ISSN: 2754-4915

Journal of Material Sciences & Manufacturing Research

SCIENTIFIC Research and Community

Research Article

Open Access

Organophilicized Bentonite for Adsorptive Removal of Methylene Blue (MB) Dye in Aqueous Medium: Thermodynamics, Kinetics and Equilibrium Studies

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ABSTRACT

HDTMA and TMPA cations intercalated bentonite clay has been assessed for the effective removal of methylene blue dye (MB) in aqueous solution. The adsorbents has been characterized by Fourier transformed infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and x-ray diffraction (XRD). Various sorption parameters like effect of initial MB concentration, contact time and pH were used to investigate the sorption process. Langmuir and Freundlich isotherms as well as Pseudo First order, Pseudo Second order and intraparticle diffusion kinetic models were applied to investigate the sorption mechanisms. Results from the adsorption experiment confirmed 180 minutes as equilibrium time for maximum sorption of MB by both organoclays. Increase in initial MB concentration resulted to a corresponding increase in the adsorption capacities of both organoclays. Adsorption of MB by the organoclays were highly influenced by pH, as maximum sorption of MB was achieved at pH of 7. Among the isotherm and kinetic models exploited, the Langmuir isotherm and Pseudo second order kinetic model gave best fit to the experimental data respectively. Results from thermodynamic studies showed that the process of adsorption of MB onto the organoclays were feasible, spontaneous and exothermic; and successful reapplication of regenerated spent organoclays (Bt-HDTMA and Bt-TMPA) yielded MB dye removal percentage of 89.6 and 85.3% respectively at 60 minutes contact time. Therefore, the results obtained from the entire study confirms the efficacy of HDTMA and TMPA intercalated bentonite clay for effective removal of cationic dyes in aqueous solution at optimal experimental conditions.

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Received: March 21, 2022; **Accepted:** March 28, 2022; **Published:** March 31, 2022

Keywords: HDTMA, TMPA, Organoclay, Methylene Blue (MB), Adsorption, Thermodynamics, Kinetics, Isotherm

Introduction

Pigments and Dye finds wide application in numerous industries today. Extensive use of dyes generates colored wastewater, leading to environmental pollution, with a loss of 10–15% of these dyes to waste streams [1]. Most dyes and pigments are toxic and difficult to biodegrade when discharged into waste streams and their presence in water affects its transparency [2, 3]. The removal of color from textile effluents is a major issue because the dyes cause remarkable environmental pollution and have toxic and carcinogenic effects on living organisms [4]. In addition, the presence of very low concentrations of colored effluents is highly visible and potentially inhibiting to photosynthesis. As a result, textile wastewater treatment has become an important problem [4-8].

Methylene blue on contact with skin may cause discoloration, feeling of cold, redness or dryness (due to chronic exposure). Ingestion of this dye may cause gastrointestinal irritation, discoloration of oral mucosa, irritation of lips, mouth and throat, paleness of complexion, lack of coordination or drowsiness. Crystal violet dye belongs to triphenyl carbocation group widely used for the dying of wool, silk, cotton, nylon. Paper, leather, etc. It also used in biological staining, as a dermatological agent, in veterinary medicine. It is the brightest class of basic dye having high tinctorial value. Crystal violet can affect human bladder and may result to cancer in the digestive system of other animals. Higher concentration ingestion causes nausea, vomiting and central nervous system depression. Discharge of Rhodamine B into the hydrosphere can cause environmental degradation. In California, Rhodamine B is suspected to be carcinogenic and thus products containing it must contain a warning on its label [9-11].

Currently, various physical, as well as, chemical and biological techniques, such as adsorption, precipitation, coagulation-flocculation, biodegradation, membrane processes, ion exchange, solvent extraction, and chemical oxidation, have been used for the removal of dyes from wastewater [12-18]. Further, several

studies dealing on the dye removal from industrial effluents, have focused on the use of the adsorption technique. In fact, this method is widely used due to its simple design, ease of operation, affordability and low operating cost, reusability of the adsorbent, selectivity, and efficiency. It should be noted that for efficient dye removal from water, the used adsorbents should have good mechanical stability, large surface areas, and must be recyclable. Several adsorbents have been studied for the removal of dyes such as wheat shell, sawdust, peanut hull, metal oxides, layered double hydroxides, fly ash, Rectorite and alumina. Other adsorbent, such as activated carbon is widely used for dyes removal from water, due to its higher surface area and/or its excellent adsorption capacity. However, many drawbacks limit the activated carbon uses, such as its high cost, and the difficulty of its regeneration. The Bentonite clay mineral has attracted the attention of researchers owing to its high surface area, its high cation exchange capacity and its swelling properties [19-27].

It is well known that the negative charge of clays is balanced by exchangeable cations, which are usually Na^+ and Ca^{2+}. Due to this negative charge, clays have little or no affinity for anionic species such as that of acid dyes. To improve their adsorption ability and capacity, the replacement of the natural inorganic cations with surfactant cations such as quaternary ammonium compounds (QAC) was frequently observed and the obtained surfactant-modified clays were then used to adsorb the neutral and anionic organic compounds [28-30]. On these applications, it is found that when larger organic cations (such as HDTMA (hexadecyl-trimethyl-ammonium) ions) are used, the hydrophobic tails interact with each other, producing an organic phase which act as a partition medium into which non-ionic organic molecules partition from water [30]. In addition to the adsorption of nonionic organic compounds, QAC-clay complexes have been shown to have the ability to removal inorganic anions from aqueous solution with an adsorption mechanism that appears to be replacement of counter ion of the surfactant by anionic species, i.e., an ion exchange mechanism was operative [30,31].

