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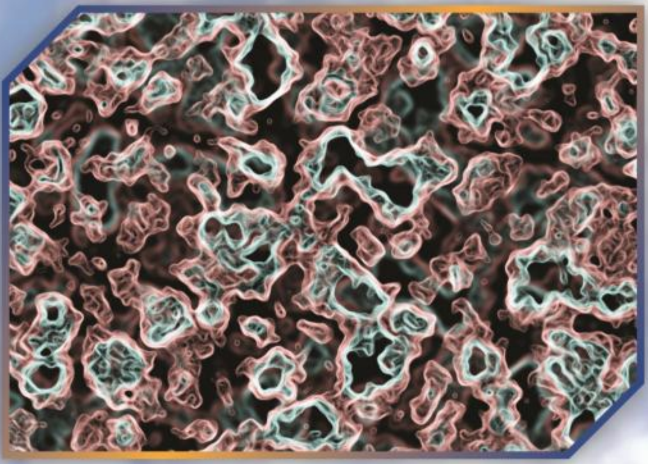

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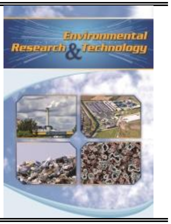

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RESEARCH ARTICLE

Assessment of physicochemical characteristics of groundwater collected from different taluks, Dindigul district, Tamilnadu, India

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ABSTRACT

To evaluate the physicochemical characteristics, water samples were collected from thirty-three villages at Dindigul district. From the analysis, pH of the all samples were varying from 6.64 to 8.17. The pH values are within the permissible limit. In Natham taluk, bore wells samples showed extreme (991, 963 and 951 mg L^{-1}) total dissolved solids (TDS) values when compared to maximum permissible TDS is 600 mg L^{-1}. The taste of water comes under poor TDS rating. The highest total hardness (TH) 725 mg L^{-1} was tested at Silukuvarpatti bore well in Nilakottai taluk. Residual free Chlorine and Iron were not detected in any of the samples. All samples showed Nitrate (NO_3^-) concentrations were ranged from 0 to 25 mg L^{-1}. The values are less than NO_3^- desirable limit, that is 45 mg L^{-1} respectively. Maximum number of samples showed chloride (Cl^-) values were higher than Cl^- permissible limit (1000 mg L^{-1}) as referenced by BIS. The highest Cl^- values were obtained at 2950 and 2000 mg L^{-1} in Pudukkottai well and Sengulam bore well taken from Reddiyarchatiram and Natham taluks. In regards to fluoride (F^-) contamination, thirty-four samples showed < 0.5 ppm F^- and rest of fourteen samples viewed <1ppm F^-. According to BIS and WHO standard, low concentration of F- below 0.5 ppm may increase the risk of tooth decay.

Keywords: Groundwater, fluoride, physicochemical parameters

1. INTRODUCTION

Water is a necessary component for everyday life [1]. Underground water is the main source of drinking water, used for agricultural and industrial activities [2]. All over 0.2 billion people from 25 nations have health risks because high fluoride concentration in underground water [3]. Approximately 80% of the diseases in the world are due to poor quality of drinking water [4]. Contamination of groundwater can result in poor drinking water quality, loss of water supply, high clean-up costs, high expenses for alternate water supplies, and feasible health issues [5]. There is a rising worldwide consumption of anionic pollutants from industries have been concerned due to their potential risk for environment and human health [6-10]. Fluoride is a toxic element present in the groundwater due to natural and or anthropogenic sources [11]. In small amounts, F^- is a necessary component for normal mineralization of bones and formation of dental enamel [12]. It is harmful when it exceeds the permissible limit 1.5 mg L^{-1} of F^- in water [13, 14]. A very small amount of F^- can cause several biochemical alterations [15] and excessive F^- intake causes fluorosis and severe skeletal problems [16-19]. The major sources of F^- in groundwater are due to dissolution of F- bearing minerals such as fluorspar, cryolite, fluorapatite, and hydroxyapatite in rocks [20]. Some anthropogenic activities due to agricultural usage of fertilizers, pesticides and discharge of sewage and sludge have also been indicated as a cause for the increase in F^- concentration in groundwater [21]. In this work to assess the physicochemical characteristics of groundwater samples were collected in and around Dindigul district, Tamil Nadu, South India.

2. DESCRIPTION OF STUDY AREA AND SAMPLING SITES

Dindigul district is situated between latitude 10.4747°N longitude 77.8367°E. It divided into six

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different taluks. The water samples were collected from Nilakottai (latitude 10.165497, longitude 77.852451), Athoor (latitude 10.288646, longitude 77.853165), Reddiyarchatiram (latitude 10.474745, longitude 77.836728) and Natham (latitude 10.222202, longitude 78.233374) in Dindigul district. Nilakottai taluk is located in the southern part of the Dindigul district and covers about 261.12 square km and is distributed in 23 panchayat villages. Athoor is located 16 KM towards west from Dindigul district. Reddiyarchatiram taluk is a revenue block consists of 24 panchayat villages. It is bounded by Athoor taluk towards South, Dindigul block towards East, and Oddanchatram block towards west. Natham taluk is located 37 KM towards East from Dindigul district (Fig 1).

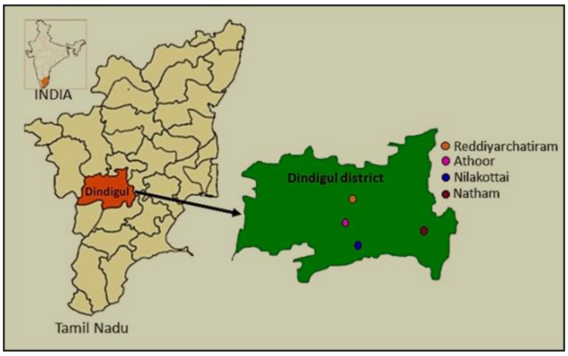

Fig 1. Samples collected in and around four taluks of Dindigul district

3. METHODOLOGY AND ANALYSIS

A total of forty-eight groundwater samples were taken from thirty-three villages of Dindigul district (Table 1). It includes 43 bore wells, 2 wells and 3 hand pumps samples were collected in sterile plastic bottles and then carefully sealed, labelled and transferred to laboratory for the analysis. The physicochemical parameters like pH, electrical conductivity (EC), total dissolved solid (TDS), and salinity was tested by multiparameter tester (PCSTestr 35, EUTECH instrument, ThermoScientific). Other characteristics, total hardness (TH), residual (free) chlorine, chloride, iron and nitrate were analysed by using multiparameter water analysis kit (Hi-media). The concentration of fluoride was estimated by LABMAN ion meter (lumion-40) with fluoride electrode combination.

4. RESULTS AND DISCUSSION

The observed pH values of all sampling sites ranged from 6.64 to 8.17 with an average value of 7.52, exhibiting the marginally alkaline condition of groundwater (Table 2). Similarly, groundwater pH (7.3-8.4) slightly basic, was collected from Dindigul district [22]. The safe limit of pH for drinking water is specified as 6.6-8.5 [23, 24] and tested water samples showed pH values were within the safe limits. The study area, EC values are in the range of 2.06 to 1890 µS cm^{-1} with an average value 826.59 µS cm^{-1} respectively (Table 2). In another finding, EC of the groundwater ranged from 150 to 5,020 µS cm^{-1} [22]. The EC of the water is one of the important parameter used to determine the suitability of water for irrigation. It is also suitable indicator for salinity or total salt content of waste water [25]. Salinity in the groundwater occurs due to the high concentration of TDS [26]. The salinity index or hazard which is correlated by EC values are the most important groundwater quality criteria for crop production [27]. The EC values of less than 750 µS cm^{-1} in the groundwater are categorized as excellent to good quality for the agricultural needs (Table 3). In this study, 20 groundwater samples are classified as class I and low to medium salinity levels suitable for high salt tolerant crops [27]. The remaining 28 samples are grouping under Class II with high salt level and permissible water quality. According to Handa [28], the samples classification are mentioned in Table 3. Based on Bureau of Indian Standards (BIS) guidelines, the ideal TDS for drinking water is below 300 mg L^{-1} and the maximum permissible limit is 600 mg L^{-1}. According to the taste of drinking water, TDS ratings can be classified as excellent (300 mg L^{-1}), good (300-600 mg L^{-1}), fair (600-900 mg L^{-1}) and poor (900-1200 mg L^{-1}) categories. The highest value of TDS 991 mg L^{-1} was observed at Karakundu bore well, Natham taluk. High level of TDS in the groundwater is due to leaching of salts from soil and also domestic sewage may penetrate into the groundwater, which may lead to increase in TDS values [29]. Consumption of water with high concentrations of TDS has been reported to cause disorders of alimentary canal, respiratory and nervous system, coronary system besides, causing miscarriage and cancer [30]. Total hardness (TH) of water samples are varying from 125 to 725 mg L^{-1}. However, TH permissible value is 600 mg L^{-1} as referenced by BIS [31]. Hardness is expressed in mg L^{-1} as $CaCO_3$, used to characterize the types of water (Table 4). In this work, few samples exhibited high TH values such as 625, 650, 675, and 725 mg L^{-1} respectively (Table 2). The highest value of 725 mg L^{-1} TH was estimated from Silukuvarpatti at Nilakottai. The increase in the maximum level of TH is due to presence of carbonate and non-carbonate compounds [32]. Iron and residual free Chlorine values were not found in any of the samples. In general nitrate and nitrite are the forms of nitrogen most commonly associated with groundwater contamination [33]. In this study, nitrate concentration of all samples ranged from 0 to 25 mg L^{-1} nitrate (NO_3^-) and also below the admissible limit. According to the WHO and BIS, the acceptable limit of NO_3^- is 45 mg L^{-1} respectively.

The origin of chloride ions (Cl^-) in groundwater may be from different sources such as weathering, intrusion of saltwater, leaching of sedimentary rocks and soils, domestic and industrial waste discharges and municipal effluents [34]. In Reddiyarchatiram and Natham taluks, maximum number of samples exhibited higher than Cl^- permissible limits (1000 mg L^{-1}, BIS; 600 mg L^{-1}, WHO). Among the samples, the highest Cl^- concentration was obtained at 2950 and 2000 mg L^{-1} from Pudukkottai and Sengulam bore wells (Table 2). The higher consumption of Cl^- which lead to high blood pressure, risk for stroke and left ventricular hypertension, osteoporosis, renal stones and asthma and heart and kidney diseases [35-37]. Besides, the excess of Cl^- in water is usually taken as an index of pollution and considered as tracer from groundwater contamination [38]. In other side only nine samples showed under Cl^- desirable values 50-150 mg L^{-1} tested in Athoor and Nilakottai taluks when compared to BIS specified Cl^- desirable limit is 250 mg L^{-1} respectively.

The F^- content in water was estimated by ion selective electrode method. From the analysis, thirty-four samples showed < 0.5 ppm F^- and rest of fourteen samples viewed <1ppm F^- values. Fluoride when consumed at < 0.5 mg L^{-1} produces adverse health effects including dental caries, lack of formation of dental enamel, and deficiency of mineralization of bones, especially in children [39]. The previous studies also concluded that the development of dental fluorosis even if the people consume drinking water with fluoride less than 1.0 mg L^{-1} [40-44; 2; 45-48]. In addition, WHO [49] evidenced that fluoride as one of the very few chemicals that have been shown to cause significant effects on people's health through drinking water.

Table 1. The latitude and longitudes of sampling sites in Dindigul district

S.no	Sampling sites	Samples type	Latitude	Longitude
1A	Pallapatti near A	Bore water	10.775355	77.908899
1B	Pallapatti near B	Bore water	10.775355	77.908899
2A	Pallapatti entrance	Bore water	10.775355	77.908899
2B	Gopalapuram	Bore water	10.465829	77.656895
2C	Pallapatti A	Bore water	10.775355	77.908899
2D	Pallapatti B	Bore water	10.775355	77.908899
2E	Pallapatti C	Bore water	10.775355	77.908899
3A	Goundanpatty	Bore water	10.112552	77.868582
4A	Velayuthapuram	Bore water	10.136868	77.906681
5A	Chokkanchettipatti	Bore water	10.149698	77.910763
6A	Malayakoundapatti A	Bore water	10.361782	77.984819
6B	Malayakoundapatti B	Bore water	10.361782	77.984819
7A	Silukuvarpatti	Bore water	10.153256	77.885264
7B	Silukuvarpatti Outer	Bore water	10.153256	77.885264
7C	Silukuvarpatti (Nilakkottai road)	Bore water	10.153256	77.885264
7D	Vellathathanpatty	Bore water	10.200874	77.870219
9A	Kamupillaichatiram	Bore water	10.274134	77.877210
10A	Vakkampatti	Bore water	10.3205137	77.907378
11A	Mutakusalai near	Bore water	10.3205137	77.907378
12A	Thathankottai	Bore water	10.441592	77.848782
13A	K. Pudukkottai	Well water	10.361782	77.984819
13B	K. Pudukkottai A	Well water	10.361782	77.984819
13C	K. Pudukkottai B	Bore water	10.361782	77.984819
14A	Alagupatti	Bore water	10.444765	77.871901
14B	Alagupatti A	Bore water	10.444765	77.871901
14C	Alagupatti extension	Bore water	10.444765	77.871901
15A	Teppakulathupatti	Bore water	10.46225	77.97535
16A	Ketchanaipatti	Hand Pump	10.391912	77.918352
17A	Silvarpatti	Hand Pump	10.367330	77.908103
18A	Kannimanuthu	Bore water	10.433159	77.909283
18B	Kannimanuthu	Bore water	10.433159	77.909283
19A	Muthanampatty pudur	Bore water	10.407465	77.910601
20A	Nochi Odaipatti	Bore water	9.832280	77.439090
21A	Gopalpatti	Bore water	10.257303	78.148081
22A	Kanavaipatti	Hand pump	10.246503	78.147480
22B	Kanavaikaruppu kovil	Bore water	10.247685	78.196340
23A	Karagundu	Bore water	10.251152	78.196340
23B	Karagundu A	Bore water	10.251152	78.196340
24A	Uluppagudi	Bore water	10.243148	78.196707
25A	RMTC nagar	Bore water	10.314977	78.018352
26A	Narasimmapuram	Bore water	10.316870	77.960692
26B	NarasimmapuramA	Bore water	10.316870	77.960692
27A	Sengulam	Bore water	10.238285	78.253094
28A	N. Pudupatti	Bore water	10.361782	77.984819
29A	Kuttupatti Pudur	Bore water	10.270504	78.261442
30A	Kuttupatti Thottam	Bore water	10.272441	78.261366
30B	Kuttupatti Thottam A	Bore water	10.272441	78.261366
31A	Kuttupatti	Bore water	10.272441	78.261366

