

Performance of Libyan Bentonite as Adsorbent for Methylene Blue Dye: Isotherms, Kinetics and Thermodynamic Studies

A. A. Jangher (Corresponding Author)

Department of Chemistry, Faculty of Sciences, University of Tripoli, Tripoli, Libya

Email: a.jangher@uot.edu.ly

S. M. Aghila

Libyan Polymer Research Center3, Tripoli, Libya

H. A. Jamhour

Libyan Polymer Research Center3, Tripoli, Libya

B. M. Mahara

Department of Chemistry, Faculty of Sciences, University of Tripoli, Tripoli, Libya

Article History

Received: 25 October 2022

Revised: 28 December 2022

Accepted: 5 January 2023

Published: 9 January 2023

Copyright © 2023 ARPG & Author

This work is licensed under the Creative Commons Attribution International

Attribution International

 CC BY: Creative Commons Attribution License 4.0

Abstract

This study provides an overview of natural and activated of Umm-Al- Razam, Libyan bentonite clay (north east of Libya region), as an offered adsorbent of anionic dye, methylene blue (MB) dye from aqueous solution; where the adsorption isotherms applied experimentally to investigate the effect of adsorbent dosage in a batch mode range from (0.1-1.2g), pH (1,3,5,7,9 and 11), initial MB concentration (5,10,20,30,40 and 50ppm), temperature (25,35,45 and 55°C) and contact time range from (5 - 120min). The Characterization of natural Libyan bentonite (NLBn) and activated Libyan bentonite (ALBn) was carried out firstly by infrared spectroscopy (FT-IR), electronic scanning microscopy (SEM) and X-ray diffraction (XRD) technique. The data analyzed by different models (Langmuir, Freundlich and Temkin) to describe the equilibrium isotherms and thermodynamic parameters such as Gibbs free energy change (ΔG) The data analyzed by different models (Langmuir, Freundlich and Temkin) to describe the equilibrium isotherms and thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) of the system were calculated. The results showed the equilibrium adsorption data of (NLBn) was fit better the Langmuir adsorption model but for (ALBn) was fit better to Temkin. The adsorption capacity for the removal of MB was 4.3 mg/g and 4.9 mg/g at different concentration on (NLBn) and (ALBn) respectively. Kinetics of dye removal was investigated and found to follow pseudo second order rate constant. The sorption and desorption capacity of MB was found to be 95% and 99% by both (NLBn and ALBn) respectively.

Keywords: Adsorption; Libyan bentonite; MB; Isotherm models; Kinetic studies; Thermodynamics parameters.

1. Introduction

Dyes waste represents one of the great problematic groups of pollutants because they can be simply viewed by the human eye and are difficult to biodegrade. However, The dyes are used in many industrial sectors such as textiles, paper and leather dyeing, as well as in the food and cosmetics industry. Dyes are known to be toxic and persistent in the environment and require physico-chemical techniques to degrade them [1]. Noteworthy removal of disposal dye in precious water resource could be done by the methods include biological treatment, catalytic oxidation, filtration, sorption process and combination treatment [2].

Among various types of methods adsorption was represented a prominent place in dye removal where the low cost elective adsorbents developed interest for proficient and less cost treatment techniques for adsorption processes [3]. Optimistic colour, basic and water soluble reactive effective on expulsion of basic dyes from the waste gushing. Several studies have been executed on adsorption of basic dyes by clay minerals [4].

Generally, the adsorption capacity for basic dyes (anionic dyes) is much lower than for acidic dyes (cationic dyes), as result of powerless attractions between acidic charges on the dyes and the negative surface of clay. Bentonite includes one octahedral alumina sheet lying between two tetrahedral layers of silica. Personality pessimistic charge of bentonite is ascribed to the isomorphs swap of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer. This negative charge is changed by the presence of replaceable cations (Ca^{2+} , Na^{+} , and so forth) in the lattice structure, which improve adsorbing cationic poisons [5-7]. In spite of the fact that, bentonite pathetically adsorbs acidic foreign substances due to repulsion force between the anion and the negative charge on the outer layer of the bentonite [8, 9]. A few creators have educated the utilization regarding bentonite modified and organo-bentonite with a cationic surfactant for acidic color end by means of loading quantity of surfactant [10, 11].

Methylene blue dye usually used in cotton and wool manufacturing, can cause serious health problems for human. for human such as hard breathing and mental disorder. The development of an effective treatment technique that can remove such pollutants into non-toxic is highly required.

Natural Libyan bentonite (NLBn) and activated Libyan bentonite (ALBn) have been investigated; investigation and characterization of the properties using many techniques such as infrared spectral analysis (FT-IR), X-ray diffraction analysis (XRD) and Scanning Electron Microscopy (SEM),

This work is concerned with the investigation on methylene blue dye which includes the effects of contact time, initial dye concentration, pH of solution, adsorbent dose and temperature in order to determine the optimum conditions of adsorption, as well as evaluating the equilibrium adsorption isotherms models including Langmuir, Freundlich and Temkin and kinetics and thermodynamics parameters.

Methylene blue dye is usually used in cotton and wool manufacturing, can cause serious health problems for humans. For humans such as difficulty breathing and mental disorder. The development of an effective treatment technique that can remove such pollutants into non-toxic is highly required.

Natural Libyan bentonite (NLBn) and activated Libyan bentonite (ALBn) have been investigated; investigation and characterization of the properties using many techniques such as infrared spectral analysis (FT-IR), X-ray diffraction analysis (XRD) and Scanning Electron Microscopy (SEM),

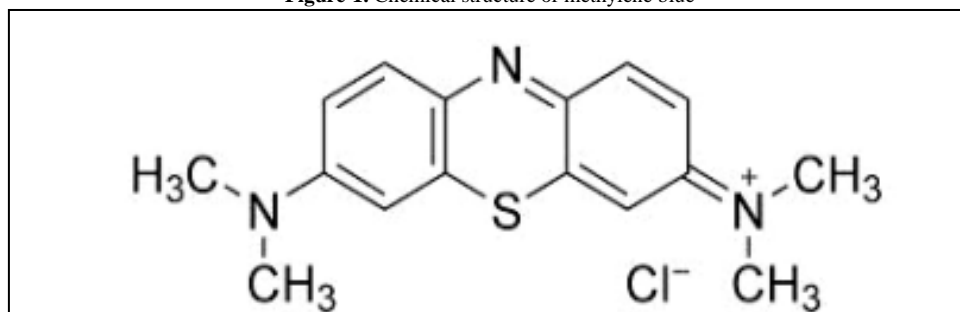
This work is concerned with the investigation on methylene blue dye which includes the effects of contact time, initial dye concentration, pH of solution, adsorbent dose and temperature in order to determine the optimum conditions of adsorption, as well as evaluating the equilibrium adsorption isotherms models including Langmuir, Freundlich and Temkin and kinetics and thermodynamics parameters.