Therefore, current study investigates the adsorption potential of hexadecyltrimethyl ammonium (HDTMA) and trimethylphenyl ammonium (TMPA) cations intercalated bentonite for uptake of methylene blue dye in aqueous solution. Adsorption experimental conditions such as effect of contact time, initial dye concentration and pH were used to study the sorption process. Adsorption kinetics and isotherms were applied to investigate the mechanism of sorption, and thermodynamics of the adsorption process was also duly studied.

Experimental

Materials

The bentonite clay (CEC = 30.94 meq/100 g) used in this study was procured from Mansid Chem. Nigeria Ltd, Port Harcourt, Rivers State Nigeria and was beneficiated according to our previous research [32]. The Quaternary alkyl ammonium compounds (Surfactants): hexadecyltrimethyl ammonium bromide (HDTMA-Br, C19H42BrN and MW. 364.45) and trimethylphenyl ammonium chloride (TMPA-Cl, C9H14ClN, MW. 171.5) were procured from Sigma Aldrich Switzerland. The methylene Blue dye (C16H18ClN3S purity =98%) was purchased from Aladdin Co. Ltd and was used without any further purification. All other chemicals used were products of BDH Chemicals, England and all the solutions used were prepared in double distilled water. The chemical structures of the Alkyl ammonium surfactants used as organic modifiers and that of the Methylene blue is shown in Fig 1.

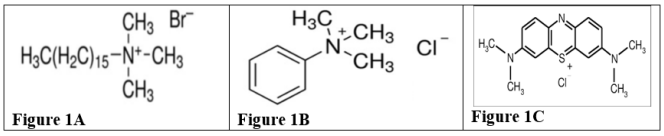


Figure 1: Chemical Structures of the Alkyl Ammonium Surfactants used in Bentonite Modification: HDTMA-Bromide (A), TMPA-Chloride (B); Chemical Structure of Methylene Blue Dye (C).

Synthesis and Characterization of HDTMA and TMPA Organoclays

Synthesis of bentonite organoclays by HDTMA and TMPA cationic intercalations has been described in detail in a previously published paper, and was characterized for specific surface area by Sear's method, cation exchange capacity (CEC) by ammonium acetate procedure , IR spectra properties by FTIR spectrophotometer (Buck scientific M530 USA FTIR), basal spacing by X-ray diffraction (Bruker, D8ADVANCE, Germany) using Ni-filtered Cu K$\alpha\alpha$ radiation (1.5406 Å), and morphology by scanning electron microscope (Seron, AIS-2100, Republic of Korea). The values obtained for CEC and specific surface area; Characteristics and physical properties of the unmodified bentonite (Bt) and the organo-modified bentonite (Bt-HDTMA and Bt-TMPA) were described by our previous work [32-34].

Batch Adsorption Experiment

The functions of initial dye concentration (25-300 mg L^{-1}), temperature (30-40 °C), pH (2-11) and contact time (5-180 minutes) on the dye adsorption were investigated. These studies were carried out in 100 mL conical flasks containing 50 mL of the adsorption solution with desired dye concentration and adsorbent value. These flasks were stirred on the orbital shaker (Nüve, ST 402) at different temperatures for various time periods. During adsorption studies, the supernatants of the solutions were separated by centrifugation from the organoclay by using a centrifuge (Nüve, NF 400). Before absorbance measurement, the clay was filtered from the dye liquor to assure that small clay particles did not interfere with the absorbance measurement. The residual dye concentration in the supernatant liquid was quantified by UV-vis spectrophotometer (model Jasco model V-530) at 662 nm. Each data point was the mean of three independent adsorption studies.

The data were used to calculate the adsorption capacity (mg/g),q_e, of the adsorbent. Finally, the adsorption capacity was plotted against the equilibrium concentration (mg/l), Ce. The dye concentration on the adsorbent surface at equilibrium was calculated by

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (1)$$

Where C_0, initial dye concentration in liquid phase (mg/l); V, total volume of dye solution used (L); m, mass of adsorbent used (g). Kinetic studies were also carried out by shaking the dispersions, which contained Methylene blue (MB) dye at 100 mgL^{-1} initial concentration, over a time interval of 5-180 minutes for 0.125 g organoclay adsorbent at room temperature of 28±2°C.

Thermodynamic Studies

To understand the adsorption behavior of Bt-HDTMA and Bt-TMPA at different temperatures, 0.125 g of Bt-HDTMA and Bt-TMPA were separately added to 100 mg L^{-1} of 50 mL MB dye solution. The contents were shaken for 180 min on orbital

shaker at different temperatures (298, 308 and 318K). The obtained solutions were then filtered and supernatant analyzed with UV–Vis spectrophotometer. Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were evaluated to determine the nature of the adsorption process.