Table 2. Physiochemical characteristics of groundwater samples

Sample No.	pH	EC (µS cm^{-1})	TDS (mg L^{-1})	Salinity (ppt)	TH (mg L^{-1})	Nitrate (mg L^{-1})	Chloride (mg L^{-1})	Fluoride (ppm)
1A	7.68	1245	885	621	250	25	100	0.819
1B	7.56	1225	870	612	250	25	100	0.785
2A	8.16	2.19	1.56	1.12	250	25	300	0.864
2B	7.47	1469	1.04	737	175	25	150	0.815
2C	7.78	2.53	1.78	1.29	425	25	300	0.429
2D	7.3	2.53	1.8	1.3	450	25	450	0.431
2E	7.89	2.40	1.7	1.23	375	25	250	0.578
3A	7.85	863	612	424	225	0	100	0.535
4A	7.15	3.26	2.3	1.7	575	25	300	0.435
5A	7.7	3.39	2.38	1.75	575	0	450	0.267
6A	7.6	2.74	1.93	1.41	325	25	400	0.124
6B	7.43	3.71	3.62	1.93	650	25	700	0.149
7A	7.52	2.06	1.46	1.05	375	25	350	0.265
7B	7.43	3.72	2.63	7.95	**725**	0	450	0.131
7C	7.17	688	486	333	150	25	50	0.144
7D	8.02	1848	1.31	935	450	0	350	0.184
9A	**8.17**	762	540	72	250	25	100	0.375
10A	7.32	220	157	108	125	0	50	0.078
11A	6.84	2.21	1.56	1.13	500	25	550	0.377
12A	7.58	1373	976	688	275	25	350	0.078
13A	7.46	1159	824	577	275	25	2500	0.148
13B	7.47	2.19	1.55	1.12	675	25	2600	0.08
13C	7.49	1531	1.09	770	375	25	**2950**	0.06
14A	7.76	1711	1.22	865	325	0	2650	0.287
14B	8.16	1612	1.15	813	250	0	2000	0.221
14C	7.6	1681	1.19	846	375	25	2700	0.226
15A	7.64	2.24	1.59	1.14	625	25	2550	0.165
16A	6.92	**1890**	1.34	**954**	500	0	2000	0.143
17A	7.64	1594	1.13	806	375	25	2200	0.3
18A	8.01	1664	1.18	839	300	25	2750	0.999
18B	8.08	1582	1.12	794	300	25	2500	**1.1**
19A	7.55	3.03	2.15	1.58	500	0	2800	0.393
20A	8.05	770	547	377	175	0	550	0.161
21A	7.98	918	652	452	175	0	2150	0.204
22A	6.93	1539	1.09	773	425	0	2400	0.344
22B	8.08	744	529	364	125	0	2750	0.188
23A	7.75	1355	963	678	300	0	2750	0.63
23B	7.80	1397	**991**	699	300	0	2750	0.704
24A	6.85	1652	1.17	832	550	25	2100	0.206
25A	7.65	1341	952	670	425	0	1850	0.37
26A	7.31	901	640	447	250	0	2100	0.736
26B	7.21	928	659	456	175	0	2000	0.667
27A	7.27	1022	726	505	250	0	2900	0.435
28A	7.20	2.18	1.55	1.11	625	25	2150	0.204
29A	6.64	423	301	205	125	0	2450	0.112
30A	7.11	475	337	230	200	0	2100	0.109
30B	7.22	1079	767	535	375	25	2250	0.188
31A	7.39	1184	840	586	325	25	1700	0.17

Note: High values denoted in bold and underlined

Table 3. Classification of water based on Electrical Condctivity [28]

EC (µS/cm)	Salinity level	Water quality	No. of samples	Category
0-250	Low	Excellent	**16** (2A, 2C, 2D, 2E, 4A, 5A, 6A, 6B, 7A, 7B, 10A, 11A, 13B, 15A, 19A, 28A)	Class I
251-750	Medium	Good	**4** (7C, 22B, 29A, 30A)	Class I
751-2500	High	Permissible	**28** (1A, 1B, 2B, 3A, 7D, 9A, 12A, 13A, 13C, 14A, 14B, 14C, 16A, 17A, 18A, 18B, 20A, 21A, 22A, 23A, 23B, 24A, 25A, 26A, 26B, 27A, 30B, 31A)	Class II

Table 4. Total hardness (TH)

Total hardness (mg/l of CaCo3)	Types of water	No. of present study samples showed values	Samples No.
0-50	Soft water	-	-
50-100	Moderately soft	-	-
100-150	Neither hard or soft	4	7C, 10A, 22B, 29A.
150-200	Moderately hard	5	2B, 20A, 21A, 26B, 30A.
200-300	Hard	15	1A, 1B, 2A, 3A, 9A, 12A, 13A, 14B, 18A, 18B, 19A, 23A, 23B, 26A,27A.
>300	Very hard	24	2C, 2D, 2E, 4A, 5A, 6A, 6B, 7A, 7B, 7D, 11A, 13B, 13C, 14A, 14C, 15A, 16A, 17A, 22A, 24A, 25A, 28A, 30B, 31A

5. CONCLUSIONS

The study results concluded that pH values are within the safe limits. In addition 66% of the samples showed greater than 300 μS cm^{-1} EC values as suggested by WHO. Water samples are hard and vary hard types incontrast excellent and good TDS rating. Alomost maximum number of samples showed chloride values are higher than permissible limit. Predominant samples found less than 0.5 ppm fluoride and rest of them viewed <1ppm fluoirde values, its were beyond the daily fluoride desirable limit (1mg L^{-1}). It may prone to dental caries in childran. According to the results, water is only suitable for household non drinking purposes.

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RESEARCH ARTICLE

Phenol removal from synthetic wastewater with powdered activated carbon: Isotherms, kinetics and thermodynamics

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ABSTRACT

Phenol is the 11th most toxic 126 chemical substance and causes cancer by accumulating in the food chain. Adsorption of phenol is an effective and also environmentally friendly method for its removal. In this study, phenol removal by using powdered activated carbon (PAC) was optimized and modeled for various isotherms at constant mixing rate (150 rpm) and sample volume (100 mL); adsorbent dose (0.01-2 g), contact time (1-180 min), and initial phenol concentration (50-1000 mg L^{-1}). Moreover, adsorption studies were carried out at different temperatures for kinetic and thermodynamic calculations. In this study, optimum adsorbent dose and contact time of PAC were determined as 0.3 g 100 mL^{-1} (3 g L^{-1}) and 10 minute, respectively. It can be concluded that it provides discharge standards for a wastewater containing 100 mg L^{-1} phenol. It was observed that the adsorption capacity decreased with increasing temperature and the adsorption process fits well with Langmuir isotherm. It has been concluded that the adsorption of phenol with PAC is an exothermic reaction. As a result of the kinetic studies, it was found to be suitable for the Pseudo Second Order (R^2 0.9999-1.0000). ΔS, ΔH and ΔG were calculated as -0.02 J mol^{-1} K^{-1}, -14.15 kJ mol^{-1} and between -8.16 and -7.76 kJ mol^{-1}, respectively.

Keywords: Adsorption, isotherm, kinetic, phenol, powdered activated carbon (PAC)

1. INTRODUCTION

Phenol (C_6H_5OH), an aromatic compound, is one of the 126 most toxic chemicals. In addition to their toxicity, they cause carcinogenic effect by accumulating in the food chain. The permissible values in water are less than 0.002 mg L^{-1}. Phenol is obtained from coal tar or benzene. It is a common pollutant in wastewater as a result of its widespread use in different industrial fields (pharmaceutical, steel, textile industry, plastics, dyestuff, paper, epoxy, phenolic resin, pesticide, insecticide, petroleum refinery, coal gasification, olive water, etc.). Biological treatment methods (lagoons, aerated stabilization ponds, trickling filters and activated sludge) may be preferred due to their resistance to moderate phenol pollution, while adsorption is preferred for high pollution removal and toxic pollutants [1].

Adsorption is an environmentally friendly advanced treatment method for pollutant removal. Various adsorption studies on phenol removal have been conducted [2-10], especially high removal yields were obtained with commercial adsorbents. Adsorption method provides organic/inorganic pollutant removal as well as taste, colour and odour removal [11]. Phenol is also a compound that causes bad taste and odour in waters [12]. Therefore, the adsorption method provides solutions for many purposes.

In this study, the removal of phenol, which is an important pollutant in industrial wastewater, with powdered activated carbon (PAC) was investigated. PAC is a very active and wide surface area adsorbent to eliminate high concentrations in industrial production plants. For this purpose, at constant mixing speed and sample volume; adsorbent dosage (0.01-2 g), contact time (1-180 minutes), initial phenol concentration (50-1000 mg L^{-1}) were optimized. Different isotherms (Freundlich, Langmuir, Temkin, Elovich, Dubinin-Radushkevich and Redlich-Peterson), kinetics (Pseudo First Order, Pseudo Second Order and Interparticle Diffusion) and

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thermodynamic coefficients were determined by analysing at different temperatures under optimum conditions. Moreover, the adsorption process was evaluated for benefit, cost and risk.

2. MATERIALS AND METHODS

The powdered activated carbon used as adsorbent in this study was obtained from Sigma Aldrich (Activated Charcoal DARCO-100 mesh=<0.142 mm). The powdered activated carbon is commercial and has not been undergone any activation process (pre-treatment). Phenol (> 99% purity) from Sigma Aldrich was used as synthetic wastewater (SWW) (1000 mg L^{-1}). Phenol analyses were carried out according to APHA Standard Methods [13].

100 mL of the phenol solution diluted in the appropriate ratio was put into a 250 mL flask, an appropriate amount of PAC was added and operated at a mixing speed of 150 rpm. As a result of the study, it was filtered through a 0.45 µm filter and phenol analysis was performed. The system used in the study is given in Fig 1.

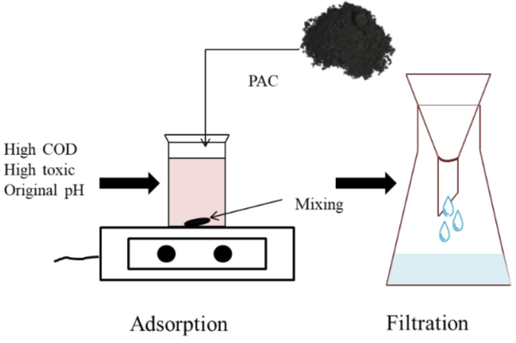

Fig 1. Schematic view of the system used in the study

At constant mixing speed (150 rpm) and sample volume (100 mL), adsorbent dosage (0.01-2 g), contact time (1-180 minutes), initial phenol concentrations (50-1000 mg L^{-1}) were optimized at 298 ºK. Analyses were carried out at 3 different temperatures (298-308-318 °K) under the optimum conditions. Different isotherm (Freundlich, Langmuir, Temkin, Elovich, Dubinin-Radushkevich and Redlich-Peterson), kinetic (Pseudo First Order, Pseudo Second Order and Interparticle Diffusion) and thermodynamic coefficients were determined and the mechanism of adsorption of phenol on PAC was explained.

3. RESULTS

3.1. Optimization

In the first step, the optimization of PAC amount was determined by shaking for 4 hours at 298°K, 150 rpm mixing speed in 100 mL SWW, 100 mg L^{-1} phenol concentration. The results obtained are given in Fig 2. As can be seen in Fig 2, the concentration decreased from 100 mg L^{-1} to 0.12 mg L^{-1} when 0.5 grams of PAC were added, and a large amount of phenol was removed. The removal efficiency is quite high. Even when 0.1 g of PAC was added, the concentration decreased to 15.6 mg L^{-1} and a removal efficiency of 84.4% was achieved. Accordingly, the addition of PAC resulted in high removal efficiencies, even in very small amounts. This high removal may be related to the high activity of PAC and the large surface area. In other words, increasing amount of adsorbent increases active regions for the retention of phenol pollutants and accordingly increases the removal efficiency. The initial activated carbon dosage at which 99% removal is achieved is 0.3 grams. After this value, the increase in removal efficiency was negligible. While the dosage amount can be selected higher, the dosage of 0.3 g 100 mL^{-1} PAC was chosen as the optimum value considering the supply and cost of PAC.

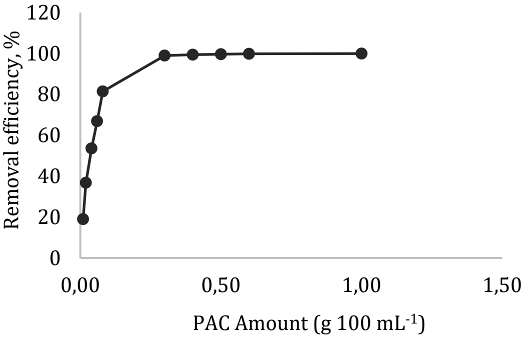

Fig 2. Optimizing the amount of adsorbent (150 rpm, 100 mL SWW, 100 mg L^{-1} phenol, 4 hours, 298°K)

After determining the optimum value of PAC amount (0.3 g 100 mL^{-1}), the optimum the contact time was studied at different reaction times (150 rpm, 298 °K, 100 mL SWW, 100 mg L^{-1}). After 5 minutes, the concentration of the solution decreased to 1.76 mg L^{-1} and 98.2% of the phenol was removed. As time was increased, the removal efficiency increased continuously and most of the phenol was removed within the first 5 minutes (Fig. 3). Subsequently, no significant increase in removal efficiency was observed with the increase in time. In other words, rapid phenol adsorption occurred at first and then slowed down. As a result of the observations, the optimum reaction time was selected as 10 minutes. It can be concluded that the increase of the adherence of phenol on the surface with the increase in the adsorbent amount shows the width of the surface area and the absence of decrease in the efficiency over time shows the suitability of mixing speed. It can also be explained by decreasing the active regions over time and decreasing the adsorption rate [14].

Different concentrations were studied to optimize the pollutant concentration, and in other words, to examine the effect of pollutant concentration on removal efficiency. The concentration range is kept wide (50-1000 mg L^{-1}), since PAC activity can occur at different concentrations in wastewater in industries.

