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Adsorption of methylene blue dye by using modified Fe/Attapulgite clay

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ABSTRACT

In this work, attapulgite clay was modified iron to obtained (Fe/attapulgite) and its capacity for the removal of a typical cationic dye, methylene blue, was studied. The modified samples were characterized by SEM, EDX, nitrogen-adsorption surface area (BET) and FTIR techniques. Various operational parameters such as pH, initial dye concentration, mass dosage and solution temperature in batch systems were investigated on the use of Fe/attapulgite in the adsorption of methylene blue (MB) dye. The amount of dye removed was dependent on initial dye concentration, mass dosage pH of solution and solution temperature. Experimental data were analyzed using three model equations: Langmuir, Freundlich, and Temkin isotherms and it was found that the Freundlich isotherm model fitted the adsorption data most with the highest correlation ($R^2 \geq 0.986$). Thermodynamic parameters, such as Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated. The adsorption of MB dye onto Fe/attapulgite was found to be spontaneous and endothermic in nature, this study shows that the adsorption confirm physisorption mechanism.

Keywords: Attapulgite, Fe/Attapulgite, Methylene blue, Adsorption, Water treatment.

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INTRODUCTION

In the manufacturing of highly industry advances large amounts of dyes are used to color the products, which are partly discharged in effluents with no previous treatment. The presence of dyes in effluents, even in low concentrations, is a major concern because they are highly visible, toxic to microorganisms and harmful to human health[1].

Various physical and chemical methods have been employed for the treatment of dyes, including coagulation, flocculation, precipitation[2], photocatalysis[3-6], and ultrasound irradiation[7]. All these methods have some economic and environmental drawbacks, such as high capital and operating cost, sludge production and complexity of the treatment processes [2, 8].

Adsorption process is broadly used for removal of odor, oil, colors and organic contaminants especially from a liquid-phase system, because it is considered an effective way to remove dyes from wastewater, since it is not destructive and easy to apply[9]. The process cost for dye removal by adsorption lies mainly on the cost of the adsorbent and the regeneration of adsorbent. As knowing the activated carbon is currently the most widely used adsorbent due to its large surface area and high adsorption capacity. However, the use of activated carbon is becoming restricted by its high cost and regeneration difficulties. Several nonconventional, low-cost adsorbents have also been tried for dye removal; some of them are peat[10], activated coconut[11], activated apricot stones[12], activated rice husks[13], sawdust[14], and red mud[15]. Many low-cost adsorbents are being developed worldwide to replace activated carbon.

Clays are very good substitute for costly commercial activated carbon used in adsorption operations [16, 17]. Ordinarily these low-cost adsorbents have a low adsorption capacity. In association these clay minerals have many benefits over other low cost adsorbents such as archaically, ion exchange capability, high adsorption capacity and surface area, mechanical and chemical stability, and several structural and surface characteristics.[18, 19]

In view of this study, we will characterize and determine key operating parameters: adsorbent dosage, pH of solution, initial dye concentration and temperature, so as to maximize the adsorption capacity and efficiency of the modified attapulgite by iron (Fe/attapulgite) as a new low cost adsorbent for the removal of methylene blue dye. The experimental data will be appraised by Langmuir, Freundlich and Temkin adsorption isotherms, as well as the equilibrium, and thermodynamics.

MATERIALS AND METHODS

Materials

Methylene blue (MB) dye, which has the chemical structure shown in Fig. 1, presents decentralizing positive charge on the organic skeletal structure, which could play a major role in keeping the species on the surface of the clay. It has a maximum visible absorbance at a wavelength of 664 nm.

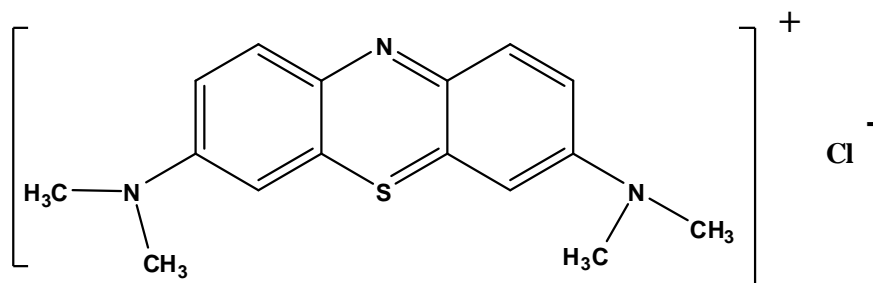


Figure 1: The chemical structure of MB.