Regeneration of MB Saturated Organoclays

The method of Noumoradi et al. was applied in the regeneration experiment [35]. This was performed by heating. For this, the organoclays were separately subjected to the adsorption as follows. Initially 0.5 g of the adsorbent was equilibrated in 50 mL of 100 mg/L MB at the optimum contact time and pH at 25°C. After mixing, the supernatant was centrifuged and analysed. The saturated clay was then separated and dried at room temperature for 48 h. The MB that saturated the organoclays were then placed in oven at 150°C for 10, 30, 50 and 60 minutes. The adsorption experiments were then conducted using the regenerated adsorbents.

Results and Discussions

Adsorption Kinetics

The characterized adsorbents (Bt-HDTMA and Bt-TMPA) were used to measure their individual adsorption capacities for the removal of methylene blue (MB) from aqueous solutions. The effect of contact times of 5-180 minutes on the adsorption of MB (Fig. 2) shows that the adsorbents had similar adsorption behavior for methylene blue (MB), with all adsorption processes controlled by two stages. In the first 50 minutes of the sorption process, a rapid adsorption of methylene blue (MB) onto the organoclays was observed (26.78 and 21.75 mg/g for Bt-HDTMA and Bt-TMPA respectively), occasioned by the presence of active vacant sites on the surface of the organoclays, followed by slower adsorption rate, until equilibrium was achieved at 180 minutes [36].

To further investigate the kinetics of the sorption process, the experimental data for the adsorption of methylene blue (MB) by the organoclays were modeled into three major kinetic models, namely: pseudo first order (Fig. 3), pseudo second order (Fig. 4) and intra-particle diffusion model (Fig. 5) according to equation (2) - (4) respectively:

$$log(q_e - q_t) = log\, q_e - \left(\frac{k_1}{2.303}\right)t \quad (2)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

$$q_t = k_{id}t^{1/2} + C \quad (4)$$

where qe (mg/g) is the amount of methylene blue (MB) adsorbed at equilibrium, qt amount of methylene blue (MB) adsorbed at any given time t (mg/g), k is the rate constant for the pseudo-first-order model, k_2 (g/mg·h) is the rate constant of pseudo-second order, k_{id} (g/mg·h) is the rate of the intraparticle diffusion kinetic model and C is the intraparticle diffusion constant. The obtained values for these kinetic models are summarized in Table 1. Judging from the values of their correlation coefficient (R^2), the pseudo second order kinetic model displayed highest R^2 values of 0.998 and 0.999 (Figures 3-5) for Bt-HDTMA and Bt-TMPA respectively, compared to other kinetic models suggesting that pseudo second order kinetic model gave best fit to the experimental data.

Table 1. Parameters for the Pseudo first order, Pseudo second order and Intraparticle diffusion kinetic models for the adsorption of MB by Bt-HDTMA and Bt-TMPA

	Pseudo first Order			Pseudo second Order				Intra-particle diffusion		
Adsorbents	k_1 (min^{-1})	q_e(mg/g)	R^2	k_2(g/mg.h)	$q_{e\,cal}$(mg/g)	$q_{e\,exp}$(mg/g)	R^2	K_{id}	C	R^2
Bt-HDTMA	0.029	94.51	0.602	0.065	27.77	27.34	0.998	1.384	12.32	0.684
Bt-TMPA	0.03	68.12	0.118	0.031	21.98	21.62	0.999	0.71	14.06	0.581

Furthermore, the values of qe calculated for Bt-HDTMA and Bt-TMPA evaluated as 27.77 mg/g and 21.98 mg/g respectively were similar to that of qe experimental founds as 27.34 mg/g and 21.62 mg/g for Bt-HDTMA and Bt-TMPA respectively, compared to other kinetic models whose qe values were found to vary widely from the experimental qe values, confirming pseudo second order model as best fit to experimental data. In addition, it can be seen that the pseudo second order rate constant (k_2) of methylene blue (MB) adsorption unto Bt-HDTMA and Bt-TMPA was found as 0.065 g/mg.h and 0.031 g/mg.h respectively; k_2 value of methylene blue (MB) adsorption on Bt-TMPA ions was observed to be about two times that of Bt-HDTMA, consequence of size variations of the organic cations. In other words, organoclays intercalated with smaller organic cations (TMPA+) tend to attain equilibrium concentration faster than those intercalated with larger organic cations (HDTMA+) [37, 38]. However, this accounts for the wide differences observed in k_2 values between Bt-HDTMA and Bt-TMPA for the adsorption of methylene blue (MB). In comparison to other adsorbents, HDTMA and TMPA cationic modified bentonite are more efficient adsorbents for adsorption of methylene blue (MB) in aqueous solution.

