. The most prevalent isolate was klebsiella pneumoniae ssp pneumonia (23.6%) which is known to cause serious nosocomial infections in addition to pneumonia in elderly and compromised patients (Lee et al., 2008; McCabe et al., 2010). Other members of the Enterobacteriaceae such as Proteus mirabilis, Serratia marcescens, Enterobacter cloacae, Esch. coli, were of high incidence rate >10%, whereas, Klebsiella oxytoca and Providencia rettgeri were of moderate incidence rate <10%. These species are usually incriminated in nosocomial
infections such as urinary; lower respiratory, biliary tracts and surgical wounds especially in compromised patients. Moreover, some of the previous isolates were found to be the cause of skin ulcers and necrotizing fasciitis in intravenous drug abusers. (Mandell et al., 2005). The isolates of Esch. coli namely capsulated and non lactose fermenting at the present study, share some characters of the Enterohaemorrhagic and enteroinvasive Esch. coli which were also isolated by others (Levine & Edelman, 1984; Greenwood et al., 1992) and are considered as emerging infectious agents. Furthermore, Kobayashi et al. (1999) and Ahmad et al. (2007) confirmed the role of houseflies as transmitters of enterohemorrhagic Esch. coli 0157:H7. Unfortunately, immunological and molecular studies could not be done at the present study for further identification of the isolated strains of Esch. coli, but indeed it would be ideal for future work.

On the other hand, low incidence rate <5% were recorded for Klebsiella pneumoniae ssp rhinoscleromatis, Klebsiella oxytoca ssp pneumoniae Enterobacter agglomerans Enterobacter aerogenes, Cedecea spp, Serratia rubidae, Serratia liquefaciens, Providencia stuartii, Providencia alcalfaciens, Proteus vulgaris, Morganella morganii, Kluvyera sp, Klebsiella pneumonia ssp rhinoscleromatis. All the previous isolates have been recognized as increasingly important pathogens in recent years due to their innate resistant to older antimicrobial agents and have the ability to rapidly develop resistance to newer agents (Sanders & Sanders, 1997). Surprisingly, Salmonella sp. and Shigella sp. were conspicuously absent from all the isolates of different areas. In contrast, Salmonella spp., Yersinia enterocolitica and Edwardsiella tarda were isolated from flies collected from the streets and in the abattoir by Rahuma et al. (2005). Furthermore, Grubel et al. (1997) and Kamal (1974) reported that house fly played a role in Helicobacter pylori and V. cholerae transmission, respectively.

In Misurata city of Libyan, Rahuma et al., (2005) isolated bacteria that are potentially pathogenic to humans from 150 fly at higher incidence rate and found that 32-42% of the flies were positive for Escherichia coli, 50-70% % for Klebsiella spp., 2-20% for Aeromonas spp.

This work showed that members of the Enterobacteriaceae such as Klebsiella pneumoniae ssp pneumoniae (40%), Enterobacter cloacae (34.6%) and Proteus mirabilis (32.7) prevailed in the flies collected from low socio-economic areas. These findings could be attributed to the poor environmental conditions, including over-crowding, substandard housing, poor sanitation and low educational level of people who do not practice hygienic measures (Evans, 1990). During summer Nazni et al. (2005), managed to isolate from faeces, vomitus, external surfaces and internal organs of house flies Enterobacter sp., Proteus sp., Escherichia sp., and Klebsiella sp. Moreover, Fotedar (2001) found that V. cholerae El Tor was acquired by house flies from garbage and human excreta lying exposed in the outbreak area since they have easy access to such area which provided an opportunity for the flies to pick up the pathogen. Transmission of pathogens from house flies to humans during an outbreak, suggests that houseflies may also function as additional epidemiological link between human beings and human excreta particularly in tropical and third world countries (Chavasse et al., 1999). Rahnella aquatilis which has been isolated at the present work, known to inhabit fresh water and is rarely isolated from clinical specimens, was reported to cause urinary tract infection in a renal transplant patient (Alballaa et al., 1992) and in a patient with relapsed acute lymphoblastic leukemia (Carinder et al., 2001).

The result of Fotedar (2001) revealed that M. domestica was the predominant fly species collected from different areas with outbreak of infections, and it is the commonest fly species reported from residential areas, hospitals and market places in India and other countries (Echeverria et al., 1983; Fotedar et al., 1992a; Fotedar et al., 1992b). The house fly carriage rate of Salmonella spp, Klebsiella pneumoniae and V. cholerae is also known to increase significantly during summer season and in low socioeconomic level habitats (Greenberg, 1973). At the present study house flies captured from the poultry farm, yeilded Klebsiella oxytoca 1 which was the main common isolate, followed by Providencia alcalfaciens, Enterobacter cloacae and Enterobacter agglomerans 4. However, the absence of both Salmonella and Shigella spp. was really surprising but might indicate the proper hygiene taken at that particular farm. In contrast, Dogra and Aggarwal (2010) reported that all the conditions on the poultry farm were in favor of housefly breeding where eggs of the houseflies continue to thrive in the manure as it is ideal environment for housefly breeding. They also isolated Enterobacter cloacae, Providencia alcalfaciens , Klebsiella oxytoca, Enterobacter agglomerans and
Acinetobacter baumannii from flies collected from poultry farms. They reported that poultry farm and the environment of the farm could be the source of these organisms.