All solutions used were prepared with deionized water and all reagents were of analytical grade. Working solutions of MB were prepared from a stock solution of 1000 mg L^{-1} to give the required initial concentrations ($C_0 = 30$ to 300 mg L^{-1}) for each experimental run.

Modified adsorbent

The attapulgite clay used in this study was supplied by the Ministry of Industry and Minerals (Mining geology-Baghdad/Iraq). Before the experiments the attapulgite was washing with deionized water for several times, after this washing by HCl (1 M) to remove all bicarbonates and carbonates ions, then dried for 24 hr in oven (100 °C).

Samples of Fe/attapulgite were prepared using a solution of FeCl₃ (3 M) was slowly added to a solution containing on attapulgite by a method based on co-precipitation, under mechanical stirring at 600 rpm. The resultant material (Fe/attapulgite) was dried in an oven at 80 °C for 24 h, and calcinated at 400 °C for 2 h then, washed with deionized water for several times until pH of around 6.7, dried in an oven at 100 °C for 24 h, , then sieved to give a standard particle size in the range of 100–150 µm. The Fe/attapulgite was stored in a desiccators for characterization and batch adsorption experiments.

Characterization of adsorbent

Morphological studies were carried out using field-emission scanning electron microscopy (FE-SEM; JEOL microscope model JSM-6701F) coupled with energy-dispersive X-ray spectroscopy (EDX) for elemental analysis. The samples were sprinkled over a piece of conducting carbon tape and coated with a thin gold layer to give them conductive properties.

Fourier transformed infrared (FTIR) spectroscopy (SHIMADZU, model: FTIR-8400S) analysis was performed in the range of 4000–400 cm⁻¹. The samples were ground with KBr (analytical grade) and the mixture was pressed under vacuum conditions to produce disks for the FTIR analysis. The specific surface areas (SSA) of the samples were determined using an AUTOSORB surface area analyzer, Quantachrome (BET). Prior to the measurements, the samples were degassed at 573 K for 2 h, and then the nitrogen adsorption and desorption were measured at 77 K.

Adsorption studies

Adsorption studies were carried out in batch mode to investigate the effect of experimental factors (adsorbent dose, pH, initial dye conc., and temperature) on the adsorption of MB on Fe/attapulgite. The effect of experimental factors such as pH (3–11), Fe/attapulgite dose (0.05–2.5 g.L⁻¹), MB dye concentration (30–300 mg.L⁻¹), and temperature (10–50 °C), was investigated employing one factor one time approach.

MB experimental solutions (V = 100 mL) were taken in glass flasks (250 mL), and mixed with known amount of Fe/attapulgite at predefined experimental conditions. The detail of experimental conditions has been presented for each experiment in the relevant sections of result and discussion. The solution was then gently agitated in an isothermal water bath shaker to achieve the equilibrium between Fe/attapulgite–MB suspensions. After the experiment, the suspensions were centrifuged, for two times to remove Fe/attapulgite particles, and the final concentrations of MB solution in the flasks after equilibrium were determined using UV–vis spectrophotometer (Shimadzu UV/Vis 1650 spectrophotometer, Japan) at maximum wavelength of 664 for MB. Removal efficiency (R %), and adsorption capacity (q_e) was calculated as followed:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (2)$$

where C₀ (mg/L) is the initial concentration of dye, C_e (mg/L) is the concentration of dye at equilibrium, V(L) is the volume of dye solution, and W (g) is the mass of adsorbent.

RESULTS AND DISCUSSION

Characterizations

The EDX spectrum for elemental analysis in Fe/attapulgite showed a high presence of Fe which were virtually absent in the attapulgite spectrum; the Fe/attapulgite had 7.55% of Fe while attapulgite had 2.52%, and there was variation of oxygen element percentage between the Fe/attapulgite and attapulgite. This could be attributed to acid treatment and cation exchange with ferric ions of the attapulgite clay that were carried out.

