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Kinetic and Isotherm Studies of Methylene Blue (MB) Dye Adsorption from Textile wastewater onto Metakaolin

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Abstract

In this study, Metakaolin was successfully prepared and characterized from Kankara Kaolinite Clay and utilized in the removal of Methylene blue (MB) dye from synthetic Textile wastewater. pH point of zero charge of the Metakaolin was determined from which a working pH was chosen for further studies. Batch adsorption experiment was employed and the effect of process variables; contact time, adsorbent dosage and initial concentration were investigated. Adsorption equilibrium was attained at 60 minutes and adsorbent dosage of 2.0 g of which 99.86% removal of MB was achieved. Kinetic studies showed that pseudo-second order model best described the sorption kinetics with R^2 value of 0.9695. The adsorption equilibrium data were fitted to adsorption isotherm models, and Langmuir isotherm best described the sorption process as indicated by the R^2 value of 0.9818. Thus, monolayer of adsorbates molecules (MB) are formed on the adsorbent surface. The maximum adsorption capacity (q_m) of Methylene blue adsorption onto metakaolin was found to be 4.99 mg/g. The research generally revealed that metakaolin is a promising adsorbent that could be utilized in the removal of Methylene Blue (MB) dye and other colored pollutants from aqueous solution.

Keywords: Methylene Blue (MB) dye, Metakaolin, Adsorption, Kinetics, Isotherms.

Introduction

The release of wastewater into water bodies from industries such as textiles, leather, printing, paper, cosmetics and pharmaceutical usually contains synthetic dyestuffs that causes environmental degradation and poses significant threat to both human and aquatic living organisms. (Roy and Mondal 2017; Kandisa *et al*., 2018; Bamroongwongdee *et al*.,2019). Dyes are basically organic substances with different chemical structures and molecular weights (Ozyaman *et al*., 2023).

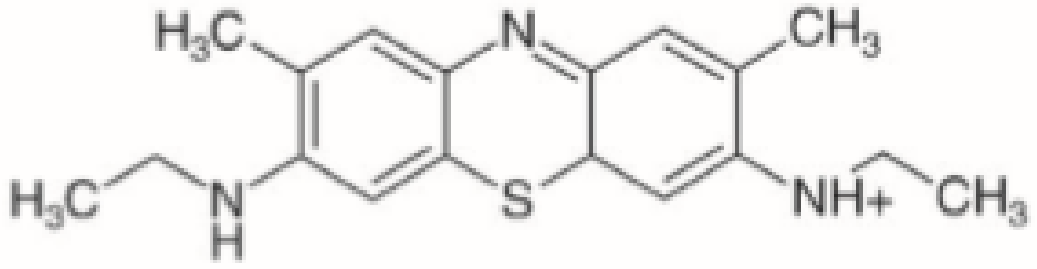
Chemically and thermally stable dyes are usually first choice of textile industries because of their long-term effect results when applied (Ravi *et al*., 2016; Kandisa *et al*., 2018). Industrial wastewaters containing dyestuffs usually exhibit high chemical and biochemical oxygen demands (Amode *et al*., 2016). Methylene blue is a synthetic dye widely used in textile industries. It's a cationic dye and chemically stable as a result of its aromatic structure (Husaini *et al*., 2023; Kandisa *et al*., 2018; Ariyanto *et al*., 2014).

It can cause serious damages to vital organs in human body such as; liver, kidney and also causes irritations of the eye, skin, digestive and respiratory tract when inhaled or swallowed and also prevent photosynthetic activity in aquatic environment by reducing light penetration. (Mekonnen and Sime, 2018; Ozyaman *et al*., 2023; Husaini *et al*., 2023). There is need to reduce the negative effects of dye contaminated wastewaters on human and the environment by treatment of the effluent before discharge into main streams (Amode *et al*., 2016; Gupta *et al*., 2015).

Several Physical, Chemical and Biological methods, including membrane separation, ion exchange, biological degradation, Photodegradation, electrochemical techniques,chemical oxidation and adsorption have been employed to remove Methylene blue (MB) and other dyes from wastewaters (Yakubu *et al*., 2024; Husaini *et al*., 2023; Yunus and Nuhu, 2020; Gupta *et al*., 2015; Khaniabadi *et al*., 2017).