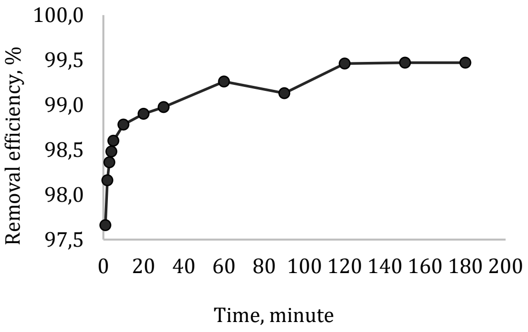

Fig 3. Optimizing contact time (150 rpm, 100 mL SWW, 100 mg L^{-1} phenol, 0.3 g PAC, 298 °K)

When the removal efficiency amounts were compared (Fig 4), the removal rates calculated as 99.0% at 50 mg L^{-1}; 97.7% at 100 mg L^{-1}; 94.7%, 90.0% and 84.5%, respectively, at 200 mg L^{-1}, 300 mg $L^{-1}$and 400 mg L^{-1}; and the efficiency decreased while the concentration increased. When there was a higher phenol content in water, it was more difficult to remove all of the phenol with the same amount of PAC. This was observed at all contact times. The decrease in efficiency as concentration increases indicates that the active area/surface area of the optimally determined 0.3 g is insufficient. In this case, a higher contact time may be provided, or more adsorbents may be added, so that the removal efficiency does not decrease as the initial concentration increases. It is stated that the removal efficiency increased as the concentration of pollutant increases in the adsorption of cationic dyes on the soil since there is not mass transfer limitation/it is the driving force for mass transfer [15]. However, there was no such effect on the removal of phenol pollutant by PAC. The reason for this difference may be related to the type of pollutant and/or type of adsorbent. Moreover, diffusion path may be prolonged for the phenols to reach to open active areas due to the decrease of active areas, because adsorbent is coated with pollutants [16]. This can also be explained by the increase in the adsorption efficiency by increasing the time as a result of prolongation of the diffusion path.

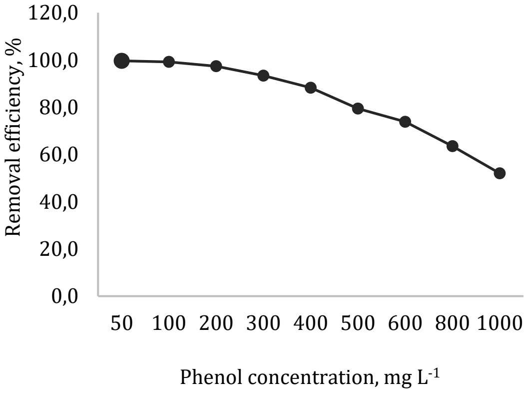

Fig 4. Optimization of phenol concentration (150 rpm, 100 mL SWW, 0.3 g PAC, 10 minute, 298°K)

3.2. Isotherms

Isotherms are equations that give an idea about the adsorption mechanism. Isotherm coefficients were determined for three different temperatures and values are given in Table 1. While temperature generally served as a catalyst for reactions, it had no positive effect on the removal of phenol by adsorption. As the temperature increased, the removal efficiency and adsorption capacity decreased and the best phenol removal was obtained at 298 °K. In the adsorption process, as the temperature increases, it may go away from the adsorbent as a result of the mobility of the pollutant molecules in the water; and a decrease in the amount of phenol retained by the adsorbent was observed as a result. Adsorption capacity decreased with temperature. This shows that the adsorption of phenol with PAC is an exothermic reaction. In a study carried out using wheat bran, the removal of pollutants increased with increasing temperature. It was stated that the temperature increased the active regions in the adsorbent [14]. Furthermore, the solubility of phenol may be increased with increasing temperature and the interaction of the pollutant with the adsorbent (physical bond) may be reduced. In other words, Brownian movement of phenol molecules may be increased [17].

Since R^2 values are very close to 1, it was shown that experimental data can be explained quite well with Langmuir and Elovich isotherms at all temperatures. Other isotherms were observed to vary depending on temperature. The suitability to Langmuir isotherm shows that the surface of the adsorbent is homogeneous, and the adsorbent surface is energetically identical (monolayer). The order of suitability of the isotherms is Langmuir=Elovich>Temkin=Redlich-Peterson>Freundlich>Dubinin-Radushkevich, respectively. The high K_F (Freundlich isotherm coefficient, L g^{-1}) values show the close proximity of the PAC with phenol and the strong relationship between them. The decrease of K_F values with increasing temperature gives an idea that the adsorption capacity decreased. This means that the temperature increase decreases the adsorption rate in the study [18]. In Dubinin-Radushkevich isotherm, the energy value calculated by formula 1 gives information that adsorption occurred as a result of physical or chemical interaction. Since energy (E) values calculated with K_{DR} (Dubinin-Radushkevich isotherm coefficient, (mol^2 J^{-2}) values obtained in the study are between 1-8 kJ mol^{-1}, it was concluded that the interaction between the adsorbent and the pollutant was physical [19].

$$\mathrm{E} = \frac{1}{\sqrt{2 * \mathrm{K_{DR}}}} \qquad (1)$$

The balance factor (R_L) is calculated by the following formula.

$$R_L = \frac{1}{(1+K_L * C_0)} \qquad (2)$$

where, R_L is balance factor (unitless) and Co is the initial phenol concentration (mg L^{-1}). The calculated R_L values are given in Table 2. Whereas $R_L>1$, it can be said that the adsorbent is suitable for the adsorption of pollutants. If $R_L=0$, it is irreversible and whereas $0<R_L<1$, it is suitable for adsorption [20]. Since $R_L<1$, it can be said that the interaction between the pollutant-PAC is physical, the adsorption process is favorable and the adsorption occurs spontaneously.

Table 1. Coefficients of different isotherms

Isotherm Models	Isotherm Equations	Isotherm Parameters	298°K	308°K	318°K
Freundlich	$Qe = K_F * Ce^{1/n}$	K_F	29.1455	26.2456	23.4179
		n	0.3714	0.3732	0.4022
		R^2	0.9847	0.9780	0.9626
Langmuir	$Qe = \frac{(b * K_L * Ce)}{(1 + b * Ce)}$	b	0.2531	0.2104	0.1797
		K_L	121.9512	117.6471	117.6471
		R^2	0.9926	0.9931	0.9949
Temkin	$Qe = b_T * Ln(K_T\text{*Ce})$	b_T	19.0600	18.8820	20.4750
		K_T	6.2146	4.7370	3.1215
		R^2	0.9837	0.9913	0.9975
Redlich-Peterson	Ln(Ce/Qe)=β∗LnCe-LnA	β	0.6286	0.6268	0.5978
		A	29.1455	26.2456	23.4179
		R^2	0.9946	0.9921	0.9827
Elovich	$Ln(Qe/Ce)=LnK_E*Qm-Qe/Qm$	Qm	30.5810	30.1205	34.1297
		K_E	0.8630	0.8687	0.8936
		R^2	0.9955	0.9999	0.9924
Dubinin Radushkevich	$LnQe=LnQs-K_{DR}*\varepsilon^2$	Qs	75.5660	75.7170	77.4010
		ε	2.0990	1.7560	1.3650
		K_{DR}	0.1140	0.1620	0.2684
		R^2	0.7680	0.7990	0.8297

Table 2. R_L (equilibrium factor) values calculated for Langmuir isotherm

Inital Concentration (mg L^{-1})	Temperature (°K)		
	298	308	318
50	0.000164	0.000170	0.000170
100	0.000082	0.000085	0.000085
200	0.000041	0.000042	0.000042
300	0.000027	0.000028	0.000028
400	0.000020	0.000021	0.000021

3.3. Kinetics

Kinetic models are used to determine the speed of the adsorption process. Pseudo First Order (Lagergen) and Pseudo Second Order (Ho-McKay) considering the chemical interaction with the results obtained at 298-308-318 °K; and interparticle diffusion coefficients were determined (Table 3). It was concluded that it conforms to Pseudo Second Order kinetics. Pseudo Second Order kinetic model is based on the assumption that it may be a chemical sorption including valence forces through the share or exchange of electrons between the adsorbent and the solution [14].

3.4. Thermodynamics

During the adsorption, heat is generated due to the interaction between molecules attached to the solid surface. Since this heat occurs spontaneously at constant temperature and pressure, the free enthalpy change, in other words, the adsorption free enthalpy ΔG is always minus-signed. As the more irregular molecules in the gas or liquid environment become more stable by holding on the solid surface, the entropy change during adsorption, in other words, the adsorption entropy (ΔS) is always minus-signed. The fact that adsorption free enthalpy and adsorption entropy are always minus-signed requires the adsorption enthalpy in Equation 3 to be always minus-signed.

$$\Delta H = \Delta G + T * \Delta S \quad (3)$$

As the adsorption process is exothermic, the adsorption capacity decreases in parallel with the increase in temperature. As a result of thermodynamic calculations, enthalpy, Gibbs free energy and entropy changes were determined to be minus (-) (Fig 5 and Table 4). The fact that these thermodynamic coefficients are minus (-), shows that adsorption is applicable, it is physisorption, sorption reaction is exothermic/spontaneous (ΔH) and it is less structural change, less random adsorption (ΔS) [19, 21]. Entropy, in other words, irregularity decreased. The reason for this is that it becomes more regular with adsorbed agent accumulation/adhesion in the adsorption process. The fact that ΔH<84 kJ mol^{-1} and ΔG are obtained between -20 and 0 kJ mol^{-1}, means that adsorption occurs by physical interaction [19].

Table 3. Kinetic coefficients

Temperature (°K)	Pseudo First Order		Pseudo Second Order		Interparticle Diffusion	
	k_1 (dk^{-1})	R^2	k_2 (g mg^{-1} dk^{-1})	R^2	Kip (mg gr^{-1} dk$^{-0.5}$	R^2
298	0.2467	0.9595	0.1063	0.9999	0.1028	0.7604
308	0.1849	0.9441	0.0171	1.0000	0.1262	0.8505
318	0.1765	0.9398	0.0175	1.0000	0.0733	0.3232

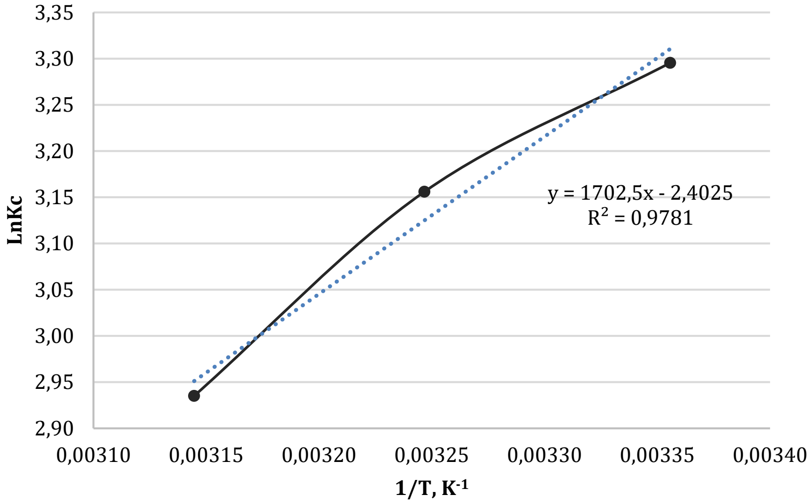

Fig 5. Thermodynamics coefficients

Table 4. Gibbs free, enthalpy and entropy energies

°K	ΔG (kJ mol^{-1})	ΔH(kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
298	-8.16	-14.15	-0.02
308	-8.08		
318	-7.76		

4. EVALUATION IN TERMS OF BENEFIT, COST AND RISK

Adsorption is one of the advanced treatment methods. It is a physical/physicochemical method based on the adsorption of pollutants on solids. The benefits of adsorption are that it can be used as a pre-treatment and can be used as a post-treatment; it provides recovery of water because it provides high efficiency removal, it is easy to operate and the design of the system is simple. Moreover, biological treatment of a toxic pollutant is difficult to perform while it can be successfully treated by adsorption [22, 23]. PAC has high specific surface area, wide usability, and structural stability at acidic/basic environment and high temperatures and it is an effective adsorbent used for removal of a wide range of pollutants (inorganic, organic, taste, odour, colour, etc.) [24]. Simplicity of the adsorption method is that, it does not require much manpower. Disadvantages are that it is disposable and sometimes causes turbidity [25].

When the cost of adsorption with PAC is taken into consideration, the investment cost is economic because it is not a complicated system. Considering 10 minutes reaction time, 10 years treatment unit life, treatment unit cost 10000 \$ m^{-3} [26] and annual interest rate of 4%, The investment cost for treatment with adsorption was calculated as 0.31 \$ m^{-3} by operating annual 30000 m^3 wastewater in 8 hours a day, 300 days a year. The operating cost depends on the price of the adsorbent and the regeneration of the adsorbent. Disposal of the polluted adsorbent is also an element that increases the cost. However, it is not correct to say that there is a big problem because there is a waste that needs to be disposed as solid or liquid in all treatment methods. In the calculation of operating cost, adsorbent, energy consumption and maintenance cost (with 2% acceptance of investment cost) were considered. When the cost of commercial activated carbon is taken as 0.8-1.1 \$ m^{-3} (according to optimum value 3 g L^{-1}), maintenance cost was calculated as 0.006 \$ m^{-3} (2% of investment cost). The cost of electricity was accepted as 0.133 \$ m^{-3} [26]. Thus, total operating cost was determined as 2.54 \$ m^{-3} and total cost (investment + operation) was determined as 2.85 \$ m^{-3}. PAC cost constitutes approximately 89% of the total cost and investment cost constitutes 11% of the total cost. Considering these data, it is very important to reduce the cost of adsorbent. Magnetic properties can be imparted to the PAC to eliminate the disadvantages such as difficult separation of the adsorbent from the water environment and a secondary pollution. If the adsorbent is magnetized (no necessary regeneration) or if new adsorbents can be produced more economically in commercial activated carbon properties (surface area, pore diameter, high stability, etc.), adsorption is a very economical method.

The adsorption process does not pose a great risk due to the simplicity of operation and no extreme operating conditions. Accidents that may occur during operation and spills, leakage during disposal of polluted adsorbents (especially if they contain hazardous contents) may pose a risk to human and environmental health. The burden of these methods (incineration, landfill) can also be increased with disposal by incineration or landfill of polluted adsorbents [27]. However, there is a waste generated/concentrated in each treatment process and management is required for this waste. The important thing is that the amount of waste is low. For this, much activated adsorbent or magnetic adsorbent should be preferred.

5. CONCLUSIONS AND RECOMMENDATIONS

In this study, the removal of phenol, which is a toxic substance and can cause negative effects on living organisms, by the adsorption method with PAC from water and the parameters affecting the adsorption process were investigated. It was determined that phenol was removed at high efficiency with PAC. Optimum operating conditions were determined as 0.3 g 100 mL^{-1} SWW (3 g L^{-1}), 10 min, and 100 mg L^{-1} phenol. It is found that it is suitable to Langmuir and Elovich isotherms for all temperatures, but it changes according to temperature for other isotherms. It is concluded from isotherm coefficients that adsorbent surface has homogeneous/same energy; adsorption occurs in one layer, interaction between pollutant-PAC is physical and adsorption occurs spontaneously. As a result of kinetic studies, it was found to be suitable for Pseudo Second Order kinetics (R^2>0, 99). As a result of thermodynamic calculations, enthalpy, Gibbs free energy and entropy change were determined to be negative (-). The negative (-) values of these thermodynamic coefficients show that the adsorption was applicable and physisorption; sorption reaction was exothermic/spontaneous; there was less structural change and less random adsorption.