The morphological structure (SEM) showed agglomerated and approximately equal sizes of particles in the Fe/attapulgite micrograph as compared with the scattered uneven clay particles of the attapulgite micrograph. This could be attributed to loss of some cations during acid treatment; and, loss of some volatile organic substances during calcinations which all occurred during the surface area developmental modification Fe element of the surface of attapulgite. The attapulgite sample was examined using SEM to analyze their morphological characteristics with respect to the Fe/attapulgite modification. Herein, we present a representative SEM images and EDX spectra of modified attapulgite in Fig. 2.

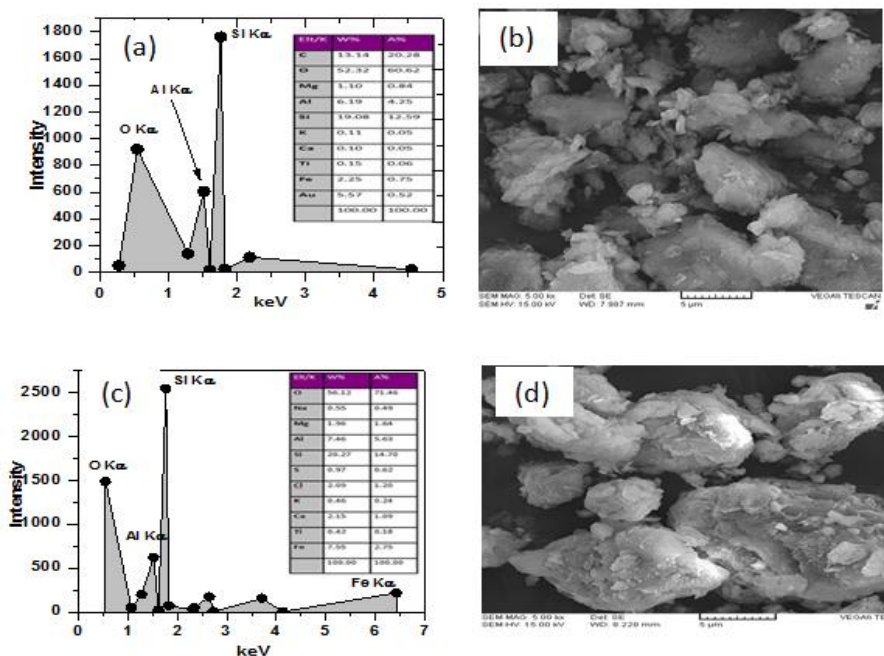


Figure 2: EDX and SEM analysis: (a) attapulgite spectrum, (b) attapulgite micrograph, (c) Fe/attapulgite spectrum, (d) Fe/attapulgite micrograph.

Table 1 presents changes of the total surface area and specific surface areas of the modified attapulgite by ferric chloride. The surface area of the modified attapulgites decreased significantly from 143.84 m².g⁻¹ (attapulgite) to 40.57 m².g⁻¹ (Fe/attapulgite). The decrease in surface area resulted from the iron attached on the surface of the attapulgite, also from the effect of calcinations of Fe/attapulgite at a high temperature can alter its chemical and physical properties of the attapulgite. The changes in molecular structure and chemical composition of the attapulgite upon the activation methods and limiting can be variable, depending on the chemical composition of the clays and the heating regime.

Table 1: Surface area analyzer of attapulgite and Fe/attapulgite

Characteristics	Total surface area	Specific Surface area (m ² g ⁻¹)
attapulgite	7.192 ± 0.03	143.84 ± 0.13
Fe/attapulgite	4.868 ± 0.09	40.57 ± 0.15

The FTIR spectra for attapulgite, Fe/attapulgite and MB/Fe-attapulgite are shown in Fig. 3. The FTIR spectra (Fig. 3a, & 3b) of attapulgite clay and Fe/attapulgite showed several absorption peaks, corresponding to different types of functional groups. The bands at 3620 cm^{-1} correspond to the hydroxyl linkage.

The broad band at $1200\text{--}1380\text{ cm}^{-1}$ shows $\nu(\text{Si-O-Si})$, [20] whereas the band at 570 cm^{-1} , which can be attributed mainly to Fe-O stretching vibrations and it is typical of magnetite. [21], also there is no new peak appears in Fig.3c, this is contributed to adsorption process have a physical behavior.