However each technology has its own inherent limitations, such as high cost, complexity, high energy input and sludge generation. Among these technologies, adsorption has been found to be simple, effective and economical (Husaini *et al*., 2023; Hamza *et al*., 2019). Adsorption process is one of the physical treatment methods, where by adsorbate molecules or ions accumulated onto the surface of an adsorbent via physical or chemical bond. (Isah *et al.*, 2022; Mustapha *et al.*, 2019). In adsorption process, activated carbon (AC) has been reported as one of the most effective adsorbent used for the removal of many pollutants (organic and inorganic), including dyes and other colored compounds. However, production of activated carbon by carbonizing and

activating the organic substances from the proper materials is relatively costly, and thus requires the search for alternatives and low-cost adsorbents (Hamza *et al*., 2019; Rehman *et al*., 2018). A low-cost adsorbent should be inexpensive material and does not require many processing and can be found in the environment naturally in abundance or produced as a by-product or a waste from an industry or agriculture (Abdulmalik *et al*., 2020; Mustapha *et al*., 2019; Akpomie and Dawodu, 2016; Sivakumar, 2015). There has been a lot of research interest on the development of cheaper adsorbents from clay minerals, because they are relatively cheap, non-toxic and chemically stable (Hamza *et al*., 2019; Uddin *et al*., 2017). Nigeria is abundantly blessed with clay minerals which can be used as cheap alternative adsorbent for the removal of dyes and other colored pollutant from solution. However, clay minerals usually have small surface area and cation exchange capacities (Hamza *et al.*, 2019). This limits the application of kaolin as an adsorbent. However, the adsorption properties of clays can be enhanced by modifying their structures and chemical compositions using various chemical additives and thermal treatment (Akpomie and Dawodu, 2016; Hamza *et al.*, 2019; Bhattacharyya and Gupta, 2008). Crystalline structure of clay minerals is usually lost during calcination process. However, calcined clays usually exhibit higher specific surface area and adsorption capacities when compared to raw clays. (Uddin, 2017; Edomwonyi-Otu *et al*., 2013). Metakaolin with chemical formular $2Al_2Si_2O_7$ is the dehydroxylated amorphous form of kaolin that is obtained through calcination of kaolin at a temperature range of 500^0C to 850^0C (Edomwonyi-Otu *et al*., 2013). There have been some research works reported on the removal of Methylene blue (MB) dye from aqueous solution using kaolin. However, there have been limited works on the adsorption of Methylene blue (MB) dye onto metakaolin. Thus, this research focuses on the utilization of thermally treated kaolinite clay mineral (Metakaolin) as an adsorbent as alternative to chemical treatment, to remove Methylene blue (MB) dye from synthetic wastewater.



Scheme 1. Chemical Structure of Methylene Blue (Moeinian and Mahmoud 2019).

Materials and Method

Preparation of Adsorbent

Kaolinite clay was obtained from Kankara Local Government Area of Katsina State, Nigeria. The raw kaolin was pulverized and beneficiated to remove impurities and improve it quality as described by Nurudeen *et al*., 2013. The beneficiated kaolin was then charged into a furnace and calcined at a temperature range of 500 – 850^{0}C for 3-hours. It was then ball milled to eliminate agglomerates, ensure particle size uniformity and sieved using 100 µm sieve to obtained metakaolin adsorbent. It was then characterized using X-ray fluorescence (XRF) and Brunauer - Emmett - Teller (BET) analysis to determine, chemical composition and specific surface area respectively.

Equation of Transformation of Kanakara Kaolinite Clay to Metakaolin

$$\underset{\text{Kaolin}}{Al_2Si_2O_5(OH)_5} \xrightarrow{500 - 850^0C} \underset{\text{Metakaolin}}{2Al_2Si_2O_7 + 4H_2O} \quad (1)$$

(Edomwonyi-Otu *et al*., 2013).

Preparation of the Adsorbate

Methylene Blue (MB) dye analytical grade with molecular formular $C_{16}H_{18}N_3SCl$ was obtained from Steeve-Moore Chemical Store Samaru, Zaria, Kaduna, Nigeria. A stock solution of 1000 mg/L of Methylene blue (MB) was prepared by dissolving 1g of MB powder with distilled water in a 1 litre volumetric flask stirred and making it up to the mark. Other experimental working concentrations were prepared from the stock solution by serial dilutions.

The dilution formula is given as:

$$C_1V_1 = C_2V_2 \quad (2)$$

Where:

V_1 = Volume of stock solution

C_1 = Concentration of stock solution

V_2 = Final volume of new solution

C_2 = Final concentration of new solution

Determination of pH Point of Zero Charge of the Adsorbent (Metakaolin).

