Attenuation of Methylene Blue From Aqua-media on Acid Activated Montmorillonite of Nigerian Origin

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ABSTRACT

This study evaluated the performance of an Unmodified Ugwuoba-montmorillonite Clay (UUC) and the Acid Modified Ugwuoba-montmorillonite Clay (AMUC) of Nigerian origin as low-cost materials for attenuation of Methylene Blue (MB). Batch sorption methodology was applied in adsorption and desorption studies. AMUC was found to have higher adsorption of MB than UUC under all experimental conditions. Optimum experimental conditions were achieved at pH 8.0, adsorbent particle size 100 μm, MB concentration 200 mg/L and contact time of 60 and 90 min for AMUC and UUC, respectively. Equilibrium isotherm analysis was performed by the application of the Langmuir, Freundlich, Flory-Huggins, Tempkin, Dubinin-Radushkevich and Scatchard isotherm models. The Langmuir isotherm was found to be applicable (R^2 of 0.999) in the sorption of MB on UUC while the Freundlich gave the best fit (R^2 of 0.990) for AMUC. Kinetic analysis was evaluated by the Pseudo First Order (PFO), Pseudo Second Order (PSO), Elovich, Bangham, Intraparticle diffusion and liquid film diffusion models. The PSO model was found to be applicable in the kinetics with an initial sorption rate of 0.647 and 1.477mg g^{-1} min^{-1} for the respective adsorbents. Thermodynamics revealed a spontaneous, feasible and exothermic adsorption process, while desorption studies showed a physical adsorption mechanism.

Key words: *Acid-modification, desorption, dye, thermodynamics, water treatment*

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INTRODUCTION

Dyes are used extensively by many industries, such as plastic, textile, and paper in the coloring of their products. Due to the presence of these organic chemicals, the effluents from these industries are usually colored (*Rauf et al. 2009*), which impede light penetration, damaging the quality of the receiving water bodies and toxic to food chain organisms (*Tan et al. 2008*). Methylene Blue (MB) is the cationic dye that is most commonly used for coloring among all others in its category and is generally used for dyeing silk, wool and cotton (*Yang and Qiu 2010*). MB can cause eye burns, gastrointestinal irritations, vomiting, diarrhea, methemoglobinemia, cyanosis, convulsions, dyspnea, and skin irritations when ingested or misused (*Fil et al. 2012*). Therefore, removal of such dyes from effluents is very important before discharge into receiving water bodies due to their harmful effects. The most commonly used method for dye removal is biological oxidation and chemical precipitation. However, these processes are effective only in the case where the solute concentrations are relatively high and also have the disadvantages of high cost, formation of hazardous by-products and intensive energy requirements (*Vadivelan and Kumar 2005*). The

adsorption technique has been found to be the most effective among all techniques for water de-colorization in terms of initial cost, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants, does not result in the formation of hazardous by-products, and is effective even in the case of low solute concentrations (*Rauf et al. 2009; Fil et al. 2012*). Activated carbon is the adsorbent of choice for dye removal due to its very high adsorption capacity (*Iqbal and Ashiq 2007*), but it is expensive which limits its widespread use (*Vieira et al. 2012*). This led to the use of several low cost adsorbents for MB removal such as agricultural waste, perlite, hair, kaoline, bentonite and montmorillonite, palygorskite, zeolite, fly ash, vermiculite, and clinoptilolite (*Ozer et al. 2007; Almeida et al. 2009; Fil et al. 2012*). Clay minerals in general have been used by some workers and found to be very effective for the removal of different types of dyes (*Fil and Ozmetin 2012; Aladag et al. 2014; Fil 2016*). Acid activation of clays such as montmorillonite has also been found to increase greatly the adsorption capacity for MB (*Sarma et al. 2011; Gil et al. 2013*). However, clay mineral may vary slightly in its adsorptive properties as a result of variations in its purity,

the saturating cation, and environmental location. Nigeria is blessed with a huge deposit of montmorillonite clay, but despite successful reports on the use of montmorillonite and its acid modified derivates obtained elsewhere for MB removal, no report on the use of Nigerian montmorillonite and its acid modified form have been documented. However, they have successfully been used in the adsorption of heavy metals, in which the acid treated form recorded an improvement in its adsorption capacity (*Akpomie and Dawodu 2016*). This research therefore aims to establish the adsorption potential of a Nigerian montmorillonite and its acid activated derivates for the removal of MB from contaminated solution.