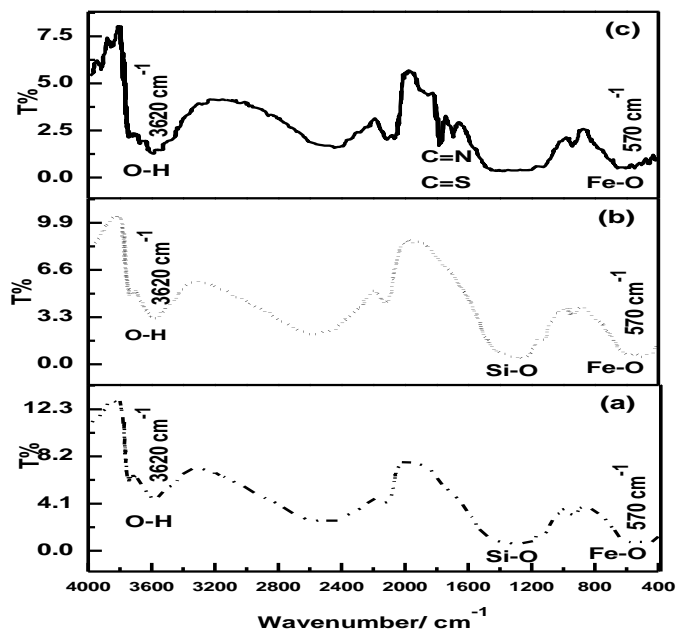


Figure 3. FTIR spectra. a) attapulgite; b) Fe/attapulgite; c) MB/Fe-attapulgite.

Effect of adsorption parameters

Effect of adsorbent concentration

Initial adsorbent dose requires proper selection because it controls adsorption via available surface area and binding sites [22]. The effect of Fe/attapulgite concentration on MB adsorption at a contact time of 2 h was studied by varying the adsorbent dose from 0.05 to $2.5\text{ g}\cdot\text{L}^{-1}$ in a $30\text{ mg}\cdot\text{L}^{-1}$ MB solution. The effect of adsorbent dose is shown in Fig 4. The results exhibit that adsorption efficiency and adsorption capacity showed inverse relationship with adsorbent dose.

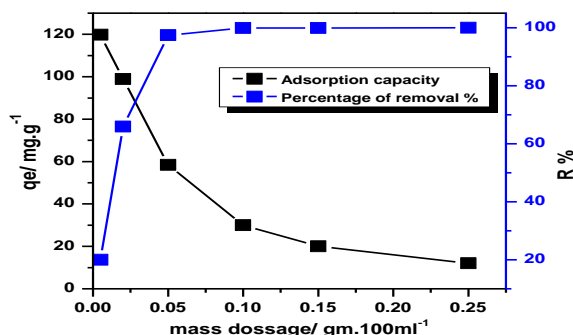


Figure 4: The effect of Fe/attapulgite concentration on MB dye. Exp. conditions: MB conc. $30\text{ mg}\cdot\text{L}^{-1}$ pH 6, agitation speed 120 rpm, contact time 2 h, Temp. 303 K.

Dye uptake increased from 19.96% to 99.84%, whereas the adsorption capacity decreased from 119.81 mg.g⁻¹ to 29.95 mg.g⁻¹ against the adsorbent dose (0.05–1.0 g.L⁻¹), respectively. Increasing the adsorbent concentration is thus seen to enhance the percentage removal of MB. Increased adsorbent concentration implies a greater surface area of Fe/attapulgitite and, consequently, a greater number of possible binding sites. At adsorbent doses greater than 0.5 g .L⁻¹, there was little change in either the rate of attaining adsorption equilibrium of the MB, or the dye uptake of MB.

Effect of pH

The measure of the basicity or acidity (pH) of the dye solution was carried out to enhance comprehensive evaluation of the adsorption process as pH is an invaluable integral part of aqueous solution studies[23, 24]. Some experiments were therefore performed at 30 °C with 75 mg .L⁻¹ solutions to study the MB adsorption on Fe/attapulgitite as a function of solution pH, results are shown in Fig.5.