As described by (Eletta *et al*., 2016; Haruna, 2020) ,0.2g of the metakaolin was weighed and put into five (5) well cleaned beakers. 50ml of 0.01MNaCl was then added to each of the five beakers containing the adsorbent and the mixtures stirred thoroughly. The pH of the first beaker was adjusted to 2.0 by adding appropriate amount of 0.1MHCl or 0.1MNaOH solutions using well calibrated pH-meter in monitoring the adjustment. Same procedure was repeated for the remaining beakers by adjusting the pH to 4,6,8 and 10

respectively. Thus, initial pH values are 2,4,6,8 and 10. Each content of the beakers were then poured into well tagged sample bottles and then taken to a shaker and operated for 48 hours. Final pH values were taken and subsequently the pH differentials were determined. A graph of ΔpH against $pH_{initial}$ was plotted and the pH point of zero charge (pHpzc) was determined.

Adsorption Experiments

Batch adsorption experiments were carried out in 250ml beaker by mixing 100ml of Methylene blue (MB) dye solution of the desired concentration with the required amount of the adsorbent (Metakaolin). The pH of the Methylene blue (MB) dye solutions were adjusted using 0.1MNaOH solution. The mixture was then stirred thoroughly with a magnetic stirrer at room temperature (27^0C) and 350 rpm for desired contact time. The mixture was then rapidly filtered using vacuum pump filter and the resulting supernatant was analyzed using UV-visible spectrophotometer at maximum absorption wavelength (λ_{max} = 665nm) to determine the amount of MB remaining in the solution. The same procedure was repeated for other runs and the percentage removal of Methylene blue (MB) dye was calculated using the relation in equation 3a.

$$\text{Percentage Removal (MB)} = \frac{C_o - C_t}{C_o} \times 100 \quad (3a)$$

$$q_e = \frac{C_o - C_e}{m} \times V \quad (3b)$$

Where; C_o and C_t represent initial and final concentrations of MB (mg/L) respectively.
q_e is the equilibrium adsorption capacity (mg/g), Ce is the equilibrium concentration (mg/L), V, Volume of solution and m is the mass (g) of the adsorbent.

Results and Discussion

Characterization of Raw Kaolin, Beneficiated and Metakaolin

Table 1. presents the chemical composition of Raw kaolin, Beneficiated kaolin and Metakaolin prepared. The decrease in silica content observed of the beneficiated kaolin could be attributed to the washing away of some silica component during the beneficiation process of the raw kaolin, while increase in silica content observed in metakaolin could be attributed to removal of non-clay minerals, combustible and volatile impurities during the calcination process (Edomwonyi-Otu *et al*., 2013). Meanwhile, the increase in loss on ignition (LoI) after Metakaolinization could be attributed to dehydroxylation of the clay during calcination process leading to removal of chemically bonded water in the clay (Hamza *et al*., 2019).

Table 1. XRF Results of the samples

Oxide(wt%)	Raw Kaolin	Beneficiated	Kaolin	Metakaolin
SiO_2	48.20	45.87		53.48
Al_2O_3	27.35	28.43		32.83
CaO	0.343	0.332		0.301
Fe_2O_3	0.555	0.302		0.142
K_2O	0.693	0.523		0.413
MgO	1.90	0.962		0.030
Na_2O	0.019	0.012		0.010
TiO_2	0.100	0.096		0.037
LoI	-	9.17		13.24
SiO_2/ Al_2O_3	1.76	1.61		1.67

Table 2 presents the BET analysis results of Beneficiated kaolin and Metakaolin. The increase in specific surface area and average pore size observed of metakaolin compared to beneficiated kaolin could be attributed to loss of crystallinity of the kaolin during calcination as well as elimination of combustible and volatile impurities blocking the pores of the kaolinite clay.

Table 2. BET results of Beneficiated kaolin and metakaolin

S/N	Parameters	Beneficiated Kaolin (BKC)	Lit.Value (BKC)*	Metakaolin (MKC)	Lit. Value MKC**
1	Surface area (m^2/g)	19.64	12.95	25.73	24.68
2	Pore volume (cm^3/g)	0.075	0.038	0.257	0.261
3	Average Pore size (nm)	1.453	1.302	2.054	2.031

