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Research Paper

Assessing Household Solid Waste Management and Disposal Practices in Biu Local Government, Nigeria

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Abstract: Solid waste generation is inseparable from mankind, the unprecedented increase in global population inevitably means an increase in waste generation. This study designed household surveys, to assess current waste management practices in Biu. Biu town becomes important particularly due to the establishment of tertiary institutions which recently increased the population of households. Waste disposal approaches indicated that the majority (76%) engaged in unsustainable disposal measures. These measures include burning, disposing of waste along water drains, disposal along the roadside, and burying waste. Although the study results indicate that majority (89.4%) of the respondents were aware of the implications of these approaches, only a few practice reuse of waste (8.6%), recycling (10.4%), and waste segregation (22%). The drawbacks of achieving effective waste disposal and management system within the study area were the inability of the local authority to provide a waste collection and disposal system (83.3%), the lack of a well-designated waste disposal site (98%), and the high cost of waste handling charges by unregistered and unmonitored waste collectors within the municipality (57.6%). Findings of this study show that in Biu LGA, lapses in waste management by the local authorities are responsible for most of the waste management problems encountered and, at the same time, there are areas of opportunity to improve the efficiency of management particularly in the physical aspects, such as collection, treatment, and safe disposal systems and services.

Keywords: *Household waste, Waste disposal, Waste management, Sustainability*

Introduction

Solid waste generation has become inseparable from humankind since humans use materials and resources for survival. More so, the increase in population accompanied by an increase in consumption from agricultural and industrial development has contributed to the unprecedented rise in the volume of solid waste in many developing countries (Alamgir *et al.,* 2012; Asase *et al.,* 2009). In addition, the poor management of waste disposal systems within rural and urban cities in many developing countries constitutes environmental degradation, with cities dealing with high pollution levels from solid waste and wastewater. The non-degradable composite of household wastes such as plastics and polyethylene, blocks drainages, leading to widespread flooding and the spread of diseases in many cities (Wilson *et al.,* 2015; Wilson *et al.,* 2013). Some unsustainable waste management practices such as burning and open dumping waste have polluted air, soil, and water systems, posing serious public health concerns (Ndum, 2013). These practices have imposed challenges on the government and environmental managers due to the volume of waste that must be managed.

The management of waste consists of careful planning, collection, treatment (when required), and disposal (Abdulredha *et al.,* 2020). It in addition involves, collecting reliable and valid data relating to the amount of waste generated, the factors that influence the volume of waste generated, and the predictions for future waste generation (Godfrey *et al.,* 2012; Salau *et al.,* 2021; Singh *et al.,* 2014). This means that adequate waste disposal and management system is now a key driver in achieving sustainable development goals (SDGs), particularly in making cities safe, resilient, and sustainable (Gunarathne *et al.,* 2019). However, sustainable solid waste management is yet to be adopted as a practice in most cities in developing countries. This is partly due to the attitudes of the residents towards waste disposal and, the government's failure to provide landfill and waste collection and disposal systems. The benefits of

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waste management have been numerous, ranging from a better quality of life within the environment, reducing pollution, conservation of energy, and achieving sustainable development (Batista *et al.,* 2021; Ikhlayel, 2018; Ferronato *et al.,* 2020). Waste has been utilized as raw material in the construction and manufacturing sectors. Plastics and polyethylene have been used as addictive in brick and paving constructions in many Sub-Saharan cities. The waste to energy management approach has converted non-recyclable waste into heat and fuel to drive development (Joseph & Prasad, 2020; Nguyen *et al.,* 2021; Zhang *et al.,* 2020). However, the benefits accrued from effective management have not been adopted in many semi-urban to rural cities in Nigeria, hence, the need for waste managers to begin to explore these novel opportunities.

With a fast-growing population, Nigeria will have a high consumption rate which will mean a high volume of waste generated across most cities. The volume of waste generated is already alarming and therefore requires urgent attention (Salau *et al.,* 2021). Although the amount of waste generated will vary depending on the region, season, lifestyle, frequency of waste collection, population characteristics, thus, the type of waste produced (Obongo *et al.,* 2021). Consequently, the waste composition will depend upon similar factors like culture, geography, income, and therefore the proximity of the town to other economic activities. Pollution of soil and water from waste will also depend on the proximity of such a system to the population and disposal sites (Joshua, 2021). Therefore, the reuse and recycling of waste particularly in the global South needs to be adopted as a sustainable approach to reducing the actual waste that ends up in landfills and other waste disposal sites (Azevedo *et al.,* 2021; Mekonnen and Tokai, 2020; Schoot *et al.,* 2011).

Due to its growing population, waste management in Biu local government area is expected to increase exponentially. The establishment of the new Army University and the existing College of Education has seen an increase in the number of persons coming in to settle for work or study. In addition, the insurgency in other parts of the state has increased the number of displaced persons coming into the town for safety thereby contributing to the volume of waste generated. There is, however, a lack of a waste management system within the local area, and most individuals have been solely responsible for the collection and disposal of their waste. Personal waste disposal is unsustainable, resulting in contamination of the air, soil, and water. As a result, this study examined existing waste management practices within households to identify inefficient practices.

Material and Methods

Study Design and Administration of Survey Questionnaires

The study adopted the NBS, (2012) general community survey procedures and practical guidelines for designing household surveys. The survey questions were designed in two parts: the respondents' demographic data and the waste and environmental management practices within the homes and communities. The questionnaire was tested through a pilot survey with a small number of participants in the Wukari community of Taraba state. The pilot testing helped to verify the question items investigated for clarity, viability, feasibility, and completion time of the questionnaire. The revised questionnaire from the pilot test was tested for thorough reflection of the intended objectives by collecting expert opinions. The opinions and advice of the two experts who were consulted were followed. The improved copy of the questionnaire obtained through reliability and validity tests was retained as the research study's ready copy.

The study sample design was adopted from Sandelowski, (1995) using the equation:

$$\mathbf{Sample\ size\ (n)\ SD(1-SD)\times\left(\frac{Zscore}{ME}\right)^2} \quad (1)$$

Where Z-score is the critical value of confidence level, taken as a 95% confidence level
SD is the standard deviation (0.5), ME is the margin of error at a confidence interval of ±5%

The minimum number of households covering the study area was determined to be about 385 using equation (1). Specifically, the survey has a statistical margin of error of ±5% at a 95% confidence level. A purposive sampling technique was used to achieve the minimum sample size, as described in related social research by Sandelowski, (1995); James *et al.,* (2001); Sim *et al.,* (2018).

A total of 451 of the 700 questionnaires were distributed (within Galtimare, Mbulamel, Mbulachive, Tabbra, Tashan-Danfulani, Ungwan sarki, and Zara-wuyaku) were returned. 55 of the 451 completed questionnaires were discarded from the sample due to missing information. The total number of questionnaires used in the analysis stands at 396 (56.6 %). Between September and December 2020, questionnaires were distributed to a representative sample of households. The heads of households were the ones who were targeted. However, household members with knowledgeable information on the waste management and disposal system in the home were asked to complete the survey on behalf of the family to avoid a low return rate.

The data collected were analyzed using descriptive approaches. Descriptive statistics using frequency distributions and percentage rating gave a critical understanding of measurement terms used. The distributions of the participants using frequency and percentage were presented in tables and charts.

Results and Discussion

Demographic Data of Respondents

The questionnaire's result was grouped and tabulated according to the key components and sub-topics that will inform the discussion of the study. The demographic distribution showed that 59.8% of the representative households were males while 40.2% were female. The age distribution showed that the age range of 26-33 had the highest turnout of representatives with 34.1%, followed by 34-41 (31.1%), 42-49 (14.6%), 18-25 (12.4%), and age range above 50 constituted 7.8% respectively. Educational qualification shows that 44.4% of the participants had at least a bachelor's degree, 26% had NCE/HND/Diploma, and 18.7% had attended secondary and primary certificates, while 10.9% had no formal form of education. In addition, the family size distribution showed that a family size of 5-8 persons constituted 52.3%, a family size above 9 was 32%, and 1-4 constituted 15.7%. Household income with the highest distribution was within ₦19,000-50,000 (35.6%), ₦51,000-100,000 (26.3%), ₦100,000 and above (19.9%), and those below the minimum wage of ₦18,000 constituted 18.2% respectively as can be seen in Figure 1 ($1 = ₦450).

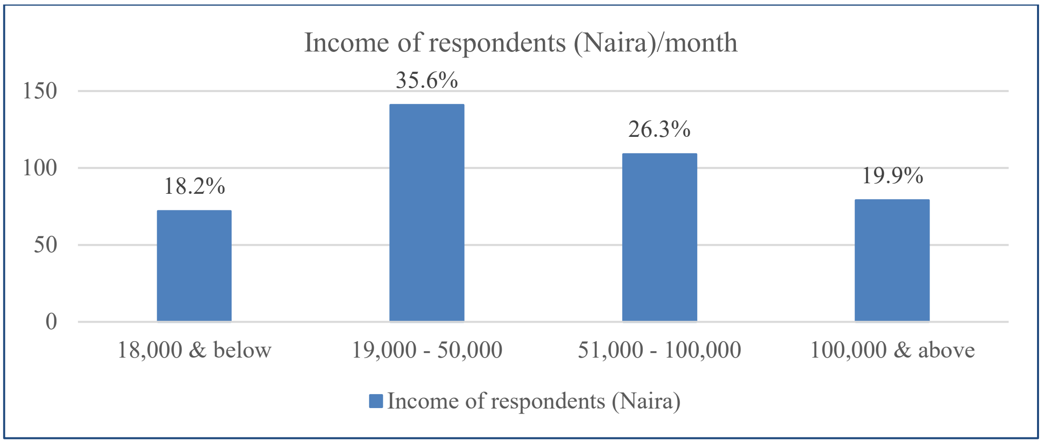

Figure 1: Distribution of income per month of households within the study area

Waste Disposal measures used by the sampled households

Table 1 shows the different solid waste disposal measures used by the households in Biu Local Government Area. The results indicated that the majority (76%) of households are currently engaged in unsustainable solid waste disposal practices that can likely impact human health and the environment. The distribution of unsustainable practices shows that open burning of wastes within the household (26.4%), dump-pit/burying wastes (22.5%), waste disposed of along the roadside (14.5%), and waste disposed of within water drains (12.6%), account for the unsustainable ways households have been using to dispose of their wastes (Figure 3). These disposal measures have been known to contribute to Air, soil, and water pollution (Joshua, 2021; Ajah *et al.,* 2015) which can result in severe health impacts. Consequently, it has also increased the presence of rodents, mosquitoes, snakes, scavenger birds, and other parasitic insects that can likely impact the overall health of the community and environment including environmental aesthetics as seen in Figure 2.

Furthermore, the findings indicate that most of the households (88.9%) dispose of their waste weekly as against monthly and this was regardless of the category (organic, paper, plastics, glass, metals, and others) of waste. Although most of the waste generated was organic waste from leftover food and vegetables, there were other chemicals including heavy metals from batteries that were disposed of. These can be dangerous to ground and surface water sources particularly residents that burry waste and those that dispose of waste along water drains that can equally be washed into surface water bodies. Similar findings were observed by Ajah *et al.,* (2015); Azodo and Ismaila, (2016); Egun, (2012); Miezah *et al.,* (2015), which suggests that the unsustainable disposal of waste within the study site can likely pose a severe risk to water quality which can directly impact health due to the lack of water treatment facility within the area. Similarly, environmental aesthetics and air quality are often impaired by the indiscriminate disposal of waste. Just as poor water quality affects health, poor air quality can also increase the likelihood of health implications.

Figure 2: Waste disposal points along the roadside within different points in Biu municipality

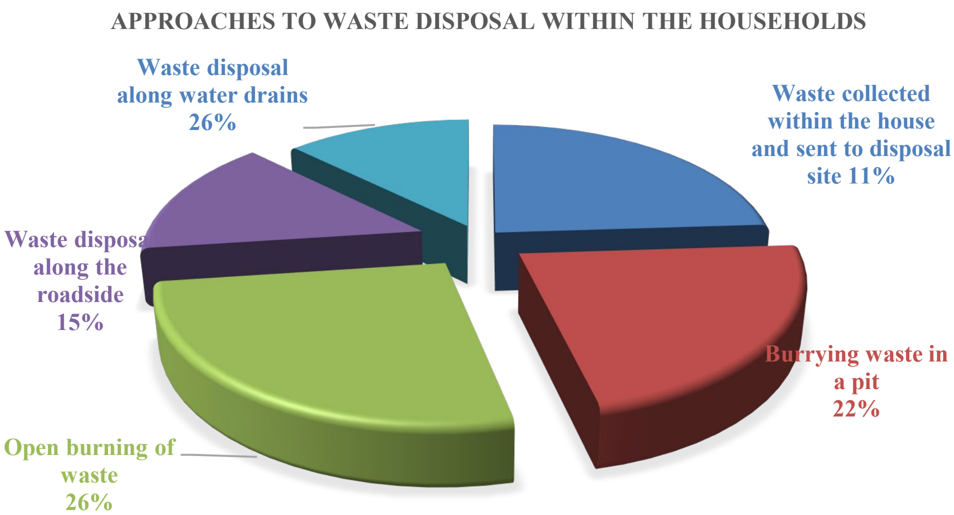

Figure 3: Approaches to the different types of waste disposal within the study area

Table 1: Waste Disposal practices among Households (n = 396)

Variables	Frequency (n)	Percentage (%)
Waste disposal system in use within households		
Waste bin within the house	94	12.9
Dump pit within or around the house	164	22.5
Direct burning of waste within or around the house	193	26.4
Waste collected and sent to the designated dump site	81	11.1
Waste disposed of by the roadside	106	14.5
Waste disposed within water drain	92	12.6
Frequency of household waste disposal		
Daily	44	11.1
Weekly	352	88.9

Other negative consequences of indiscriminate and unsustainable disposal of waste include unpleasant odor which often attracts flies and other disease-carrying pathogens, emission of gases such as methane (CH_4), and groundwater contamination through leachate (Ohaka *et al.,* 2013). Waste disposed of within drains was found to block drainages, while open burning is associated with the release of toxic gasses into the environment (Ndum, 2013; Abdulredha *et al.,* 2020; Oumarou *et al.,* 2012).