Finally, adsorption is an effective method for phenol removal despite of some disadvantages (particularly adsorbent cost). Total cost (investment + operation) is determined as 2.85 \$ m^{-3}. PAC cost constitutes approximately 89% of the total cost and investment cost constitutes 11% of the total cost. The adsorption process is an important alternative that can be preferred for wastewater treatment, especially with the use of low cost adsorbents. Studies were conducted with inexpensive adsorbents or magnetic adsorbents which can be easily regenerated under different operating conditions (pH, effect of different ions, real wastewater, etc.).

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RESEARCH ARTICLE

The optimization of growth parameters in a anodic chamber of a microbial fuel cell

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ABSTRACT

The pollution is a result of drastically rising fossil fuel usage due to increased global population and industrialization. Today's world needs to replace fossil fuels with new and renewable energy sources. Microbial Fuel Cells (MFCs) are devices that convert the chemical energy to direct electricity by microbial metabolic activity. Microbial growth was actualized at the anodic chamber of MFC and must be controlled carefully by microbial methods. The main aim of this study is optimizing the growth parameters of microorganisms in two-chambered MFC with optical density, dried and wet weight of microorganisms that were grown at the anode chamber of MFC. Moreover, the Chemical Oxygen Demand (COD) values of medium were determined at fed cycles of MFC. The total volume of MFC was 0.7 L and the connection was made with the salt bridge between anode and cathode compartments. The anode chamber was used for bacterial growth that was taken from Akkaya Dam slime, was fed with molasses medium at 5 days intervals. The OD values were determined with a spectrophotometer at 600 nm, COD values were determined with the standard method and wet-dry weight also determined as a function of the incubation period.

Keywords: COD removal, growth parameters, microbial fuel cells (MFCs), microbial growth, q_m value

1. INTRODUCTION

The usage of fossil fuels has been increasing day by day, resulting in problems such as the greenhouse effect, global warming, and environmental pollution. Renewable and sustainable energy use is recommended as one of the most important solutions to get rid of the growing energy and environmental crisis. As a renewable energy source, alternative energy production methods are being investigated for electricity production through bacterial metabolism in microbial fuel cell and hydrogen cells. The main aim of microbial fuel cells (MFCs) is bioremediation of different wastes with microbial activity and during this process can provide electricity [1 – 9].

A biofuel cell is a device that directly converts the chemical bond energy to the electricity by microbial metabolism or enzymes. Chemical energy can convert the biocatalytic oxidation of organic or inorganic compounds into electrical energy by combining the oxidation of an oxidant at the interface between the anode and cathode. Microbial fuel cells are new biotechnological systems that use microorganisms as catalysts while converting the chemical bond energy directly into electrical energy. In addition to these obvious benefits, they are likely to be used for wastewater treatment during bioelectricity generation and are therefore one of the areas of interest for researchers [10 – 15].

The fermented or non-fermented organic compounds in MFC might affect the power production of MFC. In microbial fuel cells, the microbial community development changed by the substrate which was used in anodic chamber, directly. In addition, the substrate used in the fuel cell also changes the strength and columbic efficiency of MFCs. Many different carbon sources that have simple (glucose, acetate, butyrate) or complex structure (starch, food processing wastes, synthetic or real wastewater, etc.) would be used as substrate in MFCs. Molasses produced in the sugar production process; animal feed, green manure or various fermentation processes in industrial use with low cost is preferred as raw material. Decolorization or remediation of molasses is a very difficult process due to the molasses high organic matter content, biological and chemical oxygen demand and dark brown melanoid pigment. On the other hand, molasses might

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be used as organic substrate for supported microbial growth in anodic chamber of MFC [12, 13, 16 – 18].

The performance of MFCs (voltage or power generation, removal of pollutants) is affected by microbial growth in microbial fuel cells. The microbial growth is depended to bacterial culture, substrate, temperature, and MFC cell type and these factors affected power production in MFCs. In studies related to microbial fuel cells, COD monitoring should be performed in order to determine the power efficiency as well as the treatment rate of wastewater. In addition, the degradation of the substrate that used in MFCs and reducing the Chemical Oxygen Demand (COD) is depending on the microbial growth at the anodic chamber of MFC [10 – 15].

Microbial communities have direct relationship with the usefulness of the substrate, pollutant removal and electricity generation of a MFC. It is understood from the literature that the biomass and microbial growth analysis achieved importance because of determine quality and standard property of the microbial community. The most important parameter affecting COD removal rate is the structure of microbial community developing in MFCs [4, 13, 19, 22 – 24]. Researchers need to determine the microbial growth parameters because of usage in the MFCs. The main aim of this work is to determine the microbial growth parameters such as optical density and microbial biomass in the incubation period. Moreover, the wet and dry weight of the microbial community will be given information about not only biological conditions but also biodegradation or bioremediation capacity for organic substrates or organof the MFC. The COD removal of microbial culture in the anodic chamber of MFC also determined and the COD removal for a dry weight of microbial culture was calculated from COD values.

2. MATERIALS AND METHODS

2.1. Microbial growth medium

In the anode chamber, molasses was used to provide bacterial growth. In the anode and cathode chamber, a 50 mM phosphate buffer solution was used, and 0.13 g L^{-1} KCl was added to buffer to increase the conductivity of the solution. 50 mL L-1 of molasses solution was added to 1.0 g L^{-1} $(NH_4)_2SO_4$ and 0.5 g L^{-1} KH_2PO_4 50 mM 1 L phosphate buffer and the pH of the medium was settled at 7 [25]. In the cathode chamber, ferricyanide was used as the last electron acceptor to capture the electrons produced by the bacterial metabolism. 50 mM $[K_3Fe(CN)_6]$ was added to 50 mM 1 L phosphate buffer solution [12, 20].

2.2. Microorganism source and growth conditions

The sediment sludge of Akkaya Dam was used as an initial source of microorganism. The growth of microorganisms determined as a function of optical density and biomass. Incubation conditions were conducted with an orbital shaker. The MFC was mixed at 50 rpm shaker incubator at 35°C. The optical density values were measured with a spectrophotometer at 600 nm. The biomass weight values were determined as milligrams, microorganism biomass cleaned with saline solution three times and weighed by balance. After determining wet weight the samples were dried at 60°C for 24 hours and dry weight of samples weighed by balance [26].

2.3. MFC construction

In the study, glass MFC was used for voltage generation at total volume as 750 mL. 300 mL anode compartment was filled with molasses medium. The connection between anode and cathode compartment was made with a 150 ml salt bridge that was prepared with agar agar and a saturated KCl solution. The anode compartment fed with fresh molasses medium every 48 hours and sparged N_2 gaseous to ensure the anaerobic conditions [22].

2.4. Determination of chemical oxygen demand

The organic matter pollution was determined with the COD removal, which was determined with the standard potassium dichromate technique before and after the feeding of MFC at all the incubation period [21]. The ΔCOD referred to wasted COD and calculated by subtracting the COD values at the beginning and the end of the feeding period.

$$\Delta \mathrm{COD} = \mathrm{CODbeginning} - \mathrm{CODend} \quad (1)$$

The removed COD amount was calculated with the dry weight of microbial cells at the given formula for every feeding period [25].

$$qm = \frac{\Delta \mathrm{COD}}{\mathrm{Dry\ weight}} \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. The microbial growth parameters

The microbial growth parameters such as optical density, wet and dry weight of biomass were determined to decide about the usefulness of the microbial community for removal of pollutants or power generation in a MFC. In this work the microbial growth parameters obtained from the incubation period were shown in the graphs below. The obtained data and equations are used to determine microbial growth at five days intervals of the incubation period in the anodic chamber of MFCs. The charts below were showed the correlation between the optical density and wet weight (Fig 1), and optical density and dry weight (Fig 2) of the microbial community that was grown at the anodic chamber.

The increase of microbial growth was slow at first feeding periods, on the other hand after 4th feeding period the increase of microbial growth was determined fastly. The optical density increase determination is a good way to set the wet weight of microbial biomass (Fig 1).

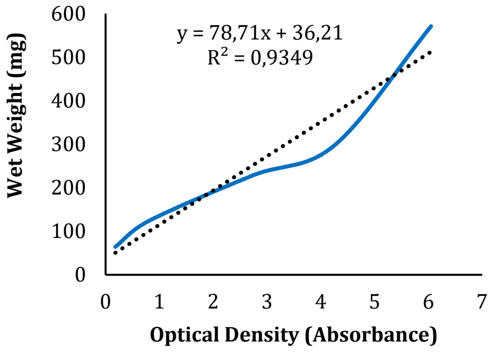


Fig 1. The optical density vs wet weight of biomass at 5 days interval feeding periods

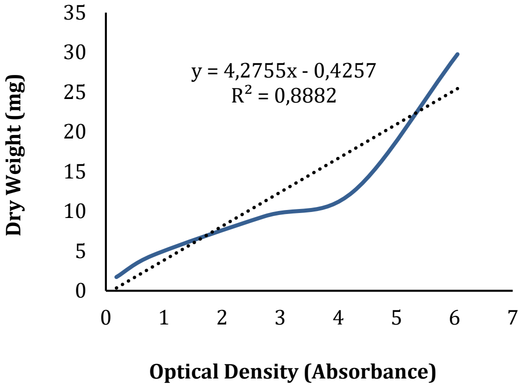
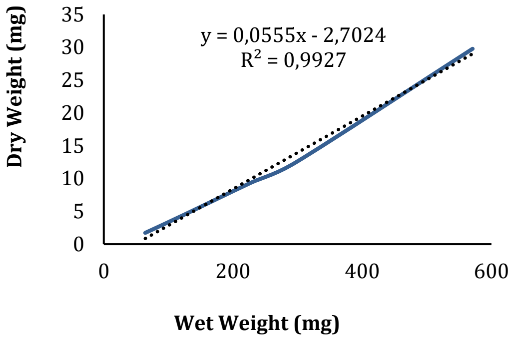


Fig 2. The optical density vs dry weight of biomass at 5 days interval feeding periods

As understood from the results mentioned at Fig 1 and Fig 2 that the microbial growth parameters could give information about biomass in the anode chamber and should be used for understanding the usefulness of the biomass for pollutant removal or power generation in MFCs. In Fig 1 and Fig 2, the determined correlations between optical density, wet and dry weights should be used for calculate the wet and dry weight values based on the increase in optical density for the microbial growth and biomass increase in anodic chamber of MFC.

Fig 3 is shown that the correlation with wet and dry weight of biomass at MFC. The correlation between wet weight and dry weight of microbial biomass was showed that the researcher could use the wet or dry weight of biomass interchangeably. The dry weight of biomass was depended to the wet weight of biomass directly and could be used for calculation of the pollutant removal rate per mg microbial biomass (q_m) with these values. Therefore, the optical density values could be used for calculations of biomass weights.



3.2. The relationship between dry weight of biomass and COD removal

In Table 1 the biodegradation of organic compounds was determined by COD decrease at the feeding cycle of the anodic chamber of MFC. The q_m (mg ΔCOD mg^{-1} dry biomass) value refers to the COD removal for 1 mg dry biomass. The q_m values were showed that the maximum COD removal was determined at the 5 days intervals at incubation period and the prolonged incubation did not increase the COD removal for bacterial weight.

The COD removal was demonstrated as ΔCOD, determined by the given formula at material and method section, at the beginning and end of feeding periods were determined as 1741 and 3305 mg at minimum and maximum level at 7th and 5th feeding periods sequentially. Moreover, the q_m values were calculated as 497 mg mg^{-1} and 1372 mg mg^{-1} as maximum and minimum level at 7th and 5th feeding periods.

Table 1. The ΔCOD, dry weight of bacterial cells and qm values at the different feeding periods at incubation period

Feeding cycle	ΔCOD (mg)	Dry Weight (mg)	q_m (mg mg^{-1})
1	2021	2.64	766
5	2496	2.54	983
10	2903	2.76	1051
15	2931	2.67	1096
20	3305	2.41	1372
25	2068	2.65	780
30	1741	3.50	497

4. CONCLUSION

Industrialization has increased rapidly to meet the needs of the growing population and society. A large portion of domestic and industrial energy is derived from fossil fuels. The use of fossil fuels has been increasing day by day, resulting in problems such as greenhouse effect, global warming and environmental pollution. Fossil fuels are expected to run out in the near future. As a renewable energy source, alternative energy production methods such as electricity production through bacterial metabolism, microbial fuel cell and hydrogen cell are being investigated. Microbial fuel cells are new biotechnological systems that use microorganisms as catalysts while converting the chemical bond energy directly into electrical energy. Microbial fuel cells can generate energy at low costs and at the same time produce very little sludge waste. There are many factors affecting bacterial growth and thus electricity production in microbial fuel cells. Bacterial culture, substrate, mediator compound and MFC cell type used are the most important factors affecting power production in MFCs. As it understood from results above mentioned that the microbial growth parameters could give some information about biomass in the anode chamber. On the other hand, researchers must have to define the microorganisms that are found in microbial community.

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RESEARCH ARTICLE

An investigation on the application of CaII-FeII-FeIII magnetic hydrotalcite-like-compounds for the removal of impurities in aqueous systems

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ABSTRACT

The main aim of this study is to investigate the feasibility of utilizing novel hydrotalcite-like-compounds as ion-exchangers for the removal of anionic impurities from aqueous solution. Hydrotalcite is naturally occurring, rarely found anionic clay. It has a positively charged layered structure consisting of two metal oxide layers and an interlayer of carbonate anions. Hydrotalcites can, therefore, be used as ion-exchangers. However, the carbonate anion is highly selected by natural hydrotalcite, making the ion-exchange capacity for other anions very low. In this study, several synthetic hydrotalcite-like compounds and a magnetic hydrotalcite-like compound samples were prepared in order to remove anionic impurities from waters. The physical structure and chemical properties of these anionic clays were characterized using standard characterisation techniques. The removal capacities of the synthetic products obtained were then investigated. Magnetic hydrotalcite-like-compound, namely, CaII-FeII-FeIII, was proved to be a good ion-exchanger.