(Nurudeen, 2018)* (Hamza *et al*., 2019)**

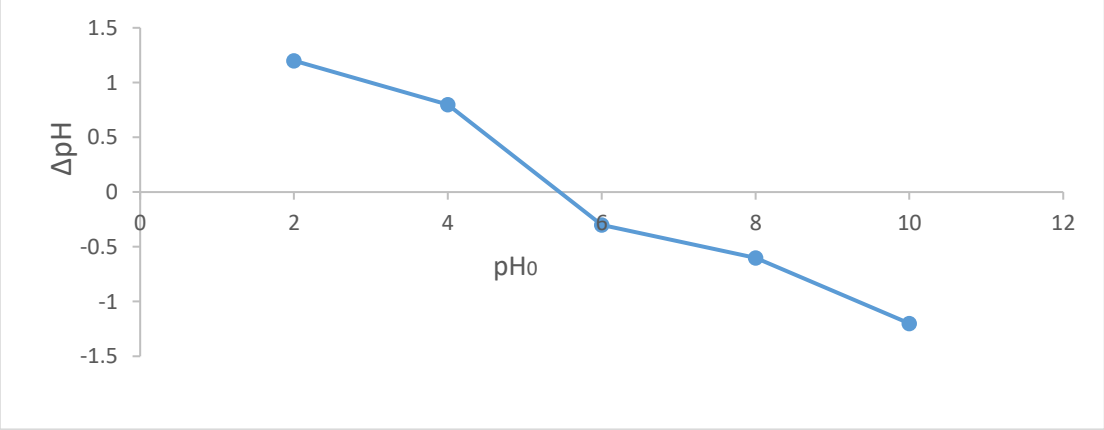


Figure 1. pH at point of zero charge (pH_{PZC}) of Metakaolin

The pH point of zero charge, pH_{PZC} is the pH at which the adsorbent has a neutral charge (zero) on the surface. The pH_{PZC} of the adsorbent was determined by using the solid addition method (Haruna, 2020; Eletta *et al*., 2016). The pH_{PZC} of the metakaolin was determined to be 5.6 as shown in Figure 1. Generally, when the pH of solution is less than pH_{PZC}, the adsorbents surface becomes positive and attracts negatively charged particle (anions) from the aqueous solution, and when it is greater than pH_{PZC}, the adsorbent surface becomes negatively charged and attracts cations from the solution. A working pH of 8.0 was chosen since is above the pH_{PZC} of the metakaolin adsorbent. The surface of the adsorbent becomes negatively charged and would reasonably increases the attraction of the cationic Methylene blue (MB) dye from the solution. Conversely, working below the pH_{PZC} would not favor the removal of Methylene blue as the surface of the adsorbents becomes protonated, thus increases the electrostatic repulsion between the MB ions and the adsorbents surface. Hence, the removal efficiency would decrease with decrease in pH. (Hamza *et al*., 2019).

Adsorption of Methylene blue (MB) dye from synthetic wastewater onto metakaolin

Figure 2 shows the effect of contact time on percentage adsorption of Methylene blue (MB) dye onto metakaolin at time interval of 0 – 90 minutes. It can be observed that the percentage removal of MB onto metakaolin increases with increase in contact time up to around 60 minutes. At the beginning, the sorption process was due to high driving force, large surface area and availability of high number of active sorption sites of the adsorbent. The sorption proceeds until it reaches equilibrium at around 60 minutes. Subsequently, the percentage adsorption of the Methylene blue (MB) dye begins to decline, signifying desorption of the adsorbates (MB) back into the solution. This could be attributed to the saturation of active sorption sites on the adsorbent at prolonged adsorption time.

