Potential Use of Alkali Activated Clay from Common Deposit for Removal of Methylene Blue Dye

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Abstract- Common clay deposits are widespread as sources of multiple clay minerals. They are less commonly used as a base material for geopolymers than pure clay deposits. This research aims to investigate the efficiency of removing methylene blue (MB) dye from aqueous systems using alkali-activated clay from a standard warranty. The main characters of the used deposit were examined using X-ray fluorescence (XRF), X-ray diffraction (XRD), and scanning electron microscope (SEM). The chemical activation was performed using an alkaline activator (Na_2SiO_3/NaOH). The water absorption rate, cation exchange capacity (CEC), and specific surface area (SA) of alkali-activated clay were measured. Several experimental variables, including adsorbent dosage, pH value, initial dye concentration, and contact time, were studied to assess the workability of removing MB. The Langmuir and Freundlich adsorption models were used to investigate the isotherms of dye adsorption by activated clay. Intraparticle diffusion, pseudo-second-order, and pseudo-first-order models investigated the kinetics. The results indicate that the adsorption capacity increases as the MB dye concentration, adsorbent dosage, and contact time increase. The maximum removal efficiency of MB dye was achieved in a primary medium. The Freundlich isotherm best fits the adsorption data with a maximal adsorption capacity of 76.9 mg/g. The pseudo-second-order model was more appropriate for characterizing kinetic behavior in kinetic research. The results revealed that the developed activated clay from a standard deposit might be used as an adsorbent to remove the MB dye from contaminated water.

Keywords: Common clay deposit, Adsorbent, Alkali Activation, Methylene Blue Dye Removal

1.Introduction

Water is one of nature's most precious resources, yet the adverse effects of industrialization have lowered its purity. The excessive use of antibiotics, pesticides, household garbage, and industrial effluents contributes to water contamination. The demand-supply chain has been the worst hit by the population explosion and human avarice, putting pressure on all types of resources. There has been an increase in demand for industrial and agricultural products, which has led to the excessive use of various chemicals, fertilizers, and pesticides, resulting in water pollution. These toxic substances have wreaked havoc on the health of all living things in the environment. Occupational safety and health regulations in the United States are governed by the OSHA Permissible Exposure Limits (PELs). As a result of various contaminants, advanced technologies are needed to detect and degrade these compounds below OSHA PELs. Next-generation innovative technologies, such as nanotechnologies, are projected to be developed in the twenty-first century. Innovative materials, devices, and systems with wide-ranging applications can be created using the latest technology and could help solve many of the world's most pressing issues (Thakur,2020).

Water is a renewable resource that is necessary for life, food production, economic growth, and overall well-being. It is a one-of-a-kind natural resource that cannot be replicated, is challenging to depollute, and is prohibitively expensive to transport. Water can be diverted, transported, stored, and recycled, making it a valuable natural resource. All of these characteristics contribute to water's enormous human benefit. Many different types of activity rely heavily on the country's surface and underground water resources. This is true for everything from agriculture to hydropower generation to cattle production

to industry to forestry to fishing, and everything in between. More than 2.84x105 Km3 of freshwater ecosystems cover just % of the planet's surface. An extremely small percentage (0.1%) of the land surface is covered by rivers. In river channels, only 0.01% of the world's water is present. Because of this, running water has a huge impact, despite the little quantities.(Wetzel,2001)

Whether direct or indirect consequence, water's importance as a living necessity cannot be disputed, water is essential to all industrial, environmental, and physiological functions. There are numerous roles for water in living organisms, including solvent, temperature buffer, metabolite, and lubricant (Hanslmeier,2011). As a result, the water quality parameters have been hindered by unguided and anomalies from numerous anthropogenic activities, making the water unfit for its intended purpose.

The ecosystem and human life are both at risk from water contamination. Depending on the nature and source of the pollutant, the consequences can differ. Some contaminants are carcinogenic, while others are endocrine disruptors (Adeogun,2016). Environmentalists are extremely concerned about these contaminants, which enter the water body in various ways but are almost exclusively human-made, because of the numerous dangers they represent to the environment.

Heavy metal pollution: This pollutant has many detrimental consequences on aquatic species, plants, and humans. Heavy metals are at the top of the list(Cao,2017)." Heavy metals are discharged into the environment in various ways, including industrial processes, mining operations, and agricultural practices, among others. Plants can absorb soil-bound bioavailable metals, which can cause major metabolic malfunction. Besides damaging the cell membrane, heavy metal ion concentrations have also been shown to

impact the formation of chlorophyll, therefore lowering the plant's ability to photosynthesize, as well as the viability of pollen and seed. (Xun,2017)

Crustaceans' exposure to metals can cause a wide range of physiologic problems, including abnormalities in metabolic activity. Crustaceans exposed to heavy metals may also lose their appetite for food, resulting in weight loss. Adults may be unable to reproduce, and larvae may not thrive if they are constantly exposed (Zhang,2017).

Organic pollutants: A vast array of organic contaminants with a wide range of toxicity can be found. Dyes, plant and animal medications, personal care product wastes, and petroleum organic pollutants are among the organic pollutants that pose a significant hazard to aquatic species, plants, and humans. EDCs, a class of chemicals classified as emerging contaminants, including a subset of organic pollutants known as disruptive endocrine chemicals (EDCs). An EDC is an exogenous agent that disrupts the normal homeostatic reproduction, development, or behavior of an organism. (Jung,2015)

Chemicals known as dyes are large water-soluble chemicals that are widely employed in a wide range of sectors, including textiles, leathers and tanning, food, and paper, among others, to influence the colour of finished goods. Adding colours to water has a significant impact on aquatic life and plant life, and us as humans. They reduce the amount of dissolved oxygen in water, which kills aquatic life and prevents sunlight from reaching photosynthetic organisms (Pandey,2020). Vegetables and fish that bioaccumulate dyes may constitute a risk to human health. Another method of exposure to humans is using coloured paper towels for drying hands and food preparation. Dye removal from wastewater before disposal is critical due to its potential carcinogenic and mutagenic effects. (Oplatowska,2011)