Keywords: Double hydroxides, clay characterization, anionic impurities

1. INTRODUCTION

Hydrotalcite is naturally occurring, rarely found anionic clay. It has a positively charged layered structure consisting of two metal oxide layers and an interlayer of carbonate anions. The structure of hydrotalcite has been investigated by a number of researchers. Allmann [1] and Taylor [2] reported the structure of hydrotalcite by as $Mg_6Al_2(OH)_{16}CO_3.4H_2O$. Hydrotalcite has a layered structure consisting of CO_3^{2-} anions sandwiched by two metal layers [3]. The structure of hydrotalcite is very similar to the naturally occurring form of magnesium hydroxide ($Mg(OH)_2$) known as brucite. Because of its layered form, it is also called a 'Layered Double Hydroxide' (LDH). Natural hydrotalcite (Mg^{2+} and Al^{3+} as cations) is a member of LDH group of minerals [4, 5], which can be typified by the minerals pyroaurite and sjögrenite (Mg^{2+} and Fe^{3+} as cations) [6-8].

Normally, hydrotalcite stays neutral, however, randomly divalent ions (Mg^{2+}) are substituted by trivalent ions (Al^{3+}) generating positively charged layers [9]. These layers can be called host layers. This positive charge is compensated by CO_3^{2-} anions and water molecules between the two metal layers. The interlayer can be named as a guest layer because of its ion-exchange properties. Water molecules in the interlayer have hydrogen bonds with both carbonate anions and metal sheets [10].

Synthetic hydrotalcite-like compounds have been widely investigated since 1970s. Recently, there is a growing interest for the use of hydrotalcite-like compounds in the removal of aquatic inorganic and aromatic pollutants [11-13]. The general formula of hydrotalcite-like compounds is given as $[M^{2+}M^{3+}(OH)_2]^+ \times [A^{n-}.mH_2O]$ where A represents an exchangeable anion such as CO_3^{2-}, SO_4^{2-}, NO_3^- or Cl^-, having a valence of n [14, 15]. The divalent metal ion could be Mg^{2+}, Ca^{2+}, Zn^{2+} or Ni^{2+}, and the trivalent metal ion Al^{3+}, Fe^{3+} or Cr^{3+}.

The ratio of divalent metal ion to trivalent metal ion differs according to the mineral, but, in general,

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minerals belong to the pyroaurite-sjögrenite group have a ratio of 3:1 [6]. When made synthetically, M(II)/M(III) ratio could take values between 1.0 to 4.0 [16, 17].

Due to the positively charged structure of hydrotalcites, the interlayer carbonate anion can be exchanged with other anions. Hydrotalcites can, therefore, be used as ion-exchangers. However, the carbonate anion is highly selected by natural hydrotalcite, and the access to the interlayer region by other anions is restricted [18]. Hydrotalcite-like compounds that are prepared carefully under a CO_3^{2-} free environment can show significant anion-exchange capacities [19]. Jones and Chibwe [20] and Carlino [21] have reported anion-exchange capacities up to 4.1 meq g^{-1}. Therefore, compared to natural cation exchangers with cation-exchange capacities of 0.7 to 1.0 meq g^{-1} [21, 22], hydrotalcite-like compounds generally have a higher ion-exchange capacity. Numerous hydrotalcite-like-compounds have been synthesized so far in order to remove inorganic [13, 23, 24] or organic impurities [25-28] in aqueous solutions.

The magnetic CaII-FeII-FeIII type hydrotalcite-like clay mineral was synthesized in this study, in order to investigate the feasibility of utilising these derived products as an ion-exchanger, and for the easy removal of this product from the batch tank, as these clay minerals have too small particle sizes to settle with their own velocity.

2. MATERIALS AND METHODS

2.1. Synthesis of hydrotalcite-like compounds

For the preparation of hydrotalcite-like compounds, the method used by Reichle [29] was employed with slight modifications. The reason to synthesize hydrotalcite-like clays was because of hydrotalcite's selectivity for the carbonate ion. In this study, three different hydrotalcite-like compounds and one magnetic hydrotalcite-like compound have been synthesized. In these compounds, the divalent metal ion was Mg^{2+}, Ca^{2+}, Fe^{2+}, the trivalent ion was Al^{3+} or Fe^{3+} and the interlayer anion was Cl^- ion. In this paper, the hydrotalcite-like compounds were named in the form of "A-B-C", where A is the divalent metal ion, B represents the trivalent metal ion and C is the original interlayer anion.

For the synthesis of Mg-Al-Cl, a mixture of 3 M $MgCl_2 \times 6H_2O$ and 1 M $AlCl_3 \times 6H_2O$ was prepared outside the reactor. This solution was added dropwise to 4 M NaOH while the mixture was stirred vigorously using a mechanical stirrer. The temperature was kept around 35 °C during mixing. The mixing lasted around 30 minutes and the pH of the reaction mixture was adjusted to 8.5. The sample was then aged for 18 hours at 65 °C in a water bath. After ageing, the slurry was washed repeatedly using boiled cooled distilled water until it was free of ions. The slurry's initial conductivity was 10 µS, and this was reduced to approximately 0.05 µS. The sample was then dried at 110 °C in an air oven. The white powder-like product was ground and stored in an air-tight sample container in a desiccator.

The synthesis procedure of Ca-Al-Cl was exactly the same with the synthesis of Mg-Al-Cl, except 3 M of $CaCl_2 \times 6H_2O$ was used instead of 3 M $MgCl_2 \times 6H_2O$. Likewise, the synthesis procedure of Ca-Fe-Cl was exactly the same with Ca-Al-Cl. This time the trivalent metal ion was changed to Fe^{3+} using $FeCl_3 \times 6H_2O$ instead of $AlCl_3 \times 6H_2O$.

2.2. Synthesis of magnetic hydrotalcite-like compound

As the name implies, synthetic magnetite (Fe_3O_4) or magnetic floc which has a standard formula of AB_2O_4 has been used in the water treatment processes as a coagulant [30]. The letters A and B represents ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions, respectively. The advantage of magnetic floc over the common coagulants (e.g. $FeCl_3$, $FeSO_4$, etc.) is that it can be recovered easily from solution by means of a magnetic separator.

In order to obtain a hydrotalcite-like compound with magnetic properties, equal amounts of ferric and ferrous salts were mixed and the pH was adjusted to 11.0 using NaOH. 3 M of $CaCl_2 \times 6H_2O$, 0.5 M $FeCl_2 \times 4H_2O$ and 0.5 M $FeCl_3 \times 6H_2O$ were mixed and added into 4 M NaOH solution. The rest of the synthesis procedure was kept the same as Ca-Al-Cl. In order to measure magnetism, the magnetic attraction factor was measured and found as 0.95 which was very close to 1.

2.3. Characterisation methods

Zeta Potential Analysis

In order to determine the sign charges of the clay mineral particles, Zetasizer 4 (Malvern Instruments) was used. To measure the zeta potential values of the clay samples, 0.25 g of clay sample was suspended in 250 mL 0.01 M KNO_3 solution. This suspension was then homogenized in an ultrasonic bath for 20 minutes. The pH adjustments were done using KOH and HNO_3 solution at different concentrations. The readings were recorded at pH values from 2 to 12.

X-Ray Diffraction Analysis, XRD

X-ray diffraction is used to obtain information about the structure and the degree of crystallinity of clay samples. The samples were scanned by a Philips PW1830 diffractometer system using Cu K radiation. The diffractometer was fitted with a PW1820 goniometer, an automatic divergence slit and a graphite monochromator. All the samples were scanned over the angular range 1.6° – 40° 2θ at 0.15° per second.

Nitrogen Adsorption Analysis, BET

This is a standard procedure for the determination of the surface area of finely divided and highly porous materials. By determining the nitrogen adsorption and desorption isotherm of the porous materials, information such as their BET surface area, pore size and microporosity can be obtained. Approximately 0.1- 0.2 g of the samples, previously dried in oven at 110 °C, were degassed at 150 °C at a constant pressure for 3-4 hours and the isotherms were recorded at 77 K. The nitrogen adsorption and desorption isotherms of the samples were recorded on an ASAP 2000 Micromeritics apparatus.

Particle Size Analysis

The particle sizes of hydrotalcite-like compounds and their derivatives were determined using a Malvern Instruments-1200 Particle Sizer and Analyser.

2.4. Data treatment

A plot of concentration on the adsorbent against equilibrium concentration in the solution at constant temperature is referred to an isotherm. A number of isotherms are available to describe adsorption behaviour. However, there are three common isotherms used for adsorption, which are the Langmuir, Freundlich and BET isotherms. The isotherms for adsorption from aqueous media generally follow a monolayer adsorption isotherm, although under some conditions multilayer adsorption has been encountered [31]. The monolayer adsorption isotherms have also been used to describe the ion-exchange behaviour of anions. The Langmuir model has been used for phosphate [32], chromate [33] and heavy metal [34] removal using ion-exchangers. The Langmuir isotherm can therefore be defined as one of the classic adsorption isotherms used for ion-exchange correlations. The Langmuir isotherm assumes two hypotheses which are (1) adsorption is on a monolayer (i.e. there is a fixed number of accessible sites on the adsorbent) and (2) adsorption is reversible. Only when the rate of adsorption of molecules on to the surface is the same as the rate of desorption of molecules from the surface, equilibrium is reached. The Langmuir isotherm corresponds to monolayer adsorption and is expressed as follows (Eq. 1);

$$q = \frac{Q^{\circ} b C_{eq}}{1 + b C_{eq}} \qquad 1)$$

In this equation q is the concentration of the species on the adsorbent (mg g^{-1}), C_{eq} is the equilibrium concentration of solution (mg L^{-1}) and Q° and b are the Langmuir constants. Q° represents the saturation concentration of adsorbed species on the adsorbent, i.e. maximum monolayer adsorption capacity. The Langmuir constant b is related to the enthalpy of adsorption. Calculating this constant is important because it represents the binding strength of the adsorbent. The isotherm equation can be rearranged as seen in Equation 2.

$$\frac{1}{q} = \frac{1}{Q^{\circ}} + \frac{1}{bQ^{\circ}} \times \frac{1}{C_{eq}} \qquad (2)$$

Plotting 1/q against $1/C_{eq}$ should give a straight line with a positive intercept. By using the gradient and the intercept on y-axis the Langmuir constants Q° and b can be calculated.

2.5. Experimental procedure

All batch-technique experiments were carried out in 500 mL conical borosilicate glass flasks. All chemicals were supplied by BDH Chemicals Co. Ltd. in analytical reagent grade and were used without further purification. The adsorbate solutions were prepared with de-ionized water. The stock solutions (1 M) were prepared and stored accordingly. Necessary dilutions at a different range of concentrations (10-300 mg L^{-1}) were prepared prior to the experiments and a control sample was also prepared. A known amount of adsorbent, 0.1 (for chromate) or 0.25 g (for permanganate), was weighed carefully and placed in conical flasks containing solution at desired concentration. The sample solutions were then contacted with adsorbent for 18 hours. The ambient temperature was kept at 16-17 °C. The suspensions were centrifuged at 3500 rpm for 20 minutes in order to separate the adsorbent from the slurry. It should be noted that 0.1 g of adsorbent is equivalent to approximately 2000 particles of hydrotalcite, except for samples with magnetic property, where 0.1 g of adsorbent is equivalent to approximately 1500 particles. Hydrotalcite's and magnetite's densities were reported to be 1.929 and 5.197 g cm^{-3}, respectively [35]. Since a large number of particles were taken for the experiments, there is a low error due to sampling. Perkin-Elmer 1100B AAS (Atomic Absorption Spectrometry) was used to determine chromium and manganese concentrations.

3. RESULTS AND DISCUSSION

3.1. Characterisation results

The electrophoretic curves of hydrotalcite-like compounds and modified hydrotalcite were given in Fig 1. All samples showed anion exchanger behaviour with an obvious trend. Zeta potential values decrease with an increase in pH, indicating higher anion exchange capacities at lower pH. It should be noted that there is little variation in the zeta potential for the Mg-Al-Cl clay for a range of pH values. Modified hydrotalcite showed very good potential of anion exchange behaviour at low pH, however it apparently loses its anion exchange properties above pH 7.

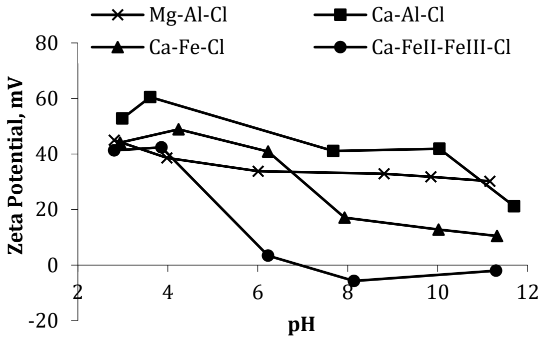

Fig 1. Zeta potential of hydrotalcite-like compounds

A summary of XRD analysis results of hydrotalcite-like compounds can be found in Table 1. The XRD analysis result of synthetic hydrotalcite was also given in this section for comparison purposes. The spacing of $d_{(003)}$ plane for synthetic hydrotalcite is 7.65 Å, which is in good agreement with synthetic hydrotalcites prepared by other researchers. The $d_{(003)}$ spacing of natural hydrotalcite was reported to be 7.67 Å [16]. The lattice parameters (a_o and c_o) of synthetic hydrotalcite can be calculated using the $d_{(003)}$ and $d_{(110)}$ reflections. The angular position of the first peak, $d_{(003)}$, gives an approximate value for the inter-lamellar distance ($c_o = 3 \times d_{(003)}$), and the $d_{(110)}$ peak situated around 60° allows the estimation for the cell dimension, a_o, which is related to the metal-metal inter-atomic distance within sheet ($a_o = 2 \times d_{(110)}$) [36].

The X-ray diffractogram of synthetic hydrotalcite (Mg-Al-CO_3) showed very narrow peaks, indicating a good degree of crystallisation. The (003), (006), (110) and (113) reflections represented a symmetrical pattern, however (003) and (006) peaks were higher and sharper compared to other reflections, which indicated a stacked layer structure. The (102), (105) and (108) reflections were broad and asymmetric which typified hydrotalcite phases. The XRD spectrum of synthetic hydrotalcite was used as a reference spectrum.