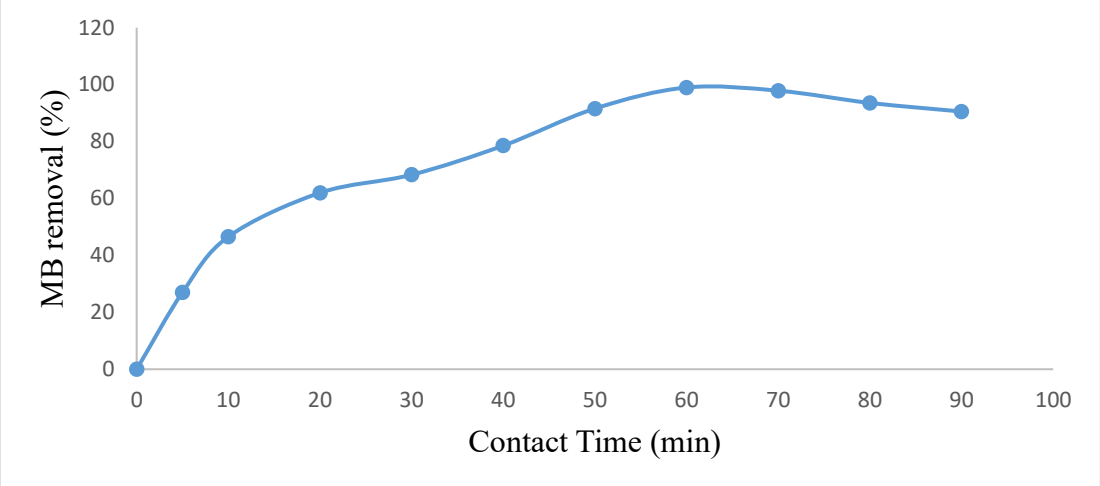


Figure 2. Effect of Contact time on Percentage removal of Methylene blue (MB) onto Metakaolin (C_0 = 100 mg/L, pH = 8)

The effect of adsorbent dosage on the adsorption of Methylene blue (MB) dye onto metakaolin was investigated as shown in figure 3. The adsorbent dosage determines the capacity of the adsorbent for a given initial concentration of the adsorbate. (Amode *et al*., 2016; Yakubu *et al*., 2017; Kyzas *et al*., 2012). The adsorbent dosage was varied from 0.5 – 2.5 g at initial concentration of adsorbate of 100mg/l. It can be observed that Methylene blue (MB) dye removal capacity increases proportionately with adsorbent dosage, and is due to large surface area and availability of more active sorption sites. After adsorbent dosage of 2.0 g, no significant removal of Methylene blue was observed, and this could be attributed to the conglomeration of the adsorbent particles due to decrease in effective surface area (Ozyaman *et al*., 2023; Pathania *et al*., 2016). Therefore, 2.0 g is the optimum adsorbent dosage for initial concentration of 100mg/l.

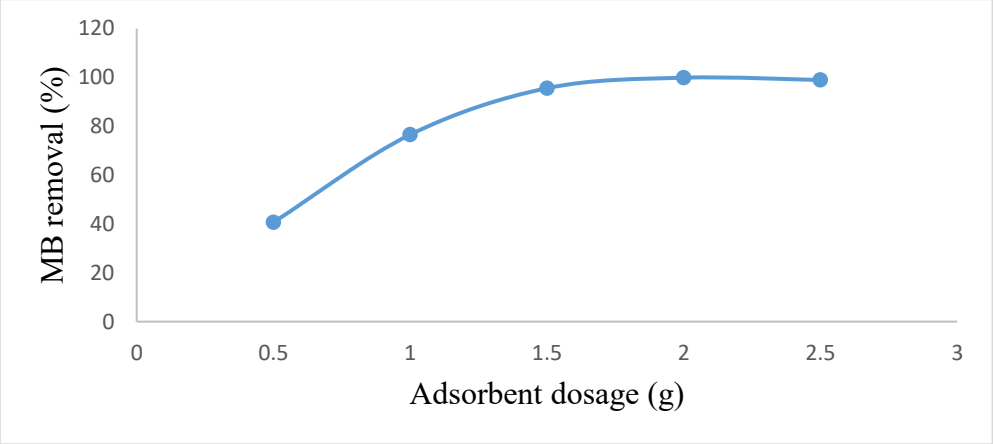


Figure 3. Effect of adsorbent dosage on percentage removal of Methylene blue (MB) onto metakaolin (C_0 = 100 mg/L, pH = 8)

Kinetic Studies

Adsorption kinetics shows the evolution of adsorption capacity through time, and is necessary to identify the type of adsorption mechanism in a given system. The kinetic data were fitted to pseudo-first order and pseudo-second order kinetic model equations. Equation 4 and 5 described the linearised pseudo-first order and second order kinetic model equations. Lagergren's first order rate equation is the earliest known to describe the adsorption rate based on adsorption capacity. The linear form of Lagergren's first order rate equation is as shown in Equation 4.

$$\ln(q_e - q_t) = lnq_e - \frac{1}{2.303}K_1 t \quad (4)$$

Where q_e is the amount of adsorbate adsorbed onto the adsorbent at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed onto the adsorbent at any time t (mg/g), and K_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption which can be calculated from the slope of the linear plot of $\ln(q_e - q_t)$ vs. t (Kandisa *et al*., 2018).

$$\frac{t}{q_t} = \frac{1}{k_2 q^2_e} + \frac{1}{q_e} t$$

(5)