Medications of the EDC family treat or prevent many diseases in humans and animals. Veterinary pharmaceuticals may also be used to improve food production efficiency(Archer,2017). One of the ways pharmaceuticals reach the environment is through indiscriminate disposal of hospital and household trash, landfill leaching, drainage water, or sewage(Kar, S.,2010 & Aguirre-Martínez,2016). Although pharmaceuticals have been identified in environmental samples at concentrations of ng/l to g/l, they are regarded as a serious threat to aquatic and human life. Pharmaceuticals in water are hazardous to aquatic creatures in acute and chronic periods. EDCs, as their name suggests, alter the human endocrine system and raise the risk of cancer. Endocrine system disturbance, diminution in egg and sperm cell production, and feminization of female aquatics are all possible outcomes of their use.(Ng,2017 & Saha,2010)

The use of dye in the textile and colourant industry is a common practice. Many of these colours are extremely harmful to aquatic life, and some are carcinogenic. Compared to anionic dyes, cationic dyes have a better track record of toxicity. Color strength and organic content are often high in effluents from diverse sectors, containing a wide range of pigments and dyes. Water clarity is reduced, photosynthetic activity is affected, and chemical oxygen demand increases, which inhibits the microbiological activities of organisms buried. Even though most dyes degrade with time and exposure to sunlight, water, soap, and oxidizing chemicals, standard wastewater treatment procedures are ineffective at removing colours because of their complex structure and synthetic origins. It's been an important and challenging field of research to treat wastewater that contains dyes(Sarma,2011).

Dyes from wastewater can now be removed, recovered, and recycled via adsorption, one of the most effective physicochemical processes at solid-liquid and solid-gas interfaces.

Using both ion exchange and adsorption mechanisms, clay minerals in soil act as natural scavengers, removing contaminants from the water they absorb. Colloid-like qualities can be found in clays composed of incredibly small particles. There are many advantages to clays as adsorbents, such as their large surface area, chemical and mechanical stability, multi-layered structure, high cation exchange capacity (CEC), and the presence of Bronsted and Lewis acids on the clay surface. Mineral weathering and genesis can be controlled by acid treatment of clay minerals which can commonly replace exchangeable cations in both Tetrahedral and Octahedral locations with H ions, leaving the SiO4 groups intact. The octahedral Al ions are preferentially liberated from the clay structure during the acid assault, and the crystalline kaolinite is thermally converted into amorphous metakaolin. This leads to the production of additional Al-OH and Si-OH bonds without disturbing the original mineral structure (Sarma,2011).

Clays are fine-grained minerals that may be plastic in nature; they can be hardened when dried or fired, and they have the required water content for drying and firing. When dried or fried, clays can become either pliable or hardened due to the presence of additional substances(Murray,2006). Mineralogy and size distinguish clays from fine-grained soils like sand. Montmorillonite, kaolinite, Illite, bentonite, and chlorite are the most common clays. Kaolinite, halloysite, and nacrites are all members of the Kaolinite mineral family. Pyrophyllite, talc, vermiculite, sauconite, saponite, nontronite, and montmorillonite are all members of the smectite group. The clay micas are part of the illite group (Adeyemo,2017).

Only the mineral illite is found in nature. In some cases, chlorites are regarded as a different category within the phyllosilicates rather than clay. Many of the "natural" clays found in the world are mixes of various forms of clay and other weathering minerals such as sand. It is possible to explore the effect of structure and layer charge on metal ion coordination to permanent charge sites because of these variations in clays(Kausar,2018). The materials are chosen for this experiment also provided a variety of aluminum and silanol surface hydroxyl arrangement possibilities. Fine-grain silicate minerals have a negative charge that affects their ability to absorb water. Adsorption of positively charged cations, such as dyes, can neutralize this negative charge. As a result, the clays have a high adsorption capacity because of their wide surface area. The sorptive capacity of montmorillonite clays is expected to be higher than that of other clays (Kausar,2018).

Natural clay is made up mostly of fine-grained minerals, and it can be pliable or complex depending on the amount of water in it. Clay is typically dried or fired to make it more durable. Phyllosilicates are common in clay, but they can also contain other substances that give clay its fluidity and cause it to solidify upon drying or firing. Materials that do not provide plasticity to clay and organic matter may be present in their associated phases. Two main building units of clay minerals are silicon-oxygen tetrahedron $(Si_2O_5)^{2-}$ and aluminum octahedron (Al_2O_3), which are both hydrous (gibbsite sheet). Individual tetrahedrons share three of the four oxygens to form tetrahedral sheets. A hexagonal arrangement with the base oxygens linked and apical oxygens pointing up/down has been used in this experiment. A typical octahedral sheet

comprises eight distinct octahedrons, each with an edge comprised of oxygen and hydroxyl anion groups. The hexagonal arrangement of these octahedrons (Adeyemo,2017).

Activated carbon can be used to remove the final 30% of water waste in a water removal system, leaving clay to handle the remaining 70%. Because of their significant interaction with natural clay and oxide minerals, the fate and mobility of the adsorbates are greatly influenced. Environmental parameters such as ionic concentration, pH, ionic strength, temperature, and kind of dye can all affect the absorption process. Metal ion uptake, the alteration of surface complexation structures, and the stability of diverse metal precipitates are all influenced by temperature (Adeyemo,2017).