The XRD diffractogram of Mg-Al-Cl represented a very similar pattern to synthetic hydrotalcite, however it was noted that $d_{(003)}$ and $d_{(006)}$ facings were broader compared to the pattern of synthetic hydrotalcite. When the XRD patterns of Ca-Al-Cl and Ca-Fe-Cl type clay samples were observed, it was seen that there were many peaks. These peaks were investigated using X-ray diffractogram database software. When these peaks related to hydrotalcite, phases were eliminated by the computer programme. It was seen that there were peaks showing $CaCl_2$, $Ca(OH)_2$, $AlCl_3$, $Al(OH)_3$ and $FeCl_3$ attached to the surface of the clay samples, resulting a loss of crystallinity. These peaks for $Ca(OH)_2$ and $Al(OH)_3$ indicated that co-precipitation might occur on the surface of the clay samples during the removal of anionic impurities from water. It was also noted that Ca-Al-Cl and Ca-Fe-Cl samples were not as crystalline as Mg-Al-CO_3 or Mg-Al-Cl samples. The XRD diffractogram of magnetic hydrotalcite-like compound did not exhibit hydrotalcite phase, but magnetite (Fe_3O_4) phase with a distinctive peak at the (111) position.

Nitrogen adsorption analysis was used to determine BET surface area, pore size and porosity of clay samples. Fig 2 shows the average pore diameter of the clay samples. As can be seen from Fig 2, the hydrotalcite-like compounds have surface areas close to each other, except Mg-Al-Cl. Differences in the surface areas between the hydrotalcite-like compounds is due to the divalent metal ions used during the synthesis. For instance, the Ca^{2+} ions have higher ionic radii compared with the Mg^{2+} ion resulting in a lower BET surface area. The effective ionic radii (r_{eff}) of some ions can be seen in Table 2. The larger sized ions occupy a greater volume of the clay surface leading to lower BET surface areas [37]. It was observed that as surface area decreased, the average pore diameter increased for the samples synthesized. The average pore diameter of modified hydrotalcite-like compounds with a magnetic property was larger compared to other hydrotalcite-like compounds.

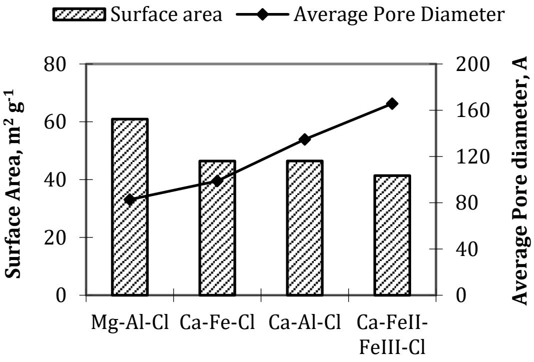

Fig 2. The surface area and average pore diameter of hydrotalcite-like compounds

Table 1. A summary of XRD results for synthetic hydrotalcite and hydrotalcite-like compounds

Compound Name	X-ray Angle (°2θ)	$d_{(003)}$ (Å)	X-ray Angle (°2θ)	$d_{(110)}$ (Å)	c_o (Å)	a_o (Å)
Mg-Al-CO_3	11.3	7.65	60.6	1.53	23.0	3.06
Mg-Al-Cl	11.3	7.67	60.5	1.51	23.0	3.02
Ca-Al-Cl	11.3	7.81	60.5	1.53	23.4	3.06
Ca-Fe-Cl	11.4	7.79	60.5	1.52	23.4	3.04

$c_o = 3 * d_{(003)}$; $a_o = 2 * d_{(110)}$

Table 2. Ionic radii of some metal ions and anions [40]

Ion	Mg^{2+}	Ca^{2+}	Al^{3+}	Fe^{2+}	Fe^{3+}	Cl^-
Ionic radius, pm	86	114	68	92	79	22

The particle size tests were conducted with a lens which could measure particles with a size less than 188 μm. According to cumulative under size curves, most of the samples were under 3 μm. The results have also shown that most of the particles were in the range of 1.0-3.0 μm (Table 3). It has been reported that there is an inverse relationship between particle size and surface area [38] and the results confirm this statement. It can be seen that an increase in the particle size resulted in lower specific surface areas.

Table 3. The mean diameters and specific surface areas of hydrotalcite-like compounds

Compound name	Mean diameter, µm	Specific Surface Area, m^2 cm^{-3}
Mg-Al-Cl	1.19	0.36
Ca-Al-Cl	2.50	0.69
Ca-Fe-Cl	2.45	0.42
Ca-FeII-FeIII-Cl	2.70	0.44

3.2. *The ion-exchange experiments*

The ion-exchange experiments were carried out using permanganate and chromate solutions. Permanganate can be found in the effluents of several industries. Permanganate ion needs to be removed from waters for aesthetic reasons because it is a strongly coloured ion. The other reason for selecting this ion was that permanganate salts are usually soluble and non-hydrolysable which can be used for ion-exchange capacity determinations. As it is known, strontium is a stable ion used in the determination of the capacity of cationic clays. The permanganate ion was used as its counterpart. The only disadvantage of permanganate ion is that it can be easily oxidized in strong light and is slightly unstable. Unlike potassium permanganate solutions, potassium dichromate solutions are generally stable. However, chromates exist in two different ionic states. These ionic states can occur between pH 0 and 7.3 as dichromate and between pH 7.3 and 14 as chromate [39]. Unfortunately, both states can be encountered in aquatic systems. During the experiments, the pH of the solution varied from 5.1 to 5.6 and 7.0 to 8.2 for $K_2Cr_2O_7$ and $KMnO_4$, respectively. The pH measured for $K_2Cr_2O_7$ solution indicated that dichromate was the dominant ion in the solution. The initial pH of the $KMnO_4$ solution increased to above neutral values during the ion-exchange process.

During the experiments, the pH of the solution varied from 5.1 to 5.6 and 7.0 to 8.2 for $K_2Cr_2O_7$ and $KMnO_4$, respectively. A comparison of adsorption isotherms for hydrotalcite-like compounds can be seen in Fig 3 and Fig 4. The data obtained from the contact tests appear to correlate well with Langmuir model. The transformed data for all the samples gave a straight line with small error, R^2 (>0.995). For MnO_4^- solution, Ca-Al-Cl showed the lowest capacity compared to other clay samples used. Although effective removal capacities were achieved with Mg-Al-Cl and Ca-Fe-Cl, the highest uptake was attained when the Ca-FeII-FeIII-Cl was used.

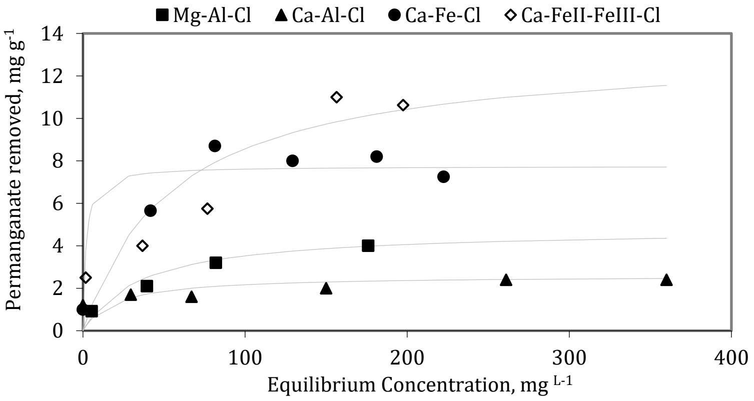

Fig 3. Adsorption isotherm plots of permanganate for different hydrotalcite-like compounds

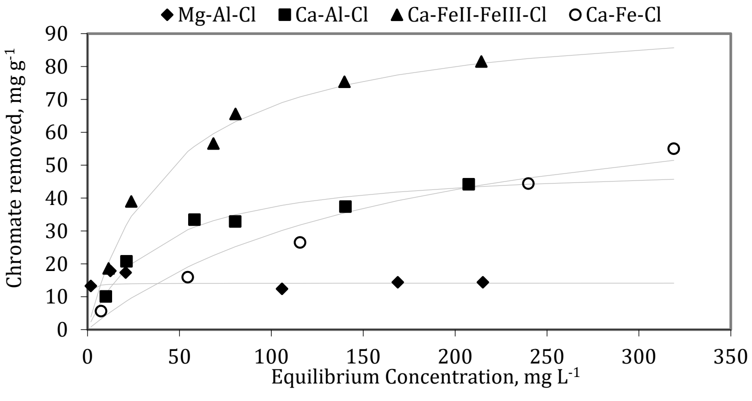

Fig 4. Adsorption isotherm plots of chromate for different hydrotalcite-like compounds

For $Cr_2O_7^{2-}$ solution, quite similar results were obtained. While Mg-Al-Cl showed the lowest adsorption capacity, Ca-Al-Cl and Ca-Fe-Cl uptake rates were close to each other, with around 40 mg g^{-1} capacity. However, as expected, the highest uptake was attained when the Ca-FeII-FeIII-Cl was used. All the results are presented in Table 4. The main reason for the highest uptake of the analytes on the Ca-FeII-FeIII-Cl was due to co-precipitation on the surface of the clay samples. Although the crystallinity of the magnetic hydrotalcite-like clay was lower compared to the other samples prepared, it showed anion exchange capacities.

Table 4. The ion-exchange experimental results

Solution	Ion-exchanger	Q°, mg g^{-1}	Q°, meq g^{-1}	b, L mg^{-1}
MnO_4^-	Mg-Al-Cl	4.70	0.04	0.028
	Ca-Al-Cl	2.51	0.02	0.053
	Ca-Fe-Cl	7.76	0.07	0.550
	Ca-FeII-FeIII-Cl	13.33	0.11	0.018
$Cr_2O_7^{2-}$	Mg-Al-Cl	14.14	0.07	0.090
	Ca-Al-Cl	50.25	0.23	0.027
	Ca-Fe-Cl	78.74	0.37	0.006
	Ca-FeII-FeIII-Cl	98.04	0.45	0.023

4. CONCLUSIONS

An investigation on CaII-FeII-FeIII hydrotalcite-like-compound for the removal of impurities in water was carried out in this study. The results of zeta potential analysis gave an indication of anion-exchange properties for the hydrotalcite-like compounds synthesized. The diffractograms obtained from XRD analysis of hydrotalcite samples indicated fairly good crystallinity and all hydrotalcite-like compounds analysed, except the one with magnetic properties, were identified as hydrotalcite structures. However, modified hydrotalcite-like compounds did not exhibit hydrotalcite phases. It has been found that hydrotalcite-like compounds have lower surface areas compared to synthetic hydrotalcite given in literature.

The overall results indicated that hydrotalcite samples prepared are able to remove anionic impurities from water. The above findings demonstrated that magnetic hydrotalcite sample (CaII-FeII-FeIII) have significantly higher capacity compared to the other hydrotalcite-like compounds prepared. Among the hydrotalcite-like compounds, Ca-Fe-Cl is the most cost-effective sample. However, magnetic hydrotalcite, CaII-FeII-FeIII, was also proved to be a good ion-exchanger. Due to easy removal of magnetic hydrotalcite by means of a magnetic separator, this anionic clay would a good material for further study.

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REVIEW ARTICLE

The overview of mechanical properties of short natural fiber reinforced geopolymer composites

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ABSTRACT

In the EU there is a pressing need for the change of the current economy into a so-called circular economy in recent years. The rational management of natural resources and the use of waste materials are becoming more and more important. It is also supported by the growing ecological awareness of society, including the consciousness of sustainable development. Nowadays, it is the construction industry that has the most significant impact on pollution. Therefore, numerous attempts are made to reduce energy consumption and the amount of waste generated by it. These are the main issues stimulating the research on new innovative materials such as geopolymer composites. They have a significantly lower carbon footprint than traditional construction materials. Moreover, the synthesis of geopolymers requires 2-3 times less energy than traditional Portland cement, not to mention the fact that 4-8 times less CO_2 is generated. In addition, the above process has another environmental benefit i.e. the possibility of using anthropogenic raw materials (minerals) such as slags and fly ashes for the production. One of the limitations for the wide use of such materials is their relatively low brittle fracture behaviour. Nowadays, one of the most important research areas is the improvement of their mechanical properties. To improve the mechanical properties it is possible to reinforce the matrix by fibres addition, especially natural fibres that are renewable resources. The main objective of the article is to analyse the mechanical properties of new composites and assessment the possibility to replace traditional building materials within eco-friendly alternatives.

Keywords: Composite, geopolymer, natural fibre, short fibre

1. INTRODUCTION

In the EU there is a pressing need for the change of the current economy into a so-called circular economy in recent years. The rational management of natural resources and the use of waste materials are becoming more and more important. It is also supported by the growing ecological awareness of society, including the consciousness of sustainable development. Nowadays the construction industry has the most significant impact on pollution. Therefore, numerous attempts are made to reduce energy consumption and the amount of waste generated by it. These are the main issues stimulating the research on new innovative materials [1, 2].

The current technology of Portland cement, developed in the 20th century, has many disadvantages. First of all, the durability of this material is questioned in many scientific studies. At the same time, its production has an adverse environmental impact, which includes both the emission of a very high amount of CO_2 and highly toxic nitrogen oxides as well as the overwhelming consumption of energy and natural resources [2, 3]. Significant energy consumption is associated with high temperature (between 1400 and 1500°C) necessary to carry out the clinker burning process. This process hardly belongs to the technologies that support the sustainable development economy [2, 4].

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The most promising alternative solutions are technologies based on alkali materials and geopolymers [5, 6]. Such technologies have a significantly lower carbon footprint than traditional construction materials. It is estimated that the production of one ton of cement is accompanied by a release of nearly a ton of CO_2 to the atmosphere. The synthesis of geopolymers requires 2-3 times less energy [1, 7], not to mention the fact that 4-8 times less CO_2 is generated. In addition, the above process has another environmental benefit i.e. the possibility of using anthropogenic raw materials (minerals) such as slags and fly ashes for the production. Modern energy, mining, and metallurgical industries produce huge amounts of post-processing waste whose deposition may cause serious ecological problems related to soil and water contamination. The geopolymer synthesis enables one to use such waste as a raw material for manufacturing new products in low energy and low emission processes [1, 3].

However, it should be noted that geopolymers are much more than environmentally friendly materials. They exhibit notable properties as construction materials. Apart from significant chemical and thermal resistance, they have excellent mechanical properties, in particular, compressive strength [8, 9]. Their main advantages are: high initial strength [10], [11], low shrinkage and dimensional stability during the production process [12, 13], good fire resistance up to 1000°C and lack of emission of toxic fumes during the burning process [14, 15], high resistance to a wide range of acids and salts [10, 16], including resistance to different environmental conditions [17], [18], good abrasion resistance [19], good adhesion to concrete, steel, glass, and ceramics [8], easiness of subjecting them to surface mapping, duplication of mould patterns [8, 12], no corrosion of steel reinforcement inside the geopolymer matrix [17], [18], availability of necessary raw materials and their cost-efficiency, including the possibility of producing geopolymer materials based on wastes such as fly ash from industrial combustion [20, 21], the possibility of immobilizing hazardous waste by enclosing it in geopolymer composites [22, 23].