MATERIALS AND METHODS

Adsorbent preparation, Characterization, Sorption and Desorption

The montmorillonite clay was obtained from ugwuoba in Oji river local government area of Enugu state, Nigeria. The clay was processed as described previously to obtain the Unmodified Ugwuoba-montmorillonite Clay (UUC) (*Akpomie and Dawodu 2014*). The Acid Modified Ugwuoba-montmorillonite Clay (AMUC) was prepared by adding 250 mL of 1.5 M H_2SO_4 to 50 g of UUC, stirred for 30 min and left for 24 hr after which the aqueous phase was decanted. Thereafter, the clay was washed with excess de-ionized water until a neutral pH of 7.0 was attained, sundried, and then oven dried at 150 ˚C for 3 hr, pulverized and passed through mesh sieves of sizes 100-500 μm (*Akpomie and Dawodu 2016*). The prepared adsorbents were characterized to determine the pH point of zero charge (pHpzc) by the method described (*Onyango et al. 2004*) while the Brunauer, Emmett and Teller (BET) surface area (SBET) was determined via nitrogen adsorption-desorption using a micrometrics ASAP 2010 model analyzer.

All the reagents used in this study were of analytical grade, obtained from sigma Aldrich (Steinheim, Germany) and used without further purification. A stock solution of 1000 mg L^{-1} of MB was prepared by dissolving appropriate amount of MB in distilled water. Thereafter, lower concentrations of MB ranging from 200-800 mg L^{-1} were prepared from the stock solution by serial dilution. The pH of the solutions was adjusted in the range 2.0-10.0 by the drop wise addition of 0.1 M NaOH or 0.1 M HCl when required. Batch adsorption methodology was applied in the sorption experiment. This was performed by contacting 0.1 g of the adsorbent with 50 mL of a given solution in 100 mL glass bottle at room temperature of 300 K. The effect of various

operating parameters were studied in the range; pH (2.0-10.0), initial MB concentration (200-1000 mg L^{-1}), adsorbent dosage (0.02-0.10 g), particle size (100-500 μm), contact time (10-180 min) and temperature (300-323 K) at optimum conditions of pH 8.0, MB concentration 200 mg L^{-1}, adsorbent particle size 100 μm and contact time of 120 min. The bottles were placed in a thermo-stated water bath for temperature regulation when the effect of temperature was investigated. In order to study the effect of a particular parameter, that parameter was varied while the others were kept constant at the optimum conditions. At the end of the given contact time for sorption, the solutions were centrifuged for 10 min at 500 rpm and the concentration of MB (mg/L) in the supernatant at equilibrium was determined using the Ultraviolent (UV)-Visible spectrophotometer (Spectrumlab 752s) at 665 nm wavelength, at which maximum absorbance occurred. Each experiment was performed in duplicate and mean value was computed in order to ensure quality assurance. The adsorption capacity of the adsorbents for MB and the percentage adsorption were calculated from following equations, respectively:

$$q\,e = v\,(C_i\text{-}\,C_e\,)\,/\,m \qquad\qquad (1)$$

$$\%adsorption = 100[(C_i\text{-}\,C_e\,)\,/\,Ci\,] \qquad\qquad (2)$$

Where *qe* (mg g^{-1}) is the adsorption capacity, *CI* (mg L^{-1}) and *Ce* (mg L^{-1}) is the initial MB concentration and the concentration at equilibrium, respectively, *v* (L) is the volume of solution used and *m* (g) is the mass of the adsorbent used in the sorption experiment.