2. Experimental

2.1. Reagents and Solutions

Methylene blue (MB), which is a basic cationic dye, was used as the adsorbate. The formula of MB is $C_{16}H_{18}N_3SCl \cdot 3H_2O$, and molecular weight 319.85 g/mol, whose chemical structure is shown in Figure 1. The MB dye was purchased from Industrial Research Center of Libya (IRC) laboratories (produced from BDH Chemical Ltd Poole England prod 26132) and was used without further purification. Stock solutions of 1000 mg/L MB were prepared in 1000 mL deionized water and working solutions were then prepared from stock solutions by using the dilution formula.

Figure-1. Chemical structure of methylene blue



2.2. Adsorbent Preparation

2.2.1. Preparation of Bentonite as Adsorbent

Bentonite was provided by Petroleum Research Center (PRC) that was obtained from Umm-Ar-Razam space located at north east of Libya.

The bentonite was crushed, then grounded and sieved. Then it was washed with distilled water for the removal of dust and other water soluble particles. The washed bentonite was dried in oven and was stored for further use as a natural Libyan bentonite (NLBn).

2.2.2. Preparation of Acid Activated Bentonite

To 100g of bentonite (NLBn). In 500 mL flask 5.0M HCl solution was added. The bentonite and with continuous stirring at room temperature for 24h. The resultant bentonite slurry was filtered, washed several times with distilled water up to pH = 6, then dried in oven at 105°C and stored for further use.

2.3. Adsorbents Characterization

The composition of bentonite for both natural and acid activated bentonite was determined using X-ray diffraction (XRD) (Model: PW 1800 of M/s Philips NV, Holland). By Transform infrared spectrometry (FT-IR). The spectra were recorded in the region of 4000-400 cm^{-1} for both natural and acid activated samples using (Thermo Scientific Nicolet iS10, Italy) to observe the functional groups. Scanning electron microscopy (SEM) analysis was carried out using (model JEOL-JSM-5610LV, Japan).

2.4. Batch Adsorption Studies

Adsorption of methylene blue (MB) onto NLBn and ALBn was conducted at different adsorption parameters. Like: different contact time, adsorbent dose, initial MB concentration, variation of pH and temperature. The residual MB concentrations of each solution were determined by measuring their absorbance characteristic using a single beam UV-Vis spectrophotometer type (HACH, DR/2400, Germany) at a wavelength of maximum absorbance (663

nm). The absorbance is then converted to concentration using the calibration curve. The batch sorption was performed on shaking water bath (HAAKE, 003-3678, Germany) at rotation speed 120rpm, to investigate the influence of NLBn and ALBn on sorption capacities of MB experiment on the mixture of 0.3g adsorbents and 30mL MB solution (initial conc. 50mg/L, pH = 9). The method was operated under shaking at 25°C till adsorption balanced was accomplished. The influence of pH on MB elimination was studied via adjusting 30mL MB solution (50mg/L MB) at different values of pH (1, 3, 5, 7, 9 and 11) using 0.1N HCl and 0.1N NaOH solutions for a period of one hour at 20 ± 2 °C.

The influence of temperature on MB elimination was done with 30mL MB (50mg/L, pH = 9) on 0.3g adsorbents up to balance was completed. The influence of contact time on MB elimination was executed in the 30mL MB solutions (50mg/L, pH = 9), by adding 0.3g adsorbent at 20 ± 2 °C for determined period of time. The influence of initial MB concentration elimination was also done using 30mL of several MB dye concentrations at (30 ml each) pH = 9; with 0.3g adsorbents at 20 ± 2 °C for 1h, contact time. Subsequently, the samples separation were done using center fugiation (speed 6500rpm; 10min)

The adsorption of residual concentrations were measured, and analyzed by UV spectrophotometer.

The quantities of MB adsorbed q_e in mg/g and removal percentage of MB adsorbed R% were calculated using the equations (1 and 2) [10]:

$$Q_e = (C_o - C_e) V / m \quad (1)$$

$$R\% = (C_o - C_e) / C_o \times 100 \quad (2)$$

Where; C_o and C_e are the MB concentrations in mg/L initially and at equilibrium, respectively, V is the volume of MB solutions in ml, and m is the weight of adsorbent in grams.

The scanning electron microscope, model IEO-1430VP Japan 200, was used to investigate particle morphology and particle size distribution of NLBn and ALBn specimens. The work was carried out at the laboratories of the Industrial Research Center (IRC), Tripoli, Libya.

2.5. Effect of Adsorption Parameters

The examination effect of adsorption experiments were conducted at 25, 35 and 45°C, respectively. The influence of the initial pH was studied at values: 1, 3, 5, 7 and 9 dye solution. The pH was adjusted using 0.1M NaOH and 0.1M HCl solutions and measured on pH meter (Jenway 3030, Italy). Adsorbent range dosages used in this study was from 5 to 25g/L.

3. Results and Discussion

3.1. Characterization of the Adsorbents

Bentonite available in Libya is considered one of the most promising natural materials that can be used for adsorption of some dyes found in waste water. The chemical composition of natural bentonite (Umm-Al- Razam) in % is given in Table 1, indicates the presence of silica, alumina, calcium oxide, iron oxide and magnesium oxide as major constituents. Traces of sodium, potassium and titanium oxides are found in the form of impurities [12].

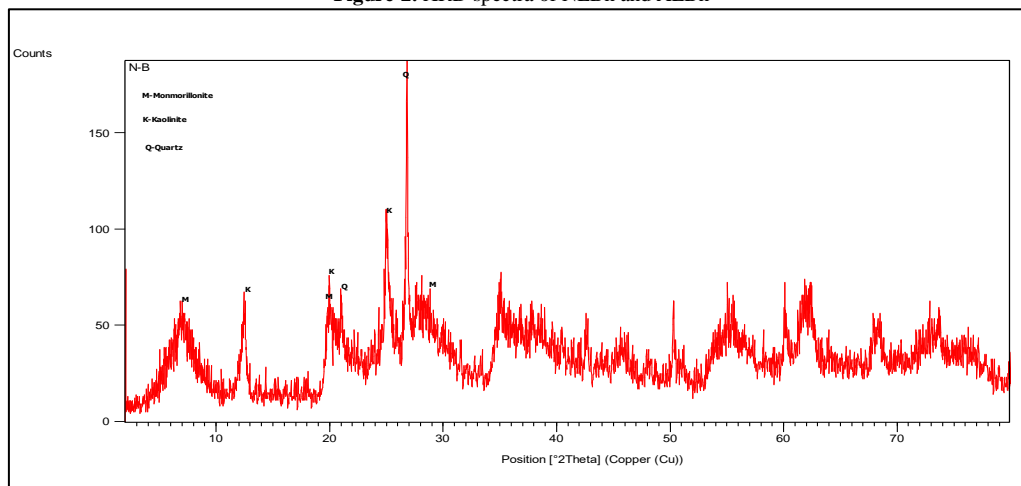
Table-1. Chemical composition of Umm-Ar- Razam bentonite ore