Amazingly, 30 isolates of Klebsiella pneumoniae, 11 isolates of Enterobacter cloacae, 8 of Esch. coli, 7 of Serratia marcesence, 7 of K. oxyioca and 4 of Proteus mirabilis were resistant to Penicillin G, while most of the other isolates were sensitive to amikacin, tobramycin, gentamicin, nalidixic acid, tetracycline and trimethoprim sulphamethoxide. As an exception, capsulated and lactose fermenter isolates of Esch. coli 2 were resistant to tetracycline and Enterobacter cloacae was resistant to trimethoprim sulphamethoxide. The sensitivity of the tested isolates to different antibiotics were recorded by Lambert and O’Grady (1992) but resistance of Esch. coli to tetracycline was similar to the finding of Pratt and Fekety (1986). However, resistance to trimethoprim sulphaemethoxide among the enteric bacteria is common (Pratt and Fakery, 1986). Furthermore, the antibiotic susceptibilities of the bacterial isolates from house flies collected from hospitals, were found to be significantly resistant to many of the commonly used antibiotics than the enterobacteria isolated from the flies caught in the streets or abattoir Rahuma et al. (2005). They also support the belief that the housefly is a potential vector of multiple-antibiotic-resistant in the hospital environment and carry the resistant pathogens from hospitals to surrounding communities, and vice versa.

This study indicates that houseflies might play an important role in disseminating pathogenic bacteria to the surrounding environment in both low and high socio-economic areas, thus well designed measures for controlling the spread of house flies are needed. The implementation of appropriate control to decrease the fly population would be certainly an ideal approach to minimize the incidence of different diseases.

References


Electrokinetic Remediation of Petroleum Hydrocarbons Spiked Soils

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Abstract: In the presented study, remediation studies were conducted to determine the effectiveness of electrokinetic method on the treatment of natural soil contaminated with petroleum hydrocarbons, in laboratory scale reactors. Electokinetic remediation of agricultural soil with an initial TPHs (Total Petroleum Hydrocarbons) concentration of 10000 ppm was investigated under 20 V or 40 V direct current by using NaOH and acetic acid as electrolyte solution, treatment efficiencies were observed according to the distance from the anode chamber and the applied electrical potential. The effect level of electrokinetic remediation on PAHs (Polycyclic Aromatic Hydrocarbons), which were announced by Environmental Protection Agency (EPA) as in high toxicity group and present in engine oil that was used as contaminant, was also included in the framework of the study. It was observed that high treatment efficiencies for PAHs and TPHs were achieved according to the distance from the anode and the electrical potential applied to the system. The achievement of the electrolytic solution on the treatment TPHs can be given as decreasing order as follows according to the average data of the sets studied: Acetic acid > NaOH. The highest PAH treatment efficiency was detected in set operated under 40 V of DC with 0.5 M of NaOH as high as 94.46%.

Keywords: Electrokinetic remediation; Soil; Total Petroleum Hydrocarbons; Polycyclic Aromatic Hydrocarbons

Introduction

Soil pollution has become more and more serious in recent years all over the world. Many organic or inorganic contaminants can be found in contaminated soil. This commonly encountered contaminants heavy metals (Kim et al., 2009), chlorinated organic compounds (Zoeteman et al., 1985, Palm et al., 1988, Sirin, 1998), total petroleum hydrocarbons (TPH) (KHuang et al., 2005) and polycyclic aromatic hydrocarbons (PAH). (Alcantara et al., 2008, Alcantara et al., 2009). PAHs are common distributed in the environment (Alcantara et al., 2009). They are chemical compounds having two or more benzene rings produced by incomplete combustion of organic material (Alcantara et al., 2009, Pathak et al., 2009). PAHs sources may be both natural and anthropogenic. Emissions from anthropogenic activities predominate, but some PAHs in the environment are originated from natural sources. Anthropogenic ones are oil spills, urban runoff, domestic and industrial wastewater discharges and vehicle exhaust (Doong & Lin, 2004). PAHs are toxic, mutagenic and carcinogenic properties due to their serious environmental problems constitute (Alcantara et al., 2008, Alcantara et al., 2009, Pathak et al., 2009). They are hydrophobic compounds and their persistence in the environment is mainly due to their low water solubility (Alcantara et al., 2008). Petroleum hydrocarbons pollution is a tough environmental problem, not only by the quantities released but also because of their toxicity. As pure chemicals, PAHs are usually colorless, white or pale yellow-green solids. There are more than 100 PAH in the environment, but only 16 of them are included in the priority pollutants list of U.S. EPA based on a number of factors including toxicity, extent of information available, source specificity, frequency of occurrence at hazardous waste sites, and potential for human exposure (ATSDR, 1995). Electrokinetic technology, a direct current (DC) is passed through the contaminated soil, causing contaminating species to be transported towards the electrodes and then removed from the soil. Three principal mechanisms of contaminant movement in electrical field are involved in this technology: electromigration, electroosmosis, and electrophoresis (Li et al., 1997). During the Electrokinetic (EK) processing, the applied current leads to water electrolysis at both anode and cathode, and the equations are as follows (Li et al., 1997, Chang & Liao , 2006, Shen et al., 2007):