Where K_2 (g/mg. min) is the rate constant of the pseudo-second-order adsorption, q_e is the amount of adsorbate adsorbed on the adsorbent at equilibrium (mg/g), and q_t is the amount of adsorbate adsorbed on the adsorbent at any time t (mg/g). K_2 (g/mg. min) can be calculated from the slope and intercept of the plot of t/q_t against t. (Isah *et al.,* 2022; Kandisa *et al*., 2018)

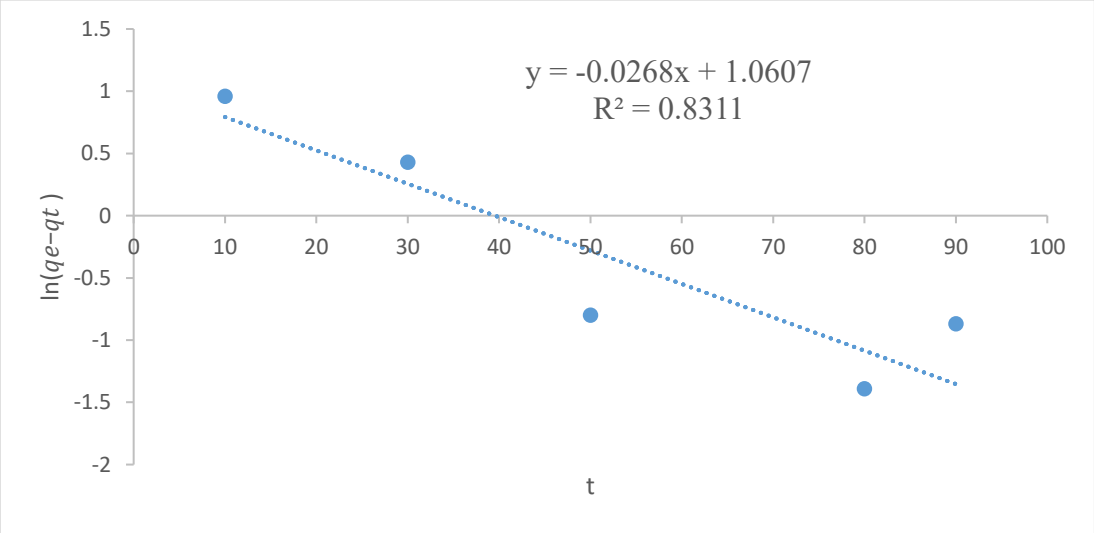


Figure 4: Pseudo-first order kinetic plot for Methylene blue (MB) adsorption onto metakaolin

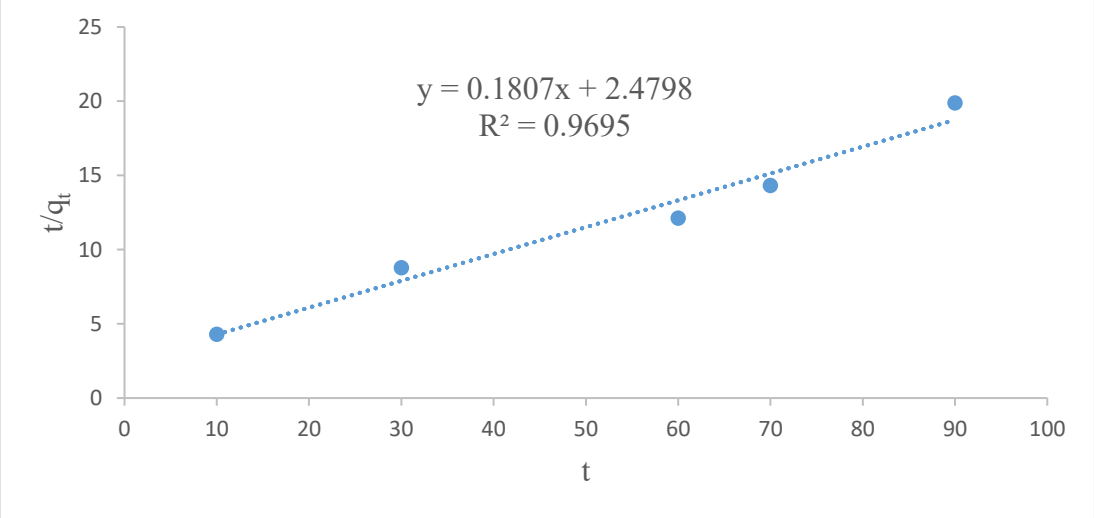


Figure 5: Pseudo-second order kinetic plot for Methylene blue (MB) adsorption onto Metakaolin

The experimental data were fitted with the kinetic models linearized equations and the linear regression analysis and constants were calculated using Microsoft excel version 2010.The result are presented in table 3.