Management of solid waste materials from source as a process of disposal

To maintain environmental quality, check human health, and protect the natural resource, effective solid waste management utilizes many waste control strategies based on the waste hierarchy, including avoidance, reduction, recycling, reuse, recovery, treatment, and disposal (Mekonnen and Tokai, 2020; Schoot *et al.,* 2011; Kabera and Nishimwe, 2019). Effective solid waste management for environmental quality and sustainability assessed in this study showed that only 28.3% of the study participants were aware of sustainable waste management practices as seen in Table 2. In addition, waste control methods in the waste handling approach by participants assessed in this study and presented in Table 3 showed that waste segregation (22%), waste reuse (8.6%), and waste recycling (10.4%) were not effectively used within the study area. The lack of awareness (71.7%) of most of the participants has been shown to contribute to the volume of waste disposed of weekly within the community. It is necessary to separate biodegradable and non-biodegradable waste to provide an environmentally friendly waste management alternative. Segregation helps in the separation of recyclables and compostables. Less than a quarter of the study population (22%) segregate the household waste. The reuse of waste materials either in part or whole reduces the volume of waste generated for disposal in households. A study by Khan *et al.,* (2016) showed that the reuse of waste practice is typical with trading the material in second-hand goods such as clothes, electronics, automobiles, furniture, and other merchandise. It is worth noting that the reuse of materials often replaces segregation because successful material reuse is accomplished by sorting at the source rather than at the disposal site. However, waste recycling is based on waste materials that cannot be reused directly but can be transformed into a new product or raw material through transformation processes (Schoot *et al.,* 2011). Pyrolysis, incineration, anaerobic digestion, gasification, palletization, and composting are some of the ways waste can be recycled (Zhang *et al.,* 2020; Hettiarachchi *et al.,* 2020). Only 41 samples of the household participants representing 10.4% of the households studied, managed their waste through waste recycling.

Table 2: Awareness of sustainable waste management practices (n = 396)

Variables	Frequency (n)	Percentage (%)
Awareness of sustainable waste management practice		
Yes	112	28.3
No	284	71.7

Table 3: Process to disposal of the solid waste management practices from the source (n = 396)

Variables	Frequency (n)	Percentage (%)
Segregating waste		
Yes	87	22
No	309	78
Reusing of waste		
Yes	34	8.6
No	362	91.4
Recycling of waste		
Yes	41	10.4
No	355	89.6

3.4. Knowledge of the implication of improper waste disposal among the households

The importance of waste management in promoting sustainable environmental management that can significantly decrease the likelihood of health-related issues due to pollution from indiscriminate disposal of waste cannot be overemphasized. The improper disposal of solid waste contributes significantly to environmental degradation, public health threats, and climate change (Jalil, 2010). Since the result of improper disposal of solid waste is hazardously harmful to the environment and human health, knowledge, and caution in the generation and disposal of these wastes are important for environmental quality and good health (Ajah *et al.,* 2015; Addo *et al.,* 2017). The knowledge and awareness of improper waste disposal to human health and the ecosystem showed that most (89.4%) of the study participants were aware of the implication of inappropriate waste management approaches, however, they indicated despite the knowledge, they have no alternatives and have to dispose of the waste. The categories of the various impact of the awareness of improper waste disposal among the households are presented in Table 4.

The consequences of improper solid waste management cut across human life and the environment. The environmental impact includes land pollution, water contamination, and environmental degradation. Exposure to the toxic materials present in solid waste are determinants of respiratory and dermatological problems, eye infections, and low life expectancy (Ajah *et al.,* 2015). Studies have shown that improper disposal of waste leads to the production of gases such as methane, carbon dioxide, carbon monoxide, nitrogen, and heavy metals, which can contribute to climate change and cause diverse health and environmental issues.

Additionally, solid waste is one of the dangerous local pollutants produced within households. This is due to the composition of waste within the waste disposal system. Waste will degrade and can have a toxic mixture effect especially waste containing metals and other chemicals. Consequently, poor waste disposal practice predisposes man's environment to all sorts of environmental hazards, including flooding, erosion, and degradation of natural resources (Ferronato *et al.,* 2020; Addo *et al.,* 2017).

Table 4: Implication of improper waste disposal among the households (n = 396)

Variable	Frequency(n)	Percentage (%)
Spread of diseases	50	8.9
Breeding of mosquitoes, rodents, and pest	66	11.7
Blocking water drain causes flooding	173	30.7
Air pollution	35	6.2
Unpleasant sights and environment	111	19.7
Release of GHG that contributes to climate change	69	12.2
Unaware of implications	60	10.6

Role of the Municipal Authorities in the Solid Waste Management in the Study Area

Generation, processing, and disposal activities involved in solid waste management include all the solid waste management activities, prevention, storage, collection, monitoring, transportation, characterization, treatment, reuse, and processing aimed at preserving the natural environment, protecting environmental quality, human health, and life in general (Godfrey *et al.,*2012; Gu *et al.,* 2015). Solid waste management for environmental quality and sustainability starts from the waste generation through to the disposal activities. Individual waste producers, as well as external support organizations and governments at all levels, are encouraged to actively participate in municipal authorities, which include the informal private sector. The study results showed that neither a waste temporary disposal system (83.3%) nor a government-designated waste site was available in the study area (98 %). This may have influenced the waste handling fees, as most of the respondents believed that waste collection and disposal fees in their municipality were excessively high in their city (57.6%). Similar findings were observed by Boateng *et al.,* (2019), therefore, a cost-effective waste management system is key to fostering sustainable management of waste particularly in poor and remote areas. This is because the waste handling fees were said to foster a negative attitude (62.1%) against waste disposal services available to households as shown by the study findings in Table 5.

Table 5: Role of local authorities in solid waste management within the study area (n = 396)

Variables	Frequency	Percentage (%)
Charges for waste collection		
Expensive	228	57.6
Moderate	93	18.9
No charges	75	23.5
People's attitudes towards waste disposal		
Positive	150	37.9
Negative	246	62.1

Provision of waste disposal system by government		
Yes	7	1.8
No	330	83.3
Not aware	59	14.9
Availability of government-designated waste site		
Yes	8	2
No	388	98

Conclusion

Controlling the generation, storage, collection, transportation, processing, and disposal of solid waste from source to disposal is part of solid waste management, aiming to protect environmental quality, human health, and natural resource protection. The existing waste management and disposal system practices among households investigated in this study identified unsustainable practices. For environmental sustainability, human health, and natural resource protection, the factors that influence wasteful activities, such as the lack of waste management and government-designated waste sites, as well as high charges on the few available, must be addressed. An attitudinal change that focuses on incorporating both the top-down and the bottom-up approach must be adopted. This will promote a participatory solution that will foster a synergy between the government, waste managers, and local people. Overall, it will create a relationship that will enhance awareness, especially on the dangers of unsustainable waste management practices within the community.

Recommendation

For an effective waste management practice that guarantees sustainable development, the following recommendations were articulated.

- Waste disposal points must be located and constructed according to standards to limit the risk of surface and groundwater contamination
- The government needs to create awareness of the dangers of unsustainable waste practices currently practiced to reduce the negative impacts
- The cost of collecting, transporting, and disposing of waste should be reviewed and sanctions placed on those who dispose of waste, particularly along waterways and drainages.

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Review Paper

Microbial Enzyme Remediation of Poly-Aromatic Hydrocarbon (PAH's) A Review

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Abstract: Pollution of soil by petroleum hydrocarbon (HC) has continued to draw serious concern due to their recalcitrant nature. The HC pollutant are majorly aliphatic and aromatic complexes of incomplete combustion of waste products from automobiles. This HC pollutant can survive in the soil for long time, causing deleterious effect to plant, animals, and humans. Microbial break down or utilization of HC by bacteria and fungi population within the polluted environment can be achieved through biostimulation or bioaugumentation technology by enzymes embedded in the microbial cells. Density, viscosity, pour-point, and solubility are some of the physicochemical parameters that may influence microbial response to HCs. Lack of nutrients, temperature, pH, oxygen are major factors that slows down HC remediation. The degradation of aliphatics by monooxygenase, attacks the terminal methyl group responsible for primary alcohol formation, which is further broken down, to aldehyde and fatty acid. The degradation of aromatics follows dioxygenase-catalyzed oxidation of arenes in aerobic microbial population to yield Vicinal and Vicinal Cis-dihydrodiols Cis, cis-muconic acid (ortho-cleavage) and 2-hydroxymuconic semialdehyde (meta-cleavage) is the final product of enzyme catechol 1,2-dioxygenase (C12O) and catechol 2,3-dioxygenase **(**C23O) catalyzed degradation of HC in the Tricarboxylic Acid Cycle (TCA). The ability of microbial isolates to produce significant enzymes such as C12O, C23O highlights their future remediation significance.

Keywords: *Hydrocarbons (HCs), Biostimulation, Bioaugumentation, Enzymes, Remediation, Ortho-cleavage, Meta-cleavage,Tricarboxylic Acid Cycle (TCA)*

Introduction

Pollution is the introduction of components such as elements, compounds, or energy into the environment at concentrations that impairs biological functioning or that present an unacceptable risk to humans or other targets that use or are linked to that environment (Fernández-Luqueño et al., 2011)**.** The major component of petroleum hydrocarbon pollution is the aliphatic and aromatic complexes formed after combustion of petroleum products (Okolafor and Ekhaise, 2021). Several researchers have reported the deleterious effect of aromatic compounds such as Polyromantic hydrocarbons (PAHs) to human and animals. PAHs are implicated to be carcinogenic, mutagenic and teratogenic to human and animal health (Dugay et al., 2002; Juhasz and Naidu, 2000; Meudec et al, 2006; Wilcke, 2000); thus PAHs have been listed as priority pollutants by United State Environmental Protection Agency (Thavamani et al., 2012)**.**

Most hydrocarbon degrading bacterial population are known to metabolize or mineralize aliphatic and aromatic by the action of enzymes embedded in the bacterial cells. These enzymes serve two main purposes such as peripheral recognition of aliphatic and aromatic compounds and conversion of degradable aliphatic and aromatic molecules by fission, thereby allowing free entry as route for carbon sequestration and energy generation (Mishra et al., 2011). However, one major challenge in the remediation of aliphatic and aromatic is the lack of sufficient nutrient to the microbial community present in the artificially or accidental polluted soil. Lack of essential nutrients such as carbon, phosphorus, nitrogen and oxygen are major factors that could affect biodegradation of hydrocarbon by microorganisms in soil and water environment (Abioye et al., 2012). The addition of inorganic or organic rich nutrients is an effective approach to improve the bioremediation processes (Hollender et al., 2003; Semple et al., 2006; Walworth et al., 2007).

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Petroleum Hydrocarbon

Petroleum are naturally occurring valuable world resources derived from the Latin word petra (rock) and oleum (oil) (Kumar et al., 2018). Petroleum HCs are made from refining and processes of crude oil. Crude oil is made up of about 50–98% HC components and non-HC component (nitrogen, Sulphur, oxygen and other trace metals) in a complex or broad group.

Report on comprehensive oil property as stated by Lee et al. (2011) revealed information on over 400 oils, posted by Environment Canada. Crude oil is classified into three types based on the origin (terrestrial or geological location), American Petroleum Institute (API) gravity (density) and sulphur content. Low density crude are known as light crude, high density crude are called heavy crude oil and Sulphur containing crude are called sour crude (Kumar et al., 2018). Petroleum HC are classified into four main groups (Table 1) based on their solubility in organic solvents. Four physical characteristics of oil that have adverse effects on the environment and cleanup responses of microorganisms are discussed below:

Density

API reported that gravity and specific gravity are commonly used to determine the density of oil. Specific gravity is the measured of the ratio of mass of oil to mass of corresponding water at known temperature. The API gravity suggests a value of 10^0 to pure water at 10 ^{0}C (60^0F). Extremely high API gravity is an indication of oils with low densities or low specific gravities. Kumar et al. (2018) reported the specific gravities of crude oil ranged from 0.79 to 1.00, which is equivalent to API gravities of 10 - 48. Density is an important index that may be used to predict the composition of oil fate in water.

Viscosity

Viscosity is the physical property of a fluid that allows it to withstands changes in shape or motion (Xu et al., 2017). The decrease in viscosity result in corresponding increase in fluid flow. The viscosity of petroleum products is associated with the oil compositions and the surrounding temperature (Saeed et al., 2016). Viscosity is an essential index of spilled HC oil spreading rate.

Pour point

Temperature in which oil stops flowing or converted to semi-solid is known as pour point. Temperature range of −57 to 32 °C is the pour point of oil (Yasin et al., 2013). Pour point is the major characteristic of oil fate and cleanup plan action of HCs.