Distilled Water (DW) and Ethanol (96%) were used as eluents in desorption of MB from the MB-loaded adsorbents. This was done by contacting 1.0 g of MB-loaded adsorbents with 50 mL of DW and ethanol solution, each performed separately. The solutions were agitated for 30 min at 100 rpm, filtered and the amounts of MB desorbed in solution were analyzed using the UV-visible spectrophotometer. The percentage MB molecules desorbed were calculated from the equation:

$$\%Desorption = 100\,[C_D\,V_D\,]\,/\,(q_e\,m) \qquad\qquad (3)$$

Where C_D (mg L^{-1}) represents the MB concentration in the desorbed solution, V_D (L) is the volume of desorbed solution, *m* (g) is the mass of adsorbent used for desorption studies and q_e (mg g^{-1}) is the adsorption capacity of the adsorbent for MB before desorption. The recyclability of the adsorbents was checked by performing three cycles of adsorption/desorption using ethanol as eluent. After each cycle, the adsorbents were washed with DW and

dried in the oven before reuse for adsorption (*Akpomie et al. 2015*).

RESULTS AND DISCUSSION

Characterization

The pHpzc of the adsorbents is the pH at which the amount of negative charge on the adsorbent surface is equal to the amount of positive charge. It can also be defined as the pH at which the net surface charge of the adsorbent is zero. At pH values higher than the pHpzc, the adsorbent surface is negative and favors adsorption of cationic species while at values below the pHpzc, it is positive and repels cationic species. Therefore, the decrease in pHpzc from 3.7 to 2.3 for AMUC is desirable for the adsorption of cationic MB molecules at pH values above 2.3. The increase in SBET from 55.76 to 96.48 m2/g suggests an increase in adsorption capacity of the acid activated derivative for MB molecules (*Akpomie and Dawodu 2016*).

Influence of operating parameters

The pH of a solution is an important factor in most adsorption processes as it affects the surface charge of the adsorbent and the degree of ionization of dye molecules (*Youssef et al. 2014*). Therefore it was determined in this study. As observed, an increase in the percentage adsorption with increase in pH from 2.0 to 8.0 was observed for both adsorbents after which the adsorption became fairly constant (**Figure 1**). An optimum pH of 8.0 was then chosen and used in this study for all subsequent experiment. As MB produces molecular cations in aqueous solution, these cations compete with excess H^+ ions in solution for the active sites on the adsorbent, at low pH values, which accounted for the low percentage removal. However, as the solution pH increases, fewer H^+ ions are available to compete with MB cations, also, the active sites on the surface becomes increasingly deprotonated, thereby increasing the number of negatively charged sorption sites (*Almeida et al. 2009*). A very important observation is that significant adsorption occurred at pH values greater than the pH^{pzc} of the adsorbents at which the surface is negatively charged, attracting the positively charged MB molecules. Similar results have been reported by some researchers (*Al-Wahbi and Dammag 2011; Guler and Sarioglu 2013*). It is clearly seen from the result that AMUC recorded a higher adsorption of MB than UUC at all pH values which suggest the effectiveness of acid treatment in enhancing the adsorption potential of the montmorillonite at any solution pH.

The adsorption of an adsorbate by an adsorbent is strongly dependent on the initial concentration of the adsorbate in solution. Therefore the sorption of MB onto UUC and AMUC as a function of initial MB concentration was determined (**Figure 2**). A decrease in the percentage adsorption of MB on both adsorbents with increase in initial MB concentration was recorded. Similar results have been reported (*Ozer et al. 2007; Hameed and El-Khaiary 2008*). The higher adsorption at lower MB concentration is due to the fact that more of the dye molecules were removed by the abundant active sites on the adsorbents, but as the dye concentration increases, the active sites becomes saturated causing less removal of MB. Also, the steric repulsions between the dye molecules at higher concentration may hinder the tendency of MB molecules to be attached to the adsorbent (*Rauf et al. 2009*). An initial MB concentration of 200 mg L^{-1} was selected and used in all experiments in this study as optimum percentage removal was obtained at this concentration. The acid treatment all proved to be effective in enhancing the adsorption of MB by the adsorbent at all MB concentrations compared to the unmodified derivative.
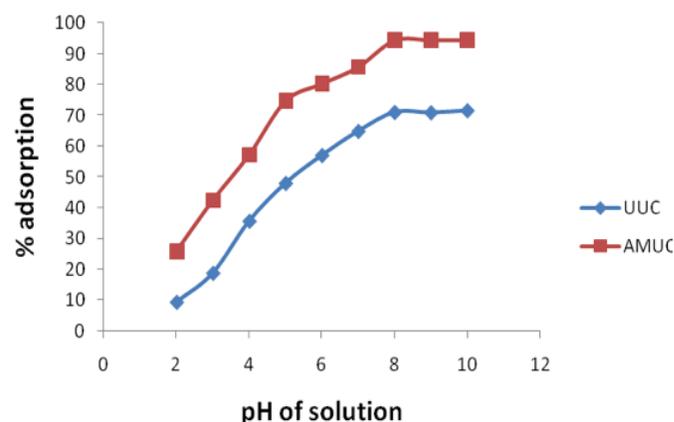