Component	Wt %
SiO ₂	44.4
Al ₂ O ₃	18.45
Fe ₂ O ₃	7.12
CaO	5.52
MgO	4.39
SO ₃	2.83
K ₂ O	1.36
TiO ₂	1.32
Na ₂ O	1.30
MnO	0.06
P ₂ O ₅	0.01

3.1.1. X-Ray Diffraction (XRD) Analysis of the Prepared Adsorbents

The ratio SiO₂/Al₂O₃ is 2.71 which indicate that the bentonite is of montmorillonite nature. This is also confirmed by the XRD analysis. The mineral phases identified along with montmorillonite were quartz and minor levels of feldspar, dolomite and calcite. The X-ray diffraction pattern of the clay and the acid activated are shown in Figure 2, found to be almost the same.

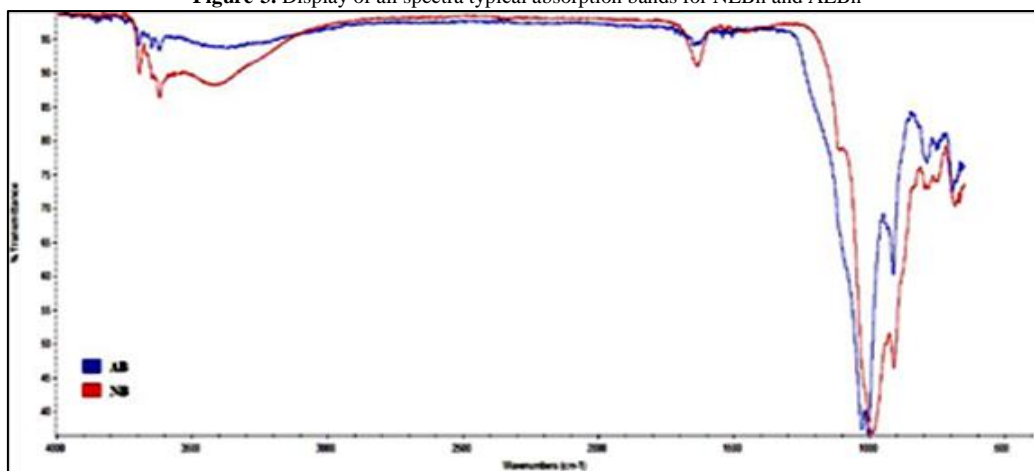
Bulk XRD analysis of Umm-Razam bentonite indicated that the prevailing presence of Ca-montmorillonite followed by kaolinite with minor quantities of impurities such as quartz and feldspar.

Figure-2. XRD spectra of NLBn and ALBn

3.1.2. FT-IR Spectra of the Prepared Adsorbents

Infrared Spectroscopy (FT-IR) was used to identify the chemical structure, functional group and obtain some bonding characteristics. The FT-IR test was carried out using Thermo Scientific Nicolet iS10 FT-IR Spectrometer. The bonding state of the NLBn and ALBn were analyzed by FT-IR absorption over a wave number range of 500 to 4000 cm^{-1} as shown within Figure 3, display of all spectra typical absorption bands. These bands is allotted [(CH₂)_n] cluster within the oftenest vary at (683.30 -759.67 cm^{-1}) of NLBn, however it absolutely was slightly shifted ranges at oftenest (694.55,787.33 cm^{-1}) for ALBn, (Al-O-Si) cluster either was a same settled by the activated treatment where it absolutely was funding within the wave vary regarding (910.59 - 992.21 cm^{-1}) of NLBn clays , however it absolutely was absorbed slightly shifted for ALBn clays where the band ascertained at oftenest (912.08 cm^{-1}).

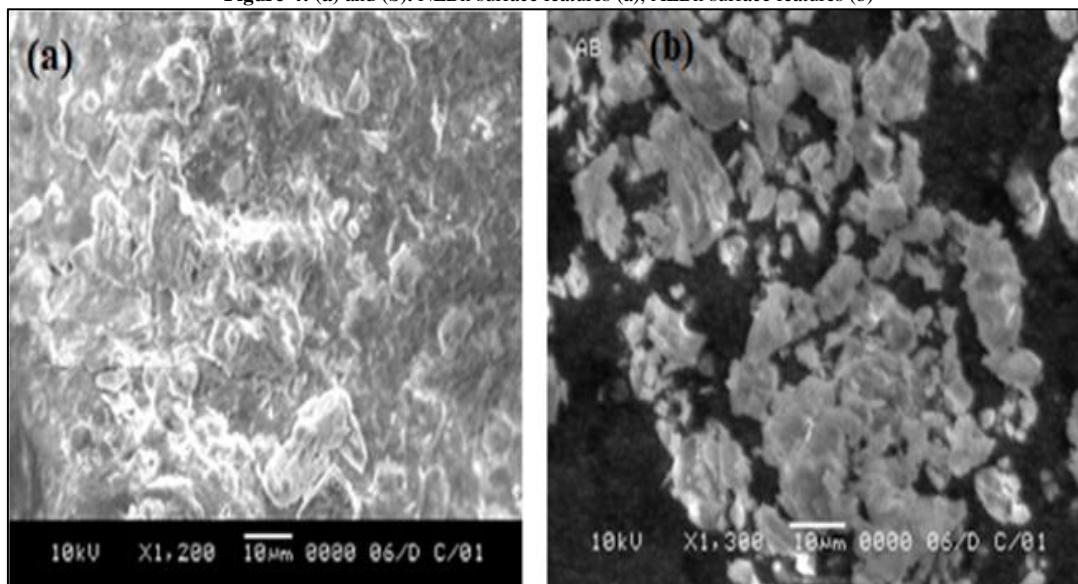
Since, there might attributed modification in nature of the chemical structure of NLBn (transformation of the tetrahedral sheet), wherever the coming into the Ca⁺² by activation method (i.e. the acid activation ends up in the formation of amorphous oxide, indicated by the inflated intensity of height, which can expose additional surface assimilation sites [13]. The stretching vibration band of (SiO₄,SiO₂) and (OH-AL-OH) teams were allotted at same wave vary (910.59 - 992.21 cm^{-1}) of each clays, stretching vibration band teams were allotted at same wave vary (3619.95-3694.24 cm^{-1}),(-OH) cluster ascertained at range (1635.38 cm^{-1}) for NLBn corresponds to the (-OH) deformation of water ,however it absolutely was attributed to dehydroxylation at wave vary (3619.95 cm^{-1}) for ALBn this is often believed to occur as a results of acid activation of clay [14, 15]. The band ascertained at (1006.36 cm^{-1}) is allotted (O-Si) and also the band ascertained (1028.86 cm^{-1}) is allotted (O-Si) for ALBn however it is not funding in NLBn since wasn't activated.