Solubility in water

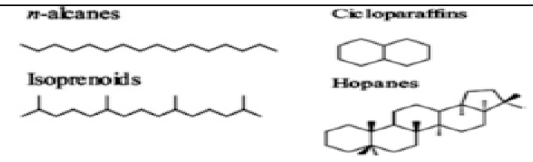
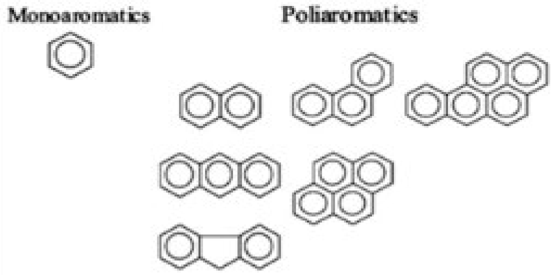
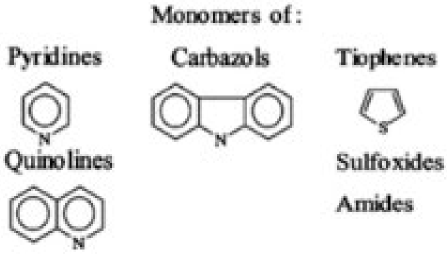
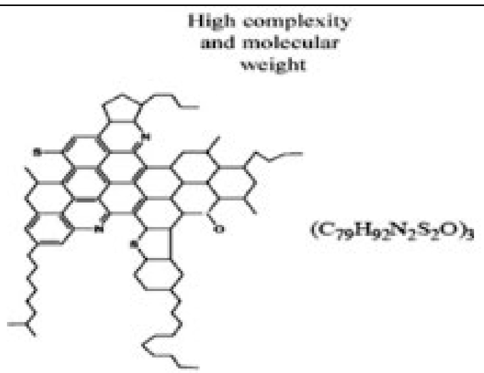
Petroleum HCs solubility in water is determined by temperature and chemical compositions of the HCs. The deficient in the solubility of common crude oil is reported to be around 30 mg/L (Adeniji et al., 2017). The solubility in water property of oil is critical in determining the oil toxicity, oil fate and appropriate bioremediation approach to follow. The most soluble oil constituents are low molecular weight aromatics compounds such as toluene, benzene and xylene (Kumar et al., 2018).

Hydrocarbon as Pollutants

Hydrocarbon (HC) pollutants in the environment can be classified as organic or inorganic (Chikere, 2013). The organic pollutants are mainly HCs in different forms. The most common are petroleum HCs which include n-alkanes and other aliphatics, aromatic compounds and other components in trace amounts (Atlas and Philp, 2005; Sarkar et al., 2005).

Spillage from crude oil and refined fuel have damaged the natural ecosystems in the Niger Delta region, South-South Nigeria and many other places worldwide. The quantity of oil spilled during accidental release of oil to the environment ranged from a few hundred tons to several hundred thousand tons (Deepwater Horizon Oil Spill, Atlantic Empress, Amoco Cadiz), but it is a limited measurement of damage or impact (Godleads et al., 2015; Stephen and Temola, 2014). Oil spills in soil reduces the ability of the soil to support the growth of plants, leaches into the ground to pollute groundwater, and increases the presence of heavy metals which bioaccumulate and biomagnify thereby causing adverse health effects to the receiving environment. Major constrains facing scientists and industrialists today is how to tackle the problem arising from pollution of soil and water by HCs; using environmental friendly, safe approach and cost implications of degrading these contaminants. Bioremediation technology is a veritable tool for HCs degradation that is intensively studied today (Godleads et al., 2015).

Table 1: Various categories of hydrocarbons

Categories	Carbon Atoms	Components	HC compound (s)
Saturated	1-45	Normal alkanes Branched alkanes	
Aromatic	4-45	Two or more fused aromatic rings	
Resins	>40	Polar compounds	
Asphaltenes	>40	NSO(s) Poorly characterized HCs High-molecular- weight compounds Heavy metals	

Adapted from (Kumar et al., 2018)

Hydrocarbon soil interactions

HCs and soil interaction at the surfaces (clay, silt and sand) are only substantial when percentage organic matter is 0.1 (Chikere et al., 2011). Thus, the importance of organic matter in the fate and behavior of organic contaminants is far-reaching. Organic matter is divided into two major phases; soft carbon (elastic) which is the expanded, flexible arrangements having fulvic, and humic acids as key components with sorption described as irreversible hard carbon (glassy) defined as rigid, condensed structures with humin, kerogen and pyrogenic carbons as commonly identified components (Chikere et al., 2011). Uptake of hydrocarbons materials within the glassy region is characterized by irreversible sequestration (Stroud et al., 2007; Van Elsas et al., 2007). HCs sequestration within the soil through sorption to organic matter and mineral elements or diffuse into the three-dimensional structure of the soil as showed in Figure 1.

The rate to which these physical interactions occur increases with time and is termed 'aging'. For aromatics fractions, their fate in the soil is dependent on their molecular size, i.e., the number of aromatic rings they possess. An increase in the size and angularity of aromatics results in a related increase in electrochemical stability, hydrophobicity, high sorption capacity and their persistence in the soil (Kanaly and Harayama, 2000; Van Hamme et al., 2003).

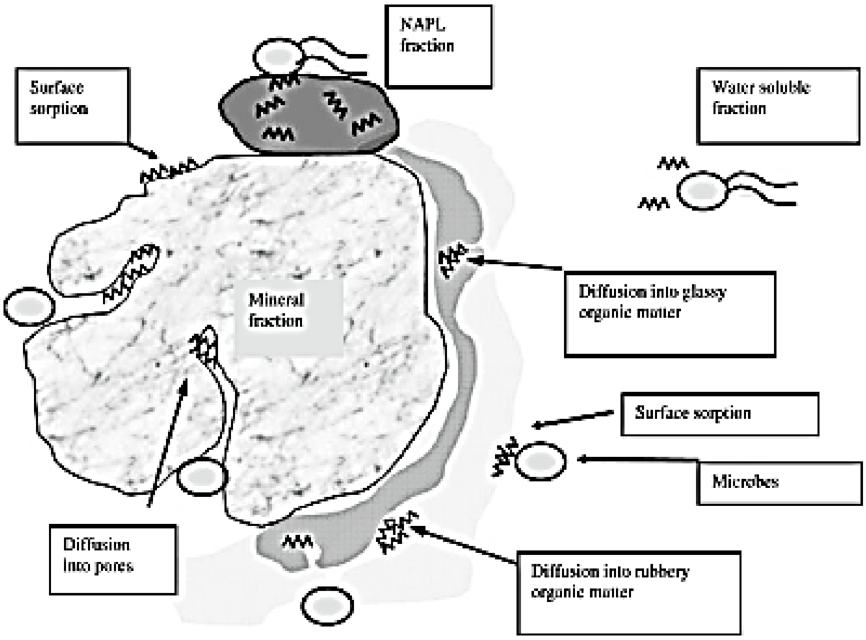


Figure 1. Interactions between soil matrices and aliphatic hydrocarbons; NAPL, non-aqueous liquid phase (Stroud et al., 2007).

Microbial hydrocarbon interactions in soil

Two major characteristics that define HCs-oxidizing microorganisms in the soil are; membrane-bound, group-specific oxygenases; and mechanisms for optimizing contact with microorganisms and the water-insoluble HCs (Chikere et al., 2011). HCs are known substrate for microbial oxidation by bioavailability and bioaccessibility (Semple et al., 2003). A compound is said to be bioavailable if it is freely available to cross an organism's membrane from the medium the organism inhabits at a given time. Bioaccessible compound is a compound available to cross an organism's cell membrane from the environment it inhabits if the organism can access the polluted environment.

Microbial diversity of HCs degradation in the soil

The degradation of HCs is mediated by diverse groups of microorganisms. it is widely reported that bacteria and fungi are primary mediators in HCs degradation. Bacteria are reported to be more versatile than fungi and therefore may play a greater role during biodegradation of HCs compounds. The most important HC-degrading bacterial genera in soil environments include *Alcaligenes*, *Bacillus*, *Achromobacter*, *Acinetobacter*, *Arthrobacter*, *Burkholderia*, *Collimonas*, *Corynebacterium*, *Dietzia*, *Flavobacterium*, *Gordonia*, *Micrococcus*, *Pseudomonas*, *Mycobacterium*, *Nocardia*, *Nocardioides*, *Ralstonia*, *Rhodococcus*, *Sphingomonas*, *Variovorax* and other unculturable bacteria (Chikere, et al., 2009; Hamamura et al., 2006; Obayori and Salam, 2010). Among fungi genera that can degrade complex HCs are *Mucor*, *Aspergillus*, *Candida*, *Cunninghamella*, *Fusarium*, *Penicillium*, *Rhodotorula*, *Phanerochaete*, *Sporobolomyces* and *Trichoderma* (Chaillan et al., 2004; Das and Chandran, 2011; Singh, 2006).

Bioremediation of HC contaminated soils

Bioremediation is the removal, destruction, or conversion of contaminants to less harmful substance (Agamuthu et al., 2013). Bioremediation remains a highly potential approach since many studies have reported its effectiveness in removing numerous pollutants from contaminated sites (Nie et al., 2009; Rimmer et al., 2006; Li et al., 2013). Generally, bioremediation technologies can be classified as *in situ* or *ex situ*. *In situ* bioremediation involves treating the contaminated material at the site while *ex situ* involves the removal of the contaminated material to be treated elsewhere (Gavrilescu, 2010).

Studies on petroleum HC biodegradation adopted various methodologies (Bidoia et al., 2010; Cerqueira et al., 2014; Zhang et al., 2016), although they all indicated that degradation can occur in exact fractions of the compound to be degraded. There is no rule of thumb in petroleum HC biodegradation as most compound showed preferential remediation of lighter HC compounds, while others directed towards heavier HCs (Huang et al., 2004).

Biodegradation is the breakdown of HCs through enzymatic activity of microorganisms (fungi and bacteria) depending on the ability of the microbes to emulsify the undissolved carbon component in the culture medium (Chrzanowski et al., 2005; Mancera-López et al., 2008). There exist three main types of bioremediations, they include biostimulation, bioaugumentation and phytoremediation.

Bioaugmentation: Bioaugmentation is a major type of bioremediation technologies today (Simarro et al., 2013). This process involves the introduction of nonindigenous organisms that possesses high degradation potentials to the soil in order to promote the bioremediation process (Wu et al., 2013). Microorganisms used in bioaugmentation must meet the requirements for effective degradation of the target pollutant, possess the ability to adapt to the environment and they must be nonpathogenic in nature (Szulc et al., 2014).

Various studies showed that bioaugmentation surges the biodegradation of HC compounds in wet land soils polluted with petroleum compounds (Suja et al., 2014; Taccari et al., 2012). The effectiveness of bioaugmentation depends on the type of inoculum and nutrient requirements (Abed et al., 2014; Suja et al., 2014).

Biostimulation: Increase in biodegradation of indigenous bacteria resulting to increase in bacterial population due to increased nutrients is referred to biostimulation. Microorganisms will proliferate and degrade compounds when nutrients and electron acceptors are sufficient. Available nitrogen compounds such as NO_3 or NH_4^+ are electron acceptor and nutrient requirements for bioremediation process (Kumar et al., 2018). Since HC biodegradation is limited by absence of physicochemical factors such as temperature, pH, moisture, oxygen, other soil properties (Al-Sulaimani et al., 2010; Atagana et al., 2008; Bundy et al., 2002), biostimulation during bioremediation process is inevitable. The advantage of biostimulation is that it will be carry out by already present indigenous microorganisms that are suitable to the subsurface soil, while the transfer of additives in a manner that permits the additives to be made available to the subsurface of the microorganisms is the major challenge (Godleads and Prekeyi, 2015).

Effect of Biological Factors in HCs Degradation

Major factors affecting microbial HCs degradation are the utilization of pollutants by microorganisms with the catabolic capability to degrade them, the activity of degrading microorganisms, limited number of degrading microbes in the soil and complex molecular structure of the organic pollutant (Semple et al., 2003). About 10^4 to 10^7 colony forming unit are present in soil, to accomplish biodegradation process; the above figure should not reduce below 10^3 per gram of soil, since it is an indication organic or inorganic contaminants in the soil (Margesin et al., 2003). Other factors that influence biodegradation are temperature, nutrient availability, moisture level, and oxygen demand of soil.

Temperature

Organic matter decay and degradation is directly influence by temperature. Biochemical activities which is the metabolic action of the organisms are hindered by temperature fluctuation. Hydrocarbon degraders (bacteria) grow best in optimized temperature conditions for a given species of the organisms. Temperature ranges of 20 - 33 ^{0}C is reported as the optimum temperature for microbial decomposition of HCs in the environment (Iranzo et al., 2001) . Temperature can slow down or increase biodegradation activity but may not affect responses to biochemical action. Temperature also affects the moisture of soil and retention potential of the soil. The rate of biodegradation increases with increase in temperature and decreases when temperature is decreases (ESTCP, 2007).

Nutrients

In chemical perspective, nutrients are grouped into macro, micro, and trace elements based on the quality and the vital requirements of HC degrading microorganisms. Carbon, phosphorus and nitrogen are mainly macronutrients comprising up to 14% of dry weight of microbial cells. Micronutrient group include sulfur, magnesium and calcium containing up to 0.5 % dry weight of a cells. Trace elements such as iron, cobalt, manganese, copper, and zinc are not required by HC degrading organisms. Graj et al. (2013) reported that oil HCs reduces the accessibility of plant nutrients in the soil. Hydrocarbon degraders in the soil consume available nutrients or fix nitrogen and phosphorus, thereby reducing the nutrient availability. Nutrients are always available for microbial growth in an HC polluted site, although nutrients can be introduced in a utilized form as organic substrate amendment (Godleads et al., 2015), which acts as electron donor to fuel bioremediation.

pH

Hydrocarbon degradation occurs more at pH range 6 to 8 (Iranzo et al., 2001; Mammitzsch et al., 2014). Bacteria and microbial growth decreases with decrease in pH less than the optimum pH level required for microbial species. The pH affects availability of carbon and nutrients and the solubility of heavy metals in the soil (Mousavi et al., 2017). Therefore, pH is an important factor for microbial community (Wang et al., 2017). Biodegradation of HCs compounds depends solely on the presence of enzymes that are dependent on pH value (Wang et al., 2017). Hydrocarbon biodegradation occurs faster at pH 7 particular fungi species compared to bacteria that can allow up to pH 5 (Das and Chandran, 2010).