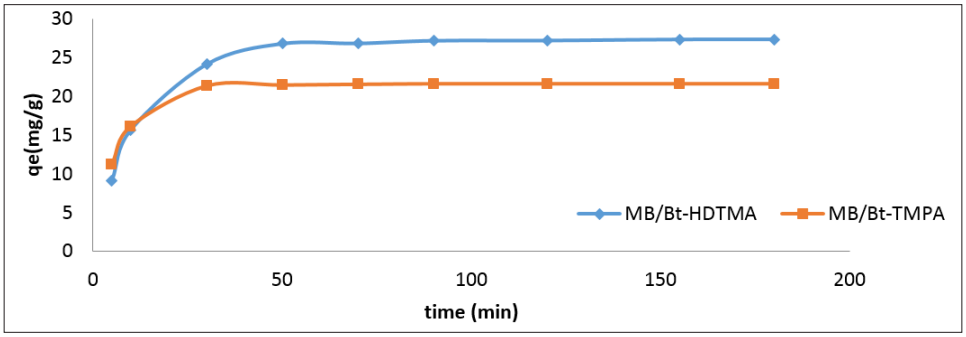


Figure 2: Effect of Contact Time on Adsorption of MB by the Organoclays (pH=7, Mass of Organoclay= 0.125 g, Temperature =28°C, MB conc =100 mg/L)

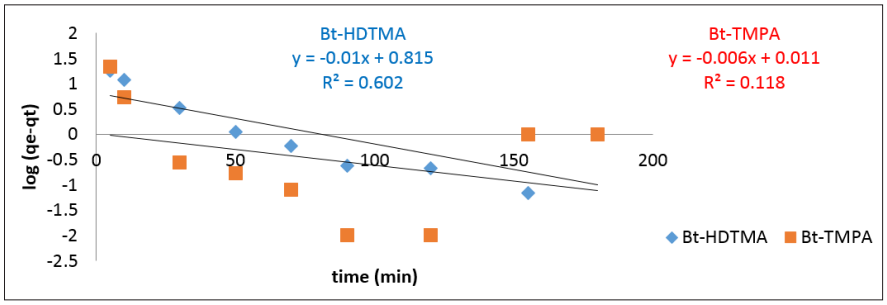


Figure 3: Pseudo First Order Kinetic Model for Mb Adsorption onto Organoclays

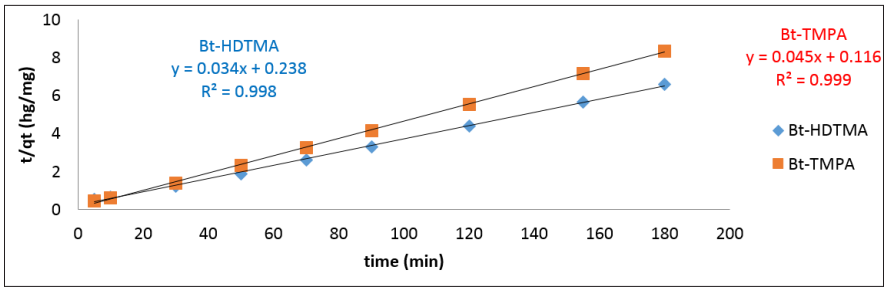


Figure 4: Pseu–do Second Order Kinetic Model for Mb Adsorption onto Organoclays

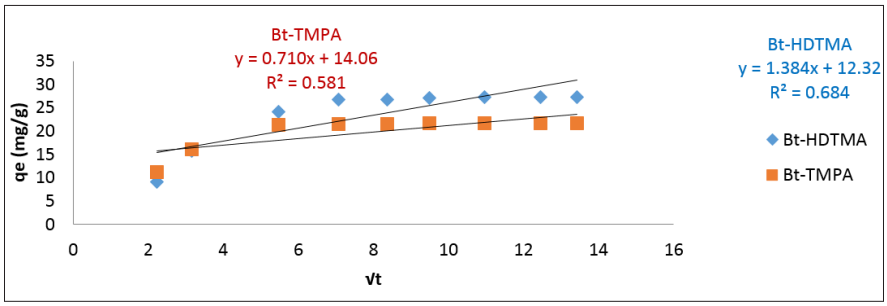


Figure 5: Intra-Particle Diffusion Kinetic Model for Mb Adsorption onto Organoclays

Adsorption Isotherms

Adsorption isotherm helps to determine some essential parameters such as capacity of adsorbents, surface properties of adsorbents and adsorption mechanism pathway, which aids in designing effective sorption system and also describes the adsorbate-adsorbent interaction [39]. Generally, it could be regarded as a curve which describes the phenomenon leading to the mobility of a substance from the aqueous aquatic environment to a solid-phase at a constant temperature and pH [39]. The Freundlich and Langmuir isotherms were applied to describe the adsorption of Methylene blue (MB) by Bt-HDTMA and Bt-TMPA according to equation (5) and (6) respectively:

$$ln\, q_e = ln\, k_f + \frac{1}{n}\, lnC_e \qquad (5)$$

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \qquad (6)$$

where Ce (mg/L) and qe (mg/g) are the concentration of adsorbate and the adsorption capacity of the adsorbents at the equilibrium time, respectively, kf (mg/g) and 1/n are the Freundlich constant, b (L/mg) is the Langmuir constant and Qm (mg/g) is maximum adsorbent capacity. The values of the isotherm parameters obtained by fitting the experimental data to these isotherm models are summarized in Table 2. Normalized deviation values (DQ) were also calculated for each isotherm according to the equation below:

$$\Delta Q = \sum \frac{1}{N}\left[\frac{Qn - Qd}{Qd}\right] \qquad (7)$$

Table 2. Isotherm parameters for the adsorption of MB by Bt-HDTMA and Bt-TMPA (adsorbent dosage= 0.125 g)