Autochrome (N2, NO, and NO2) dyes are colourful organic compounds based on functional groups in chromophoric dyes (NR2, NHR, NH2, COOH, and OH). Acid dyes are typically used for dyeing silk, wool, modified acrylics, and nylon, although other types of dyes can be used as well. Cosmetics, paper, food, ink-jet printing, and leather dyeing all employ these dyes (Gupta,2009). Azine, xanthene, anthraquinone, triphenylmethane, nitroso, nitro, and azo dyes are among the most common types of acid colours. A few of the more often used acids dyes are acid blue 2, acid red 57, methyl orange (I), and orange (II). Primary colours are employed in the textile business, the paper industry, and the pharmaceutical industry(Salleh,2011). Tannin mordanting cotton, silk, and wool can also be done with these. Insoluble in water, these dyes produce coloured cations and are known as cationic dyes because of this. For example, cyanine, thiazine, oxazine, hemicyanine, and diazahemicyanine are the principal dyes used in basic red 46, malachite green, basic yellow 28, and methylene blue(Bouatay,2016). Fibers

such as cellulose acetate and nylon are dyed with dispersed pigments. These non-ionic dyes are utilized in acrylic fibers because they are insoluble in water and aqueous solutions. Some of the most popular examples are dispersed yellow, disperse orange, and disperse red, which belong to the benzodifuranone group. Leather, cotton, rayon, and paper dyeing all use direct dyes. These colours exhibit a strong affinity for cellulosic fibers (Forgacs,2004). Oxazine, stilbenes, and poly azo compounds make up the bulk of the class. Natural orange 34, direct black, direct violet, and direct blue are just a few examples of natural colours. Among the fibers that can be dyed with reactive dyes are nylon, wool, cellulose, and cotton. Dye and fiber establish a covalent bond thanks to chromophores such as phthalocyanine and triaryl methane in these dyes. There are many well-known examples, such as remazol, reactive black 5, and reactive yellow 2. Wool, rayon, flax wool, and cotton (primarily on cellulosic fibers) can be dyed with vat dye, such as indigoids and anthraquinone, which are not water-soluble. Vat Green 6, vat blue, and indigo are common examples of vat dyes (Espantaleon,2003).

It will be less expensive to utilize adsorption with clay sorbent (Bentonite, Red Mud, and Clinoptilolite) for effluent treatment than active commercial carbon (0.8–1.1 U$/kg), natural zeolite (0.08 U$/kg), chitin (15–20 U$/kg), and cross-linked chitosan (16.5–10 U$/kg), all of which must be imported. Because of its simplicity and ease of operation and its ability to overcome issues with high energy input (reverse osmosis and UV sterilization), the adsorption method is also regarded as a preferable solution for water and wastewater treatment in underdeveloped nations (Ali,2012).

Dyes are organic compounds that are complicated (Ehrampoush et al., 2010). Textiles, paper printing, food, medicines, leather, and cosmetics are just a few industries that use

these dyes (Hassaan and El Nemr, 2017). The discharge of dye-containing industrial waste into the environment poses a major risk to the ecosystem and public health (Zhao et al., 2015). Dye pollution in liquid industrial waste is caused by complex contaminants and high colour intensity, making them challenging to disintegrate, even with biodegradation in the long term (El Alouani et al., 2019). Methylene blue (MB) or basic blue 9 are the most used industrial dyes. It is a basic dye that is water-soluble and contains heterocyclic aromatic molecules. Geopolymers have great effectiveness in removing dyes from aqueous solutions (Li et al., 2006). Materials such as fly ash (Li et al., 2006; López, 2014), rice husk (Sharma et al., 2011), and metakaolinite (Setthaya et al., 2017) have recently been employed to make geopolymers, and their efficacy in removing MB dye from aqueous solution has been examined. Several researchers focused on a variety of factors that affect sorption capacity, including mixture proportion, adsorbent dosage, pH value, temperature, and contact time (Naseem and Tahir, 2001; Bayat, 2002; van Jaarsveld et al., 2002; Bakharev, 2006; Cetin and Pehlivan, 2007).

As aluminosilicate sources, clay deposits vary in clay mineral composition and purity (Meunier, 2005). Some clay deposits are pure, containing only one dominant clay mineral, such as kaolinite, illite, halloysite, or montmorillonite, while others are complex, containing multiple clay minerals such as common clay deposits and soil (Khalifa et al., 2020). The use of pure clay deposits as precursors to produce geopolymers-based adsorbents, such as kaolin, metakaolin, and bentonite, has been reported in several investigations. They revealed that the clay-based geopolymers have excellent properties such as good absorbability, high surface area, porosity, and cooperative solid bonds (Chen et al., 2016; Kara et al., 2017; Alouani et al., 2018; El Alouani et al., 2019; Maleki et al., 2020).

Common clay deposits are divided into two types: those that include two clay minerals, such as kaolinite-illite deposits, and those that contain three clay minerals, such as kaolinite-illite-montmorillonite (Khalifa et al., 2020). Little research has been done on common clay deposits (Diop & Grutzeck, 2008; Dietel et al., 2017; Marsh et al., 2019). They indicated that hydroxy sodalite was generated, and geopolymer was formed in some cases. According to Khalifa et al. (2020), the degree of reactivity of these materials is controlled by the crystallinity of clay minerals and the purity of the resources.

Common clay deposits have never been used or evaluated for dye waste removal in aqueous systems. The interest of this research is to estimate the potential use of alkali-activated clay from common deposits as an adsorbent and its efficiency for removing MB dye from aqueous solutions. The main goal of this study is to investigate the effect of various parameters such as adsorbent dosage, pH, contact time, and initial dye concentration on the adsorption efficiency of MB from an aqueous medium. The adsorption kinetics was studied using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Langmuir and Freundlich's models were used to analyze the experimental equilibrium data.

2 Materials and Methods

2.1 Preparation, Alkali activation, and Characterization

For this study, a sample of standard clay deposit was obtained from Al-Azraq area (NE Jordan, about 110 km from Amman). The site was chosen as a common resource of common clay deposits. The sample was crushed, sieved to a grain size of less than 425 m,

and homogenized by mixing. X-ray fluorescence spectroscopy was used to identify the major elements of the used material using a SHIMADZU Sequential X-ray Fluorescence Spectrometer. At a scan rate of 2 per minute, the XRD pattern was obtained. According to the American Mineralogist Crystal Structure Database, the mineral peaks were discovered (AMCSD).