Figure 1. Effect of initial pH of solution on the adsorption of methylene blue on the adsorbents.
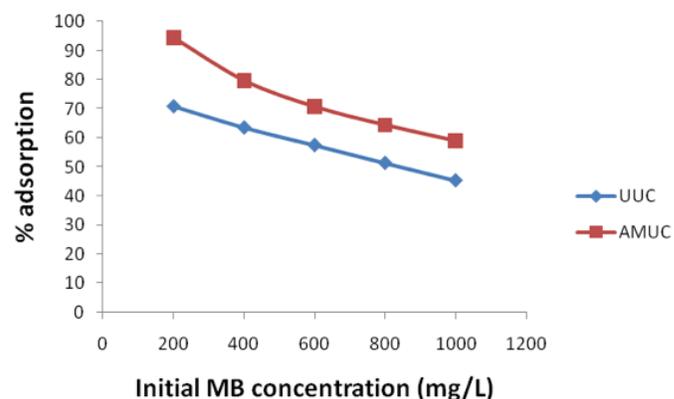

Figure 2. Effect of initial methylene blue concentration on its adsorption on the adsorbents.

It is clear than an increase in the dosage of both adsorbents from 0.02 to 0.1 g resulted to a corresponding increase in the amount of MB adsorbed (**Figure 3**). The increase is attributed to an increase in the number of sorption sites and surface area of the adsorbents (*Guler and Sarioglu 2013*). It may also be attributed to increased surface negative charge and decrease in electrostatic potential near the solid surface that favors solute-sorbent interactions (*Unuabonah et al. 2007*). Acid modification also enhanced the adsorption potential of the clay for MB at all adsorbent dose compared to UUC, which is desirable. All sorption experiments were performed at an adsorbent dose of 0.1 g as optimum sorption of MB was obtained at this dosage on both UUC and AMUC.

A decrease in the percentage adsorption with increase in the particle size of the adsorbents was obtained (**Figure 4**). This decrease was attributed to a decrease in the surface area of the adsorbents at larger particle sizes which provided less active to be utilized for the sorption of MB molecules (*Wong et al. 2003*). AMUC was also found to have a higher sorption of MB than UUC at all particle sizes, which indicated the effectiveness of
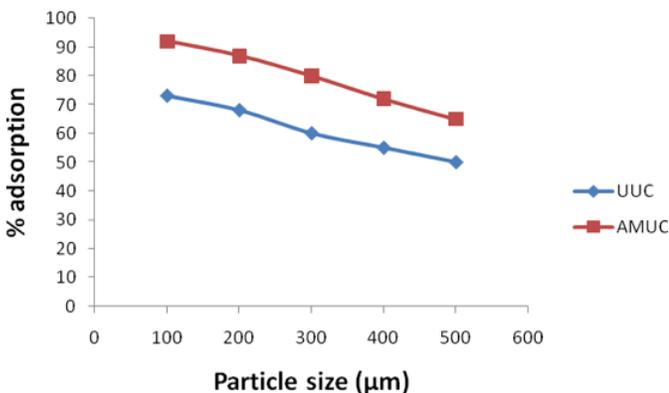
acid modification. Consequently, both adsorbents were utilized at particle size of 100 μm when the effects of other experimental parameters were studied, in order to achieve optimum adsorption.