		Langmuir				Freundlich			
Adsorbent	Temperature	Qm(mg/g)	b(L/mg)	R^2	ΔQ ($\times 10^2$)	K_f(mg/g)	1/n	R^2	ΔQ ($\times 10^2$)
Bt-HDTMA	30°C	104.7	0.64	0.926	1.04	46.82	1.66	0.777	4.89
	40°C	108.23	0.48	0.954	0.78	48.77	1.34	0.681	6.22
Bt-TMPA	30°C	94.78	0.51	0.951	0.88	65.2	1.06	0.541	7.12
	40°C	103.65	0.69	0.964	1.65	47.1	2.19	0.606	5.45

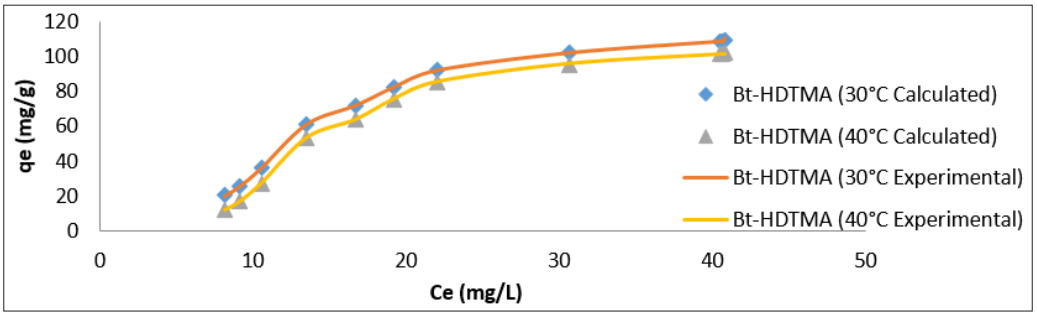


Figure 6: Langmuir Isotherm Model for Mb Adsorption onto Bt-HDTMA

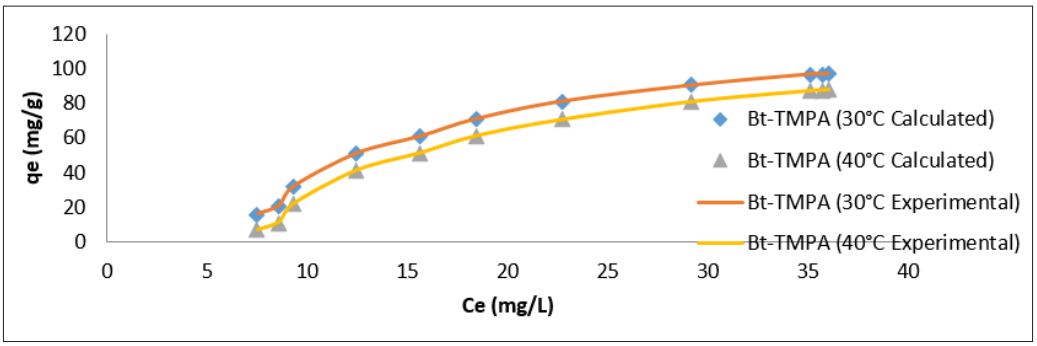


Figure 7: Langmuir Isotherm Model for Mb Adsorption onto Bt-Tmpa

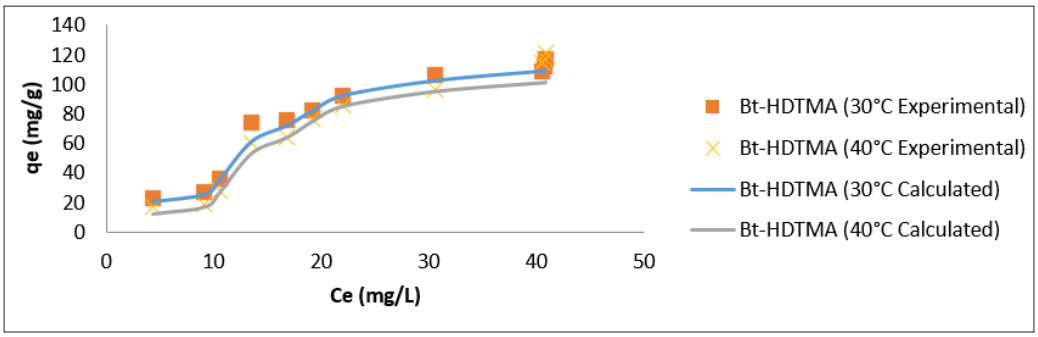


Figure 8: Freundlich Isotherm Model for Mb Adsorption onto Bt-Hdtma

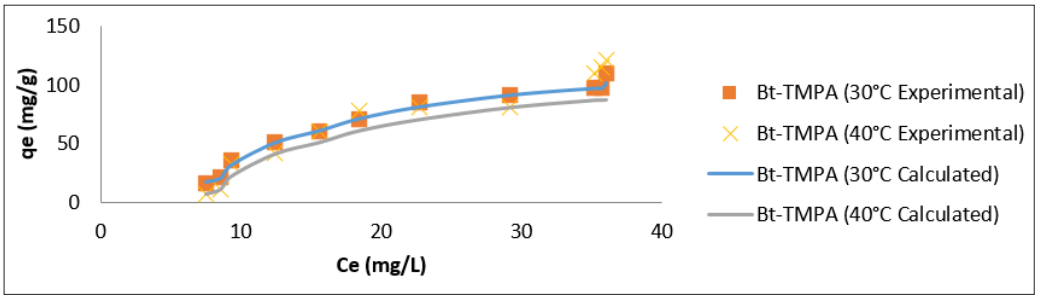
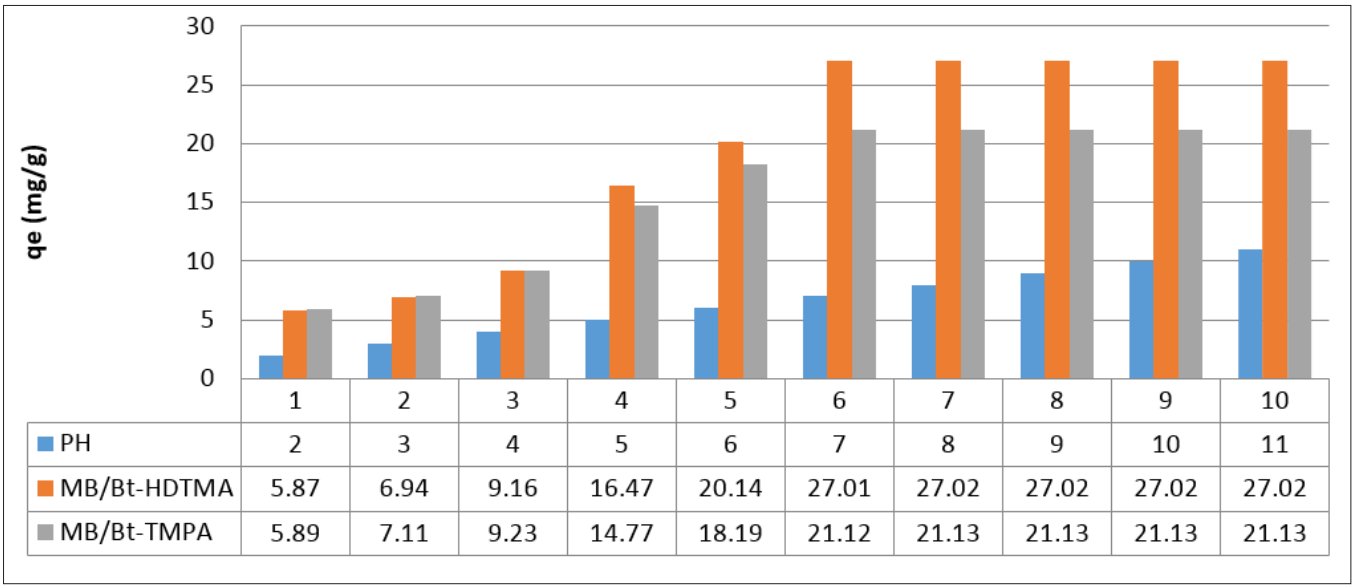


Figure 9: Freundlich Isotherm Model for Mb Adsorption onto Bt-Tmpa

Table 2 show the correlation coefficients and the normalized deviation values for the Langmuir, Freundlich sorption isotherm constants. When the R^2 and DQ values are compared, the equilibrium data of methylene blue dye (MB) onto the organo-bentonite follow the Langmuir isotherm. The correlation coefficient values of Langmuir isotherms for the organoclays indicate that there is a strong positive relationship for the data. In addition, the calculated b values which are the one of the Langmuir isotherm characteristics were found to be between 0 and 1 for all temperatures. These results indicate that adsorption is favourable according to Table 2. Also, all 1/n values obtained from the Freundlich isotherm were greater than 1, implying strong adsorption bond between the organoclays and the MB dye molecules. Adsorption isotherms with experimental and calculated data obtained from dye adsorption are shown in Fig 6-9. From Fig 6-9 it is crystal clear that the increase in initial methylene blue dye concentration