Oxygen

Hydrocarbon degradation undergoes aerobic and anaerobic conditions. Aerobic respiration involves the utilization O_2 by microorganisms as final electron acceptor during metabolic reactions and oxidation (reduction) process. Microbes use nitrate-iron, sulfate and CO_2 as electron acceptor in anaerobic respiration (Ladino-Orjuela et al., 2016). Aerobic respiration process results in the breakdown of toxic matters/compounds non-toxic substance such as CO_2 and water (Rockne and Reddy, 2003). Degradation of HC compounds occurs faster during aerobic reaction than anaerobic conditions, and then HCs are broken down to H_2O and CO_2. Therefore, the rate of bioremediation increases with increase in oxygen level.

Degradation of Aliphatic and Aromatic HCs

It is reported that aromatic component of HCs is highly toxic compared to aliphatic HCs components (Uche and Dadrasnia, 2017). The aromatic compounds possesses antagonistic effects on the native soil microflora. Compounds such as isobornyl, camphene, acetate, limonene, and α-pinene were inhibitors of many microorganisms (Kumar et al., 2018). Phenolic and quinonic naphthalene derivatives demonstrated antagonistic activity against microbial cell growth (Qingren et al., 2011).

Enzyme Activity in the Degradation of Aliphatic and Aromatics

Aliphatic HCs degradation

Aliphatic HC Degradation results in the formation of CO_2 and H_2O. Two major biodegradation pathways are involved in the degradation of alkanes. The initial step is the aerobic degradation of saturated, aliphatic HC (n-alkanes) involves the enzymes that possesses a strict prerequisite for molecular oxygen; which are monooxygenases (mixed function oxidases) or dioxygenases (Chikere et al., 2011). The common pathway depends on the activity of monooxygenase enzymes which are specific for n-alkanes (Stroud et al., 2007). Monooxygenase attacks the terminal methyl group responsible for primary alcohol formation (Van Hamme et al., 2003). The alcohol is oxidized to aldehyde and fatty acid (Fig. 2).

Secondly, a dioxygenase enzyme acts on the terminal methyl group of an n-alkane leading to the addition of two oxygen atoms, resulting in the formation of a peroxide which is converted to a fatty acid (Figure 2). The carboxylic acid groups in the fatty acids are further metabolized via the b-oxidation pathway (Figure 2), which is a common catabolic pathway in living cells, to form acetyl CoA or propionyl CoA depending on the number of carbon atoms present in the n-alkane. These compounds are further metabolized via the tricarboxylic acid cycle (TCA cycle) to CO_2 and H_2O (Turley et al., 1981; Van Elsas et al., 2007; Van Hamme et al., 2003).

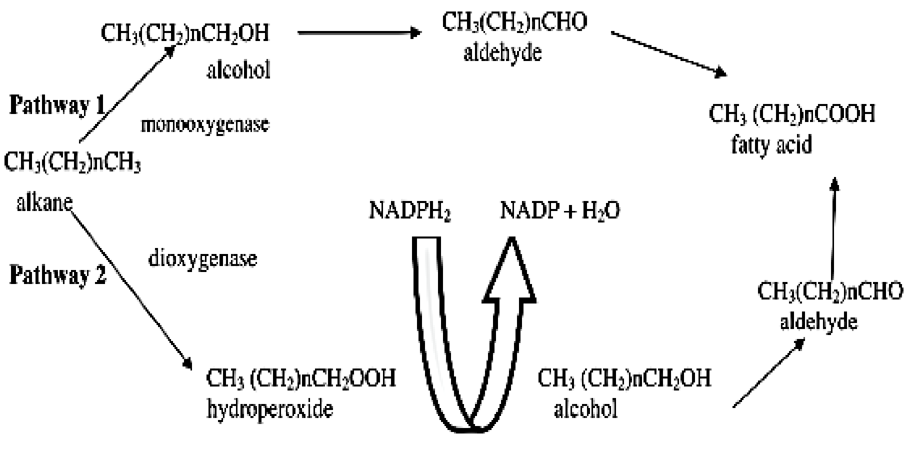


Figure 2. Pathway for the biodegradation of aliphatic HCs (alkanes) (Van Elsas *et al*., 2007)

Aromatic HCs degradation

The major reason for the low rate of biodegradation of aromatic HCs are low solubility, metabolite repression, production of toxic dead-end metabolites, presence of preferred substrates and lack of co-metabolic substrates (Kanaly and Harayama, 2000; Van Elsas et al., 2007; Van Hamme et al., 2003). While other aromatic HCs such as BTEX are present in petroleum, naphthalene, with two aromatic rings, represents the simplest form of polycyclic aromatic hydrocarbon (PAH).

No single microorganism has been able to utilize high molecular weight aromatic compounds such as benzo(a)pyrene as the sole source of energy, even though the transformations through co-metabolic activities have been reported (Van Elsas et al., 2007). The first step of aromatic HC degradation, dioxygenase-catalyzed the of oxidation of arenes in aerobic bacteria to yield vicinal vicinal cis-dihydrodiols as early intermediates by a multicomponent enzyme system (Chikere *et al*., 2011). The byproducts dihydroxylated cleave by intradiol or extradiol ring cleaving dioxygenases through either an ortho-cleavage pathway (Figure 3) or meta-cleavage pathway (Figure 4), resulting to intermediates such as protocatechuate and catechols (Fig. 5) using benzene as an example (Peng *et al*., 2008)

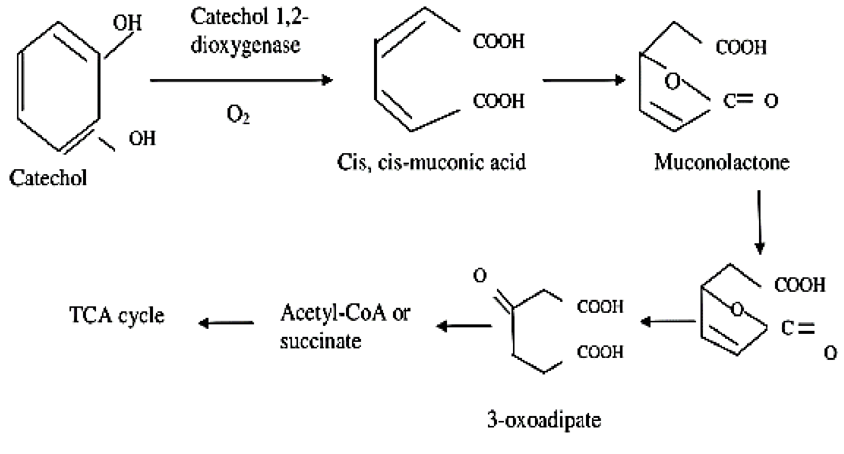


Figure 3. Ortho-cleavage of catechol in the TCA (Tricarboxylic acid) cycle (Van Elsas *et al*., 2007)

Complete breakdown of metabolites such as succinate, acetate, pyruvate or acetaldehyde from the above pathways enters the TCA cycle and are thus available as carbon or energy sources to the cell (Turley et al., 1981Turley et al., 1981; Kanaly and Harayama, 2000). Degradation of crude oil by Microbes results in the attack on aliphatic or aromatic fractions of HCs. Studies have reported removal of HCs at high rates under optimal conditions (Turley et al., 1981Turley et al., 1981; Hamamura et al., 2006; Leahy and Colwell, 1990; Maila et al., 2006; Margesin et al., 2003; Rosenberg et al., 1992). High molecular weight aromatics HCs such as resins and asphaltenes are considered recalcitrant or exhibit only slow biodegradation rates (Turley et al., 1981; Stroud et al., 2007; Van Hamme et al., 2003).

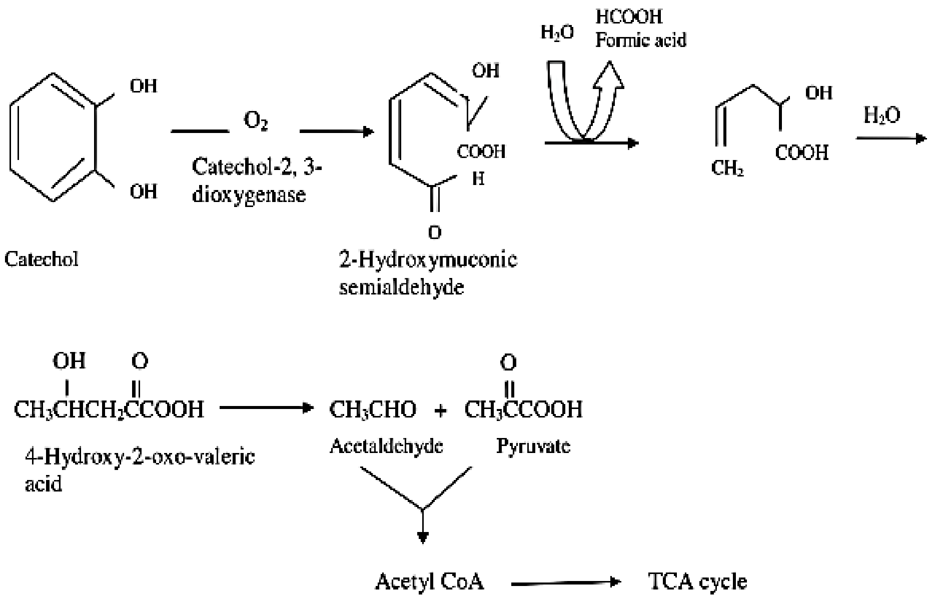


Figure 4. Meta-cleavage of catechol in the TCA (Tricarboxylic acid) cycle (Van Elsas *et al.*, 2007)

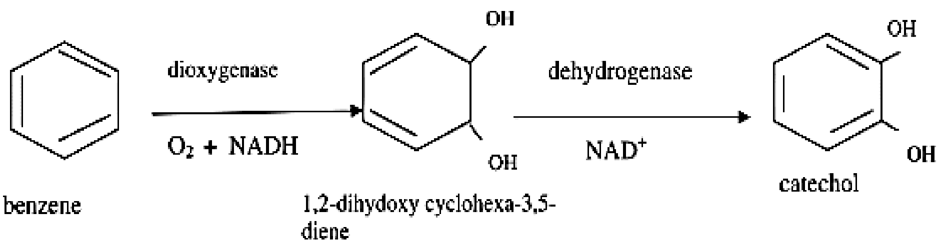


Figure 5. Biotransformation of aromatic benzene to catechol (Van Elsas *et al.*, 2007)

Conclusion

The damages incurred from aliphatic and aromatic petroleum hydrocarbon pollution remain a challenge to the environment. Since recycling of byproducts of petroleum hydrocarbon containing pollutants is not visible for the now, alternative means of remediating this waste can be explored using enzyme (monooxygenase and dioxygenase) catalyzed microbial remediation. The ability of microbial isolates to produce significant enzymes such as C12O, C23O highlights the future remediation significance of microbial population of HC polluted soils.

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Research Paper

Impact of Al_2O_3 NPs on Callus Induction, Pigment Content, Cell Damage and Enzyme Activities in *Ocimum basilicum* Linn.

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Abstract: With the advancement of nanotechnology, various potential applications of nanoparticles (NPs) have attracted considerable attention. In recent years, plant tissue culture applications in agricultural nanotechnology have become more popular. However, there are very few studies evaluating the effect of aluminum oxide nanoparticles (Al_2O_3 NPs) on enzyme activity and pigment content after plant tissue culture application. For this purpose, *Ocimum basilicum* L. callus growth effects, lipid peroxidation, hydrogen peroxide (H_2O_2) scavenging activity and chlorophyll content were investigated. As a result of this application, callus formation percentage and callus weight of the stem segment were found to be better than the leaf as the source of explants. The highest callus formation percentage (100%) was recorded as 741 mg stem and 324 mg leaf in (MS + 75 mg/l Al_2O_3) nutrient medium. In the (B5 + 75 mg/l Al_2O_3) nutrient medium, the stem was found to be 675 mg and the leaf 350 mg. Stress caused by Al_2O_3NP application was evaluated by chlorophyll and carotenoid pigment measurement. The highest Chl-a was detected at 75 mg / l Al_2O_3 NP concentration. The lowest total carotenoid was reported at 100 mg/l. The lowest Chl-a was detected at 25 mg / l. It was observed that the test groups treated with Al_2O_3 nanoparticle were significantly higher than the control group. In particular, the malondialdehit (MDA) level at 50 mg/l was quite high (7,409 times compared to control).

Keywords: *Al_2O_3, nanoparticles, plant tissue culture, MDA, chlorophyll, pigment*

Introduction

Nanotechnology is one of the fastest growing fields of advanced technology and therefore a source of hope for many branches of modern industry as well as medicine and pharmacy. In recent years, the use of nanoparticles (NP) in commercial products and industrial applications has increased significantly. However, the molecular level interaction mechanisms between NPs and biological systems have not been fully elucidated (Barrena *et al*., 2009; Khot *et al*., 2012). Moreover, certain NP properties, such as large specific surface area and greater reactivity, have raised problems due to their negative impact on human and environmental health (Andre and Mädler, 2006, Maynard *et al*., 2007). However, information on the fate of NPs in water and soil remains limited. With current research, positive and negative effects of NPs on plants have been reported, and researchers have investigated the effects of NPs on plant germination and growth (Khot *et al*., 2012). Also, some reports have confirmed that NPs can induce phytotoxicity and have a negative effect on seed germination and growth. However, specific properties of NPs such as size, shape and load can also be used to improve seed germination and crop performance (Khot et al., 2012). In a study focusing on NPs in edible plants, all plants exposed to or treated with NPs were reported to indicate toxicity.