Figure-3. Display of all spectra typical absorption bands for NLBn and ALBn

3.1.3. Scanning Electron Microscope of the Adsorbents

SEM photographic images, Figures 4a and 4b), show distinction in surface options between the natural clay that is comparatively sleek and flat, and also the activated functionalizing of surface with planned methodology provides clear visual proof for the new area generated by robust treatment. The treated sample shows several new cavities and inferior exterior in all probability thinks to removal of some acid-soluble salts.

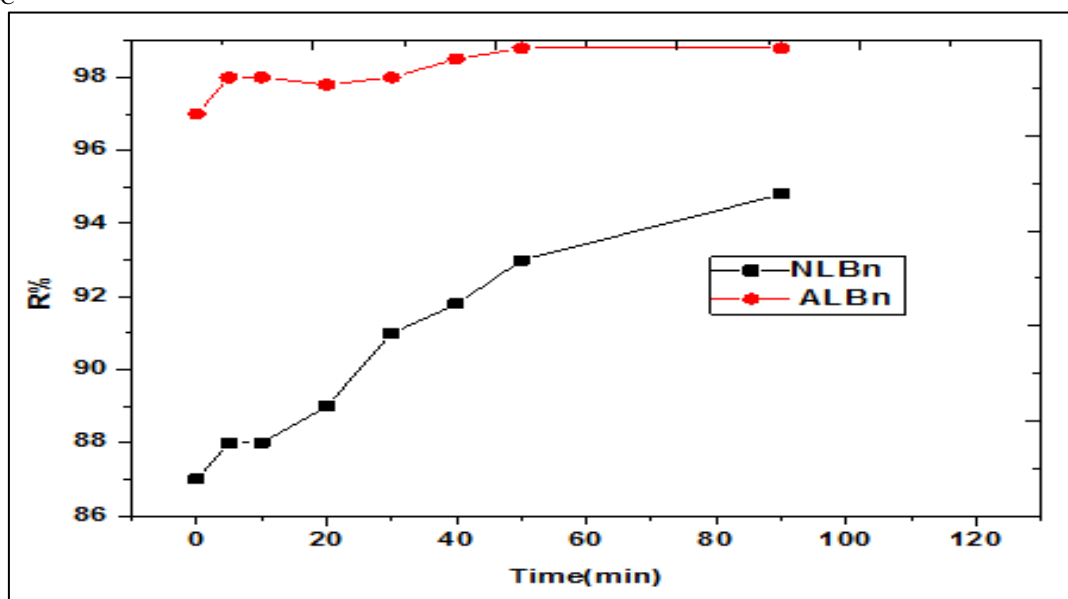
Figure-4: (a) and (b). NLBn surface features (a), ALBn surface features (b)



3.2. Effect of Contact Time

Study on the Equilibrium contact time effect for the adsorption of MB onto NLBn and ALBn adsorbents, was carried out at different time intervals ranging from 5 to 120min. The adsorption of MB onto NLBn and ALBn is shown in Figure 5, it shows that adsorption of MB onto NLBn and ALBn increases with increasing contact time up to 60 min and then becomes almost constant for each adsorbent. The maximum adsorption capacity of each NLBn and ALBn for MB was 93mg/g and 99mg/g respectively. From that it was concluded 60min is the equilibrium time for the removal of 50mg/L of MB using NLBn and ALBn as adsorbents. For further study 60min was selected as equilibrium time, it has been found that under identical conditions the ALBn presented higher adsorption capacity.

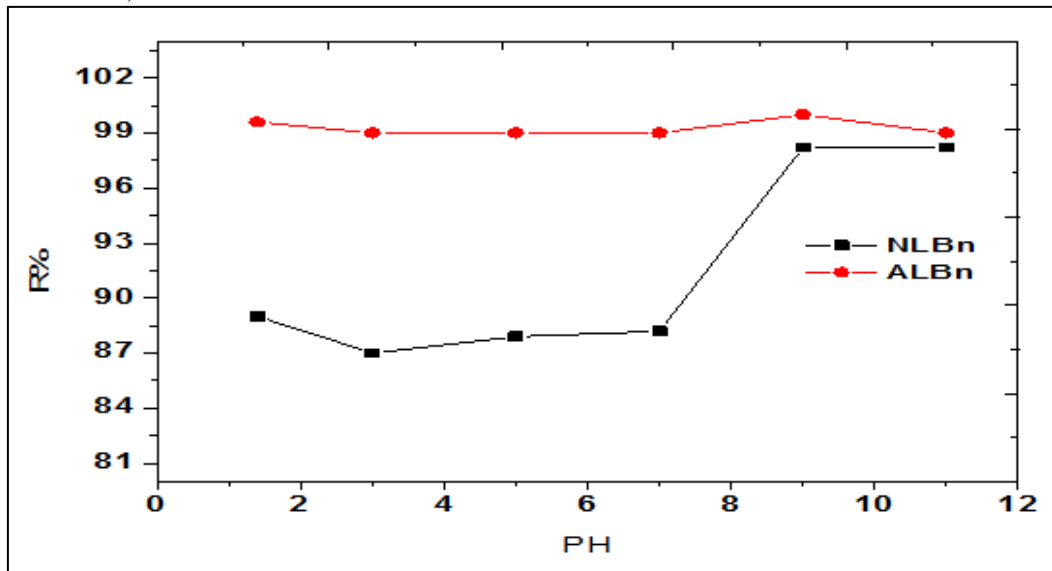
Figure-5. Effect of contact time on MB removal by NLBn (square) and ALBn (circle) at ($C_0 = 50\text{mg/L}$, dosage = 0.3g /30mL, pH = 9, and temp. = $20 \pm 2^\circ\text{C}$)



3.3. Effect of pH

The effect of pH on MB adsorption onto NLBn and ALBn, was studied through tests carried out on solutions of pH range from 1.0 to 9.0, as shown in Figure 6, the percentage of dye removal increased from 96 to 98.2% and from 99.6% to 100% for NLBn and ALBn respectively. It was observed at pH 11, the minor decrease in percent removals sorption on ALBn surface may be attributed of the repulsion between dye molecules and adsorbent where in acidic medium the positively charged surface of sorbent tends to oppose the adsorption of the cationic adsorbate [12].