results to a corresponding increase in the adsorption capacities of the organoclays. This may be due to an increase in driving forces affecting dye compounds. One of these forces is van der Waal's force that affects active adsorption sites of the adsorbent, which occurs at higher concentrations. However, there is no significant difference between the adsorption isotherms at two different temperatures of 30°C and 40°C.

Effect of pH

The initial pH of dye solution plays an important role on the adsorption of Methylene blue (MB) onto the organoclays because of its effect on the solution dye chemistry and the degree of ionization of the adsorbent surface [40]. Removal of Methylene blue (MB) dye was studied by varying pH of the aqueous solution from 3 to 11 at 25 °C with fixed dye concentration of 100 mg/L and adsorbent mass of 1 g/L. As shown in Fig. 10, the adsorption capacity increase significantly from 5.07 to 27.01 mg/g and 5.89 to 21.12 mg/g for Bt-HDTMA and Bt-TMPA respectively when the aqueous phase pH increases from 3 to 7. When the pH varies from 7 to 11, the adsorption capacities only increased by 0.1 mg/g for both organoclays. Therefore, low dye adsorption observed at acidic pH can be accredited to competition between hydrogen ion H^+ and cationic Methylene blue (MB) dye. High dye adsorption observed at high pH (7-10) is due to the decrease in the number of protons occupying the active sites of the organoclays and higher negative charge of adsorbent surface (due to OH^- ions) [41]. Thus, increasing electrostatic interaction occurs between the positively charged Methylene blue (MB) dye and the negatively charged organo composite upon the pH increase in the pH range 7-11 [12, 42, 43]. Therefore, the optimal initial pH for the Methylene blue (MB) adsorption was chosen at pH 7 for other experiments.