Aluminum is one of the most abundant metallic elements in the world. It offers wider usage possibilities with its availability in many alloys (Johnson and Sanders, 2012; Ruan & Schuh, 2012). Aluminum oxide (Al_2O_3) is used in the health and cosmetics industry due to its high mechanical strength, hardness, wear resistance, high biocompatible structure and chemical inert properties (Lukin et al., 2001). Aluminum oxide nanoparticles are among the most preferred nanoparticles. As the element aluminum has been studied for many years, its toxicity is relatively well known. However, the toxicity of Al_2O_3 nanoparticles is still not fully known (Dağlıoğlu & Öztürk 2016; Dağlıoğlu & Öztürk 2018 a,b; Dağlıoğlu & Öztürk 2021). Possible mechanisms for the cytotoxicity of aluminum oxide NPs are still

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being debated. However, oxidative stress and DNA damage may be responsible for its cytotoxic effects (Kim et al., 2009). Sweet basil *(O. basilicum* L), a species of Lamiaceae family, is an extremely valuable plant and is grown commercially in many countries of the world (Hussain et al., 2008). The flowers and leaves of the plant are used in the food industry, either fresh or dried (Makri & Kintzios, 2007). *O. basilicum* is an anesthetic, anti-inflammatory analgesic, anti-ulcerogenic, heart stimulant, anti-tuberculosis (Limma-Netto et al., 2017; Bilal et al., 2012; Siddiqui et al., 2012). Its antioxidant, antimicrobial and antifungal potentials are high (Snoussi et al., 2016; Piras et al., 2018). In addition, it is used by the public for carminative, galactagogue, digestive system and spasm (Marwat *et al.,* 2011).

In this study, Al_2O_3 NPs and *O. basilicum* species were selected due to the above-mentioned properties. The most effective concentration was determined by applying Al_2O_3 NPs prepared in different concentrations to the plant cell culture of *O. basilicum*. After cell culture studies, Al_2O_3 NP treated *O. basilicum*. was collected from plant cell cultures and chlorophyll analysis, lipid peroxidation and hydrogen peroxide level were determined.

Materials and Methods

Plant and nanoparticle materials

Seeds of sweet basil (*Ocimum basilicum* L.) was used as plant material in this study. *O. basilicum* seeds were obtained from the Department of Field Crops, Faculty of Agriculture of Ordu University, Ordu, Turkey. Aluminum oxide nanoparticles (Al_2O_3 NPs), hydrophilic with a purity of 99% and an average particle size of 20 nm, used in toxicity tests were provided from a Nanography company from Ankara, Turkey.

Preparation of Al_2O_3 NPs test solution

To prepare stock solutions at concentrations of 0, 25, 50, 75 and 100 mg/L, the test substance was prepared in a deionized water by means of the Al_2O_3 NPs dispersion medium (Dağlıoğlu and Öztürk 2018; Özturk and Dağlıoğlu 2018). The solution was then vortexed for 20 s. Ultrasonic water bath was used to prepare stock solutions of nanoparticles.

Seed germination

Sterilization process and germination according to Açıkgöz (2021). Briefly, seeds were sterilized for 30 min in 1.95% sodium hypochlorite solution and after rinsing with sterile distilled water. The seeds were then inoculated on Murashige and Skoog (MS) basal medium; supplemented with 3% (w/v) sucrose and 0.8% (w/v) agar, 1.0 mg/L GA_3, the pH was adjusted to 5.6–5.8. Later, magenta plates were kept in 25 ± 2 °C for 16/8 h light/dark cycle in the climate chamber.

Callus formation from stem and leaf explants in media (MS and B5)

Sterile seedlings (20−22 cm long, 3 months later incubation) cut leaf and stem were used as explant source for the formation of callus cultures. Stem and leaf explants were used in the study and different concentrations of Al_2O_3 (0.0, 25, 50, 75 and 100 mg/l) NPs were added to MS and B5 growth medium with 2.5 mg/L NAA (naphthalene-acetic acid)+0.5 mg/L KIN (kinetin), 3% sucrose and 0.8 % agar, kept in climate room at 25±2 °C for 16/8 h light/dark conditions. The calluses were taken to subcultures twice with four weeks interval (using the same hormone combination and growth medium).

Nanoparticle characterization

The crystal structure of the Al_2O_3 NPs was characterized by X-ray diffraction (XRD) (Rigaku Smartlab model). The diffraction patterns were recorded at 2-Theta angular range of 20^0-90^0, 40 kV and 30 mA. The diffraction patterns of Al_2O_3 powders were compared with ICDD (PDF-4 + 2015 RDB) database. Al_2O_3 NPs size and distribution were performed by scanning electron microscopy (SEM, Hitachi, SU 1510) (Fig. 1).

Preparation of Basil extract

For water and ethanol extract, 25 g of the dried basil leaves was made into a fine powder in porcelain mortar and mixed with 500 ml of boiling water with a magnetic stirrer for 15 min. The residue was re-extracted until the extract solvents became colorless. The resulting extracts were obtained by Whatman. No. 1 was filtered and collected. The ratio of leaf powder and solvent is 1: 5 (W /v/g/ml). The final mixture, Whatman No. 4 filtered under suction with 4 filter paper. The very fine particles remaining in the filtrate were separated by centrifugation using centrifugation at 7000 rpm (Mata *et al*., 2007).

Lipid peroxidation

Lipid peroxidation determines the amount of malondialdehyde (MDA) that causes cell membrane damage. MDA was determined according to the method described by Lutts et al., 1996. Briefly, 200 mg of the plant was weighed and 5 ml of 0.1% trichloroacetic acid (TCA) was added thereto, which was centrifuged at 12500 rpm for 20 minutes. 3 ml of supernatant was taken from the 5 ml extract. On this supernatant, 3 ml 0.1 %TCA in 20 % thiobarbuturic acid (TBA) was added. The mixture was kept in a hot water bath at 95 °C for 30 minutes. Then, the absorbance values of A532 and A600 nm were read in the spectrophotometer. MDA concentration was determined as μmol/g T.A using ı "extinction coefficient" of 155 mM^{-1} cm^{-1} (Sevengör et al., 2011).

H_2O_2 scavenging activity

The ability to remove hydrogen peroxide of ethanol basil extract was determined according to the method of Ruch et al., (1989). H_2O_2 solution (40 mM) in phosphate buffer (pH 7.4) was prepared. Extracts in distilled water (50 µg/mL) were added to H_2O_2 solution (0.6 mL, 40 mM). The absorbance value of the reaction mixture was recorded at 230 nm. Blank solution is phosphate buffer without H_2O_2. The ethanol basil extract and the H_2O_2 cleaning percentage of standard compounds were calculated as follows (Gülçin et al., 2003; Gülçin and Aboul-Enein 2007):

$$H_2O_2 \text{ scavenging activity} = \left(\frac{Acontrol - Asample}{Acontrol}\Big| \quad\right) x100$$

Chlorophyll analysis

At the end of the exposure period, 80% acetone solution and quartz sand were added to crushed Al_2O_3 NPs applied to fresh chlorophyll analysis. For the chlorophyll analysis, 80% acetone solution and quartz sand were added to the Al_2O_3 NPs applied basil plant and crushed. The resulting extract was taken to the centrifuge tube and 4 ml of 80% acetone was added. After centrifugation, the Whatman black band was filtered through filter paper, and the final volume was completed to 10 ml. The obtained liquid was read on the spectrophotometer at 450, 645 and 663 nm. To prevent experimental errors, three groups were studied for each sample. The amounts of chlorophyll a, chlorophyll b, total chlorophyll, and carotenoid were calculated using the following formulas.

The amounts of chlorophyll a, chlorophyll b, total chlorophyll, and carotenoid using the following formulas (Odabaş, 1981).

Chlorophyll a (mg/g texture weight)	=	[12.7x(D663)-2.69x(D645)] * (V/1000.A)
Chlorophyll b (mg/g texture weight)	=	[22.9x(D645)-4.68x(D663)] *(V/1000.A)
Total chlorophyll (mg/g texture weight)	=	[20.2xD645) +8.02x(D663)] *(V/1000.A)
Carotenoid (mg/g texture weight)	=	4.07x D450- [0.0435x Chlorophyll a + 0.3367x Chlorophyll b]

D: wavelength, V: 100% acetone final volume, A: weight of leaf tissue in grams.

Data Analysis and statistical evaluation

Significant differences between the control and the test groups were determined by multiple comparison of one-way analysis of variance (ANOVA) and Tukey test. The *P* values show significant differences of 0.05 ($P \leq 0.05$).

Results

Callus formation from stem and leaf explants in media (MS and B5),

As a result of the examinations performed after the first planting medium and subcultures, the percentage of callus formation and callus weight were found to be better than the leaf in hormone combinations where the stem segment was used as the source of explants. Callus formation percentage, callus weight and callus scoring are given in Table 1 and 2. The highest callus formation percentage (100%) and callus weight 741 mg and 675 mg were obtained from the two main nutrient media (MS+75 mg/l Al_2O_3 NPs and B5+75 mg/l Al_2O_3 NPs).

Table 1. The effect of Al_2O_3 NPs concentrations applied to leaf and stem explants on callus formation percentage (%) and callus weight (mg) (MS media)

	Leaf			Stem		
Al_2O_3 NPs 0 (control)	Percentage of explants forming callus (%)	Callus weight (mg)	Leaf Score (0-4)	Percentage of explants forming callus (%)	Callus weight (mg)	Stem Score (0-4)
	50	160	2	100	100	2
	60	90	1	100	379	3
	90	300	2	100	173	2
	90	47	1	100	325	3
	90	85	1	100	190	2
25 mg/l	90	260	2	100	574	3
	90	247	2	90	557	3
	80	220	2	100	362	2
	70	217	2	70	500	3
	80	209	2	80	554	3
50 mg/l	50	103	2	60	225	2
	40	70	1	50	72	2
	40	80	1	70	190	2
	60	200	2	60	204	2
	40	79	1	80	327	2
75 mg/l	60	40	1	90	732	3
	100	312	2	100	653	3
	100	**324**	**2**	**100**	**741**	**3**
	80	148	1	80	300	2
	80	347	2	80	276	2
100 mg/l	70	100	1	30	270	2
	100	379	2	100	245	3
	80	173	1	80	368	2
	90	325	2	90	621	3
	60	190	2	80	273	2

Footnote: Scoring is calculated over 4 points. Here, criteria such as callus formation percentage, callus formation direction, callus type and weight were taken into account. However, no information is given about the direction and type of callus formation in the Table 1. Samples meeting all of these criteria received 4 points, while those meeting only one received 1 point.

Considering the effect of Al_2O_3 NPs on the percentage (%) of explants that form callus in the MS media, 50 mg/l Al_2O_3 NPs for leaf and stem are quite low. Again, it is this concentration that has the least effect on callus weight.

In the B5 nutrient medium as seen in the above table, the percentage of the explants that produced the lowest callus for the leaf and stem and the callus weight were recorded at 100 mg/l Al_2O_3 NPs concentration.

Between the two main nutrient media (MS and B5) used in the study, the highest percentage of callus formation (100%) and callus weight were obtained from the application of 324, 741 mg and 350, 1600 mg and 75 mg/l Al2O3 NPs, respectively. When leaf and stem explants, which are callus sources, were compared themselves, it was determined that stem explants stood out with 741 and 675 mg in terms of callus weight. Many studies on the subject have shown that the medium used, hormone combination and explant source are effective in callus formation.

Table 2. Callus formation, callus weight and scoring in leaf and stem explants (B5 media)

	Leaf			Stem		
Al_2O_3 NPs	Percentage of explants forming callus (%)	Callus weight (mg)	Leaf Score (0-4)	Percentage of explants forming callus (%)	Callus weight (mg)	Stem Score (0-4)
0 (control)	20	47	1	30	100	2
	80	132	2	80	304	2
	50	047	1	50	140	2
	50	142	2	50	142	2
	10	28	1	10	54	2
25 mg/l	60	140	1	60	240	2
	100	200	2	100	500	3
	100	324	2	100	514	3
	80	156	1	80	356	2
	80	141	2	80	248	2
50 mg/l	40	127	1	50	224	2
	30	132	2	50	270	2
	40	100	1	40	175	2
	70	196	2	70	270	2
	60	128	2	60	255	2
75 mg/l	100	230	2	100	530	3
	90	198	2	90	450	3
	100	**350**	**2**	**100**	**675**	**4**
	70	356	3	70	500	3
	80	220	2	80	440	3
100 mg/l	10	50	2	10	75	2
	10	14	1	10	80	2
	10	17	1	10	64	2
	60	175	2	60	210	2
	0	0	0	40	140	2

Footnote: Scoring is calculated over 4 points. Here, criteria such as callus formation percentage, callus formation direction, callus type and weight were taken into account. However, no information is given about the direction and type of callus formation in the Table 2. Samples meeting all of these criteria received 4 points, while those meeting only one received 1 point.