One of the limitations for the wide use of such materials is their relatively low brittle fracture behaviour and their relatively low tensile and flexural strength [5, 24]. Contemporary, one of the most important research area is improving this mechanical properties by reinforce the matrix trough fibres addition [2, 3]. In mechanical point of view the reinforcement by fibres is an efficient method to improve such mechanical properties as fracture toughness. The presence of fibres reduces the general effects of cracking, limits the widths of the occurring cracks (for example reduction of the propagation of microcracks), suppresses all brittle behaviour and enhances ductility [3, 5]. It also increases the flexural strength of composites. The fibres can also improve those properties of geopolymers that are connected with their energy absorption and resistance to deformation [25, 26]. The most common additives for the composites are: fabric, long fibres (usually directional) and short fibres (usually unidirectional) [3].

Nowadays, the geopolymers reinforced by fibres are fast growing topic of research. On the Fig 1, there are presented the fibres that have been tested as a reinforced for geopolymer composites [2].

In the environmental point of view, the addition of natural fibres will be especially beneficial [2, 5]. The replacement of the synthetic fibres with their natural counterparts reduces significantly the environmental impact (closing important life cycles, including CO_2). The natural fibres have also other features such as [27-29]:

- low cost of production,
- low density,
- they are usually renewable in short time,
- non-toxic,
- easy to process.

The main objective of the article is to analyse the possibilities of using new composites in practical applications, especially taking into consideration the mechanical properties. The article presents the mechanical properties of new composites and assesses the possibility to replace traditional building materials within eco-friendly alternatives.

2. RESEARCH METHODOLOGY

The research was focused on natural fibres, such as: plants, animal and mineral one. The research was conducted with scientific articles databases such as ScienceDirect, Scopus and Google Scholar. The research was focused on geopolymers, inorganic polymers and alkali-activated materials, taking into consideration their mechanical properties. During research keywords such as: “natural fibres reinforced geopolymer” and “geopolymer composites with natural fibre” were used. Next the additional search phrases were applied. They were connected with particular kind of fibres, exemplary “flax fibres”. Additional information for articles based on contemporary conducted research in the framework of project supported by the ERANet-LAC 2nd Joint Call (http://www.eranet-lac.eu) and funded by National Centre for Research and Development, Poland, the Romanian National Authority for Scientific Research and Innovation, CCCDI – UEFISCDI, project number ERANET- LACFIBER 17/2017, within PNCDI II and the Türkiye Bilimsel ve Teknolojik Araştırma Kurumu (TÜBİTAK), under grant: “Development of eco-friendly composite materials based on geopolymer matrix and reinforced with waste fibers”.

2.1. Cellulose / Lignocellulose fibres

Among natural fibres, the most common are different types of plant fibres based on cellulose and lignocellulose. On a global scale, there are currently about 2,000 species of fibre plants, of which around 1,000 are currently used [3, 30].

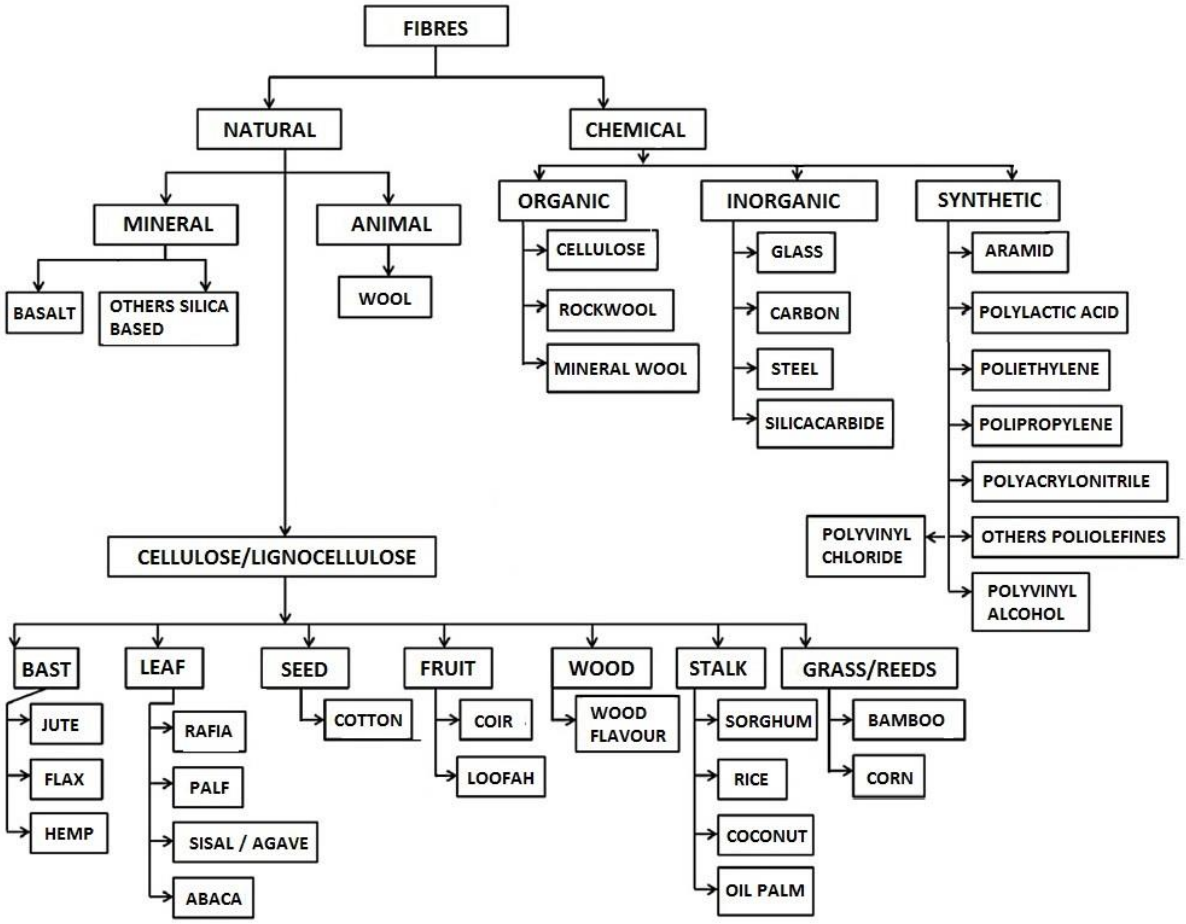

Fig 1. Classification of fibres used for reinforcment the geopolymer composities [2]

A lot of research work connected with geopolymers reinforced by cotton fibres has been conducted in years 2013-2014. The cotton was introduced to geopolymer matrix based on fly ashes (class F, collected from the Collie power station in Western Australia), as a short fibres as well as fabric layers [28, 31]. The results show that the content of cotton fibres up to 0.5 wt% increases the compressive and flexural strength, as well as fracture toughness of the materials. The content more than 0.5 wt% caused a decrease in the mechanical properties due to poor workability (mainly voids formation caused by poor dispersion of fibres within the matrix) and fibre agglomerations. [32, 33]. The other works with the short cotton fibres reinforced geopolymers based on fly ash from Skawina, Poland were conducted. They show that 1% of fibre addition improves mechanical properties in comparison with geopolymers without admixture [5]. The research with cotton fabric shows optimum value of fibre addition 2.1 wt% according to mechanical properties of the composite [33, 34]. However the mechanical properties can decrease as a result of water absorption [35]. The research results also show the dependence of properties on the fabric layers orientation [32]. The thermal stability of this kind of composites was also investigated. They have stable properties in elevated temperature thanks to geopolymer matrix [34, 36].

Other popular fibre for application in composites dedicated for construction purposes is abaca, called also as manila hemp. This fibre has very good mechanical properties [37]. The research was connected with the utilization of scrap abaca fibre as reinforcement (long fibre ca. 25 cm) for fly ash-based geopolymer matrix (fly ash from power plant situated in Luzon, Philippines). The research was focused on the abaca fibres to geopolymer matrix. The results show that proper pre-treatment of the fibre significantly increases the mechanical properties of the composites [37].

The research was made also on sisal fibres (Agave sisalana). The two types of geopolymers based on metakaolin [38] and fly ash [5, 39, 40] were manufactured. The metakaolin based matrix was reinforced by 3 wt% sisal fibres (25 mm length). The results show significant improvement of the mechanical properties in comparison with matrix without fibre addition [38]. The other research has been performed based on geopolymer based on fly ash from Satpura Thermal power station Sarni, District-Betul [40]. The short sisal fibres (length ca.1 cm) were added in the amount of 0.5, 1, 1.5, 2, 2.5 wt%. The best results for mechanical properties were obtained for 2 wt% [40]. The investigation for short sisal fibres was also conducted for geopolymers based on fly ash from Skawina, Poland [5, 39]. The results show that 1 wt% fibre addition improves mechanical properties [5, 39].

Correia et al. [38] also investigated pineapple leaf as a waste product of pineapple cultivation as a potential additive to geopolymer composites. The metakaolin based matrix was reinforced by 3 wt% leaf fibres (25 mm pineapple length) [38]. The results show that mechanical properties increases. Although the tests results for samples with pineapple leaf fibres are lower than the ones with sisal one [38]. Other research was made on geopolymer matrix based on fly ash class-C reinforced by short fibre (ca. 5.0 mm) - 0, 0.2, 0.4, 0.6, 0.8 and 1.2 wt% [41]. The results show that addition the pineapple fibres improves the compressive and flexural strength of the composites and do not change the nature of geopolymers as a fire or acid resistance material [41].

Contemporary, the flax is one of the most popular fibres used as an additive to geopolymer matrix. The research was made on different matrix based on i.a.: dehydroxylated kaolinite-type clay (New Zealand halloysite - Imerys Premium grade) [42], low calcium fly-ash (from the Eraring power station in NSW) [43], [44], fly-ash with nano-assitions [45, 46]. The flax fibres were added in amount: 4-10 wt%. The research results pointed improving mechanical properties by fibre addition, especially flexural strength. Also the research conducted in the framework of the ERANet-LAC project shows that flax is promising reinforcement for geopolimers based on clay as well as fly-ash [47, 48].

After flax and sisal, hemp (Cannabis sativa) is one of the most widely used cellulosic fibres as reinforcement in different kind of composites [38]. The research with this fibre was conducted with matrix based on foamed geopolymer. The two amounts of hemp fibres were applied 1.13 and 4.53% [49]. The results show good bonding between matrix and reinforcement, good stability to the thermal variation and improvement of mechanical properties [49]. Another research was made on geopolymer based on: fly ash from the PEGO Thermal Power Plant in Portugal, calcium hydroxide, waste glass, ordinary Portland cement (OPC), recycled aggregates and a sodium hydroxide solution [50]. The geopolymer mortar was reinforced by short hemp fibres (ca. 20–30 mm) up to 8 wt%. It caused decreasing of mechanical properties - about 50% in the compressive strength. Despite this fact, the authors stress the environmental benefits – reduce the carbon footprint, connected with using the natural fibres (the use of at least 8% hemp fibres leads to carbon negative emissions -19.7 kg CO_{2eq} m^{-3}) [50]. The research with hemp addition has also been made in the framework of the ERANet-LAC project, they show that hemp could be valuable addition to geopolymer matrix, but the properties depend on the amount and form of fibres [48].

The investigation for short coir fibres was conducted for geopolymers based on fly ash from Skawina, Poland with 1 wt% fibre addition. The result show that fibres admixture improves mechanical properties in comparison with geopolymers without fibre addition [5]. Similar research was made with coir addition between 0 to 1% and geopolymer mortar based on fly ash and silica fume [51, 52]. The research shows that optimum amount of coir is about 0.75 wt% according to mechanical properties. Additionally, a coir improves the crack resisting capacity on the mortar [52]. Other type of research was made with using short (3 – 5 cm) coconut trunk fibre and geopolymer matrix based on fly ash from Bosowa power plant in Jeneponto, South Sulawesi [53]. The results show also that mechanical properties increase up to some amount of fibres and then decrease [53]. Trindade et al. [53] also investigated the jute fibre as reinforcement for the geopolymer cement (metakaolin and sand). The test results present that the incorporation of jute fibres in geopolymers appears a viable solution to overcome its initial brittle behaviour [53].

The research for short raffia fibres was conducted for geopolymers based on fly ash from Skawina, Poland [5, 54]. The results show that the composites reinforced by raffia fibres has worse properties than synthetic fibre (PP). However they still have reasonable mechanical properties for some construction purposes [54].

Some investigations were also conducted with sweet sorghum. To the geopolymer matrix based on fly ash was implemented bagasse (waste form production) in 1, 2, 3 wt% as a fine fibre (below 10 mm) [55]. The results show that the compressive strength slightly decreases and the tensile and flexural strength increase with the content of sweet sorghum fibres up to 2% and then decrease to be lower than that of the geopolymer without fibres addition [55]. There is also change the behaviour during failure from the brittle failure (samples without fibres) to "ductile" (for samples with fibres) [55].

Not typical reinforcement is luffa (kind of tropical and subtropical vines in the cucumber family). The fibres were obtained from dried matured fruits. The composite includes about 10 vol% natural Luffa Cylindical fibres arranged as a layers [56]. The results show that the compressive and flexural strength of the final geopolymeric products respectively increase and the composites are durable (no significant deterioration in mechanical performance over a duration of 20 months) [56]. Other not typical addition used for geopolymer composite production was an Amazonian tropical bamboo - Guadua angustifolia. Geopolymer based on metakaolin was reinforced by bamboo fibres and strips [57]. The results confirm that the proper bamboo preparation allow gain the flexural tests results comparable with synthetic fibres such as polypropylene - PP [57].

Also some investigations connected with different fraction of wood waste [25, 58], including sawdust addition [59] to the geopolymers were conducted. The geopolymer matrix based on fly ash and metakaolin. The different kinds of wood aggregates were applied as an reinforcement [58], including: wood particles, wood fibres and wood flour. The research result shows that the shape and size of wood aggregates affect the properties of the geopolymer composites [58]. The wood flour show the best cohesion with matrix among investigated additions. The research with sawdust addition (0–20% by mass with an interval of 5% were investigated) was made on the fly ash based matrix [59]. The results show that 5% of sawdust addition is optimal taking into consideration all mechanical properties. However, the flexural strength increases with the content of sawdust - the highest flexural strength was for 20% of sawdust regardless of curing ages [59].

The other possibilities of reinforcement geopolymers composites are offered by some plant waste such as corn husk [60], rice husk [61] and coffee grounds [62], [63]. The research in this area is valuable not only because of designing a new composite, but also because of new possibilities of utilization some industrial waste. Moreover there is a lot of natural fibres such as: henequen, ramie, sunn, kenaf that have not been investigated yet as a reinforcement for geopolymers composites [2], [3]. It creates new research opportunities and new possibilities for application this class of composites in civil engineering [2].