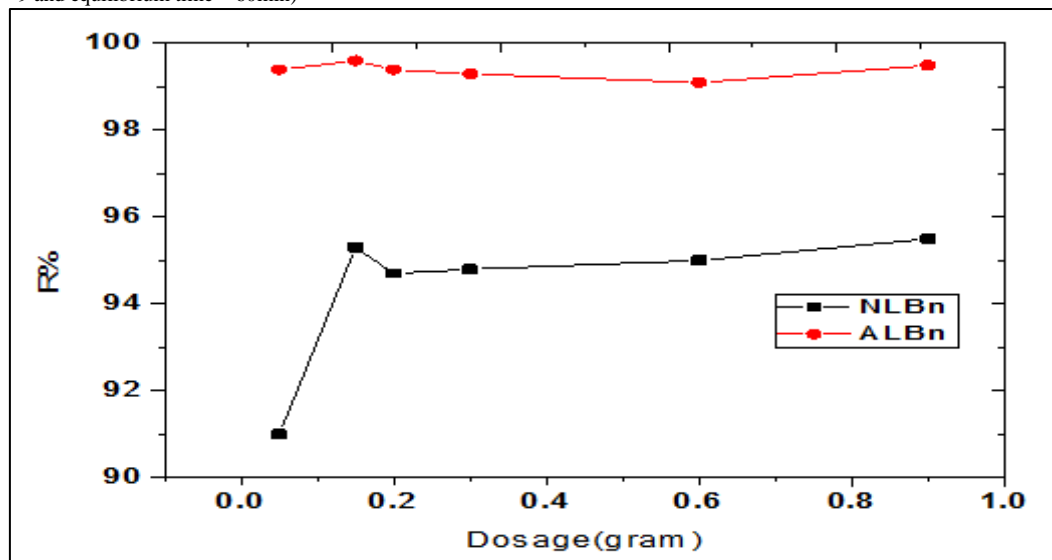
Figure-6. Effect of pH on MB removal by NLBn (square) and ALBn (circle) at ($C_0 = 50 \text{ mg/L}$, dosage = $0.3 \text{ g}/30 \text{ mL}$, temp. = $20 \pm 2^\circ \text{C}$ and equilibrium time = 60min)



3.4. Effect of Adsorbent Dosage

The studied adsorbent dosages were on 0.05, 0.15, 0.30, 0.60 and 0.90 g/L Shown in Figure 7. It was noticed that NLBn dosage gradually increase the percentage dye removal of MB from 91 to 96.5%. It was also noted that increasing the dosage of ALBn from 0.05 to 0.90 g/L. However, when the dosage of ALBn increased from 0.05 to 0.90 g/L the percent dye removal of MB was increased from 99.4 to 99.6%.

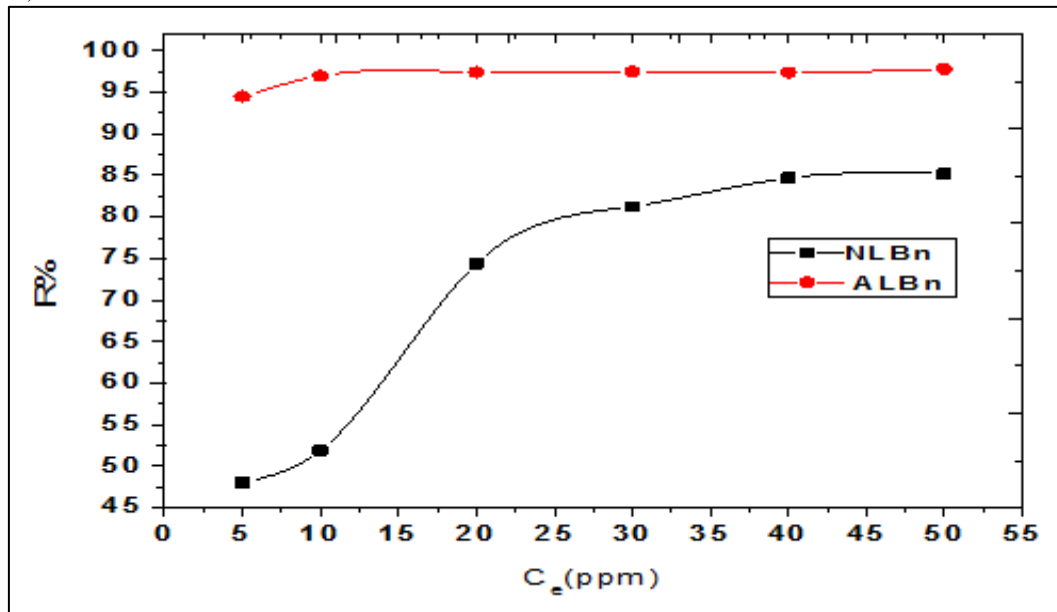
Figure-7. Effect of adsorbent dosage NLBn (square) and ALBn (circle) on MB removal % at ($C_0 = 50 \text{ mg/L}$, dosage = $0.3 \text{ g}/30 \text{ mL}$, temp. $20 \pm 2.0^\circ \text{C}$, pH = 9 and equilibrium time = 60min)



3.5. Effect of Initial Dye Concentration

The effect of initial MB concentration on the adsorption capacity of NLBn and ALBn toward MB, is shown in Figure 8, where (R %) increasing with increasing the MB concentration from 5 to 50 mg/L. The results also indicated that the amount of retained dye increased with the increase of initial dye concentration. Although the rate behavior of both NLBn and ALBn was similar, but it has been found that under identical conditions the ALBn presented higher adsorption capacity.

Figure-8. Effect initial concentration on MB removal of NLBn and ALBn at (pH = 9, dosage = 0.3g/30mL, temp. = 20 ± 2oC and equilibrium time = 60min)



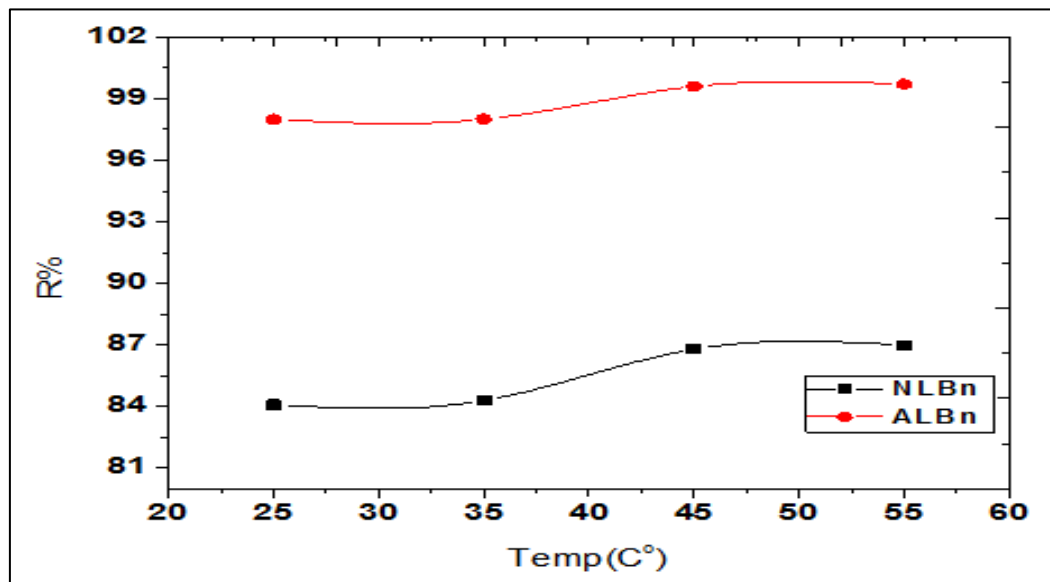
3.6. Effect of Temperature

The effect of temperature on the removal percent of MB onto both NLBn and ALBn was investigated on a concentration of 50 mg/L at 25, 35, 45 and 55°C.