Physicochemical characterization of Al_2O_3 NPs

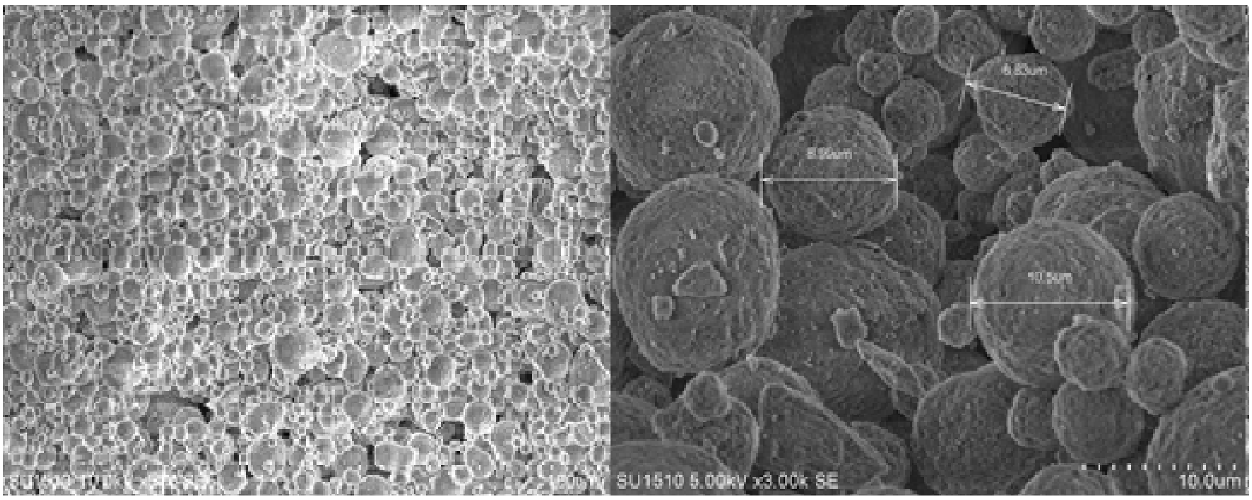

Figure 1. SEM image of the Al_2O_3 NPs

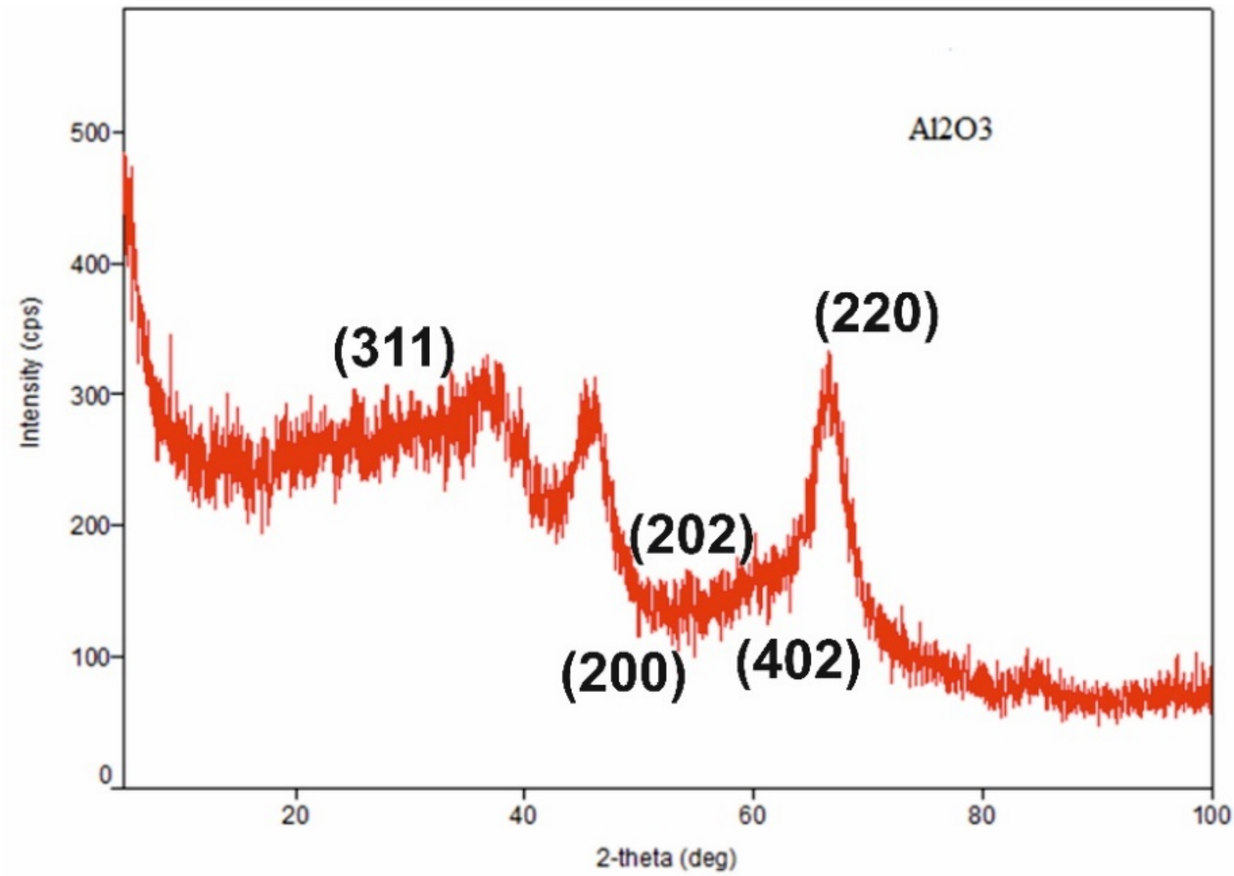

Figure 2. X-ray diffraction (XRD) analysis of powdered Al_2O_3 NPs.
Compared to standard PDF cards, the samples analyzed were found to be compatible with the Al_2O_3 element. However, some peaks did not match Al_2O_3. This is because the particles are 95% pure. This is because the particles are 95% pure.

Pigment analysis

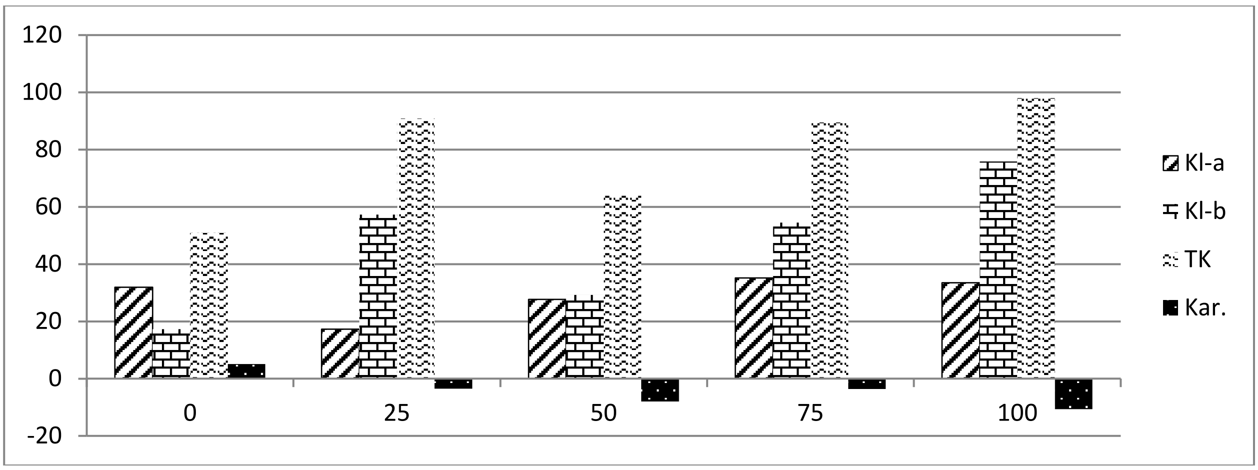

Figure 3. Pigment contents in *O. basilicum* exposed to Al_2O_3 NPs.

Considering that photosynthesis plays an important role in photosynthesis II (PSII) in response to environmental stress, analysis of chlorophyll fluorescence and evaluation of CO_2 assimilation in the administration of Al_2O_3 NPs may reflect PSII behavior (Biswal and Biswal 1999). The chlorophyll content of the extracts obtained from the *O. basilicum* leaves exposed to Al_2O_3 NPs at concentrations of 0, 25, 50, 75 and 100 mg/L was quite different. Chlorophyll a content was found to be high in low Al_2O_3 NPs concentrations compared to the control group. It was found to be low in groups exposed to high

Al_2O_3 NPs concentrations. According to the control group, it was noted that it decreased by 25, 50 mg / L, 61.7% and 13.5% and increased by 10% and 4% at 75 and 100 mg / L, respectively.

Table 3. H_2O_2 and CAT activities with MDA level in *O. basilicum* treated with AL_2O_3 NPs

Samples	MDA	H_2O_2
0 mg/L	1.158	4.00
25 mg/L	6.70*	4.00
50 mg/L	8.58*	3.972*
75 mg/L	1.212	4.00
100 mg/L	1.806	4.00

Lipid peroxidation, which was measured as the formation of MDA production, was observed to be quite high in the test groups treated with Al_2O_3 nanoparticle compared to the control group. Especially, the MDA level at 50 mg/L was quite high (7.409 times compared to the control). Lipid peroxidation at a concentration of 25 mg/L was higher than the control group (P <0.05). Lipid peroxidation at the highest dose (100 mg/L) was higher than the control (1.55 times), but reduced by 0.74 times ($P <0.05$) compared to 25 and 50 mg/L concentrations.

Discussion

Many studies on the subject have shown that the medium used, the combination of hormones and explants are effective in the formation of callus (Hariprasath et al., 2015; Dhas et al., 2016; Jin et al., 2017; Krishnan and Siril, 2017; Açıkgöz, 2020; Açıkgöz, 2021). Optimum callus formation from explant sources *in vitro* can be achieved by selecting the most appropriate source of explants (root, stem, leaf, hypocotyl and epicotylone) according to the species, using the appropriate nutrient medium (MS, B5, SH, LS and NN) and finally the correct hormone or it is provided with hormone (cytokinin + auxin) combinations. Many studies have been carried out to induce callus formation in many species. In most of these studies, stem explants induced callus formation more than leaves, while leaf explants induced more callus formation in some (Zinhari et al., 2016; Hosseini et al., 2017; Açıkgöz et al., 2018; Açıkgöz et al., 2019). It has been reported by many researchers that elicitor treatments are very effective in cell growth and callus formation. The age of cell culture (Namdeo, 2007; Kang et al., 2009), the duration of exposure to elicitors and the type of elicitor play important roles in increasing the effectiveness of these treatments (Kubeš et al., 2014). In previous studies, some researchers reported that some compounds such as CdCl2, AgNO3 inhibit cell growth and callus formation (Zhao et al., 2010; Sivanandhan et al., 2014; Zaker et al., 2015; Gonçalves et al., 2019). However, some researchers reported that some elicitors such as AgNO3 and its derivatives support cell growth and callus formation at appropriate concentrations. (Yan et al., 2006; Deepthi and Satheeshkumar, 2016; Singh et al., 2017; Roy and Bharadvaja, 2019).

In this study, the toxicological profile and general mechanisms related to the chronic toxicity of Al_2O_3 NPs applied to *O. basilicum* cell culture were investigated. Preliminary characterization of Al_2O_3 NPs was performed by SEM and XRD analyzes before testing conditions. In the SEM image of Figure 1, Al_2O_3 NPs are nearly spherical in shape. Al_2O_3 NPs appear to be agglomerated and have an approximate size of about 20 nm. Other characterization related to the shape of Al_2O_3 NPs was performed with XRD (Figure 2). In XRD analysis, the peaks were observed at 36.33, 45.07, 46.16, 62.03 and 66.70. *O. basilicum*, a well-known traditional herb in the Indian continent, has been included in several herbal preparations for the treatment of various diseases. Many types of *O. basilicum* and *O. sanctum* forms such as ethanoic extract, flavonoids, seed oil, phenolic compounds, root extract, leaf extract, aqueous extract, fixed oil, fresh leaf pulp and leaves were examined. Bone marrow radioprotection has promising results for chemo protection, hypoglycemic activity, and immune stimulatory effects (Prashar et al., 1994; Godhwani et al., 1998). The presence of xenobiotics and toxicants causes oxidative damage to cells and biomolecules. The negative effects of oxidative damage can be eliminated by antioxidant enzymes such as superoxide dismutase (SOD) and catalase (CAT) activities (Radotic et al., 2000; Lee et al., 2001; Liu et al., 2009). In this study, CAT activity remained stable in *O. basilicum* in response to Al_2O_3 NPs treatments. In addition, antioxidant activities of ethanol extracts obtained from leaf and stem of *O. basilicum* plant were investigated by various methods. When investigations with *O. basilicum* were examined, it was seen that the determination of secondary metabolites, glycosylate and volatile aromatic compounds and their volatile components were limited to studies on determination of sulfur and nitrogen content and growing conditions. After treated *O. basilicum* with Al_2O_3 NPs, it was extracted with methanol in room conditions and its effects on H_2O_2 and CAT activities and MDA levels were examined (Table 3). Malondialdehyde (MDA) is a cytotoxic product of lipid peroxidation and shows an indication of free radical production and consequently tissue damage (Ohkawa et al., 1979). MDA is the result of peroxidation of fatty acids containing three or more double bonds. MDA level is used to evaluate lipid peroxidation. Increases in MDA levels were observed in Al_2O_3 NPs treated *O. basilicum*. The highest increase was observed concentration in 50 mg/L and this increase was statistically significant ($P<0.05$). In the application of 50 mg/L Al_2O_3 NPs, the MDA level increased by 7.409 times compared to the control. At 25 mg/L, the concentration of Al_2O_3 NPs increased 7.78 times compared to the control. At a concentration of only 75 mg/L, it was noted that the level of MDA was very low compared to the control. Furthermore, it was determined that CAT and H_2O_2 sweeping activity were the same for all Al_2O_3 NPs concentrations ($P>0.05$). According to these results, the highest tissue damage of Al_2O_3 NPs was 50 mg/L and 25 mg/L respectively. 100 mg/L caused very little tissue damage. At 75 mg/L, the MDA level was much less than the control group. In the application of 25 and 50 mg/L Al_2O_3 NPs which can be said to be actively penetrated in the cells. It can be said that high doses of 75 and 100 mg/L Al_2O_3 NPs do not cause tissue damage because they do not penetrate the cell due to aggregation. Because when nanoparticles form aggregates at high doses/concentrations, their passage to the cell is prevented. MDA and pigment analysis confirm each other. The chlorophyll content of leaf provides valuable information about the physiological state of plants. It makes it possible to evaluate chlorophyll content in leaves as fast and non-destructive *in situ*. Chlorophyll a and chlorophyll b are the pigments required to convert the light energy into stored chemical energy. The amount of sunlight absorbed by the leaf is a function of the photosynthetic pigment content. Thus, the chlorophyll content can directly determine the photosynthetic potential and primary production (Curran et al., 1990, Filella et al., 1995). In addition, chlorophyll indirectly estimates the state of the nutrient because a large part of the leaf nitrogen is incorporated into the chlorophyll (Filella et al., 1995, Moran et al., 2000). Moreover, the content of leaf chlorophyll is closely related to plant stress and aging (Merzlyak and Gitelson 1995; Merzlyak et al., 1999). The pigment content of the sweet basil leaves varied considerably. (Figure 3). In this study, chlorophyll a content was examined as an indicator of productivity in basil plant. Accordingly, chlorophyll a content is low in low Al_2O_3 NPs concentrations compared to the control group; high Al_2O_3 NPs concentrations were observed to be high. Compared to the control group, it decreased 61.7% in 25 mg/L and 13.5% in 50 mg/ L. Productivity is expected to decrease with increasing concentration of toxicants compared to conventional toxicants. However, in this study, productivity increased with increasing Al_2O_3 NPs concentration and low concentration productivity decreased significantly. This may be explained by the tendency of aggregation which is one of the unique physicochemical properties of the nanoparticles. Nanoparticles indicate high affinity to each other and form an aggregation. Thus, the nanoparticle cannot penetrate the cell by increasing its size. Also, as mentioned above, the MDA level used as an indicator of cell damage showed compatibility with the content of chlorophyll a. In other words, the level of chlorophyll at the concentration of Al_2O_3 NPs (25 and 50 mg/L) with the highest MDA levels was quite low. On the contrary, chlorophyll a level was high at concentrations (75 and 100 mg/L) with low levels of MDA.