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At the Anode: $2\text{H}_2\text{O} - 4\text{e}^- = 4\text{H}^+ + \text{O}_2(\text{g})$  \hspace{1cm} (Eq. 1)
At the Cathode: $4\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^- + 2\text{H}_2(\text{g})$  \hspace{1cm} (Eq. 2)

As seen from these equations, the electrolysis reactions cause an acidic solution to be generated at the anode and an alkaline solution to be generated at the cathode. Acar & Alshawabkeh firstly introduced the electrokinetic treatment of metal contaminated soils in their article published in 1993, which explains the transfer of the process fluid and ionic species under an electric field (Acar & Alshawabkeh, 1993). Yuan & Weng (2004) investigated the remediation efficiency and electrokinetic behavior of ethylbenzene contaminated clay by a surfactant-aided electrokinetic (SAEK) process under a potential gradient of 2 V cm$^{-1}$. The removal efficiency of ethylbenzene was determined to be 63–98% in SAEK system while only 40% was achieved in an electrokinetic system with tap water as processing fluid (Yuan & Weng, 2004). Nam et. al. (2008) determined the levels and distribution of PAHs in soil samples from background locations in the UK and Norway, to investigate their spatial distribution and the controlling environmental factors (Nam et. al., 2008). Oonnittan et. al. (2009) investigated the feasibility of enhanced electrokinetic Fenton process for the remediation of hexachlorobenzene (HCB) in low permeable soil. Results show that the position of electrodes in the system and the way in which Fenton's reagent was added to the system has a significant influence on the treatment efficiency (Oonnittan et. al., 2009). Alcantara et. al. (2010) proposed electroremediation for cleaning soil contaminated by organic compounds. Model samples of kaolin clay polluted with a mixture of PAHs (fluoranthene, pyrene, and benzanthracene) were treated (Alcantara et. al., 2010).

The general objective of this study is to experimentally investigate the effectiveness and feasibility of using electrokinetic extraction technique to mobilize and/or remove organic contaminants detected frequently in polluted sites.

**Material and Methods**

**Soil sampling**

Agricultural soil used for the study was obtained from the Menemen Research Centre of Turkish Ministry of Agriculture from the sampling depth of 10 cm. The samples are stored in zip-lock plastic bags at 5°C until the experiments. The properties of soil sample are illustrated in Table 1.

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<td>Organic Matter Content ,% (dry soil )</td>
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<tr>
<td>TN dissoluble ,ppm (dry soil )</td>
<td>136</td>
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<tr>
<td>TPH ,ppm (dry soil )</td>
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**Materials used**

Engine oil was used to spike the soil samples in this study. The oil is the product of PETROFER Industrial Oils and Chemicals Company which is located in Çiğli, Izmir. The type of the oil is PETROFER Petrolube Lubrimax 20W/50 Four Seasons Engine Oil, API:

**Experimental setup**

As can be seen in Figure 1; the experimental setup used for electrokinetic remediation of engine oil contaminated soil mainly consists of; soil bed, electrolyte solution chambers, gas measurement systems attached to the electrolyte solution chambers, and power supply unit. A 24 cm long Plexiglas cylinder with 75 mm internal diameter was used to obtain fixed soil bed for the experiment. The soil
bed, which contaminated soil was placed into, has two graphite electrodes with 75 mm diameters and 3 mm thickness at the both ends connected to the electrolyte chambers. The chambers were made of industrial Teflon and each of has 66 ml of liquid volume. Gas which consisted in electrolyte solution measurement systems attached to the electrolyte chambers were made of two glass cylinders equipped with valves to control air and liquid entrance and exit. Prior to the experiments, Menemen Soil is dried and sieved under 2 mm to remove larger particles and then autoclaved to stop microbial activity. The required amount of engine oil is dissolved in Petroleum Ether (PE) and added to 1.25 kg of Menemen Soil to obtain 10000 ppm dw of TPHs in the soil. After PE is evaporated under the fume hood, the electrolytic solution used in the electrolytes is applied to the soil sample to obtain humidity that equals to the soil field capacity (31%). Then, the soil electrolyte solution mixture is placed into the soil bed and compressed by using shaking table to avoid empty spaces in the samples that may inhibit the electrical conductivity along the sample. The systems are operated constantly for 192 hours under 20 V or 40 V DC electrical potentials. The electrical intensity during the experiments are arranged to 0.01 A and remained constant.