	1	2	3	4	5	6	7	8	9	10
PH	2	3	4	5	6	7	8	9	10	11
MB/Bt-HDTMA	5.87	6.94	9.16	16.47	20.14	27.01	27.02	27.02	27.02	27.02
MB/Bt-TMPA	5.89	7.11	9.23	14.77	18.19	21.12	21.13	21.13	21.13	21.13

Figure 10: Effect of pH on Adsorption of MB by the Organoclays (Contact time= 180 mins, Mass of Organoclay= 0.125 g, Temperature =28°C, Initial MB conc =100 mg/L)

Adsorption Thermodynamics

At similar temperature ranges of 298-318 K, the thermodynamic parameters such as entropy change (ΔS°), enthalpy change (ΔH°) and Gibbs free energy (ΔG°) are calculated from the temperature-dependent adsorption isotherm to describe the adsorption process according to equation (8) - (10):

$$K = \frac{C_O - C_e}{C_e} \quad (8)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

Where C_o and C_e are the initial concentration and equilibrium concentration, R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K) [44, 45]. Plots of ln K versus 1/T for the adsorption of MB on Bt-HDTMA and Bt-TMPA, and the calculated values for entropy change (ΔS°), enthalpy change (ΔH°) and Gibbs free energy (ΔG°) are presented in Fig 11 and Table 3 respectively.

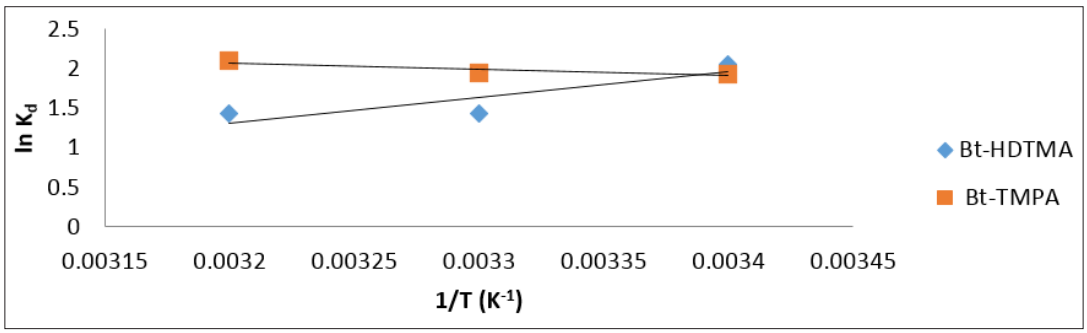


Figure 11: Plots of ln K versus 1/T for the adsorption of MB on Bt-HDTMA and Bt-TMPA: mass of adsorbent = 0.125 g, pH=7, contact time=180 mins, initial MB concentration= 100 mg/L.

Table 3: Thermodynamic parameters for the adsorption of MB onto organoclays: mass of adsorbent = 0.125 g, pH=7, contact time=180 mins, initial MB concentration= 100 mg/L

	ΔS^0 ($Jmol^{-1}K^{-1}$)	ΔH^0 ($kJmol^{-1}$)	ΔG^0 ($kJmol^{-1}$)		
Adsorbent			**298K**	**308K**	**318K**
Bt-HDTM.	0.071	-66.54	-17.564	-17.871	-17.911
Bt-TMPA	0.093	-49.12	-12.04	-12.43	-12.82

With increase in temperature, the ΔG° values also decreased which suggested an increase in the feasibility of adsorption process. ΔG° values were found to be negative which indicated that the adsorption process was spontaneous. The negative values of ΔH° suggested that it is an exothermic process. The positive values of ΔS° suggested an increase in degrees of disorder and randomness at the solid-liquid interface during the adsorption process [46-48].

Adsorption Mechanism

The intra-particle diffusion (IPD) model was applied to understand the adsorption mechanism behind the adsorption of MB onto the organoclays. The parameters are shown in Table 1 and the plots are represented in Fig. 5. The values of intercept provide an estimate of the boundary layer thickness [49]. The results showed that the Boundary layer effect was significant in adsorption of MB onto the organoclays. As observed in Fig. 7, the plotted line did not pass through the origin indicating that the intra-particle diffusion alone was not the rate-controlling factor and boundary layer diffusion also contributed to the adsorption process [48, 50].

Regeneration of Spent Organoclays

In this study, temperature of 150°C at different times (10, 30, 50 and 60 min) was used to regenerate the methylene blue dye (MB) saturated adsorbent. As seen from Figs 12 and 13, the adsorption capacity of the regenerated organoclays were increased by increasing the regeneration time. The ratio of the sorption capacity of the regenerated adsorbent to the original adsorbent was increased from 37.1–89.6% for Bt-HDTMA and 29.8 – 85.3% for regeneration time range of 10 – 60 minutes. This result implies that HDTMA and TMPA modified bentonite (Bt-HDTMA, Bt-TMPA) can be used repeatedly without a significant loss in the adsorption efficiency for methylene blue (MB) dye.