Table 3. Kinetic Models and their Parameter Values

Kinetic models	Linear expression	Parameter values
Pseudo-first order	$\ln(q_e - q_t) = lnq_e - \frac{1}{2.303}K_1 t$	k_1= 0.062 min^{-1} q_e= 2.89 mg/g, R^2= 0.8311
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q^2{}_e} + \frac{1}{q_e}t$	k_2= 0.013 g/mg.min, q_{exp} = 4.99 mg/g, q_e = 5.534 mg/g, R^2= 0.9695

The R^2 value of pseudo-second order kinetic model is very close to unity compared to that of pseudo-first order and the q_e calculated is also in good agreement with the experimental value obtained. Therefore, pseudo-second order kinetic model best described sorption process of Methylene blue (MB) dye onto Metakaolin adsorbent.

Adsorption Isotherm Studies

Adsorption isotherms show the relationships between the concentration of adsorbate on the solid adsorbent phase and its concentration in the liquid phase at equilibrium. Isotherms provide information about the capacity of adsorbents and the mechanism of adsorption (Hamza *et al*., 2019). Two adsorptions isotherm models namely, Langmuir and Freundlich isotherms were selected in this study.

Langmuir Adsorption Isotherm

The adsorption isotherms for Langmuir have been employed to describe the adsorption of adsorbate based on the concepts of monolayer on energetically uniform homogeneous solid surfaces (Ariyanto *et al*., 2014; Isah *et al*.,2022; Amode *et al*., 2016). The expression for Langmuir isotherm can be written in linear form as shown in Equation 6:

$$\frac{\mathrm{Ce}}{\mathrm{qe}} = \frac{1}{\mathrm{qm\ Kl}} + \frac{1}{\mathrm{qm}}\mathrm{Ce} \qquad (6)$$

where K_L is the Langmuir constant, which is related to the energy of adsorption (L/mg) and the affinity of the binding sites, and q_m is the maximum adsorption capacity (mg/g). K_L and q_m can be found from the intercept and slope of the plot of C_e/q_e against C_e.

Freundlich Adsorption isotherms

This isotherm model is generally used for multilayer adsorption on heterogeneous surface of adsorbent (Ariyanto *et al*., 2014; Sivakumar, 2015; Isah *et al*.,2022). The uptake model can be illustrated by equation 7.

$$lnq_e = lnK_F + \frac{1}{n} lnCe \quad (7)$$

where K_f and n are the constants of Freundlich isotherms. K_f shows adsorption capacity, while *1/n* is the adsorption intensity. The constants of Freundlich isotherm K_f and *n* can be obtained from the plot of ln q_e against ln C_e, which determine the extent of the adsorption process, and the degree of nonlinearity between solution concentration and adsorption respectively.

However, after establishing the optimum condition for MB removal, the initial dye concentration (10 – 60mg/l) were varied at constant time and adsorbent dosage and the results of the experimental data were fitted to both Langmuir and Freundlich isotherm model equation as shown in figure 6 and 7.

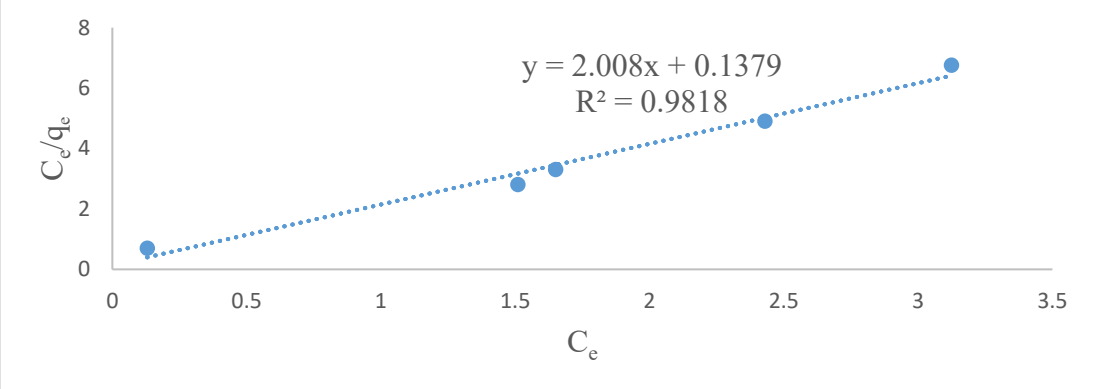


Figure 6: Langmuir Isotherm plot for Methylene blue (MB) adsorption onto Metakaolin