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Review Paper

Techno-Economic Analyses of the Moisture Adsorbed Materials

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Abstract: The use of adsorbents, which are naturally formed in nature or created in a laboratory environment, in agriculture, industry, and daily life is increasing day by day. It is possible to classify adsorbents according to different criteria, however in this study, they are considered natural and synthetic adsorbents. Considering the laborious and costly preparation of synthetic adsorbents in the laboratory environment, and the abundance, cheap costs, and accessibility of the natural adsorbents in Turkey, it is necessary for our country to have an important place in the world markets, by establishing eco-friend, clean, and high-tech production facilities and orienting towards natural adsorbents. The use of adsorbents, which are naturally formed in nature or created in a laboratory environment, in agriculture, industry, and daily life is increasing day by day. Adsorbents which can be called as also desiccants; should be non-toxic, harmless for the environment, cheap, easily obtainable, and recyclable, containing functional groups, insoluble in water, having a large surface area and scientifically accepted. It is possible to classify adsorbents according to different criteria, however in this study, they are considered natural and synthetic adsorbents. Here, these desiccants are compared and the economic importance of natural desiccants for Turkey is mentioned. Preparation of synthetic adsorbents in the laboratory environment is quite laborious and costly. Considering the abundance, cheap costs, and accessibility of the natural adsorbents in Turkey, it is necessary for our country to work on natural desiccants. In this way, it is crucial for our country to have an important place in the world markets, by establishing eco-friend, clean, and high-tech production facilities

Keywords: *adsorbent, eco-friend, natural adsorbents, synthetic adsorbents.*

Introduction

Adsorbents; they should be non-toxic, harmless for the environment, cheap, easily obtainable and recyclable, containing functional groups, insoluble in water, having a large surface area and scientifically accepted. Natural or synthetic materials used to adsorb the humidity in the environment and to protect the material from moisture are called "desiccants". Desiccants, also known as humidifiers, are chemicals that strongly attract water vapor. The main parameter in desiccant dehumidification is to capture the water vapor molecules or particles in the humid air in the labyrinths of the adsorbent-carrier materials with very large inner surfaces and remove them from the humid air (Chimeddorj, 2007). The most important factor in the realization of this process is the pores of the desiccant material, which form very large areas at the micro level (Rahle, 2006). Humidifiers, also known as desiccants, are chemicals that strongly attract water vapor. They could be broadly assorted as liquid and solid desiccants. Silica gel, activated alumina, zeolites, perlites and clays are solid desiccants that adsorb water vapor chemically or physically without chemical change. Triethylene glycol, calcium chloride, lithium bromide or chloride are grouped as liquid desiccants that adsorb water vapor. They may modify chemically when they adsorb moisture (Gandhidasan & Mohandes, 2008). The most important advantages of liquid desiccants are that their regeneration temperatures are very low, such as 50-65°C, and they also adsorb inorganic and organic contaminations in the air, thus helping to clean the air (Gandhidasan, 2004). Solid desiccants are also widely used commercially. They should have large surface areas for high mass transport rate and high capacity. The activities and bulk densities must be high for the compounds to be removed. They ought to be easily and economically regenerable. Moreover, they should have high mechanical resistance against dust formation and breakage. They must be corrosion resistant, inexpensive and non-toxic. There ought to be no noticeable change in volume

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during adsorption, desorption, and could maintain strength when wet (Gandhidasan *et al*., 2001). The most widely used solid commercial desiccants are silica gel and clay. Inorganic adsorbents, e.g. mineral clays, for moisture adsorption are widely used. Smectite and sepiolite are the most commonly used adsorbent clays. The most important competitors of adsorbents produced from clay are wood chips and cellulose compounds. However, these compounds cannot be used in every application area due to their flammability properties as well as their cheapness (Chimeddorj, 2007).

Superadsorbents are nanocomposite superadsorbents are made by loading clays like montmorillonite, kaolin, attapulgite, etc. in a polymeric network utilized to control the diffuse of fertilizers and pesticides, enhance soil moisture holding, rise seed germination, and have greater efficiency of adsorbing water (Sarkar *et al*., 2015). Along with minerals like zeolite, gypsum, clays, and calcium carbonate are also natural conditioners and modifiers of the soil environment. Some chemical, physical, and physicochemical characteristics differ clays from other soil colloids in terms of their behavior toward influencing heterogeneous soil environments (Manjaiah *et al*., 2019).

In agriculture, to deal with the rising water scarcity, several water-saving techniques have been improved to reduce irrigation water and enhance water use efficiency in rice production system, such as aerobic rice (Nie *et al*., 2012), saturated soil culture (Kima *et al*., 2014), non-flooded mulching cultivation (Qin et al., 2010), the system of rice intensification (Berkhout *et al*., 2015), alternate wetting and drying irrigation (AWD)(Cabangon *et al*., 2001; Nalley *et al*., 2015), etc. Among these methods, AWD is generally utilized worldwide, especially in China. In AWD treatment, the field does not need to be kept submerged all the time. The AWD be likely to also affect grain yield by altering the nitrogen cycle in the rice system (Dong et al., 2012). Under AWD irrigation, the soil is alternately submerged and non-submerged, which leads to anaerobic and aerobic conditions. Accordingly, the alternate wetting and drying cycle increased the nitrogen loss by accelerating nitrification-denitrification processes (Zheng *et al*., 2018). The nitrogen loss not just leads to low nitrogen use efficiency but also bring about serious environmental risk such as groundwater pollution, eutrophication, emission of greenhouse gases and so on (Ju et al., 2011). In order to incerase N use efficiency and improve rice yield, many N-saving techniques have been enhanced, i.e. N fertilizer split application, application of controlled-release N fertilizers, and adoption of soil amendments. Lately, zeolite has been widely used in agriculture as inorganic soil amendment to reduce N leaching, improve N use efficiency and increase crop yield. Although there were several studies about the effects of zeolite application on agronomic characters of rice under continuous flood irrigation, few studies have looked into its effect on rice under AWD. In addition, zeolite could also enhance water use efficiency by rising soil water retention capacity and water availability to plants (Xiubin & Zhanbin, 2001). Natural zeolites have been proved to increase crop water use efficiency (Gholamhoseini *et al*., 2013). The increase of grain yield could be attributed to reduced nitrogen leaching and increased water holding capacity in soil in the presence of zeolite which developed the nitrogen and water availability for rice growth. In order to save irrigation water and maintain rice yield simultaneously, lots of water-saving methods have been put forward.

According to the Drought in the Mediterranean report of the World Wildlife Fund, especially in Turkey, Egypt and Syria, precipitation has decreased by 25% due to global warming, one of the two main causes of drought is incorrect agricultural irrigation techniques and the other is global warming. It is stated that in the countries with coasts, the water use policies of the states in agriculture should be changed urgently. For this reason, it is necessary to increase soil fertility and reduce water use in agriculture. For this, natural and artificial adsorbents have been used recently.

Here, moisture adsorbed (desiccant) materials and their properties, which are of great importance today and can be used in many areas, are discussed. The interest in natural desiccants is increasing since synthetic desiccants are both uneconomical and require laborious laboratory procedures. In this study, zeolites, clays, and, perlites which are abundant in our country and frequently preferred due to their important properties such as humectant and ion exchange, are also discussed in terms of their economic importance. In this study, which is largely a compilation, the definition and classification of adsorbents used in agriculture, including ion exchangers in a broad sense, and their potential in Turkey, have been presented and discussed.

Moisture Adsorbents (Desicants)

Natural Desiccants

Clay minerals

Clays can be used as a dehumidifier and there are more than two hundred types of clay minerals in nature. Calcium alumina silicate clay, which is chemically inert, can adsorb more water vapor than other types of clay. The layered structure of this calcium-rich montmorillonite clay increases its water adsorption capacity. Adsorption takes place on surfaces and between layers. Since clay is a natural material, it is more economical than silica gel. They have a moisture holding capacity of up to 20% by weight at 40% relative humidity and 25 °C temperature. The advantages of clay dehumidifiers are their natural formation, chemical inertness and non-toxicity, rapid adsorption capabilities at critical humidity levels, dry and free flowing properties in all humidity conditions, high moisture adsorption capacity, and recyclability.

It is used less than silica gel, but it is relatively inexpensive, which is one of its attractive features. Clays work well at low temperatures but begin to lose water at 120ºF (50ºC). Due to this feature, it is not suitable for use in hot environments. However, this allows the clay to be used by re-activating (drying) at low temperatures (Chimeddorj, 2007). Clays that cannot get enough moisture are modified by various methods and their ability to adsorb moisture is increased. As a modification process, various dehumidifiers are added to the clay or heat activated (Cancela *et al*., 1997) For example, according to British standard BS 7529:1991, clay activated at 145±25ºC should have a moisture adsorption capacity of at least 20% by weight at 50% relative humidity. The pH of the produced desiccant clay should be minimum of 5.5 and maximum 8.0 (Chimeddorj, 2007).

The interaction of water with soil colloids has a critical role in all areas of soil science, and numerous studies have shown that exchangeable cations significantly influence soil–water relations (Dontsova *et al*., 2004). Na, Mg, Ca elements are significant for the soil in terms of water adsorption and the improvement of the soil. Exchangeable cations effect on the overall behavior of water in soils. Dispersion and clay swelling, which are enhanced by Na and Mg on the soil exchange complex, can block air- and water-conducting soil pores, thereby affecting infiltration and hydraulic conductivity. By contrast, Ca is known to promote the flocculation of soil colloids and is often used in various soil remediation strategies. Water condensation and osmotic swelling are the dominant mechanisms for retaining water molecules at high relative humidity (RH). At low water contents, the hydration characteristics of smectite depend strongly on the exchangeable cation. Layer charge also impacts on the amount of water adsorbed on clay surfaces, with more water being adsorbed on high charged smectites than on low charged ones (Dontsova *et al*., 2004). Water demand for a given consistency of clay-containing soils varies considerably, depending on the water retention capacity that in turn is determined by the crystal chemistry of clay minerals. The water retention capacity reduces in the sequence: sepiolite > Na-montmorillonite > Ca-montmorillonite> mixed layer mica/smectite > non-expandable clays. The water/(cement+clay) ratio shows a broad linear correlation with the specific surface area (BET) of all clays (He et al., 1995).

Perlites

Perlite is an acidic volcanic glass and it expands with heat and becomes very light and porous when expanded. Perlite is frequently used as a "substrate" material that increases the physical properties of the soil, to provide the necessary suitable soil conditions, to increase the compactness of the soil, to reduce water drainage and to preserve moisture, to create a breeding environment for seedlings, and to aerate the soil. It is known that perlite granules that were produced under high (>1500 ^{0}C) temperatures, could reach minimum of four times their original size and generally a 430% increase in their volume that could better hold water and support plant roots, particularly under deficit irrigation conditions. Moreover, it is reported that perlite was the optimal germination medium sterilized and free from weeds, pathogens, and other shrubs (Evans, 2004; Hanna, 2006). Therefore, perlite addition in to the crops is an attractive method to alleviate the consumption and usage of water in agriculture, nowadays. Recent studies (Fahmi *et al*., 2021) reveal that the evident improvements in soil characteristics due to perlite addition, which increased soil's water holding capacity, saved more water volumes, and reduced water requirements of plants to increase irrigation intervals. These studies also report that the addition of the perlites into the soil brings about the possibility of cultivation in even gypsiferous soils.

Zeolites

Zeolites (Gismodin Fojasite, Gonaidite, Natrolite, Analcime, Phillipsite, Chabazite, Erionite, Mordenite, Tomsonite, Mesolith, Holandite etc), known as aqueous aluminum silicates with a crystal structure of alkali and alkaline earth elements, today, it is an important industrial raw material due to its properties such as having high selectivity in ion exchange processes, resistance to an acidic environment, molecular sieve properties, and also they have low usage costs. The number of researches in the field is also very limited. While zeolites find use in many sectors in the world such as pet-litter (animal pad), paper paint, toothpaste, detergent industry, pollution control, agriculture, and energy, the technological use of natural zeolites (clinoptilolite) cannot be adequately evaluated in our country (Sabah *et al*., 2011). In laboratory-scale research, natural zeolites; in the treatment of ammonium ion from wastewater (Ülkü, 1984) and in the retention of some cations that cause pollution of water (Bürküt *et al*. 1997), as an additive in cement production, heavy metal ions in waste water (Demirel *et al*.1989), and Cs^{+}, Sr^{++} containing its use as an ion exchanger in the treatment of radioactive wastes (Akyüz *et al*., 1991) have examined (Sabah *et al*., 2011). Along with them, the relationship between the formation of natural zeolites (Suner, 1991), mineralogy (Göktekin, 1990; Köktürk, 1995), production technology, species, effects on human and environmental health (Köktürk, 1995; Yücel & Çulfaz, 1984) and the wetting temperatures and cation exchange capacities (Yörükoğulları *et al*., 1989) etc. are the different study branches of the zeolites.