**Figure 1.** Major parts of the designed reactors

**PAH’s Analysis**

For GC-MS analysis of PAHs, soil extractions are completed according to the EPA Method 3550B- Ultrasonic Extraction (USEPA, 1996). 1 g of soil is placed into a 40 mL vial and 25 mL 1:1 acetone:hexane mixture was added. Prior to extraction, all samples were spiked with PAH internal surrogate standards to monitor analytical recovery efficiencies. 0.5 mL PAH internal standard (Accustandard- 8000 mg/L each: Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12) was added into the vial and retained overnight. The vial, then, has extracted in ultrasonic extractor for 30 min with 380 Watt, filtered from glass wool and transferred to another vial. The samples were cleaned up on an alumina-silicic acid column containing 3 g of silicic acid (3% water) and 2 g of alumina (6% water) (USEPA, 1996). The column was pre-washed with 20 mL of DCM followed by 20 mL of petroleum ether. Then, 20 mL DCM is added to the column and the strain containing PAHs is collected in another 40 mL vial. This strain is transferred into the Kuderna-Danish Apparatus (water temperature 65°C, DCM boiling point: 40°C) and the volume of the extract reduced to 10 mL. 10 mL hexane was added to the system once more and the volume is reduced to 5 mL final volume by arranging the water bath to 65°C until the first 10 mL collected (for DCM collection) and then by arranging it to 95°C (Hexane boiling point: 69°C) for hexane collection. 1 mL of final volume is placed in a 1.5 mL glass vial and used for GC-MS analysis. All extracts were analyzed for 15 PAHs including acenaphthene, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, benz[a]anthracene, chrysene, benz[b]fluoranthene, benz[k]fluoranthene, benz[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[g,h,i]perylene with a gas chromatograph (GC) (Agilent 6890N) equipped with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP5ms, 30 m, 0.25 mm, 0.25 µm) was used. The initial oven temperature was held at 50°C for 1 min, was
raised to 200°C at 25°C min⁻¹ and from 200 to 300°C at 8°C min⁻¹, and was held for 5.5 min. The injector, ion source, and quadrupole temperatures were 295, 300, and 180°C, respectively. High purity helium was used as the carrier gas at constant flow mode (1.5 mL min⁻¹, 45 cm s⁻¹ linear velocity).

Results and Discussion

**pH changes in electrolytic chambers**

The pH values of electrolytic solutions were started to be measured in every 24 hours after the operation starts until the treatment period (192 h) was over. In Figure 2, the pH changes in the anode chambers are given for the DC applied and the NaOH concentration used in the systems. Changes in pH level in the cathode chambers are presented in Figure 3 for the tests conducted with NaOH solutions. In all of the three experiments conducted with NaOH, the pH in anode chambers were in alkaline levels when the systems were initiated. The pH levels were steady and around 13 in the cases with 0.5 M NaOH concentration, while it started to drop down after the first 72 hours and reached to the level of 8.4 at the end of the treatment period with 1 M of NaOH. As can be seen from the Figure 3, the initial pH levels in the cathode chambers were strongly alkaline (>10) at the beginning of the experiments and they were aligned at 13.3 in first 24 hours and remained at this level until the end of the experiments in all of the cases. The initial pH level in the anode chamber solutions were below 3.0 and the pH levels fluctuates between 2.3 and 3.8 during the test period after a slight increase in the first 24 hours, except the experiment conducted with 0.5 M acetic acid under 20 V DC which displayed a steady decrease after the 24th hour to reach a pH level of 1.67 in anode chamber (Figure 4).

As can be seen from the Figure 5, the initial pH values in the chambers were between 2.4 and 2.9. In the tests conducted under 40 V DC (0.5 M AA and 1 M AA) and in the test conducted with 1 M AA under 20 V DC, pH levels slightly increased during the tests and reached to a range between 4.4 and 5.2 at the end. In the test conducted with 20 V DC with 0.5 M AA, pH level in cathode chamber showed a sharp increase up to 11.0 in first 96 hours and then reached to 11.4 with a slight raise.

**Figure 2.** pH changes in anode chamber when NaOH used as electrolytic solution

**Figure 3.** pH changes in cathode chamber when NaOH used as electrolytic solution
Electroosmotic flow

Electroosmotic flow was varying with the type and concentration of the electrolyte solution, as well as the applied electrical potential on to the soil. In the experiments with NaOH solutions, lower concentrations performed positive electroosmotic flows; 152 cm$^3$ and 77 cm$^3$ for 20 V and 40 V DC with 0.5 M NaOH, where negative values were measured during the experimental period in the experiment under 20 V DC with 1 M NaOH (-119 cm$^3$) (Figure 6). In the first 24 hours, the direction of electroosmotic flow was negative in the experiment with 0.5 M acetic acid under 20 V DC, it reversed to positive in the 48th hour, and then again backward for the next 72 hours, and finally again moved backwards until the end of the experiment by obtaining -36.4 cm$^3$ of cumulative electroosmotic flow. The movements of electroosmotic flow in the experiments under 20 V (1 M acetic acid) and 40 V (0.5 M acetic acid) showed similar trends; moved forward in the first 96 hours and then moved backward and forward until the end of the experimental period by obtaining 82 cm$^3$ and 14 cm$^3$ cumulative scores. In the experiment with 1 M acetic acid under 40 V DC, any distinct movement of electroosmotic flow could not be observed during the experimental period (Figure 7).