The prepared sample was calcined for 2 hours at a temperature of 660-700°C to improve the reactivity of the clay minerals by increasing the surface area available for dissolution and activation (Luukkonen et al., 2018 and Buchwald et al., 2009). Four steps are involved in the production of activated clay:

1. The alkaline activator was made from a mixture of a specific mass ratio of Na_2SiO_3 and 10M NaOH solutions.

2. The alkaline solution was gradually added to the calcined clay using a mechanical overhead mixer for 10-15 minutes to achieve a homogenized mixture.

3. The mixture was placed into three cubic steel molds (50×50×50 mm) and vibrated for 2-4 minutes to release air bubbles before being covered in plastic film to prevent moisture loss.

4. The covered mold was cured for 24 hours at 80°C in a vented oven, then allowed to cool at room temperature before being de-molded and weighed.

Six mixtures were prepared with different mass ratios of Na_2SiO_3/NaOH (0.5, 0.8, 1, 1.2, and 1.5) to determine their effects on the product characters. The liquid/solid ratio of the whole prepared mixtures was 1.4. It gave the best workability. The percentage of water absorption was measured for alkali-activated specimens after immersion in sealed containers filled with tap water for 24 hours. For cation exchange capacity (CEC)

measurement, the dry samples of activated clay were ground, sieved to a particle size of 425 μm, washed with deionized water to remove the excess NaOH, and then dried at 105 °C. According to Rengasamy and Churchman (1999), the test was performed by replacing the standard mixture of cations on the exchange sites with a single cation (in this work, MB^+) and then measuring the number of cations exchanged. CEC is measured in milliequivalents per 100 grams (meq/100g). The specific surface area (SSA/m^2 g^{-1}) was measured according to the adsorption of molecules method presented by Santamarina et al. 2002. The used polar liquid for the adsorption test was methylene blue to measure the total surface.

To investigate the removal efficiency of MB dye waste, the optimal mixture was chosen based on the highest CEC and SAA values. XRD and SEM analyses were carried out.

2.2 Adsorption Tests

To utilize activated clay as adsorbent, the selected specimen was ground and sieved to a particle size of 425 m before being washed with deionized water to remove excess NaOH and dried at 105 °C. The experiment for the adsorption of MB dye from an aqueous solution was carried out by preparing a 50 ml solution of MB dye with the desired concentration for removal tests. The adsorbent was added to the dye solution. For a specific amount of time, the mixture was gently stirred at a speed of 250 rpm. The mixture was then filtered. A UV-visible spectrophotometer (Model CE 2011, Cecil Aurius Series) with a maximum wavelength of 668nm was used to measure the residual concentrations of MB. Eq.1 & 2 were used to calculate the removal efficiency and adsorption capacity.

$$Re\% = \left(\frac{(Co - Ce)}{Co}\right) \times 100 \ldots . (Eq. 1)$$

$$q = \left(V\frac{(Co - Ce)}{m}\right) \ldots . (Eq. 2)$$

Where Re% is the removal efficiency,

C_o (mg/l) is the initial concentration of MB,

C_e (mg/l) is the equilibrium concentration of MB,

q (mg/g) is the adsorption capacity,

V (ml) is the solution volume, and

M (g) is the adsorbent weight.

2.3 Adsorption Parameters

On MB dye removal experiments, the changes in experiment factors were investigated to study the removal efficiency and adsorption capacity of MB dye from an aqueous solution. Changes in starting MB concentrations (50, 100, 150, 200, 300, and 400 mg/L) and adsorbent dosage (0.50, 0.10, 0.15, 0.20, 0.25, 0.30, and 0.35g) were investigated. Changes in contact times (15, 30, 60, 90, 120, 150, and 180 minutes) as well as pH value (2.0, 3.0, 5.0, 11.0, and 12.0) were studied. Using a pH meter and 6M NaOH and 6M HCl solutions, the pH levels were adjusted. The pH of the adsorbent at the point of zero charges (pHpzc) was calculated using Pawar`s method (Pawar et al., 2016). After the system had reached equilibrium, the adsorption capacity and removal efficiency were determined.

2.4 Adsorption Kinetics and Isotherms

The kinetics of the adsorption process were investigated in this research to describe the relationship between the rate of solute uptake and adsorption time. The adsorption kinetics were described using three mathematical models: pseudo-first-order, pseudo-second-order, and intraparticle diffusion. Eq. 3 expresses the linear form of the pseudo-first-order model (Lagergren et al., 1898).

$$\ln(qe - qt) = \ln qe - K1t \dots (Eq.\,3)$$

Where q_e (mg/g) is the adsorption capacity at equilibrium,

q_t (mg/g) is the adsorbed concentration of MB at time t,

t (min) is the contact time, and

K_1 (1/min) is the adsorption process's pseudo-first-order rate constant.

Eq. 4 represents the pseudo-second-order model (Ho and McKay, 1999).

$$\frac{t}{qt} = \left(\frac{1}{K2qe^2}\right) + (\frac{t}{qe}) \dots (Eq.\,4)$$

Where t (min) is the contact time,

q_t (mg/g) is the adsorbed concentration of MB at time t,

K_2 (g/mg.min) is the pseudo-second-order rate constant for the adsorption process.

Eq. 5 can be used to test the contribution of the intraparticle diffusion mechanism (Baret, 1968).

$$qt = KIt^{1/2} + I \dots (Eq.\,5)$$

Where q_t (mg/g) is the adsorbed concentration of MB at time t,

K_I (mg/g min 0.5) is the intraparticle diffusion rate constant, and

I (mg/g) is the intercept that indicates the boundary layer thickness.

The Langmuir and Freundlich isotherms were used to determine the mechanism of

adsorbate molecule distribution between liquid and adsorbent, respectively.