From that it was clearly observed the removal percent at equilibrium increases with increasing temperature. At the temperature increasing from 25oC to 55oC, indicates the maximum removal of MB by NLBn and ALBn was found to be increased from 84 to 86 and from 98 to 99.5, respectively. As shown in Figure 9, it was also observed generally, that the removal percent of MB increases as the temperature increased.

The increase in adsorption with an increase in temperature may be due to the widening of pores of the adsorbent and some active site formation on the surface of adsorbent due to bond cleavage at higher temperature. Moreover the diffusion rate in the pore of adsorbent also increases with an increase in temperature [16].

Figure-9. Effect of the Temperature on MB removal of NLBn and ALBn at (Co = 50mg/L, dosage = 0.3g/30mL, pH = 9 and equilibrium time 60 min.)



3.7. Adsorption Kinetics

The fee regular of adsorption is unique from the first-order fee expression given through Lagergren [14] can be expressed as equation (3):

$$\ln [(q_e - q_t)] = \ln q_e - (k_1 t) / (2.303) \quad (3)$$

Where; q_e and q_t (mg/g) are the amount of MB adsorbed at equilibrium and at time t , respectively, and k_1 is the equilibrium constant (min⁻¹), which is obtained from the slope of the line plot against $\ln (q_e - q_t)$.

The pseudo-second-order model is based on the adsorbent chemisorption assumption. This model [13] can be expressed as equation (4).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where; k_2 (g/mg.min) is the equilibrium rate constant for second-order adsorption and q_e can be obtained from a plot of t/q_t versus t as in Figure 10. The comparison of the correlation coefficients and results for the first-order and second-order kinetic models is shown in the table. For NLBn and ALBn, the pseudo-second-order model is the best model for experimental kinetic data.

Consistent very well with the experimental data, R_2 is greater than 1 for all adsorbents shown Table 2. These results also showed the applicability of this equation of motion and the characterization of the secondary process of MB adsorption on clay.

Figure-10. Pseudo-second order adsorption of MB adsorbed on NLBn and ALBn for 50 ppm at $20 \pm 2^\circ\text{C}$, pH = 9 and dosage = 1.0 g L⁻¹.

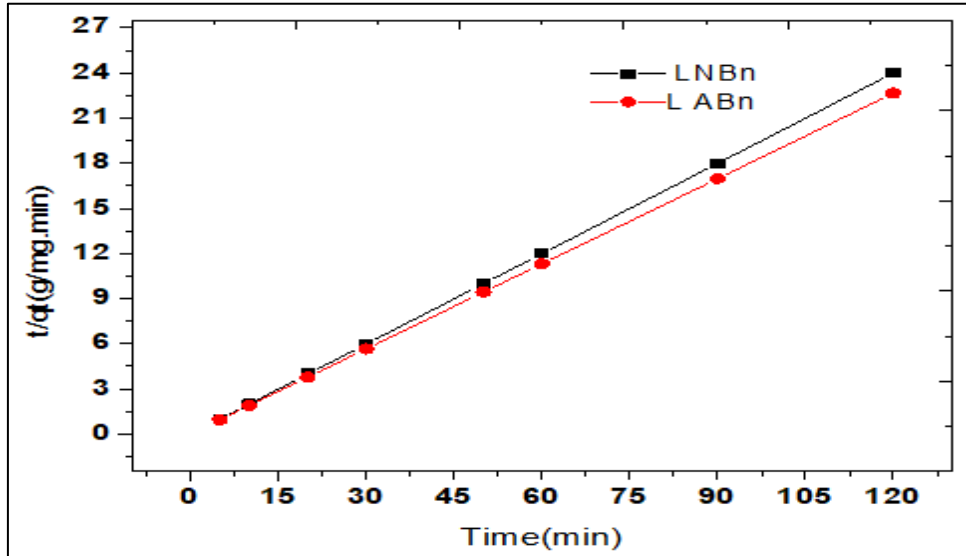


Table-2. Kinetic parameter for the adsorption of MB onto NLBn and ALBn clays

Pseudo first - order kinetic model			
Sample	$q_e(\text{ppm})$	$k_1(\text{min}^{-1})$	R_1^2
NLBn	5.0	0.7288	0.70
ALBn	5.3	0.227	0.30
Pseudo second - order kinetic model			
Sample	$q_e(\text{ppm})$	$k_2(\text{min}^{-1})$	R_2^2
NLBn	5.0	7.81×10^{-3}	1
ALBn	5.3	2.604×10^{-2}	1

3.8. Adsorption Isotherms

In the present work Langmuir, Freundlich and Kaptain adsorption isotherms were used in order to interpret the isotherm data of the adsorption of MB onto NLBn and ALBn. Equilibrium adsorption isotherms were described using Langmuir, Freundlich and kimbtain isotherm equations (5-7) [14], respectively:

$$\frac{C_e}{q_e} = \frac{1}{(b q_m)} + \frac{C_e}{q_m} \quad (5)$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (6)$$

$$q_e = k_T \ln C_e + B_T \quad (7)$$

Where; q_e and q_{max} are the equilibrium and maximum uptake capacities (mg/g), respectively, b is related to free energy of adsorption and represents the Langmuir adsorption constant, C_e is the MB concentration in solution (mg/L) at equilibrium, K_f is the Freundlich constant related to adsorption capacity (mg/g) while $1/n$ represents the adsorption intensity, B_T and K_T are Temkin isotherm parameters; B_T (kJ/mol) is related to the heat of adsorption. The optimal parameters from the fitting of Langmuir, Freundlich and kimbtain isotherm equations with experimental data are summarized in table 3 and are shown in Figures 11, 12 and 13.