Soil pH

The soil in the reactor column was removed and pH values were detected in equivalent soil slices with the width of 4 cm at the end of each experiment. After the experiments conducted with NaOH as electrolyte solution, the soil pH values were alkaline through the column and between 10.1 and 11.2 (Figure 8). When Acetic acid was used as electrolyte solution, pH of the soil column slightly raises from anode to cathode, (Figure 9) except the experiment conducted with 1 M acetic acid under 40 V DC, that the soil shows neutral levels through the reactor column.
TPHs

TPHs concentrations in the soil column were detected after the treatment period and the treatment efficiencies were determined according to the initial concentration. Figures 10, 11, and 12 present the final TPHs concentrations in the soil sections and treatment efficiencies in the case of NaOH use as electrolyte solution. In the experiment with 0.5 M NaOH and 20 V DC application, TPHs treatment efficiencies are lower (76-78 %) in the soil sections close to anode than the efficiencies obtained in the soil sections in front of the cathode (91-98%).

Figure 6. Cumulative electroosmotic flow in the experiment which NaOH was used as electrolytic solution

Figure 7. Cumulative electroosmotic flow in the experiment which Acetic acid (AA) was used as electrolytic solution

Figure 8. Soil pH levels after the experiments with NaOH solutions
Figure 9. Soil pH levels after the experiments with Acetic acid solutions

Figure 10. The TPHs concentrations and Treatment Efficiencies in Soil Sections after the Electrokinetic Remediation According to the Distance from the Anode (20 V 0.5 M NaOH)

Figure 11. The TPHs concentrations and Treatment Efficiencies in Soil Sections after the Electrokinetic Remediation According to the Distance from the Anode (20 V 1 M NaOH)

The average TPHs treatment efficiency is 85% in this experiment. In the experiment with 1 M NaOH, 20 V DC electrical potential resulted with lower treatment efficiencies than the 0.5 M NaOH concentrations under the same DC (average treatment efficiency: 72.6%). With 0.5 M NaOH and 40 V DC electrical potential the TPHs removal through the soil column has decreased and the average treatment efficiency was determined as 64.6%. The treatment efficiencies with acetic acid solutions are presented in Figures 13, 14, 15, and 16. With the 0.5 M of acetic acid, the final TPHs treatment efficiencies in anode half (78.4-97.8%) is relatively higher than the efficiencies obtained in the cathode half (70-78.5%) of the reactor. The overall treatment efficiency for TPHs was 82.7%. By increasing the acetic acid concentration under 20 V DC, treatment efficiency increased (91.4%) and the deviations between the concentrations observed in anode (90.5-93.7) and cathode (87.7-93.3) halves.
became insignificant. Increasing voltage from 20 V to 40 V in the case of 0.5 M acetic acid application also increased the overall treatment efficiencies, which were found as 82.7% for 20 V and 89.99% for 40 V. But, the TPHs treatment efficiencies just in front of the anode and cathode reservoirs (70% and 81.2% respectively) were significantly lower than the other sections of the soil column. As 1 M acetic acid was used as electrolyte solution under 40 V DC electric potential, both the overall treatment efficiency (44.5%) and the treatments in soil sections (17.9-71.2%) decreased. Furthermore, distinctive treatment efficiencies have seen in sequential soil sections of the column.

Figure 12. The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (40 V 0.5 M NaOH)

Figure 13. The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (20 V 0.5 M Acetic Acid)

Figure 14. The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (20 V 1 M Acetic Acid)
Figure 15. The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (40 V 0.5 M Acetic Acid)

Figure 16. The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (40 V 1 M Acetic Acid)

**Total PAHs**

The PAHs are also detected at the end of the electrokinetic remediation period in soil sections and the results are presented in this part of the thesis according to the electrolytic solution used. In Figure 17, the PAHs average treatment efficiencies in soil sections by using NaOH solution are illustrated according to the distance from the anode. It was seen that in the experiments conducted with 0.5 M NaOH resulted with higher PAHs treatment efficiencies. In the experiments conducted with acetic acid, the PAHs average treatment efficiency was low in all soil section when 20 V DC applied for the acetic acid solution of 0.5 M. But, the same acetic acid concentration gave the highest treatment efficiency when 40 V DC application is considered (Figure 18).

Figure 17. Average PAH treatment efficiency in soil sections by using NaOH as electrolyte solution
Figure 18. Average PAH treatment efficiency in soil sections by using Acetic acid (AA) as electrolyte solution

Conclusion

• The achievement of the electrolytic solution on the treatment TPHs can be given as decreasing order as follows according to the average data of the sets studied: Acetic acid > NaOH.
• It was observed that the treatment efficiency increases as the electroosmotic flow (EOF) increases in the sets operated with NaOH and acetic acid.
• It was also recognized that, continuous changes in the direction of EOF adversely effects the treatment of the contaminants, since they move between anode and cathode and could not be removed.
• It was detected that the direction of EOF is less important than its stability in one direction (towards anode or cathode), because in the cases with dominant reverse EOFs treatment of TPHs could be achieved.
• Electrolysis (electromigration) and electroosmosis are the major phenomenon affecting the treatment efficiency, which are controlling each other. In the systems operated, any evidence on the effects of electrophoresis could not be detected.
• PAHs are the compounds which have low solubility, and their response to applied treatment conditions is partially different from TPHs.
• The highest PAH treatment efficiency was detected in set operated under 40 V of DC with 0.5 M of NaOH as high as 94.46%.
• 0.5 M of NaOH and acetic acid obtained high PAHs removal under 40 V DC. The achievement of the electrolytic solution on the treatment PAHs can be given as decreasing order as follows according to the average data of the sets studied: NaOH > acetic acid.