Furthermore, the effect of contact time on the adsorption of MB by the adsorbents was investigated in order to determine the time needed for equilibrium sorption. An increase in adsorption with increase in contact time was established after which equilibrium was achieved around 60 min on AMUC and 90 min for UUC, thereafter becoming fairly stable (**Figure 5**). The faster rate of removal at the initial stages is due to the presence of abundant active sites on the adsorbents which becomes used up with time attaining saturation, thereby leading to equilibrium attainment. Similar results have been reported on the sorption of MB (*Almeida et al. 2009; Youssef et al. 2014*). The fast uptake of MB molecules is due to solute transfer, as there are only sorbate and sorbent interactions with negligible interferences from solute-solute interactions due to the low concentration and homogenous nature of the system. The faster rate of equilibrium attainment by the acid modified clay is desirable and may be as a result of more active sorption sites for faster sorption of MB on AMUC than UUC. Also, AMUC also recorded a higher adsorption at all contact time than UUC indicating again the significance of acid modification. In order to ensure equilibrium attainment on both adsorbents, a contact time of 120 min was used in this study for optimum sorption of MB.

Equilibrium Isotherm Modeling

Equilibrium adsorption isotherms help relate the adsorbate concentration in the bulk and adsorbed amount at the interface at equilibrium. They also provide useful information on sorption mechanism, surface properties and affinity of the adsorbents. In this study, the Langmuir, Freundlich, Flory-Huggins, Tempkin,
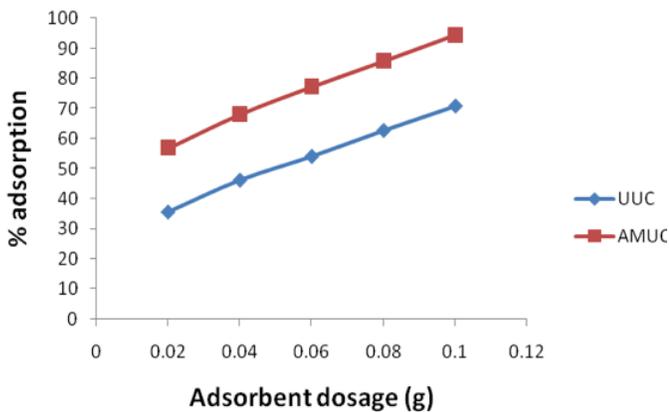

Figure 3. Effect of adsorbent dosage on the adsorption of methylene blue on the adsorbents.

Figure 4. Effect of adsorbent particle size on the adsorption of methylene blue on the adsorbents.
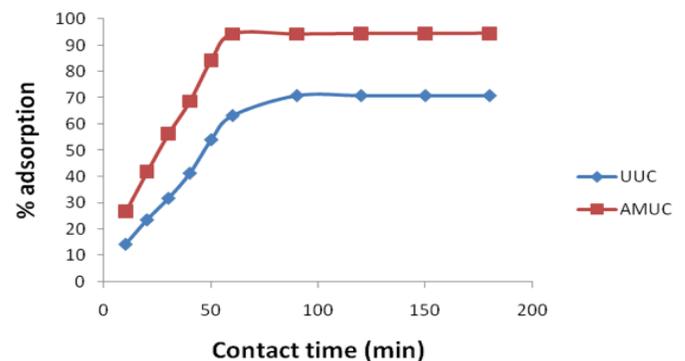

Figure 5. Effect of contact time on the adsorption of methylene blue on the adsorbents.

Dubinin-Radushkevich and Scatchard isotherm models were applied in the analysis of the equilibrium data.

The Langmuir isotherm is given in its linear form as (*Langmuir 1918*):

$$C_e / q_e = 1 / (q_L K_L) + C_e / q_e \tag{4}$$

Where q_L (mg g^{-1}) is the maximum monolayer adsorption capacity of the adsorbents, K_L (L mg^{-1}) is the Langmuir adsorption constants (**Table 1**).