Figure-11. Langmuir adsorption isotherm for MB on NLBn and ALBn at ($C_0 = 50\text{ppm}$, $\text{pH} = 9$, $\text{temp.} = 20 \pm 2\text{oC}$ and dosage = 10g/L)

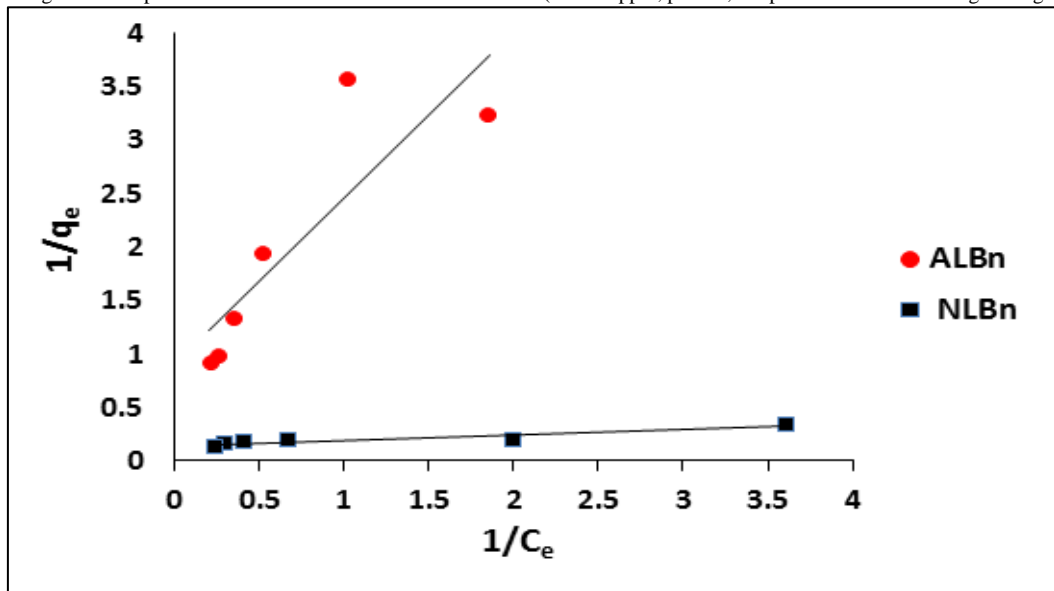


Figure-12. Freundlich adsorption and ALBn at isotherm for MB on NLBn ($C_0 = 50\text{g/L}$, $\text{pH} = 9$, $\text{temp.} = 20 \pm 2\text{oC}$ and dosage = 10g/L)

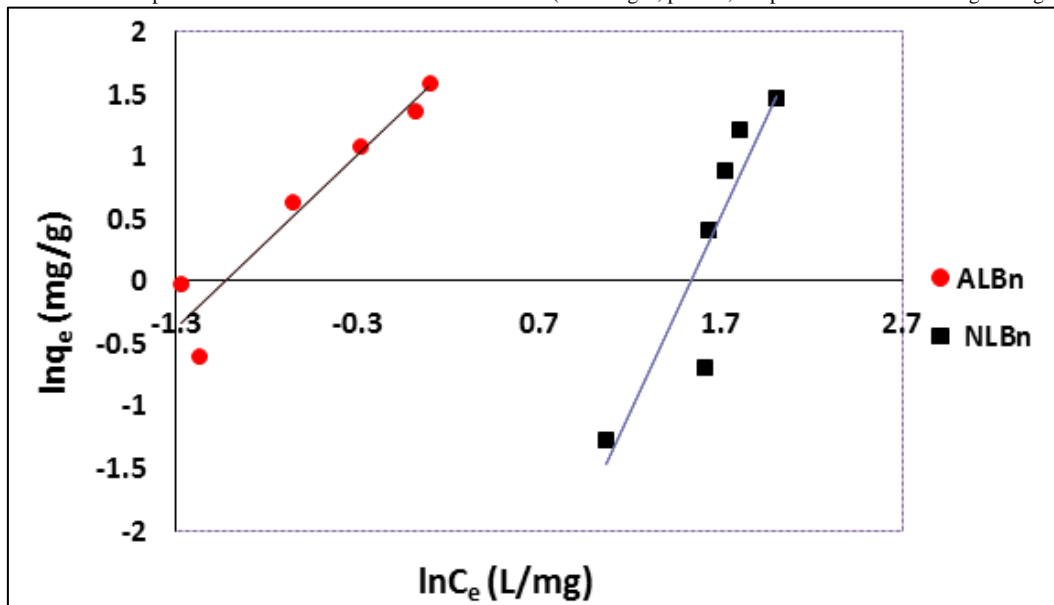


Figure-13. Kimbtain adsorption isotherm for MB on NLBn and ALBn at ($C_0 = 50 \text{ g/L}$, $\text{pH} = 9$, $\text{temp.} = 20 \pm 2\text{oC}$ and dosage = 10g/L)

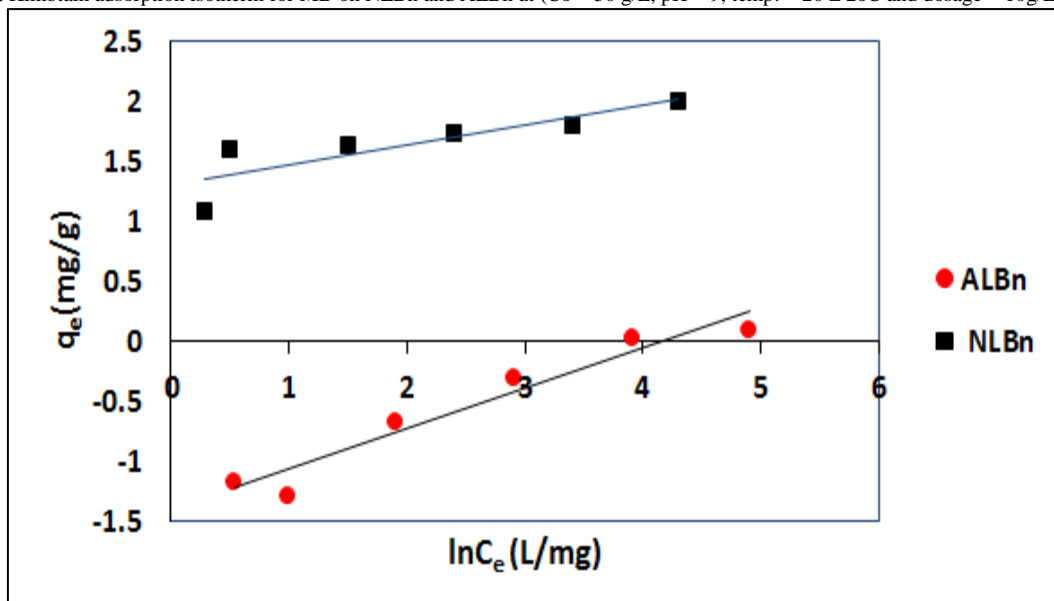


Table-3. Langmuir, Freundlich, and Temkin parameters

Model	Parameter	NLBn	ALBn
Langmuir	q_{\max} (mg/g)	4.3	4.9
	K_L (L/mg)	- 0.134	-1.895
	R^2	0.85	0.68
Freundlich	K_F (mg/g)	0.079	4.180
	n	0.317	0.722
	R^2	0.78	0.89
Temkin	K_T (mg/g)	4.316	2.793
	B_T	-5.019	4.055
	R^2	0.65	0.93

It is clear that Langmuir model gave better represented for adsorptions data for NLBn and Temkin model gave better re represented for adsorptions data of ALBn. The evidence was confirmed by better coefficient value (R^2) of models than etch other.