References


Impact of Global Warming on Flora and Fauna

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Abstract: The paper, illustrated with graphs, discusses the impact of global warming on flora & fauna, its underlying causes, and attempts to trim down it with the collaboration of all individuals. The paper relates that, as an outcome of global warming, climate changes have reached anomalous levels with rainfall and hurricanes of unusual intensity. Everyday gases such as carbon dioxide are released to warm the earth, allowing it to be a place that can be inhabited by flora & fauna. However once the fauna became higher in population, the warming of the earth was easier to identify. The paper also warns of what will happen if action is not taken in time and discusses positive and negative economic probabilities on flora & fauna. The paper concludes that it takes time for people to change their attitudes but in changing, the end result will be worth it.

Key words: Global warming, Greenhouse effect, Flora & Fauna, Causes, Ecosystem, Conservation

Introduction

Global warming is a term used to describe the trend of increases in the average temperature of the earth’s atmosphere and oceans that has been observed in the recent decades. Global warming and climate change has become a global issues and concern within the regional and international levels. In the context of national scope, these issues had grown stronger after Indonesia had been selected to become host of the 13th Conference of the Party to the United Nation Framework Convention on Climate Change (UNFCCC COP 13). The venue took place in Denpasar, Bali. Our earth has already experienced the phenomena of global warming and climate change which leads to hazardous climate events. The Intergovernmental Panel on Climate Change (IPCC) has released numbers of research which has proved that the earth is warming and climate is changing. The IPCC is an independent scientific body under the UNFCCC. The phenomena of hazardous climate events have an enormous impact to the environment and human livelihood. Global warming and pattern climate changes threatened farming for food security, clean water availability, human and ecosystem health. Global warming also threatened the existence of small island nations because of the rising of sea level.

Causes of Global Warming

As said, the major cause of global warming is the emission of green house gases like carbon dioxide, methane, nitrous oxide etc. into the atmosphere. The major source of carbon dioxide is the power plants. These power plants emit large amounts of carbon dioxide produced from burning of fossil fuels for the purpose of electricity generation. About twenty percent of carbon dioxide emitted in the atmosphere comes from burning of gasoline in the engines of the vehicles. This is true for most of the developed countries. Buildings, both commercial and residential represent a larger source of global warming pollution than cars and trucks. Building of these structures requires a lot of fuel to be burnt which emits a large amount of carbon dioxide in the atmosphere. Methane is more than 20 times as effectual as CO2 at entrapping heat in the atmosphere. Methane is obtained from resources such as rice paddies, bovine flatulence, bacteria in bogs and fossil fuel manufacture. When fields are flooded, anaerobic situation build up and the organic matter in the soil decays, releasing methane to the atmosphere. The main sources of nitrous oxide include nylon and nitric acid production, cars with catalytic converters, the use of fertilizers.
in agriculture and the burning of organic matter. Another cause of global warming is deforestation that is caused by cutting and burning of forests for the purpose of residence and industrialization.

**Impact of Global Warming on Earth**

Everyone has a responsibility to keep the earth safe and secure for the coming generations. Some immediate actions have to be taken for its security and to bring down the carbon dioxide emission and thus global warming:

1. Electricity has to be stored and used judiciously. Replace all incandescent bulbs with compact fluorescent lamps as it consumes only a little energy. Replace electric heaters with solar heaters. It is non-polluting and eco friendly.
2. Give more attention while constructing buildings. Properly insulated houses retain heat in winter. Avoid the use of huge glass walls as it increases heat inside and thus naturally increase the use of air conditioners during summer.
3. Turn off computers, fans and bulbs while not in use and this help to reduce the energy consumption.
4. It is advisable to use sprinklers or drip–irrigation for plants and vegetables. It helps to reduce the loss of too much water at the same time make the surroundings more cool.
5. Vehicles are to be properly maintained so that the fuel consumption is reduced and emission of toxic gases is minimal. Pool a car to office or work place and walk to nearby places.
6. Buy only energy efficient home appliances. Be selective while you purchase and thus reduce the waste of products.
7. Wastes are to be properly treated. Use compost pit to dump degradable waste and recycle the plastic wastes. Proper sewage system is a necessary to protect rivers and lakes.
8. Use water judiciously, as it is going to be a scarce commodity. Protect the rivers and lakes properly.
9. The use of wind power is an efficient method and factories must try to use this as source of electricity where ever possible.
10. Reduce the use of plastics as it destroys both atmosphere and land.
11. Plant as much trees as you can. Trees and plants can protect the atmosphere and soil as it is the best source of oxygen.
12. Avoid the use of fossil fuels and rely on gas energy since the carbon compounds emitted by this is comparatively smaller.
13. Protect oceans as it is the rich reservoir of vast amount of valuable flora and fauna. Educate the masses so that everyone is aware of the problem his action causes to earth.