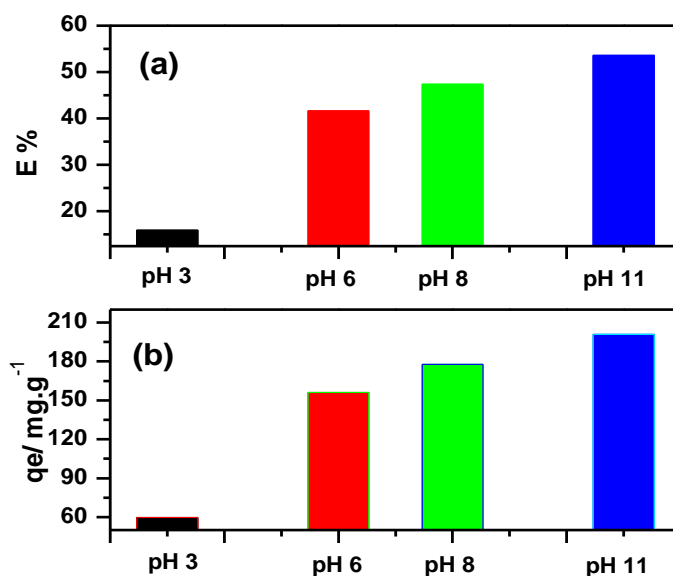


Figure 5: Effect of solution pH on the adsorption of MB dye on Fe/attapulgitite. Exp. Conditions: T = 303 K, C₀ = 75 mg.L⁻¹, adsorbent conc. = 0.2 g.L⁻¹, t = 2 h, agitation speed = 120 rpm.

The amount and the percentage of MB adsorbed from four solutions were as follows: un-buffered, 59.6 mg. g⁻¹, 15.90%; pH 3, 156.16 mg. g⁻¹, 41.64%; pH 6, 177.59 mg. g⁻¹, 47.35%; pH 8, 201.06 mg. g⁻¹, 53.61%; pH 11. Hence it is clear from the results that the adsorption process is pH solution dependent, the adsorption capacity and the percentage of MB adsorbed increasing with pH and being at a maximum at pH 11. This is attributed that the silanol groups on this surface become increasingly de-protonated as the pH of the adsorption system rises, thereby increasing the number of negatively charged adsorbent sites[25], or may be the electrostatic attraction due to columbic forces between the positive MB molecules and the negatively charged active sites on the adsorbents surfaces. While at lower pH 3–4 where protonation of H⁺ activities dominated and influencing the adsorbent surfaces to become positively charged, repulsion reaction between the MB molecules and the adsorbent active surfaces resulted [26].

Adsorption isotherms

The adsorption process is proportional to the initial dye concentration because it drives the mass transfer rate under a higher concentration gradient between dye solution and Fe/attapulgitite surface. The effect of initial dye concentration (30–300 mg/L) on the sorption efficiency and adsorption capacity Fe/attapulgitite is given in Fig. 6. Dye molecules have to compete with each other for the fixed number of binding sites at higher initial concentration[27]. Thus, some of dye molecules do not get adsorbed and remain in the solution[28].

The adsorption equilibrium isotherm is an important for describing how the adsorbate molecules distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state[29].

It is expressed by relating the amount of adsorbate taken up per gram of adsorbent, q_e ($\text{mg} \cdot \text{g}^{-1}$), to the equilibrium solution concentration, C_e ($\text{mg} \cdot \text{L}^{-1}$), at a fixed temperature, pH of solution and mass dosage.

The Langmuir[30], Freundlich[31]and Temkin[32] models are commonly used to describe the adsorption isotherm, and their constants afford significant parameters for predicting adsorption capacities[33].

The assumptions of the Langmuir model include considering that the surface is uniform and there are no interactions among adsorbed molecules on the surface. Also, each molecule occupies a specific site, with only one molecule per site, and is unable to move over the surface, each having the same energy, until the formation of a monolayer[34]. The Freundlich equation is based on an empirical relationship between the adsorption and adsorbate concentration[34].

The non-linear form of the Langmuir isotherm model[30] is given as:

$$q_e = \frac{K_L q_{\max} C_e}{1 + q_{\max} C_e} \quad (3)$$

where C_e (mg/L), is the equilibrium concentration of MB adsorbed; q_e ($\text{mg} \cdot \text{g}^{-1}$), is the amount of MB adsorbed; q_{\max} and K_L (Langmuir constants), the monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively. Langmuir constants generated from sorption data plot of q_e against C_e as shown in Fig. 6