Eq. 6 defines the Langmuir isotherm model's linear expression (Singh et al., 2016).

$$\frac{Ce}{qe} = \left(\frac{Ce}{qm}\right) + \left(\frac{1}{KLqm}\right) \ldots . (Eq.\,6)$$

Where C_e (mg/L) is the pollutant's equilibrium concentration,

q_e (mg/g) is the amount of dye at equilibrium,

q_m (mg/g) is the amount of monolayer adsorption capacity, and

K_L (L/mg) is the Langmuir constant.

The Freundlich isotherm's linear model can be represented logarithmically as in

Eq. 7. (Foo and Hameed, 2010).

$$\ln qe = \ln Kf + \frac{1}{n}\ln Ce \ldots . (Eq.\,7)$$

Where K_F (mg $^{(1-n)}$ L^{n}g^{-1}) is the adsorption capacity,

1/n is the adsorption intensity, and

C_e (mg/L) is the pollutant's equilibrium concentration.

The system is homogeneous if the n value is more than or equal to 1 (n 1), and it is heterogeneous if the n value is less than 1 (n 1) (Neolaka et al., 2017). In addition, the value of KF indicates whether the system is adsorption-friendly or not.

3 Results and Discussion

3.1 Characterization

The chemical composition of clay-based material is listed in **Table 1**. The clays contain a total of 76.47% silica (SiO_2) and alumina, according to the results (Al_2O_3). The SiO_2/Al_2O_3 ratio is 4.67. CEC is the total number of cations clay particles can replace and hold. The higher the CEC, the higher cations that can be saved (Yukselen and Kaya, 2006). At the same time, the specific surface area is the total surface area contained in a unit mass of clay materials (Sokolowska, 2011). As demonstrated in **Table 2**, the results indicate that as the $Na_2SiO_3/NaOH$ ratio decreases, the percentage of water absorption, CEC, and SSA rise practically linearly. Because extra water leaves pores after evaporation, an increase in water absorption could suggest the creation of high porosity (Alshaaer et al., 2016). The reduction in water absorption was due to the new mineral phases blocking the pore space after alkali activation. The silica content increases and the activation process is supported by a higher ratio of $Na_2SiO_3/NaOH$. The pore size reduces, and the structures become closer to each other, according to Farhana et al. (2015). The results show that the SSA influences water absorption and CEC values. According to Crini et al. (2018), a larger surface area equals a higher adsorption capacity. Studies have shown a strong relationship between SSA

and CEC (Yukselen, and Kaya, 2006). The water sorption capacity and sorption of organic and inorganic substances depend on the SSA (Sokolowska, 2011).

Table 1 Major elements of the clay deposit

Oxide	Al_2O_3	CaO	Fe_2O_3	K_2O	L.O.I	MgO	Na_2O	SiO_2	SO_3	TiO_2
Wt.%	13.49	0.69	7.15	3.58	7.21	2.40	0.27	62.98	0.08	1.62

Table 2. Results of water absorption, cation exchange capacity, and specific surface area of different mixtures of alkali-activated clays

$Na_2SiO_3/NaOH$	Water absorption%	CEC (meq/100g)	SSA (m²/g)
0.5	14.11	19.21	44.03
0.8	17.20	21.45	49.50
1	11.38	16.37	30.39

Table 1 Major elements of the clay deposit

			2
	9.24	1	6
1.2		2.	.
		1	1
		8	0
	6.95	9	2
		.	2
1.5		5	.
		4	2
			2

XRD results of raw material compared to alkali-activated clays (M2) revealed the appearance of quartz as a significant phase in the clays after reaction, along with the remnants of kaolinite, montmorillonite, and illite. A new phase of tectosilicate, namely hydroxy sodalite ($Na_2Si_2Al_2O_5 (H_2O)_6$), has been identified (**Fig.1**). SEM micrographs showed the morphological and structural features in **Fig**. 2. On the surface of clay particles and aggregates filling the pore spaces, the new sodium aluminosilicate phases were seen as circle-type 'shells.' The unreacted clay particles confirm the XRD results by indicating that the reaction is not complete.
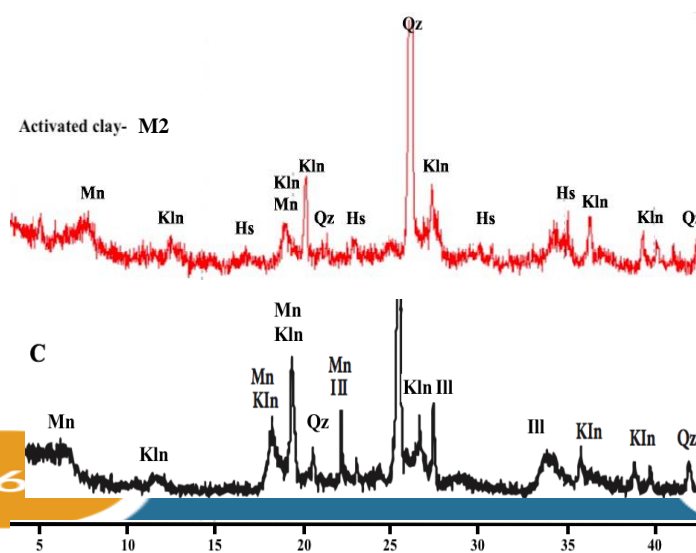
Fig.1 XRD patterns of clays before and after alkali activation. Qz: quartz, Mn:

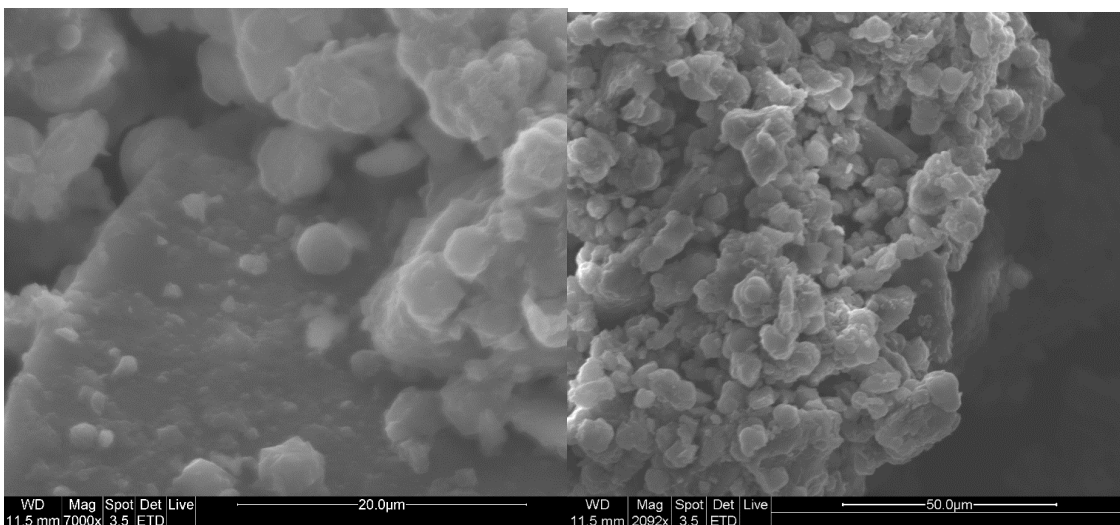montmorillonite, Ill: illite, Kln: kaolinite, and Hs:hydroxysodalite

Fig.2 SEM micrographs of alkali-activated clays

3.2 Removal of MB Dye

The effects of the initial concentration of MB dye, adsorbent mass, pH medium, and

contact time were examined to determine the removal efficiencies and adsorption capacities

of the activated product, denoted by M2, as an adsorbent.

3.2.1 Effect of initial MB dye concentration

The effects of varying the initial MB dye concentration on the adsorption capacity were

examined by adding 0.2g of adsorbent to a dye solution with various concentrations in the

range of 50-600 mg/l at pH 5 for 120 minutes at room temperature (**Fig.**3). The adsorption capacity increased at equilibrium from 12.37 to 45.32 mg/g, increasing the initial dye concentration from 50 to 400 mg/L. It was concluded that as the concentration of MB increased, the adsorption capacity increased. This was due to the sufficient number of available pores on the adsorbents. The adsorption capacity did not improve sufficiently after 400 mg/L. This is probably because the geopolymer reached its maximum adsorption capacity, the sites of the adsorbent were filled with MB dye molecules, and there were no sites available for binding. Generally, adsorption capacity increases with increased concentrations of the adsorbate, but the removal efficiency decreases (Lewinsky, 2007; Shi, 2019). A similar trend was observed by Alouani et al. (2018), Maleki et al. (2020); Sharifpour et al. (2018); Al-Ghouti et al. (2020); and Yagub et al. (2014). They concluded that the increase in MB concentration increased the adsorption capacity.
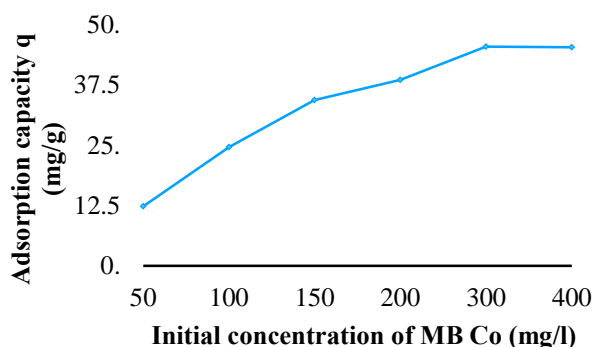

Fig.3 Effect of initial concentration of MB dye on the adsorption capacity

3.2.2 Effect of Adsorbent Dosage

Adsorbent mass is the main factor in the determination of removal efficiency. The effect of adsorbent dosage on the removal efficiency of 200 mg/l of MB dye solution was investigated by adding various adsorbent dosages (0.05-0.35g) at pH 5 for 120 minutes at

room temperature. The results revealed that as the mass of added adsorbent increases from

0.05 to 0.35g, the removal efficiency increases from 22.35% to 99.63%, as seen in **Fig.**4.

These results might be attributed to an increased amount of adsorbent on the reacted

material surface caused by more adsorbents (Isaac and Sivakumar, 2013). Alouani et

al. (2018), Maleki et al. (2020), Al-Zboon et al. (2011), and Xu et al. (2011) found a similar

trend (2008). They observed that increasing the amount of activated particles increased dye

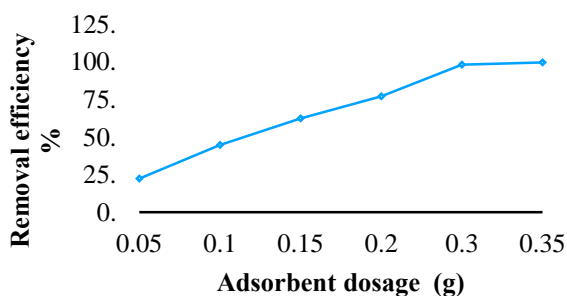adsorption from the solution on the adsorbent material.

Fig.4 Effect of adsorbent dosage on the removal efficiency

3.2.3 Effect of pH

The pH has a significant impact on the dye removal efficiency. Changes in the pH of

the solution affect MB adsorption onto the adsorbent (Al-Ghouti et al., 2020). The pH effect

on MB adsorption capacity and dye removal was investigated. The removal efficiency

increased from 70.28% to 98.43% as the pH value increased from 2 to 12. This result

indicates that in an acidic environment, there are a lot of H^+ ions around the adsorbent's

surface, which decreases the interaction of the solute ions (MB^+) with the adsorbent's sites.