**Global Warming Affecting the Various Ecosystems**

Pollution is the real threat to mankind, as we emit contaminants into the environment. Since it being the main cause of instability and disorder of ecosystem, it has to be eradicated or at least controlled. The nature and all its components are interrelated and man relies on these components for its existence. The action of one affects the others and human evasion has caused the extinction of many species. The nature exists with us, both go side by side and both are inevitable. We have a responsibility to take care of the nature in an appropriate manner.

One of the main threats which the Earth faces is global warming. It strips Mother Earth of her aura of invincibility. As the effect of global warming the sea level arises, and the catastrophic floods which follows, displace millions of people living in the coastal belt all over the world from their home land. The rise in global sea level affects the ocean circulation.

The plains are being stripped of its moisture rich soil and we are on the verge of a fodder crisis. Many of the native temperature resistant plant species are being wiped out of the earth. Vector borne diseases like dengue malaria are expected to increase sharply across the globe as the temperature variations make it more conducive for mosquitoes to thrive. Diarrhoeal disease which is associated with drought and flood is also expected to register a sudden increase.

The effect which global warming has on the flora and fauna of sea is unprecedented. Warmer sea ocean temperatures destroy vast coral reefs and the balance of marine life is lost. The increase in the
number of violent hurricanes, unnaturally torrential rains, unusually hot summers are all indicators of the treacherous days which are yet to come.

Renewable energy reduces the global warming. Hydroelectric energy, one of the dependable and eco-friendly renewable energy produces minimum pollution. The construction of dams for this purpose helps to control floods, provide water for irrigation and at the same time produce electricity. This energy source never pollutes water; but the vegetation, that is submerged on decaying produces methane, one of the deadly accelerators of global warming. This effect is more prominent in tropical region. The positive benefits of the hydroelectric power overweigh and hence people tend to turn a blind eye towards this problem. But we must not forget the fact that even though the source is localized the effect is universal.

The present change in the Arctic Glaciers is the clear indicator of negative impacts of global warming. The temperature in the Arctic region is increasing gradually. It reduces the snow cover, the wide spread glaciers are melting down and the sea level is rising alarmingly. The frequency and intensity of floods are increasing. During autumn and winter, rain is occurring, rising permafrost temperature. The depletion of highly reflective Arctic cover is increasing the pace with which global warming is affecting our environment. The changes in ocean circulation pattern, which is another direct impact of glacier melting, are gradually affecting the global climate. Some birds are migratory and they rely on Arctic for breeding. The melting down of glaciers affects the biodiversity and extinction of these species. Polar bears are an example of a species which is on the verge of extinction as a result of this unwanted phenomenon.

The reduction in sea level damages the marine habitat also. The coastal areas which are exposed to storms lead to coastal erosion. Change over ways so that we can protect the Arctic Ice Cap before it is too late. There is an increase in heat related deaths. The rise in average temperature increases the diseases carrying organisms like mosquitoes, rodents and bats. The respiratory illness increases due to global warming because grasses and allergic pollen grow more profusely in warmer environment. Violent storms and other extreme climate carrying deadly diseases occur frequently.

The climate change is also affecting the ecosystem. Some widespread species like Indian leopard is facing extinction. Birds migrate to different places to survive. Ecosystem habitat have isolated due to human settlements and infrastructure. All these things affect economy of both the developed and developing countries. The extreme weather events, droughts and floods are occurring frequently and severely. The weather related disasters are increasing. As the atmosphere gets warmer, the climate gets hotter and more unstable. The frequency of earthquakes has risen and it directly affects the economy of countries. Weather related disasters cripple the economy and health of humans and especially children.

Majority of global greenhouse gas emissions occur in developed nations, but the developing countries suffer more as most of them are located in the tropics. The increase in heat and humidity is a major problem. Heat is released to the environment mainly human activities. The signs of development, the concrete buildings and black roads are real threat to the rise in heat. It absorbs heat and emits back to the environment at night. It becomes hot and humid in major cities at night. It increases the use of air-conditioners which in turn emits greenhouse gases.

**Flora and Fauna**

Flora is basically the plant life that is present in a particular region or habitat or at a particular time and fauna is the animal life that is present in a particular region or habitat or at a particular time. Biodiversity is a very large topic and somewhat difficult to define adequately in only a sentence or two. In the very simplest terms, "biodiversity" means the diversity of life on our planet, which includes genetic diversity, species diversity, and habitat diversity. US Congress Office of Technology Assessment has defined biodiversity as "Biological diversity is the variety and variability among living organisms and the ecological complexes in which they occur. Diversity can be defined as the number of different items and their relative frequency. For biological diversity, these items are organized at many levels, ranging from complete ecosystems to the chemical structures that are the molecular basis of heredity. Thus, the term encompasses different ecosystems, species, genes, and their relative abundance." The area of flora, fauna and biodiversity is quite interrelated. Flora and fauna forms a major part of biodiversity.
India is a land of varied flora, fauna and biodiversity. India is one of the twelve mega diverse nations of the World. Two of India's great mountain ranges, the Eastern Himalayas and the Western Ghats have been designated among the world's eighteen 'hotspots' of biodiversity. But in the last few decades we have seen a steady increase in the extinction rate of flora, fauna etc. all over world including India and so now, conservation of biological diversity is of paramount importance to the survival of man. Conservation of biological diversity leads to conservation of essential ecological diversity to preserve the continuity of food chains. The genetic diversity of plants and animals is preserved. It ensures the sustainable utilization of life support systems on earth. It provides a vast knowledge of potential use to the scientific community. A reservoir of wild animals and plants is preserved, thus enabling them to be introduced, if need be, in the surrounding areas. Biological diversity provides immediate benefits to the society such as recreation and tourism. Biodiversity conservation serves as an insurance policy for the future.