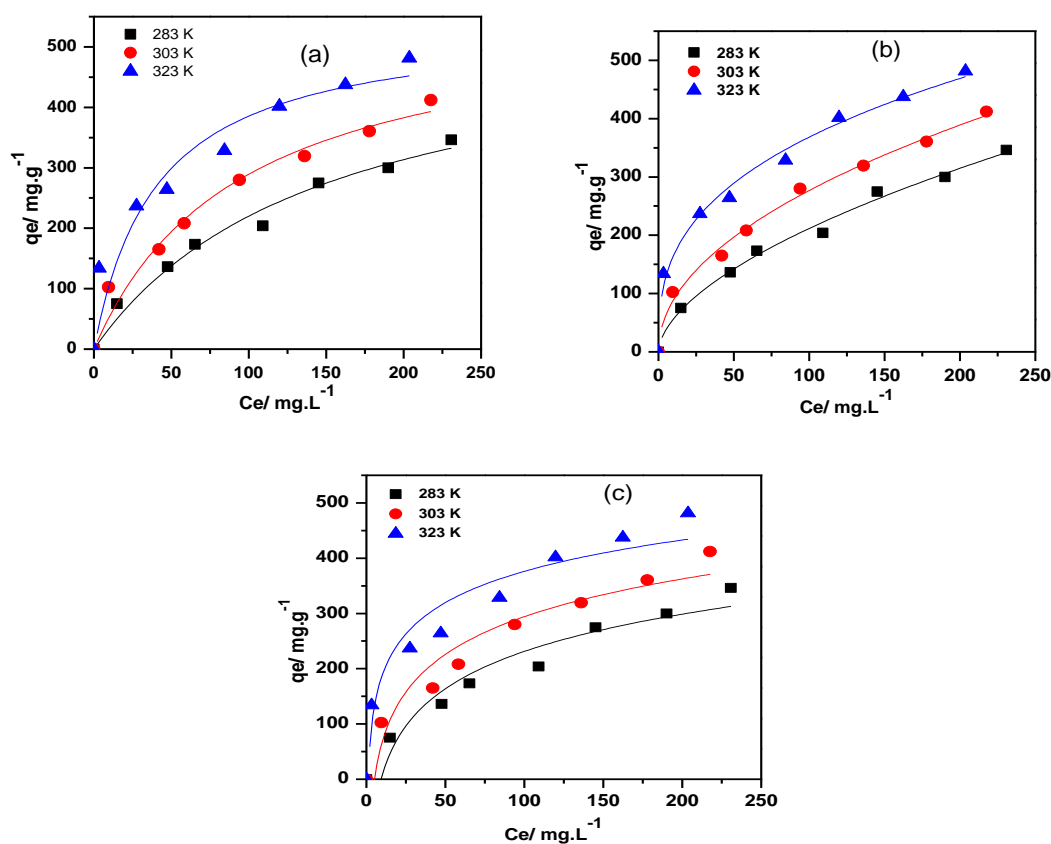


Figure 6: a) Langmuir, b) Freundlich and c) Temkin isotherms models plot of MB adsorbed by Fe/attapulgite at different temperatures. Exp. Conditions: $T = 303 \text{ K}$, adsorbent conc. = $0.2 \text{ g} \cdot \text{L}^{-1}$, $t = 2 \text{ h}$, agitation speed = 120 rpm , $\text{pH} 6$.

The Freundlich equation, which is essentially empirical, is the earliest known relationship describing the adsorption process. The isotherm assumes that adsorbent surface sites have a spectrum of different binding energies.

The Freundlich isotherm is based on the premise that adsorption occurs on rare heterogeneous surfaces sites with different energy of adsorption and are also non-identical. The non-linear form of the Freundlich isotherm was used to investigate the adsorption process adherence to the model, the equation[31] is given as:

The logarithmic form of the Freundlich isotherm is given as:

$$q_e = K_f C_e^{1/n} \quad (4)$$

where q_e ($\text{mg} \cdot \text{g}^{-1}$) is the amount of dye adsorbed at equilibrium; C_e ($\text{mg} \cdot \text{L}^{-1}$) is the equilibrium concentration of the adsorbate; K_f ($(\text{mg} \cdot \text{g}^{-1})(\text{L}/\text{mg})^{1/n}$) and n (dimensionless) are the Freundlich equilibrium coefficients. The value of 'n' a heterogeneous factor, gives information on favorability of adsorption process; while $1/n$ relays information on adsorption intensity and, K_f is the adsorption capacity of the adsorbate. The values of the model parameters obtained from the plot of Q_e against C_e shown in Fig. 6 are presented in Table 2. The Temkin model proposes into account the effects of the interaction of the adsorbate and the adsorbing species [32]. By ignoring the extremely low and large concentration values, the model assumes that the heat of adsorption (a function of temperature) of all of the molecules in the layer would decrease linearly rather than logarithmically with coverage due to adsorbate-adsorbent interactions[35], the equation is stated as follows:

$$q_e = \frac{RT}{b} \log(K_T C_e) \quad (5)$$

where b Temkin constant related to the heat of adsorption($\text{kJ} \cdot \text{mol}^{-1}$), and K_T empirical Temkin constant related to the equilibrium binding constant related to the maximum binding energy ($\text{L} \cdot \text{mg}^{-1}$).