The higher regression coefficient (R^2) of 0.999 and 0.969 for UUC and AMUC, respectively is very close to one. This indicates a monolayer sorption of MB on a homogenous adsorbent surface. Also, the maximum monolayer adsorption capacity (q_m) of AMUC was found to be higher than UUC, indicating an improved adsorption of MB after acid treatment. A Langmuir dimensionless constant referred to as equilibrium parameter (R_L) was calculated from the equation:

$$R_L = 1 / [1 + K_L C_i] \tag{5}$$

The value of R_L indicates the type of adsorption to be irreversible ($R_L = 0$), linear (RL = 1), favorable ($0 < R_L < 1$) and unfavorable ($R_L > 1$). The RL values calculated for MB sorption on UUC and AMUC was found to be in the range 0.17-0.5 and 0.07-0.26, respectively, indicating a favorable adsorption unto the adsorbents.

The Freundlich isotherm is presented in its linear form as (*Freundlich 1906*):

$$log q_e = log K_F + [1 / n] log C_e \tag{6}$$

Where K_F (mg g^{-1}) and n are the Freundlich constants (**Table 1**). The Freundlich isotherm also presented good R^2 values for both adsorbents, however, the value (0.990) obtained for AMUC was higher than that of the Langmuir model (0.969). This suggested that acid activation of the clay tend to make the surface of AMUC heterogeneous and involved a multilayer sorption of MB. Also, values of n between 1 and 10 indicated a favorable adsorption. The values of n obtained are 1.901 and 3.185 for UUC and AMUC, respectively, indicated again a favorable sorption of MB unto the adsorbents.

The linear form of the Flory-Huggins isotherm model is given in the equation (*Foo and Hameed 2010*):

$$log (\theta / C_i) = log K_{FH} + nFH log (1 - \theta) \tag{7}$$

Where $\theta = (1 - C_e/C_i)$ is the degree of surface coverage, KFH (L g^{-1}) and nFH represents the Flory-Huggins equilibrium isotherm constant and model exponent, respectively. The correlation coefficient (R^2) of 0.912 and 0.924 obtained for UUC and AMUC, respectively were lower than those of the Langmuir and Freundlich model (**Table 1**). Therefore this isotherm was not appropriate in the description of the sorption process of MB on the adsorbents.

The Temkin isotherm model was applied in its linear form as (*Foo and Hameed 2010*):

$$q_e = BlnA + BlnC_e \tag{8}$$

Where B is related to the heat of adsorption and *A* (L mg^{-1}) is the equilibrium binding constant. The R^2 values obtained from the Temkin model (**Table 1**) for MB on the adsorbents were low (<0.9). Therefore, this isotherm was not suitable in the description of the sorption of MB molecules.

The Dubinin-Radushkevich (D-R) isotherm is expressed linearly as (F*oo and Hameed 2010*):

Table 1. Equilibrium isotherm parameters for the adsorption of methylene blue on the adsorbents.

Isotherm Model	UUC	AMUC
Langmuir		
q_L (mg g^{-1})	125	142.9
K_L (L mg^{-1})	0.005	0.0141
R^2	0.999	0.969
Freundlich		
K_F (mg g^{-1})(mg L^{-1})1/n	1.728	3.43
N	1.901	3.185
R^2	0.984	0.990
Flory-Huggins		
K_{FH} (L g^{-1})	0.04	0.08
n_{FH}	1.31	1.87
R^2	0.912	0.924
Tempkin		
B (mg g^{-1})	12.46	17.34
A (L g^{-1})	0.042	0.047
R^2	0.842	0.817
Dubinin-Radushkevich		
qm (mg g^{-1})	48.64	55.81
β (mol^2 kJ^{-2})	0.0001	0.0001
R^2	0.678	0.749
Scatchard		
qs (mg g^{-1})	154.2	167.3
b (L mg^{-1})	0.08	0.11
R^2	0.994	0.793

$$lnq_e = lnq_m - \beta\varepsilon^2 \qquad (9)$$

Where q_m (mg g^{-1}) is the saturation capacity of the adsorbent, β (mol2 J^{-2}) corresponds to the sorption free energy and ε is the Polanyi potential expressed as:

$$\varepsilon = RTln\,(1 + 1/C_e) \qquad (10)$$

Where T (K) is the absolute temperature and R is the gas constant (8.314 J mol^{-1}K^{-1}). The very low R^2 values (< 0.8) obtained for MB on both adsorbents (**Table 1**) showed clearly that the D-R model was not suitable in the description of the sorption process.