**Conservation of Flora & Fauna in Global Warming:**

Even though climate changes have become global issue, but there are still many communities around the world who has not known and understand what is global warming and climate changes. Many of us living in developing countries are limited to information on global warming and climate changes. For many developing countries like Indonesia, efforts to develop public awareness on global warming and climate changes are urgently needed in order to enhance public understanding on the issues. In the efforts of spreading awareness on global warming and climate change, Peka Indonesia collaborating with ISES and TMII conducted one day seminar on global warming and climate change. The seminar was conducted on January 22nd 2007 in Indonesian Miniature Garden, Jakarta with seminar theme "Conservation of Flora and Fauna in the middle of changing climate and global warming"

**Global Warming is Inspiring Scientists to Fight for Awareness:**

Scientists all over the world are making predictions about the ill effects of Global warming and connecting some of the events that have taken place in the past few decades as an alarm of global warming. The effect of global warming is increasing the average temperature of the earth. A rise in earth’s temperatures can in turn root to other alterations in the ecology, including an increasing sea level and modifying the quantity and pattern of rainfall. These modifications may boost the occurrence and concentration of severe climate events, such as floods, famines, heat waves, tornados, and twisters. Other consequences may comprise of higher or lower agricultural outputs, glacier melting, lesser summer stream flows, genus extinctions and rise in the ranges of disease vectors. As an effect of global warming species like golden toad, harlequin frog of Costa Rica has already become extinct. There are number of species that have a threat of disappearing soon as an effect of global warming. As an effect of global warming various new diseases have emerged lately. These diseases are occurring frequently due to the increase in earth’s average temperature since the bacteria can survive better in elevated temperatures and even multiply faster when the conditions are favourable. The global warming is extending the distribution of mosquitoes due to the increase in humidity levels and their frequent growth in warmer atmosphere. Various diseases due to Ebola, hanta and matchup virus are expected due to warmer climates. The marine life is also very sensitive to the increase in temperatures. The effect of global warming will definitely be seen on some species in the water. A survey was made in which the marine life reacted significantly to the changes in water temperatures. It is expected that many species will die off or become extinct due to the increase in the temperatures of the water, whereas various other species, which prefer warmer waters, will increase tremendously. Perhaps the most disturbing changes are expected in the coral reefs that are expected to die off as an effect of global warming. The global warming is expected to cause irreversible changes in the ecosystem and the behaviour of animals.

**Conclusion**

Global Warming The beginning of the Industrial Revolution brought many new, exciting inventions into our lives to simplify our lives and made them more efficient. The Union of Concerned Scientists,
UCS, explains that one of the most important actions that need to be taken at any level is the amount of fossil fuels burned for energy at any level. It is suggested by many organizations that natural gases should replace other fuels such as coal, oil and gasoline, and that we should still limit the burning of even natural gases. It is also suggested that the government should create car-less cities, where citizens can only walk, ride bikes or use public transportation to get around inside the city. Yet another suggestion is to require citizens to drive electric cars, or electric hybrid cars, to reduce the amount of pollution put into the atmosphere by driving. A less popular action would be to limit the amount of gasoline available to each citizen over a certain amount of time, making them unable to contribute any more pollutants than anyone else is allowed. Transportation is not the only area where action can be taken, household appliances, heating or cooling equipment, consumer electronics, or office equipment also have an effect on the environment. According to the Consumer Federation of America Foundation, CFAF, the average home causes more air pollution than the average car. The CFAF also states that a household that buys “energy efficient equipment” instead of standard new equipment can considerably lower the emissions of carbon dioxide over the lifetime of the appliances that is a pollution savings comparable to taking a car off the road for seven years. As well as lowering the amount of pollutants being put into the air, citizens can reduce their energy bills by around 30% by replacing their home appliances by energy efficient products in their home. Individuals can make a big difference in global warming also. Citizens can get involved with organizations to attract the attention of the government as well as following a couple of the suggestions made above. People can drive less, or use more efficient cars, smoke less, even cigarette and pipe smoke are pollutants, and replace their appliances and household products with more energy efficient ones. Global warming is a problem, and it won’t go away without the cooperation of the world and its inhabitants.

The IPCC is also agenda-driven to exaggerate the threat of anthropogenic global warming and overlook the role of natural variations in climate and the benefits of a warmer world. It is not surprising that every report from the IPCC finds global warming to be an even greater threat than it was in the previous report.

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