The advantages of zeolite water-storing are their natural formation, chemical inertness, and non-toxicity, rapid adsorption capabilities at critical humidity levels.Zeolites, which have a smooth and porous crystal structure with a certain aperture, can act selectively by allowing cations of certain sizes to enter these pores during ion exchange (Sherman *et al*., 1978). Again, with the ion exchange method, the types, numbers, and positions of the cations in the pores of the zeolites can be changed to increase the effective pore volume of the zeolites (Breck, 1974).

In recent years, it is of great importance that this mineral is used in agricultural activities to remove the hardness of water, clean wastewater, and as a water-storing. Due to this importance, besides natural zeolites, synthetic zeolites with better purification ability are produced. However, although synthetic zeolites have better ion exchange capacity compared to natural zeolites, their high cost limits the possibilities of use, and the use of natural zeolites is increasing day by day (Sabah *et al*., 2011).

Natural zeolites have only recently begun to be accepted in many market areas, despite their widespread use and great market potential. In addition to contributing to the national economy by determining our natural zeolite potential in our country, which has a significant reserve potential, it will also provide great benefits by using it to prevent the drought in agriculture, the infertility of soil, and environmental pollution that seriously threatens humanity in our country. Recently, zeolites have widely used as alternative materials in semi-arid and arid regions in our country as well as in the world, as they can support the saplings in terms of water until they survive the dry period. The drought in the Central Anatolia Region and the wrong policies applied in agriculture have caused the lakes to dry up and the waters to recede and have recently brought about the formation of sinkholes in the Konya-Karapınar region. Studies about agriculture in the Konya-Karapınar region indicate that zeolites increase soil fertility and reduce water usage (Mumpton, 1999; Ozbahce *et al*., 2015; Yapparov *et al*., 1988).

Synthetic Desiccants

Artificial adsorbents; are substances that are difficult to produce in factories, have high costs, can be toxic and adversely affect environmental health. The only positive side is that they can be designed with the desired feature. In recent years, many cheap and environmentally friendly artificial adsorbents have also been produced (Demir & Yalçın, 2014). Silica gel and activated alumina from activated carbon and oxide adsorbents, fly ash from industrial wastes; furthermore, resins and polymers (single, multiple and/or hybrid) are the most commonly used commercial types (Demir & Yalçın, 2014).

Silica Gel

It is one of the high capacity synthetic adsorbents. They are the materials used in every point where a dry environment is desired, which keeps the humidity in its body with high efficiency. Silica gels are utilized as adsorbent in several drying processes in industry. Low cost, long service life, high wear resistance and low regeneration energy requirement are the most significant advantages of silica gel. When examined microscopically, it consists of micro-level pores (pores) and a capillary network system.

Due to this feature, they are inert materials in the form of granules with a high surface area. With the physical adsorption method, it attracts moisture and gas molecules with a molecular diameter that can enter through the pore structure and keeps them by condensing them in micropores. In addition to white silica gels, there are silica gels with blue and orange indicators that allow visual control.

Activated Alumina

The source of the aluminum element is corundum Al_2O_3, gibbsite/hydrargillite $Al(OH)_3$, diaspore-boehmite AlO(OH) minerals (Demir & Yalçın, 2014). Activated alumina is a type of aluminum oxide and can be used in almost all industrial drying processes. It is an adsorbent with superior surface properties used as a drier in industrial facilities, especially in dynamic adsorption conditions. In compressors, taking moisture from liquid liquids and dry air systems are used safely for a long time. It provides efficient drying at very low condensation points. This product, which can be used for drying all kinds of liquids and gases, also shows high performance in the retention of impurities such as carbon dioxide, heavy metals, sulfides, and hydrocarbons.

Activated Carbon

Today, activated carbon, with the effect of its high porosity, is the most important adsorbent widely used in Turkey and the world in order to control industrial environmental pollution. Commercially activated carbons; wood, coal (peat, lignite, stone coal) They are produced by activating carbons obtained from shells (coconut, rice, wheat, cocoa, citrus, hazelnuts), fruit seeds, and oil products by passing through various processes. Activated carbons obtained from these materials are generally hard and dense and can be used for a long time without decomposing in water (Demir & Yalçın, 2014).

Polymers

Many applications have been developed to enhance the water holding capacity of the soil, especially for agriculture in semi-arid and arid regions. One of these applications is the use of water-retaining adsorbent known as superadsorbent polymer (SAP). Hydrogels, which are called "water traps" due to their high water holding capacity, support plant growth, and development in the soils of arid and semi-arid regions where water shortage is one of the main problems for agricultural production (Johnson and Piper, 1997). These superadsorbent polymers, which generally consist of a cross-linked polymer chain, can retain much more water than conventional adsorbent materials (Esposito *et al*., 1996). These water-storing polymers can hold water up to five hundred times their weight (Kazanskii & Dubrovskii, 1992) and when applied to the soil, they can increase the water holding capacity of the soils up to twice (Bhardwaj *et al*., 2007; Karimi *et al*., 2009). In many studies carried out; It has been stated that the use of water-retaining polymers provides many benefits such as reducing the water stress of the plant, increasing the water holding capacity of the soil, extending the time between successive irrigations, rising the plant growth rate and performance and root weight (Ekebafe *et al*., 2011; Hüttermann *et al*., 1999; Pill & Jacono, 1984; Viero *et al*., 2002). The polymer used in the study by Yakupoğlu et al. (2019) is a cross-linked, acrylic acid potassium acrylate copolymer. A certain amount of straw was added to the composition of this polymer and a water retainer named Natural Aquatic® was obtained. This superadsorbent has a more natural structure thanks to the straw in its composition. The composition of the straw is 65-75% cellulose, 15-20% hemicellulose and pentosans, 5-10% lignin, 1-3% wax and protein. It consists of minerals such as 2-10% silica and a small amount of starch. This water trap developed with straw contains different ratios of C, H, O ,K and elements that can come from straw. The purpose of modifying the Natural Aquatic® polymer with straw is to increase the water holding capacity even more and to develop a waterstop that is partially composed of organic materials. Natural Aquatic® is an easy-to-use soil additive that can retain water and nutrients. This product adsorbs rain and irrigation water and retains 200-300 times its volume in the plant root zone. Natural Aquatic® also acts as a ready-made water tank in the root zone of the plant and offers the water needed by the plant for the plant's consumption (Yakupoğlu *et al*., 2019). According to the results obtained from Yakupoğlu *et al*. (2019), 0.2% and 0.4% doses of the straw bearing water-retaining polymer called Natural Aquatic® in semi-arid climate zone soils, the slope of which did not exceed 9%, in terms of its effect on soil and water losses, It is suitable for clay textured soils where corn cultivation will be done. In areas where the slope is < 9% where soybean will be grown, higher doses can be used. Although it is not an economical application in today's conditions, if it is preferred to apply these water stops to fallow areas in semi-arid climate regions, 0.8% and above application dose of this polymer for areas with slopes up to 9% is inconvenient because it will cause excessive soil and water losses. There are still great unknowns about the behavior of water-retaining polymers in the soil and their behavior in different conditions. In addition, Yakupoğlu *et al*. (2019) reveal that intermediate doses of Natural Aquatic® superadsorbent should be tested in order to gain more clarity on the subject, the straw ratio in its content should be calibrated according to different soil types, and experiments should be carried out under synthetic precipitation with different characteristics and in different slope groups.

Comparison of Some Desiccants

Natural zeolites, clay minerals and perlites have a huge potential to improve nutrient use efficiency through controlled release as well as environmental remediation from toxic organic and inorganic pollutants. Along with that, these minerals and their modified products are significant materials to hold soil moisture. Usage of these minerals as soil conditioners, modifiers, and compost also enhances soil quality and nutritional conditions, which broadly targets the sustainable development of soil fertility through increasing the yield of crops (Manjaiah *et al*., 2019). Not just adsorbing water, zeolites and modified clays along with clay minerals are also being used for environmental cleanup (Boddu *et al*., 2008; Sarkar *et al*., 2012; Kumararaja *et al*., 2017; Mukhopadhyay *et al*., 2017a). Recently, these materials have become very popular because of their low cost of production, easy availability, and multiple uses. The average price information obtained from various laboratories for some absorbents is given in table 1. Along with that, table 2 displays the basic properties of some natural and synthetic desiccants. Natural adsorbents have more higher adsorption capacity relative to those for synthetic adsorbents. Adsorption capacities of clay minerals (montmorillonite, bentonite, fibrous clay minerals, NaOH-treated pure kaolin, NaOH-treated raw kaolin, etc.) and zeolite minerals differ according to mineral types and different researchers (Rafatullah *et al*., 2010) (Table 1).

Table 1 Adsorption capacities and prices of 1 kg of moisture-retaining desiccant material on average

Synthetic Desiccants	Price/Amount (€/kg)	*Adsorption capacity (mg/g)
Silica gel	20 €/kg	28-312
Activated alumina	3.2 €/kg	2.49
Activated carbon	10 €/kg	9.81-980
Molecular sieve zeolite	18 €/kg	0.2
Synthetic perlite	1.5 €/kg	couldn't find
Zeolite minerals	Low cost	10.82-53.1
Perlite	Low cost	162.3
Clay minerals	Low cost	6.3-300

*Adsorption capacities of the desiccants were taken from Rafatullah et al. (2010) and references therein.

Table 2 Properties of some adsorbents

Physicochemical properties	Zeolite	Perlite	Montmorillonite Clay	Silica Gel	CaO quicklime	CaSO4 gypsum
Adsorptive Capacity at low H_20 Concentrations	Excellent	Excellent	Fair	Poor	Excellent	Good
Capacity for Water @77° F, 40% RH	High	High	Medium	High	High	Low
Separation by Molecular Sizes	Yes	Yes	No	No	No	No
Rate of Adsorption	Excellent	Excellent	Good	Good	Poor	Good
Root development and soil improvement	Excellent	Medium	Poor	Poor	Poor	Poor
Adsorptive Capacity at Elevated Temperatures	Excellent	Excellent	Poor	Poor	Good	Good

Reserves of Natural desiccants in Turkey and the World

Clay minerals can be formed by alteration of feldspar minerals, volcanic rocks, and tuffs, hydrothermal alteration, and precipitation in an aqueous environment (lake). Especially in Turkey, where volcanic rocks and young volcanism are common, clay minerals are widely observed. There are significant clay deposits in Tokat, Eskişehir, Afyon, Ankara, Çankırı, Çorum, Balıkesir, Edirne, Ordu, Artvin, Giresun and Trabzon, Konya. Bentonite is found in igneous rocks, alteration, or sediments of volcanic bedrock in Turkey. It shows irregular bedding along with the lens, pocket, mass intermediate levels, and fractures. Turkey's total potential bentonite reserve is approximately 281,000,000 tons. In order to get a share from the raw bentonite and cat litter markets, which have low added value in the world markets, private entrepreneurs who are strong in terms of finance need to invest in this sector (İpekoğlu *et al*., 1997). Clay mineral reserves are quite high in the world. Bentonite reserve, which is frequently used in agriculture, in fields such as cat litter and drilling mud, is around 1870 million tons. The world's most important bentonite reserves are in the USA, CIS, Japan, Greece, Cyprus, Italy, Germany, England, Spain, Bulgaria, and Milos Island (Greece), Cyprus and Sardinia Island (Italy) have significant advantages in terms of their geographical locations (İpekoğlu *et al*., 1997).

USA, Armenia, Japan, Italy, Turkey, Greece are rich countries in terms of perlite resources. The USA purchases perlite from Greece and the EU from Turkey. Most of the perlite produced and consumed in countries such as the USA is used as construction material and building material. Turkey alone has 74% of the world's perlite reserves, which are approximately 7.7 billion tons. 34% of the country's perlite reserves are within the borders of Kars province. Turkey's perlite reserves are around 4.5 billion tons. Nevşehir, Niğde, Aksaray, Çankırı, Bitlis, Van, Erzurum and Kars have the richest perlite and pumice deposits in the world and can be used in soil improvement with its mineral richness, water holding capacity and aeration porosity in agriculture. In addition, with its thermal insulation and light construction material, it can be used as a strainer in energy and iron saving, petroleum and chemical industries, and various industries in the region. It is thought that Turkey will have a significant say in world trade with low cost and high technology investments in perlite and pumice deposits (Özgüner, 2004).

In Turkey, there are rich zeolite deposits in regions such as Balıkesir, Bigadiç, Manisa, Gördes, Kütahya, İzmir, Bolu, Cappadocia (Çetinel, 1993). It is recorded that there are over 50 billion tons of zeolite reserves in Turkey (Özaydın 2008). About 60% of world production is carried out by Cuba. Other important producers are Japan, the USA, South Africa, Hungary, Bulgaria, and Italy. World zeolite consumption is 750 000 tons per year, 70% of this consumption is in detergents, 10% in catalyst and adsorbent production, 8% in desiccant (desiccant) production and 12% in other areas (Köktürk, 1995).

Discussion and Conclusion

In this study, desiccants and their properties, which are of great importance today and can be used in many areas, are discussed. Although expenditure on low-cost adsorbents may be negligible, further cost-benefit analysis needs to take into account any spending associated with regeneration or operation including chemicals, laboratory, electricity, labor, transportation, and maintenance (Krishnan & Anirudhan, 2003). Natural adsorbents are economically attractive for our country because of their both molecular properties and abundant reservoir.

Considering the abundance, cheap cost and easy accessibility of natural adsorbents in our country, there is no need for synthetic adsorbents, which are more expensive and difficult to prepare and obtain with laboratory applications, except for special applications areas. Considering the environmental awareness at the highest level during the operation of natural mines, as well as the establishment of production facilities with superior and environmentally friendly technologies, are considered very important for the environmental and economic future of our society.

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