On the contrary, in a basic environment, the amount of H^+ ions surrounding the

adsorbent's surface decreases, resulting in a good interaction between the MB^+ and the

active sites (Tang et al., 2017). Using 10M NaOH solution during the activation process

demonstrates the activated material's strong basicity in this study. Furthermore, at higher

pH levels, the hydroxide ions interact with dye adsorption (Ayari et al., 2007; Xu et al.,

2008). As presented in **Fig.5**, the lowest adsorption efficiency occurred at pH value 2. There

are fewer cations in the solution to be adsorbed onto the negatively charged adsorbent. The

pH at the point of zero charges for the adsorbent surface (pHpzc) should be defined to

determine the type of surface-active centers and the ability of the surface adsorb. When the

pH of the media is less than pHzpc, the surface charge of the adsorbent is positive; when

the pH is greater than pHzpc, the surface charge is negative (Mbuv et al., 2017; Shi, 2019).

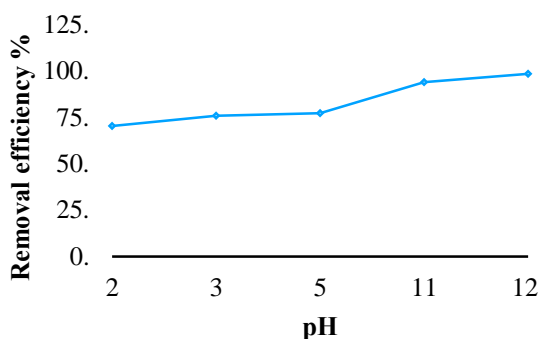**Fig**.6 presents the adsorbent's pHpzc was determined to be 8.98.

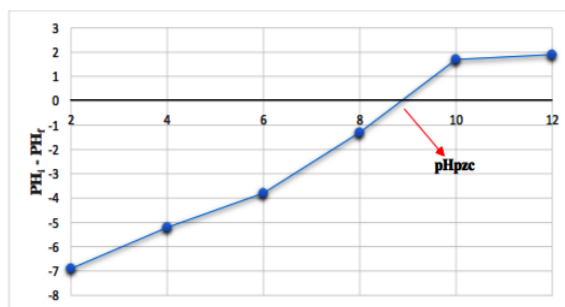**Fig. 5** Effect of pH medium on the removal efficiency

Fig.6 Point of zero charges (pH$_{pzc}$) of adsorbent

This result indicated that the activated material had a surface net positive charge below the pH of 8.98 and a net negative charge above the pH of 8.98. (Pawar et al. 2016). Alouani et al. (2018&2019), Kavitha and Namasivayam (2007), and Deng et al. (2007) got a similar trend in the adsorption of MB on synthesized adsorbents (2009). According to Kavitha and Namasivayam (2007), the removal increase is caused by electrostatic attraction between the negatively charged particles of the geopolymer and the positively charged particles of the cationic dye.

3.2.4 Effect of Contact Time

According to Vilarinho et al. (2015), the adsorption increases as the contact time increases. The impact of contact time on removal effectiveness for the MB dye solution 200 mg/l was examined by adding 0.2g of adsorbent at pH 5 and different intervals ranging from 0 to 120 minutes at room temperature. **Fig.7** shows the results, which reveal that during the first 30 minutes of contact time, the removal % of MB is quick. The most significant value is seen at 120 minutes. Following the equilibrium, there was no significant change in the removal percentage. Alouani et al. (2018 & 2019), Maleki et al. (2020), and Hamid et al. (2019) all observed that contact duration had a comparable impact on the removal effectiveness of MB dye by geopolymer paste (2017). The results show that time is an important factor in dye adsorption from the aqueous phase.
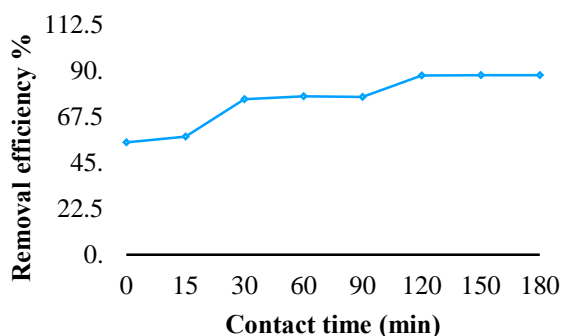
Fig. 7 Effect of contact time on the adsorption capacity and removal efficiency

3.3 Kinetics Studies

To match the experimental data for kinetics models, intraparticle-diffusion, pseudo-first-order, and pseudo-second-order models were used. For intraparticle-diffusion, pseudo-first-order, and pseudo-second-order equations, **table 3** presents the calculated kinetics constants and correlation coefficients. **Fig. 8** (a–c) illustrates the relevant results. The model's expected compatibility with the experimental data was expressed using correlation coefficients (R2). The R2value of the model is relatively high, indicating that it well predicts MB dye removal kinetics. The high correlation coefficient pseudo-second-order kinetic model (0.989) best predicts the removal of MB on activated product (M2), and the calculated qe (cal) values match the experimental QE (exp) values. These findings show that a chemical reaction between MB and the geopolymer's functional groups (electron sharing and ion exchange) triggered the removal experiment (EL Alouani et al., 2019). For the adsorption of MB, Boukhemkhem and Rida (2017) and Zhu et al. (2017) found similar kinetic results (2018).