2.2. Animal fibres

Other possibilities are offered by animal fibres such as wool and related mammalian fibres [4, 64, 65]. Among the animal fibres the widest test were conducted on wool [65, 66]. The research was carried out using high-quality wool (merino wool), as well as low-quality wool, for example carpet wool and wool from waste [65]. The matrix was a geopolymer made of kaolinite type halloysite clay originating from New Zealand, while the reinforcement was made of 2 types of high quality merino wool (18-25 μm) and low quality wool - mixed carpet wool (30-35 μm). The fibres were added in an amount of 5% by weight of the composite. In addition, the fibres were subjected to various types of pre-treatment - they were applied in three forms to composites [64]: in the form received without any action, after purification and pre-prepared by soaking in a solution of formaldehyde. After 14 days, flexural strength tests were carried out on the prepared samples. This strength for the matrix material was 5.8 MPa. For composites with the addition of fibres, the best properties were obtained for pre-prepared low-quality wool and treated high-quality wool - 8.7 MPa and 9.1 MPa, respectively. Studies have also shown a change in the nature of the fracture from brittle to ductile [65].

The research conducted on waste wool was carried out on a metakaolin matrix with the addition of 23% and 31% by volume of fibre (which gave 10% and 15% by weight, respectively) [66]. Obtained mechanical properties for the matrix, after 4 days, are respectively 1.4 MPa bending strength and 5.5 MPa compressive strength, 4.7 MPa bending strength and 8.6 MPa compressive strength were obtained for the composite with 10% wool, and 4.0 MPa and 8.3 MPa, respectively, for composite with 15% fibre [66]. The results also show that the obtained insulating properties at the level of $k = 0.20\ W\ mK^{-1}$ and the mechanical strength of the new composites are comparable with other commercial products, such as calcium silicate boards, and can be used in similar applications [66].

Other types of animal-derived fibres have not yet been studied as reinforcements of geopolymers. Therefore, it is possible to conduct research with accessories, such as animal hair (e.g. pigs), silk or bird feathers.

2.3. Mineral fibres

The mineral fibres such as basalt and diatomite when there are applied as reinforcement they usually give better results than plant fibres, but using this kind of fibres is not so beneficial for environment as plant ones [3], [4]. Among the mineral additives, the widest research was conducted on basalt fibres. They were implemented to geopolymer matrix as fabrics [66], [67], long fibres [68], as well as short fibres and microfibers. The short basalt fibres were investigated in different types of matrix, including: metakaolin, slag and fly ash.

For example the research was conducted on matrix based on fly ash from Raichur Thermal Power Station, Karnataka, India, with the addition of slag, basalt fibre, plasticizer (MYK Remicrete PC 5) and two types of aggregates (fine and coarse) [69]. The composition with fibres had higher values than basic matrix. The best result for compressive strength was achieved for 2% fibre content - 58.4 MPa after 28 days [69]. This composition gives also the best values for tensile strength - 3.6 MPa [69]. Tests on the mechanical properties of composites with the addition of basalt fibres were also carried out on the basis of a matrix consisting of fly ash, slag after processing of steel and sand [70]. The basalt fibres (diameter: 7-30 μm and lengths: 12 mm), were added in following amount: 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5% by volume [70]. The compressive strength test shows that all composites achieved higher values than the plain matrix material. The highest values were obtained for 0.4% volume addition of basalt fibres, it was 40.3 MPa, compared to values around 35 MPa for basic matrix [70]. For bending strength, the highest values were obtained for 0.3% by volume of fibres, it was 7.3 MPa [70]. The research with basalt fibres was also carried out on the basis of a geopolymer matrix composed of metakaolin, slag from the Bolu Cement Company in Turkey, sand and collemanite waste (borate mineral) from the Eti Mining Company mine in Turkey [71]. The tests were carried out with 0.4, 0.8 and 1.2% fibres (diameter - 20 μm and lengths - 12 mm) addition by volume. The best results for mechanical properties were obtained for a sample containing 1.2% of basalt fibres: 64.8 MPa after 28 days, compared to the sample without reinforcement - 61.6 MPa for compressive strength and - 12.6 MPa, compared to the basic matrix - 8.8 MPa for flexural strength [71].

Another tests were carried out on a metakaolin matrix reinforced with basalt microfibers up to 10 μm, 5, 10 and 15% of microfibers by weight were used [72]. The composite with 15% microfibers showed the highest strength properties. Its compressive strength was 38.1 MPa, compared to 28.4 MPa for the plain matrix [72]. Similar works with the addition of short basalt fibres were carried out on a geopolymer matrix based on fly ash from the Gladstone power plant in

Queensland, Australia [19]. The fibres (diameter - 13 µm and length - 12.7 mm) were added in amounts of 0, 0.5, 1 and 1.5% by weight. [73]. The results of the compressive strength at ambient temperature showed an increasing for samples with short fibres compared to the material without additives. Studies [72, 73] confirmed also the resistance of basalt fibre geopolymers to elevated temperatures. It is also worth paying attention to the research on the addition of basalt fibres to fly ash from the power plant in Thailand. In these studies, a very high weight proportion of basalt fibres was used: 0, 10, 15, 20, 25 and 30% [74]. The results show that all composites with the addition of basalt fibres obtained higher compressive strength than the basic matrix. The optimal addition was 10 - 15% of fibres [74].

Another tested mineral additives in geopolymers were composition: silica, alumina and zirconium (diameter about 3.5 µm and length 20 - 35 mm) [75]. These fibres were introduced into a geopolymer matrix based on metakaolin with the addition of particles after grinding bricks (so-called refractory bricks) in amounts: 0.5 and 1% by weight. [75]. The highest compressive strength values were obtained for a matrix with the addition of 15% ground refractory brick about 56 MPa and for the same matrix reinforced with 1% fibres. For bending strength, the values obtained for reinforced composite are significantly better. In this case, the crack modulus was compared, which was 8.4 MPa for the matrix material, and 14.4 MPa for the composite with 1% fibres [75]. Other mineral additives used in geopolymer composites include diatomaceous earth [76], however, this additive was not introduced in the form of fibres, but grains with a diameter of 1.2 µm and wollastonite, also introduced in the form of micro-additives [77, 78].

Test results for mineral fibres give interesting results (mechanical properties are usually better than for reinforcements in the form of plant fibres), but the use of this type of fibre does not have so many advantages for the environment. First of all, these fibres are not quickly renewable, have a higher density than vegetable fibres and do not give benefits in the form of CO2 reduction during the product's life cycle, including the production process.

3. DISCUSSION

The undisputed advantages of geopolymer materials are good compressive strength and good thermal properties (high fire and heat resistance), as well as resistance to corrosive environments. The weaknesses of this type of composites is brittle cracking, which limits their use in many areas [55], [79]. That is main reason why the research into introducing fibres as a reinforcement into a geopolymer matrix is conducted.

The research shows the addition of fibres is an efficient method for improving such mechanical properties as fracture toughness [3]. The presence of fibres reduces the general effect of cracking, limits the widths of the occurring cracks (exemplary reduction of the propagation of microcracks), suppresses all brittle behaviour and enhances ductility. The fibers can also improve those properties of geopolymers that are connected with their energy absorption and resistance to deformation. Fibres increase the amount of energy absorbed by geopolymer before damage occurs [3, 55]. In particular, the introduction of short fibres, due to their easy fibre dispersion and fibre shape factor, is an effective way to strengthen geopolymer materials [3].

Research carried out so far for fiber-reinforced geopolymer composites show that their addition is an effective method of improving mechanical properties. Most of the research has shown both an improvement in compressive strength and bending of composites (Table 1).

Table 1. Mechanical properties for the natural fibres reinforcement geopolymers

No.	Fibres	Matrix	Mechanical properties	Mx. vs com.	Time	Reference, comments
1	Cotton 0.5 wt. (10 mm x 0,2 mm)	Fly ash	Bending (B): 10.4 MPa matrix (mx) 11.7 MPa composite (com)	+12.5%	28 days	[36]
2	Cotton 0.5 wt. (10 mm x 0.2 mm)	Fly ash	Compressive strength (CS): 19.1 MPa mx 48.0 MPa com	+151.3%	28 days	[32]
3	Cotton 1.0 wt. (30 mm x 1 mm)	Fly ash	B: 5.5 MPa mx 5.8 MPa com CS: 24.8 MPa mx 28.4 MPa com	+5.4% +14.7%	28 days	[5]
4	Abaca 8% wt. (0.1-0.2 mm)	Metakaolin	B: 2.5 MPa mx 27 MPa CS: 7.0 MPa mx 50 MPa com	+980% +614.3%	28 days	[37]; very high value for com – needs to be verified.

5	Sisal 3% wt. (ca. 25 mm)	Metakaolin	CS: 6.9 MPa mx 6.0 MPa com B: 1.4 MPa mx 2.7 MPa com	CS: Decreasing (D), B: +96.4%	Lack of information	[38]
6	Sisal 3% wt. (ca. 10 mm)	Fly ash	B: 3.3 MPa mx 4.5 MPa com CS: 27.2 MPa mx 41 MPa com	+36.4% +50.5%	14 days	[40]; low value for B.
7	Sisal 1% wt. (3 mm x 0,5 mm)	Fly ash	B: 5.5 MPa mx 5.9 MPa com CS: 24.8 MPa mx 25.2 MPa com	+6.3% +1.5%	28 days	[5]
8	Pineapple leaf 3% wt. (ca.25 mm)	Metakaolin	CS: 6.9 MPa mx 3.3 MPa com B: 1.4 MPa mx 2.0 MPa com	CS: D B: +42.8%	Lack of information	[38]
9	Pineapple leaf 1.2% wt. (ca.50 mm)	Fly ash	B: 6,0 MPa mx 7.1 MPa com CS: 23.3 MPa mx 58.2 MPa com	+17.8% +149.6%	28 days	[41]
10	Flax 10% wt. (0.01-0.08 mm)	Clay	B: 5.8 MPa mx 70.2 MPa com	+1110,3%	28 days	[42]; results required verification
11	Hemp 8% wt. (20-30 mm)	Fly ash, waste glass, OPC, recycled aggregates	B: 3.4 MPa mx 2.1 MPa com CS: 45 MPa mx 12 MPa com	D	28 days	[50]; low value for B.
12	Coir 1% wt. (3 mm x 0.5 mm)	Fly ash,	B: 5.5 MPa mx 5.2 MPa com CS: 24.8 MPa mx 31.4 MPa com	B: D, CS: +26,5%	28 days	[5]
13	Coir 0.75% wt. (25 mm)	Fly ash, silica	CS: 45.5 MPa mx 51.2 MPa com	+12,5%	28 days	[51]
14	Coir 0.5% wt. (30-50 mm)	Fly ash	B: 74.4 MPa mx 76.4 MPa com CS: 80.7 MPa mx 89.4 MPa com	+2,7% +10,8%	28 days	[52]; very high value for B.
15	Raffia 1% wt. (3 mm x 1 mm)	Fly ash	B: 5.5 MPa mx 3.0 MPa com CS: 24.8 MPa mx 13.7 MPa com	D	28 days	[5]
16	Sorgum 2.0% wt. (< 10 mm)	Fly ash	B: 3,4 MPa mx 5.4 MPa com CS: 27.7 MPa mx 22.9 MPa com	B: +58.8% CS:	7 days	[55]
17	Bamboo 5% wt. (12.5-40 mm & <1,25 mm)	76% metakaolin, 24% silica	B: 4.5 MPa mx 27.6 MPa com CS: 55.7 MPa mx 33.1 MPa com	B: +513.3% CS: D	7 days	[58]; 4 points B
18	Wood 10% wt. (0.7 mm)	Fly ash and metakaolin	CS: 76.5 MPa mx 30 MPa com	D	28 days	[59]

19	Wool 5% wt. (18-35 μm)	Clay	CS: 5.8 MPa mx 9.1 MPa com	+56.9%	14 days	[65]; 4 points B
20	Wool - waste 10% wt. (ca. 50 μm)	Metakaolin	CS: 5.5 MPa mx 8.6 MPa com B: 1.4 MPa mx 4.7 MPa com	+56.4% +235.7%	4 days	[66]; very low value of compressive strength
21	Basalt fibre 2.0% wt.	Popiół lotny	CS: 43.3 MPa mx 58.4 MPa com	+34.7%	28 days	[69]
22	Basalt fibre 1.0% wt.	Metakaolin	CS: 39.5 MPa mx 36.9 MPa com	D	28 days	[71]
23	Basalt fibre 15% wt. (10μm)	Metakaolin	CS: 28.4 MPa mx 38.10 MPa com	+74.61%	28 days	[72]
24	Silica, alumina & zirconium, 1% wt. (3.5 μm x 20-35 mm)	Metakaolin and clay bricks	CS: 56 MPa mx 56 MPa com	Without change	15 days	[75]; tested at 60oC.

Contemporary, the reinforcements used in geopolymer composites are often based on inorganic fibers, such as carbon or glass fibres [3, 80] or synthetic fibres [81]. However, the research direction is clearly visible, undertaking work on reinforcements from natural fibres [5, 82]. This solution is to be an environmentally friendly alternative. However, it is worth noting that the reinforcements with natural fibre give lower mechanical properties, which does not always allow their desirable applications. In addition, only selected from these fibres are tested in terms of providing materials with other properties, i.e. resistance to temperature or corrosive environments. A separate problem is the lower dimensional repeatability of natural fibres.

4. CONCLUSIONS

The main motivation of research work is growing environmental awareness and importance of development of sustainable construction materials for decreasing environmental impact of building industry. Nowadays, the geopolymer composites are most promise alternative for traditional building materials based on concrete. One of the limitations for these materials is brittle behaviour. To improve their mechanical properties it is possible to reinforce the matrix by fibres. In the environmental point of view, the addition of natural fibres is especially beneficial. The article presents exemplary solution in this area based on up-to-date literature.

Various types of fibers, both natural and chemical, were tested as geopolymer reinforcements. The results show that the geopolymer composites based on natural fibres could be a low-cost and an effective construction material with comparable properties as composites reinforced by synthetic fibres. In many cases, however, these studies were only a preliminary analysis of the subject, limited to basic microstructure and mechanical tests on a small number of samples.

The natural fibres could replace the conventional additives. They could have similar mechanical properties and positive environmental effects - reduce greenhouse gas emissions and negative environmental impacts. The contemporary research gives promising results, but the further research are required. The practice applications require further tests to optimize the mechanical properties of the composites as well as investigate the other properties such as absorptivity and resistance for different environment, including long-durability issues and the LCA analysis for the chosen products.

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