The Scatchard isotherm was used to verify the homogenous or heterogonous surface of the adsorbents as deduced from the Langmuir and Freundlich isotherm models. The linear form of the Scatchard isotherm model is expressed as (*Anirudhan and Suchithra 2010*):

$$q_e/(C_e = qSb - q_eb) \qquad (11)$$

Where q_S (mg g^{-1}) and b (L mg^{-1}) represent the Scatchard model adsorption parameters. If a straight line is obtained from the linear plot of q_e/C_e against q_e, then the adsorbent presents only one type of binding site (Homogenous surface), but if a deviation from linearity is obtained, then the adsorbent has more than one type of binding site (heterogonous surface) (*Anirudhan and Suchithra 2010*). The Scatchard isotherm constants q_S and b were obtained from the slope and intercept of the plot, respectively. The values of correlation coefficient obtained for UUC showed linearity with R^2 of 0.994 indicating that the surface of UUC is homogenous in nature. However, an opposite result was obtained for AMUC in which a deviation from linearity (R^2 = 0.793) indicating a heterogeneous surface of the adsorbent. This result clearly corroborated that of the Langmuir and Freundlich models indicating that acid activation made the surface of AMUC heterogeneous. The obtained adsorption capacity of UUC and AMUC was compared to previously reported works of other low-cost adsorbents (**Table 2**). The adsorption capacity of the adsorbents in this study was found to be higher than those of many other adsorbents in literature.

Kinetic Analysis

The kinetic mechanism of sorption was analyzed by the application of the Pseudo-First Order (PFO), Pseudo-Second-Order (PSO), Elovich, Bangham, Intraparticle diffusion and liquid film diffusion kinetic models.

The linear form of the PFO model is given as (*Lagergren 1898*):

$$log(q_e-q_t) = logq_e - (k_it)/2.303) \qquad (12)$$

Where Ki (min^{-1}) is the PFO rate constant, qt (mg g^{-1}) and qe (mg g^{-1}) are the amounts of MB adsorbed at time t and equilibrium respectively. The values of R^2 (**Table 3**) obtained for sorption of MB on both UUC and AMUC were low which suggested an inadequate representation of the kinetics by this model.

The PSO model is expressed linearly as (*Ho and Mckay 1998*):

$$t/q^t = 1/K_2\,q_{e^2} + t/q_e \qquad (13)$$

Table 2. Comparison of maximum monolayer adsorption capacities of different adsorbent for methylene blue.

Adsorbent	q_{max} (mg g^{-1})	Reference
Aspergillus Fumigatus	125	(*Abdallah and Taha 2012*)
Raw Spirogyra Sp	50.7	(*Guler and Sarioglu 2013*)
Pretreated Spirogyra Sp	64.61	(*Guler and Sarioglu 2013*)
Brazilian Montmorillonite	289.12	(*Almeida et al. 2009*)
Egyptian bentonite	336.7	(*Youssef et al. 2014*)
Acid activated bentonite	127.58	(*Youssef et al. 2014*)
Yemen bentonite	435.1	(*Al-Wahbi and Dammag 2011*)
Macumba palm cake	27.75	(*Vieira et al. 2012*)
Thermally treated macauba palm	32.30	(*Vieira et al. 2012*)
Brazilian pine fruit shell	252	(*Royer et al. 2009*)
NaOH-modified rejected tea	242.1	(*Nashua and Hameed 2011*)
Coffee husk	90.1	(*Oliveira et al. 2008*)
Rice husk	40.58	(*Vadivelan and Kumar 2005*)
Magnetic peanut hulls	8.9605	(*Taha and El-Maghraby 2016*)
Nigerian montmorillonite	125	Present study
Acid activated Nigerian montorillonite	142.9	Present study