Table 3. Kinetic parameters for adsorption
of MB onto activated clay

	Absorbent
Raw clay	q_e (mg/g)
Pseudo-first-order kinetics	q_e (mg/g)

K_1 (1/min)

$R^2{}_1$

Pseudo-second-order kinetics

q_e (mg/g)

k_2 (g/mg. min)

$R^2{}_2$

Intraparticle diffusion model

I (mg/g)

K_1 (mg/g.min 0.5)

R^2

a. t (min)

b. t (min)

c. t 1/2
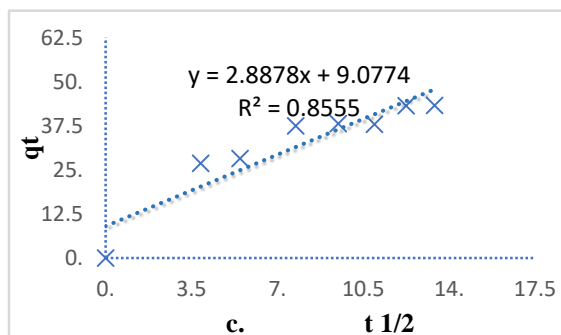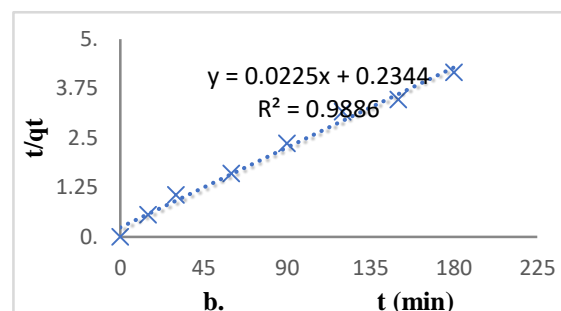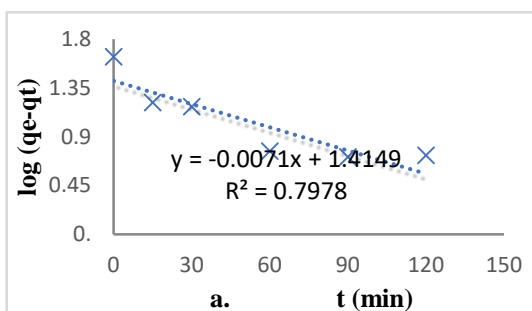
Figs.8 Pseudo-first-order (a), Pseudo-second-order (b), and Intraparticle diffusion

(c) plots for removal of MB by activated clays (M2)

3.4 Adsorption isotherms

The adsorption isotherm is an important consideration when designing adsorption

systems. It must be measured to determine and optimize the adsorbent capacity. The

Freundlich and Langmuir adsorption models were used to fit the experimental data in this study. The coefficient of determination was used to demonstrate the fit of the regression equation to the sample data. The constants were calculated according to **Table 4**. As shown in **Fig.9**, the value of R^2 obtained from the Langmuir isotherm equation (0.955) was greater than that obtained from the Freundlich (0.937) isotherm equations. These results suggest that the data from the removal studies could be effectively represented by the Langmuir model of monolayer adsorption on a homogeneous surface. This result is similar to the dye adsorption results of Ilgin (2020) and Onyeocha et al. (2016). The maximum monolayer adsorption capacity was 76.9 mg/g (q_{max}). The R_L value ranges from 0 to 1 (0.038-0.322), indicating that cationic dye adsorption on the geopolymer material is favorable.

Table 4. Models isotherm constants for adsorption of MB using activated clays

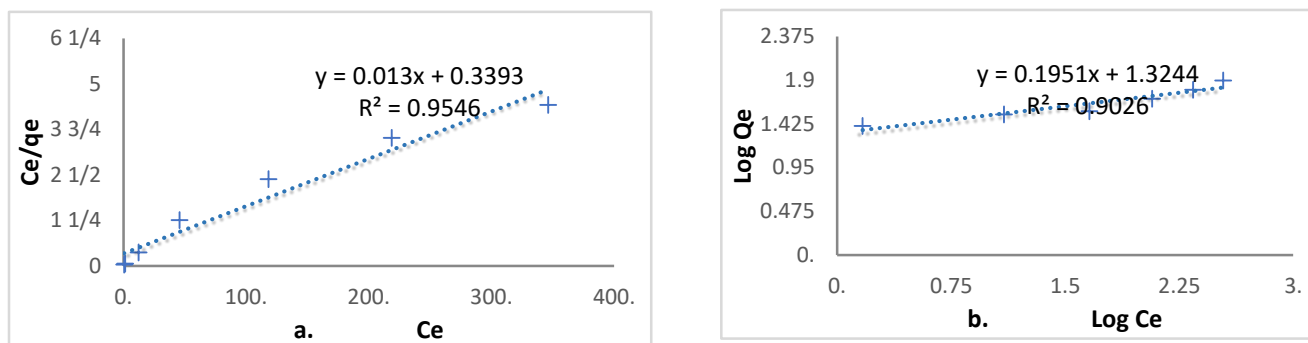|		
Langmuir	q_m (mg /g)	76.9
	K_L (L/ mg)	0.038
	R^2	0.955
	Range R_L	0.038 - 0.322
Freundlich	K_F (1/g)	18.4
	1/n	0.2254
	R^2	0.937

Fig. 9 a. Langmuir isotherms b. Freundlich isotherms for removal of MB by

activated clays

4.Conclusions

A standard clay deposit is activated by an alkaline solution and then used as an adsorbent to remove the methylene blue dye. The water absorption of activated specimens is affected by the sodium silicate to sodium hydroxide ratio in an alkaline activator. As sodium silicate in the water has risen, water absorption has decreased. Hydroxysodalite, a new sodium aluminosilicate phase from the feldspathoid group, was formed due to the alkali activation. As the adsorbent dosage, pH value, and contract duration were increased, the removal efficiency improved. As the original methylene blue concentration grew, the amount of dye was adsorbed. The maximum adsorption capacity was discovered in the primary medium. According to the results of kinetic fitting for MB removal studies, ion exchange is assumed to be the fundamental mechanism for MB removal by activated clays, and the removal process may be monolayer. The dye adsorption data is neatly described by the Freundlich isotherm. Overall, the results show that alkali-activated clay from a standard clay deposit has high efficiency in removing methylene blue from an aqueous medium.

Declarations

Ethics Statement: This article does not contain any studies with human participants or animals performed by the authors.

Conflicts of interest: The authors have no conflicts of interest to declare.

Data availability: Any data that support the findings of this study are included within the article.

Code availability: 'Not applicable.'

Reference :

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