The three isotherms under study all described the adsorption of MB on Fe/attapulgitite but not without some level of variance of their fitness. The best fit of isotherm was selected based on the highest correlation coefficient (R^2) value (closest to unity) which described the fitness of the isotherm to the experimental data.

Results show Freundlich isotherm model had the best fit than the other two parameters models for the adsorption of MB on Fe/attapulgitite; this was evident in the R^2 values presented in Table 2.

Table 2: Langmuir, Freundlich and Temkin isotherms parameters for MB adsorption by Fe/attapulgitite.

Isotherm	283 K	303 K	323 K
<i>Langmuir isotherm</i>			
K_L ($\text{L} \cdot \text{mg}^{-1}$)	0.00674	0.02457	0.01048
Q ($\text{mg} \cdot \text{g}^{-1}$)	542.3354	546.01982	565.54821
R^2	0.96325	0.94682	0.83897
<i>Freundlich isotherm</i>			
K_f ($\text{L} \cdot \text{mg}^{-1}$)	15.08882	28.77754	73.97969
$1/n$	0.57342	0.49148	0.34853
R^2	0.98624	0.98858	0.98137
<i>Temkin isotherm</i>			
b	97.35965	98.43166	81.7218
K_T	0.10755	0.19863	0.99851
R^2	0.95005	0.94436	0.94208

The Freundlich isotherm model involves surface heterogeneity of the MB adsorption process while the homogeneous behavior of MB adsorption process was informed by Langmuir isotherm model. This is going by the values of $n > 1$ and $0 < 1/n < 1$ which were obtained as shown in Table 2, satisfying favorable and heterogenous conditions, respectively of the model. The monolayer coverage obtained from this work by Langmuir model can be compared with similar published data as shown in Table 3.

Table 3: Comparison of monolayer adsorption of MB onto various adsorbents

Adsorbent	Adsorption capacity (mg/g)	Reference
RHC	58.02	[1]
Montmorillonite clay	289.12	[36]
Persian Kaolin	29.85	[37]
NaOH-treated pure kaolin	20.49	[38]
NaOH-treated raw kaolin	16.34	[38]
Fe/attapulgit	411.94	This work

Effect of temperature

Changing the temperature can have two different effects on the adsorption process: before equilibrium is reached it can alter the dye adsorption rate while after the equilibrium has been reached it can affect the adsorption equilibrium of the adsorbent for a particular adsorbate.

A study of the temperature dependence of the adsorption processes therefore gives valuable information about the enthalpy and entropy changes accompanying adsorption[39]. Fig. 7 illustrates the effect of temperature on the adsorption of MB, onto Fe/attapulgit as a function of initial MB concentration.

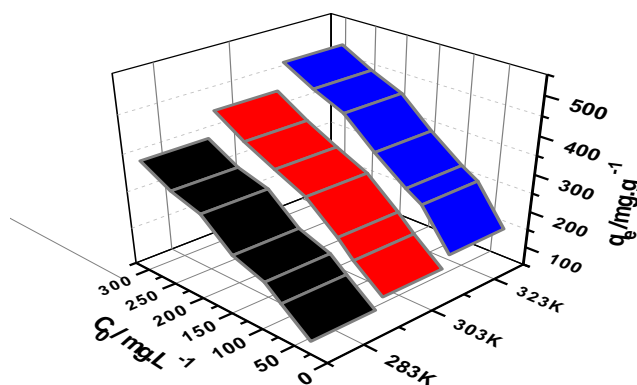


Figure 7: Effect of temperature on the adsorption of MB onto Fe/attapulgit for a solution initially containing (30-300 mg.L⁻¹) of MB as a function of adsorption capacity. Exp. Conditions: adsorbent conc. = 0.2 g/L, t = 2 h, agitation speed = 120 rpm, pH 6.