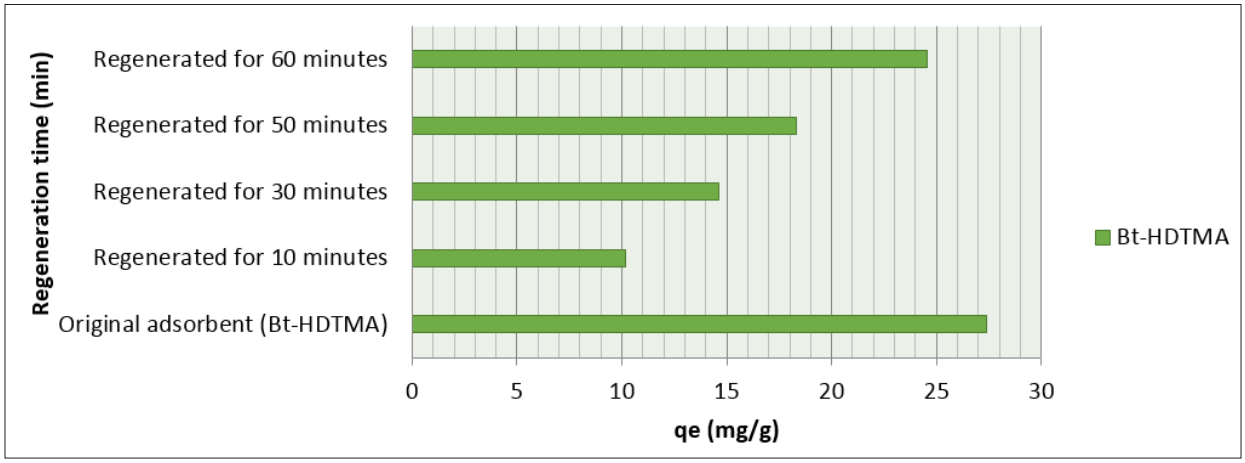


Figure 12: Effect of temperature of 1500C at various times (10, 30, 50 and 60 min) on the regeneration of the Bt-HDTMA. (MB solution = 100 mg/L, initial pH = 7 ± 0.5, contact time = 180 mins and adsorbent conc. = 5 g/L).

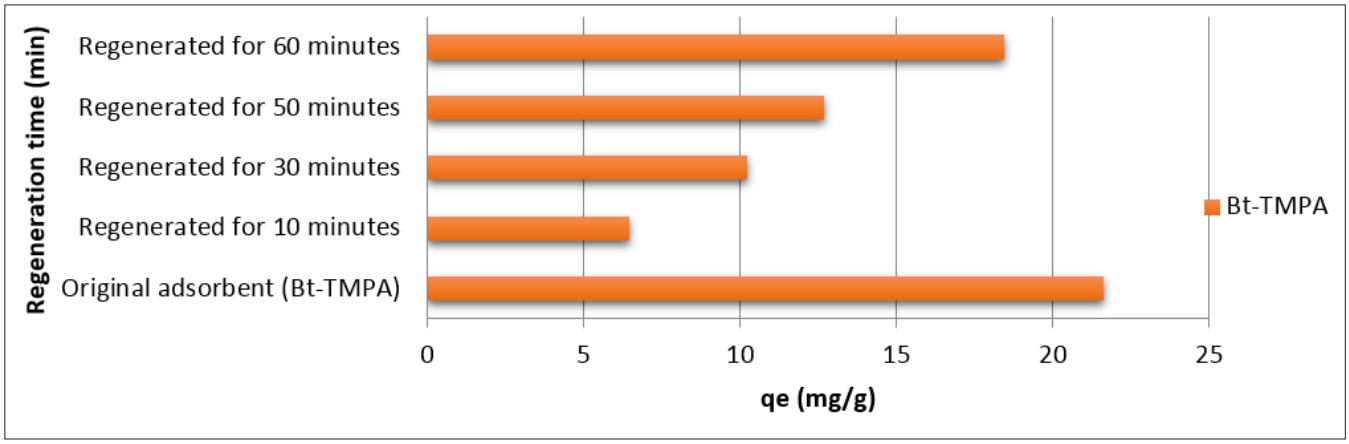


Figure 13: Effect of temperature of 150°C at various times (10, 30, 50 and 60 min) on the regeneration of the Bt-TMPA. (MB solution = 100 mg/L, initial pH = 7 ± 0.5, contact time = 180 mins and adsorbent conc. = 5 g/L).

Conclusion

Effective removal of methylene blue dye by hexadecyltrimethylammonium (HDTMA) and trimethylpenylammonium (TMPA) cations intercalated bentonite in aqueous solution has been investigated. The sorption of methylene blue dye by the organoclays were highly influenced by the effect of contact time, initial methylene blue concentration and pH. Sorption data were best described by the Langmuir isotherm and Pseudo second order kinetic model. From the thermodynamic point of view, the process of methylene blue dye adsorption onto the organclays were feasible, spontaneous and exothermic. About 89.6 and 85.3% removal of methylene blue dye by regenerated MB saturated organoclay (Bt-HDTMA and Bt-TMPA respectively) were recorded. However, it is a statement of fact that these organoclays (Bt-HDTMA and Bt-TMPA) which are readily available, eco-friendly, cost effective exhibits great adsorption efficiency for removal of cationic dyes in aqueous medium, and also promises wide scale future application.

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