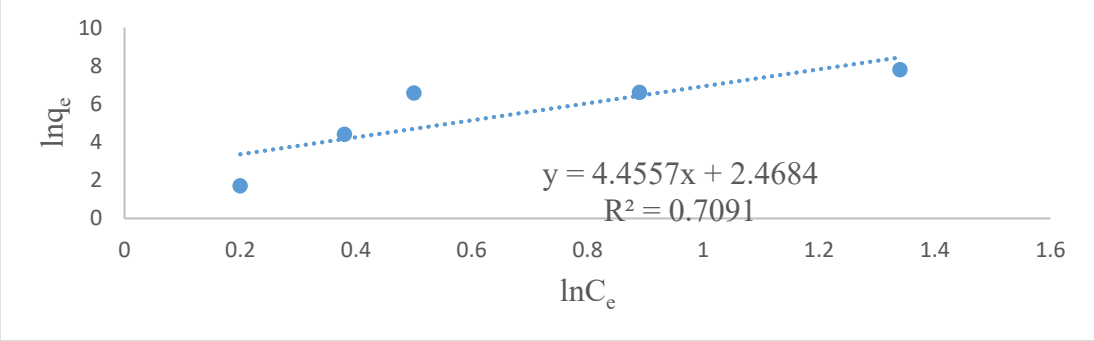


Figure 7: Freundlich Isotherm plot for Methylene blue (MB) adsorption onto Metakaolin

Figure 6 and 7 shows the linearized plots of the two isotherms, while table 4 presents the isotherms parameters and correlation coefficients (R^2) that were derived from the slope and intercept of the plots. By comparing the regression coefficients, adsorption of Methylene blue (MB) onto metakaolin is best described by the Langmuir isotherm model with R^2 value of 0.9818. Therefore, this shows that adsorption of MB involves the formation of monolayers of the adsorbates molecules (Methylene blue dye) on the adsorbent surface (metakaolin). Similar trend were observed by other studies in which Langmuir model described a much better fit than the Freundlich model in relation to Methylene blue dye adsorption (Amode *et al*., 2016; Ariyanto *et al*., 2014; Mekonnen and Sime 2018; Abdulmalik *et al*., 2020).

Table 3. Adsorption Isotherm parameters for Methylene blue Adsorption onto Metakaolin

Isotherm models	Equation	Parameter values
Langmuir	$\frac{1}{qe} = \frac{1}{qmklCe} + \frac{1}{qm}$	K_L= 14.49 L/mg , q_m= 4.98 mg/g R^2= 0.9818
Freundlich	$lnq_e = lnK_F + \frac{1}{n} ln\text{Ce}$	1/n = 4.4557 , n = 0.224, K_F= 11.80 R^2= 0.7091

Conclusion

Metakaolin was successfully prepared and characterized from Kankara Kaolinite Clay and utilized in the removal of Methylene blue (MB) dye from aqueous solution. BET analysis shows that the adsorbent has Specific surface area of 25.73 m^2/g, pore volume of 0.257 cm^3/g and average pore size of 2.054 nm. The pH point of zero charge of the Metakaolin was determine to be 5.6 from which a working pH was chosen for further studies. The effects of process variables; contact time (0 – 90 min), initial concentration (10 – 60 mg/L) and adsorbent dosage (0.5 – 2.5 g) on the uptake of Methylene blue (MB) onto Metakaolin were investigated. Adsorption equilibrium was attained at 60 minute and adsorbent dosage of 2.0 g of which 99.86% removal of Methylene blue (MB) was achieved. The kinetic data showed that pseudo-second order model best described the sorption kinetics with R^2 value of 0.9695. Adsorption equilibrium data were also fitted to adsorption isotherm models of which Langmuir Isotherm best described the sorption process as indicated by the R^2 value of 0.9818. Thus, monolayer of adsorbates molecules were formed on the adsorbent surface. The maximum adsorption capacity (q_m) of MB adsorption onto metakaolin was found to be 4.99 mg/g. Moreover, this natural adsorbent has advantages such as; environmentally friendly, relatively low cost and non-toxic and thus can be considered as promising adsorbent for the removal of Methylene blue (MB) dye from aqueous solution.

Recommendation

Pilot Textile wastewater treatment plant should be fabricated locally so that the adsorbent produced (Metakaolin) in this research work could be utilized.

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