Results show an increase in the amount of MB adsorbed, after equilibrium was reached, when the temperature was raised from 283 to 323 K for most of the initial MB concentrations, indicating an endothermic adsorption process [40, 41] Before equilibrium was reached, increased temperature led to an increase in the rate of dye adsorption, implying a kinetically controlling process, as found in many other systems[40, 41].

Adsorption thermodynamics

Thermodynamic parameters, such as the change in enthalpy (ΔH), entropy (ΔS) or Gibbs free energy (ΔG), are important as indicators for the practical application of a process[42, 43] Thermodynamic studies for adsorption of MB on Fe/attapulgit at various temperatures of 10, 30 and 50 °C were carried out. This was done to determine the spontaneity of the adsorption process.

The experimental values obtained from the following equations inform whether the adsorption process was spontaneous or non spontaneous[44].

$$\Delta G = -RT \ln K_d \tag{6}$$

where R is the universal gas constant (8.314 J/Kmol); T, the absolute temperature (K); K_d is the distribution coefficient expressed as $K_d = q_e/C_e$; and ΔG is the Gibbs free energy.

Van't Hoff equation was used to determine the average standard enthalpy change, the equation is expressed as:

$$\ln(k_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

A plot of $\ln K_d$ against $1/T$ gives a graph (Fig. 8) where we can obtain entropy ΔS , from the intercept and enthalpy ΔH , from the slope; which are parameters that provides information on movement of solute (MB) from the bulk to the adsorbent Fe/attapulgitite surface. Summary of the thermodynamic parameters obtained are summarized in Table 4.

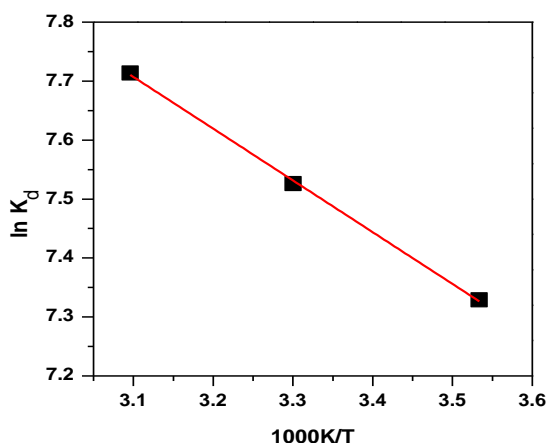


Figure 8: Linearized form of Van-Hoff's equation for adsorption of MB by Fe/attapulgitite surface.

Table 4 indicate the negative value of the Gibbs free energy change (ΔG) reveals that the adsorption process was spontaneous in nature[45] and the changed value of ΔG with increasing temperature it can be concluded that the adsorption mechanism is dominated by physisorption[46], in keeping with the finding that the adsorption is rapid and more spontaneous at higher temperature.

Table 4: Thermodynamic functions ΔG , ΔS , ΔH , of MB dye adsorbed on the Fe/Attapulgitite.

T/K	K_d	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/K .mol)
283	1523.81	-17.2441	7.298029	86.69839
303	1857.143	-18.9611		
323	2238.095	-20.7137		

As can be seen in Table 4 the ΔH value is positive confirming the endothermic nature of the adsorption process. This feature may be an indication of the occurrence of monolayer adsorption[46]. The entropy change ΔS shows positive value, this confirms that the increasing randomness between the solid–solution interfaces during the adsorption process, probably due to the desorption of solvent molecules prior to MB dye adsorption [44].

CONCLUSION

The equilibrium between MB dye in the solution and on the Fe/attapulgitite surface was achieved in 2 h. The isotherm parameters obtained from models revealed that, Freundlich ($R^2 = 0.968$) was the best isotherm that described the adsorption process and then followed Langmuir and Temkin isotherms, respectively. Isothermal studies showed that MB adsorption was favorable on Fe/attapulgitite and followed multilayer adsorption. According to results of thermodynamics studies, negative values of ΔG showed that the adsorption process was spontaneous, favorable and physisorptive. Moreover, adsorption process followed endothermic trend with temperature. The maximum adsorption capacity of MB on Fe/attapulgitite was found to

be 481 mg/g. These results showed that MB dye can be effectively removed from aqueous solution employing Fe/attapulgite as a cheap adsorbent.

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