3.9. Thermodynamic Studies

The temperature effect on the adsorption of MB onto NLBn and ALBn was explained further by thermodynamic parameters. Thermodynamic parameters i.e. change in free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) were investigated by the following equations (8-10):

$$\ln K_D = - RT \ln K_D \quad (8)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

$$\ln K_D = qe/Ce \quad (10)$$

Where; K_D is the distribution coefficient, R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature in kelvin. The value of ΔH° and ΔS° was calculated from the slopes and intercepts of linear plot of $\ln K_D$ versus $1/T$ while the value of ΔH° was calculated through equation (8). The value of ΔG° , ΔH° and ΔS° is given in Table 4.

The value of ΔG° is negative which indicates that the adsorption was spontaneous. The value of ΔS° is positive which suggests that the MB molecule was adsorbed randomly on the surface of adsorbent; while the positive value of ΔH° confirms that the adsorption process was endothermic.

Table-4. Thermodynamic parameter for adsorption of MB onto NLBn and ALBn

ΔH° (J / mol)	ΔS° (J / mol K)	ΔG° (KJ / mol)			
		25 °C	35°C	45°C	55°C
MB on NLBn					
0.72996	28.30	- 8.433	- 8.716	- 8.999	- 9.282
MB on ALBn					
0.8654	30.85	- 9.195	- 9.503	- 9.812	- 10.121

4. Conclusion

This study concern with investigation on the equilibrium adsorption of methylene blue on to natural and activated of Umm-Al-Razam bentonite. The percentage of MB dye removal was found to 96% for NLBn and 99.5% for ALBn. The experimental isotherm data was found to have the best fit Langmuir model where gave better representing adsorptions data for NLBn and Temkin model gave better represented for ALBn. The removal of MB is a rapid process and the adsorption process obeys the pseudo-second order model, indicating cation dye has a very strong affinity on the NLBn and ALBn surface. Adsorption of dye increases with increasing pH using NLBn and there was no effect of solution pH on removal percentage of MB dye by ALBn; this may be attributed to the surface charge of the NLBn and Bentonite is positively charged at low pH values and negatively charged. Rate of adsorbed MB onto ALBn was relatively constant. On the other hand, Rate of adsorbed MB on NLBn was initially high and then slowed down gradually until PH of about 7 where it increased rapidly and equilibrium was attained.

5. Acknowledgment

The authors wish to thank the Institute of Libyan Petroleum (ILP) for supplying bentonite samples. Also, the authors would gratitude to Engineers Wedad Alakrash for their help in conducting some experiments FT-IR, XRD Engineers Nasren Azeez A. Masoud, Mohamed A. Omar, SEM Amar Atakaly, Dr. Shaban Wains Al-Rmalli which founded the idea of work before he died and Prof. Dr S. K. Shahooki for his help, Department of Chemistry, Faculty of Science, Tripoli University, and Tripoli, Libya.

References

- [1] Hmeid, H. A., Akodad, M., Baghourm., Moumen, A., Skalli, A., G., Azizi, G., Anjjar, Laoulm, A., and Daoudi, L. L., 2021. "Adsorption of a basic dye, Methylene Blue, in aqueous solution on bentonite." *Mor. J. Chem.*, vol. 9, pp. 416-433.
- [2] Ong, S., Keng, P., Lee, W., Lee, Ha, S., and Hung, Y., 2011. "Dye waste treatment." *Water (Switzerland)*, vol. 3, p. 157.
- [3] Gupta, V. and Suhas, D., 2009. "Application of low-cost adsorbents for dye removal - A review." *J. Environ Manage*, vol. 90, p. 2313.
- [4] Ghosh, D. and Bhattacharyya, K., 2002. "Adsorption of methylene blue on kaolinite." *Appl. Clay Sci.*, vol. 20, p. 295.
- [5] Baskaralingam, P., Pulikesi, M., Elango, D., Ramamurthi, V., and Sivanesan, S., 2006. "Adsorption of acid dye onto organobentonite." *J. Hazard. Mater*, vol. 128, p. 138.
- [6] Hu, Q., Qiao, S., Haghseresht, F., Wilson, M., and Lu, G., 2006. "Adsorption study for removal of basic red dye using bentonite." *Ind. Eng. Chem. Res.*, vol. 45, p. 733.
- [7] Wang, C., Juang, L., Hsu, T., Lee, C., Lee, J., and Huang, F., 2004. "Adsorption of basic dyes onto montmorillonite." *J. Colloid Interface Sci.*, vol. 273, p. 80.
- [8] Crini, G., 2006. "Non-conventional low-cost adsorbents for dye removal: a review." *Bioresour. Technol.*, vol. 97, p. 1061.
- [9] Özcan, A., Erdem, B., and Özcan, A., 2004. "Adsorption of Acid Blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite." *J. Colloid Interface Sci.*, vol. 280, p. 44.
- [10] Al-Khatib, L., Fraige, F., Al-Hwaiti, M., and Al-Khashman, O., 2006. "Adsorption from aqueous solution onto natural and acid activated bentonite." *Am. J. Environ. Sci.*, vol. 8, p. 510.
- [11] Ma, J., Cui, B., Dai, J., and Li, D. D., 2011. "Mechanism of adsorption of anionic dye from aqueous solutions onto organobentonite." *J. Hazard. Mater*, vol. 186, p. 1758.
- [12] Srivastava, V., Swamy, M., Mall, I., Prasad, B., and Mishra, I. I., 2006. "Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics. Colloids surfaces a physicochem." *Eng. Asp.*, vol. 272, p. 89.
- [13] Al-Wahbi, A., 2011. "Removal of methylene blue from aqueous solutions using Yemen bentonite." *Diyala J. Eng. Sci.*, vol. 4, p. 30.
- [14] Khan, M., 2020. "Adsorption of methylene blue onto natural Saudi Red Clay: Isotherms, kinetics and thermodynamic studies." *Materials Research Express*, vol. 7, pp. 1-13.
- [15] Hong, S., Wen, C., He, J., Gan, F., and Ho, Y. Y., 2009. "Adsorption thermodynamics of Methylene Blue onto bentonite." *J. Hazard. Mater*, vol. 167, p. 630.
- [16] Eren, E. E. and Afsin, B., 2008. "Investigation of basic dye adsorption from aqueous solution onto raw and pre-treated bentonite surface." *Dyes Pigments*, vol. 76, p. 220.