Where K_2 (g mg^{-1} min^{-1}) is the PSO rate constant of sorption. The very good R^2 values obtained for MB sorption on UUC and AMUC showed that this model presented a good fit to the kinetic data (**Table 3**). The PSO model has been found to present the best fit in most sorption processes (*Dawodu and Akpomie 2014*). Also, the initial sorption rate (h) of MB on AMUC was found to be higher than that of UUC which corroborated the faster rate of sorption and equilibrium attainment by the former, when the effect of contact time was studied. However, despite the fact that most researchers conclude chemisorptions process from the good fit of the PSO model alone, such conclusion was not applied in this study. This is because the PSO model is based on an assumption and it was reported in our previous study that an accurate and reasonable conclusion can be drawn if this model is also compared with the magnitude of the enthalpy change ΔH^0 values obtained from thermodynamic analysis (*Akpomie and Dawodu 2015*).

The Elovich kinetic model equation is given in its linear form as (*Low 1960*):

$$q_t = 1 / (\beta ln (\alpha\beta) + 1 \ /\beta lnt) \quad (14)$$

Table 3. Kinetic model parameters for the adsorption of methylene blue.

Kinetic and Thermodynamic Models	UUC	AMUC
Pseudo-first-order		
q_e (mg g^{-1})	46.76	38.47
K_i (min^{-1})	0.006	0.01
R^2	0.876	0.770
Pseudo-second-order		
q_e (mg g^{-1})	52.63	55.14
h (mg g^{-1} min^{-1})	0.647	1.477
K_2 (g mg^{-1} min^{-1})	2.34×10^{-4}	5.33×10^{-4}
R^2	0.907	0.960
Elovich		
α (mg g^{-1} min^{-1})	0.625	0.713
β (g min^{-1})	0.063	0.081
R^2	0.901	0.943
Bangham		
a_B	0.204	0.273
K_o	2.57	3.92
R^2	0.781	0.724
Intraparticle diffusion		
K_d (mg g^{-1} min$^{-1/2}$)	2.13	2.68
I	1.742	3.619
R^2	0.794	0.803
Liquid film diffusion		
K_{fd} (mg g^{-1} min^{-1})	0.027	0.032
D	0.742	0.813
R^2	0.957	0.942

where α represents the initial adsorption rate constant (mg g^{-1} min^{-1}) and β correspond to the extent of surface coverage and activation energy of chemisorptions (g mg^{-1}). The R^2 values (**Table 3**) obtained for the adsorption of MB on UUC and AMUC were high (> 0.9) which indicated a good fit of the Elovich kinetic model to the process. However, the values were lower than those obtained for the PSO model.

The Banghams kinetic model equation was applied to the adsorption process in its linear form as (*Mane et al. 2007*):

$$loglog[C_i/(C_i - q_t m)] = log(K_O m)/2.303V) + aBlog(t) \quad (15)$$

Where V (mL) represents the volume of solution, K_O (g) and a_B (< 1) are the Bangham's model constants. The R^2 values (**Table 3**) obtained from this model were 0.781 and 0.724 for MB adsorption on UUC and AMUC respectively, and showed significant deviations from linearity. This suggested that intraparticle diffusion mechanism was not the major mechanism in the sorption of MB on the adsorbents and the process would likely be dominated by the liquid film diffusion mechanism. This was verified by the application of the respective rate model equations.

The Weber and Morris intraparticle diffusion model was applied to the kinetic data to elucidate the diffusion mechanism and is expressed as (*Weber and Morris 1963*):

$$q_t = K_d t^{1/2} + I \quad (16)$$

Where K_d (mg g^{-1} min$^{-1/2}$) is the intraparticle diffusion rate constant and I is the intercept. Intraparticle diffusion is the only rate controlling step if the plot of qt versus $t^{1/2}$ is linear and passes through the origin ($I = 0$). The intercept (I) indicates the occurrence of the boundary layer effect (film diffusion) and the greater the value of I the greater the effect. The R^2 values (**Table 3**) obtained for MB on both UUC and AMUC were less than 0.81 indicating that intraparticle diffusion is not the major mechanism of the sorption process. Moreover, the presence of the boundary layer effect (I) showed the existence of the surface sorption or film diffusion mechanism.

To verify if the liquid film diffusion is the major or rate controlling mechanism, it was therefore necessary to apply the liquid film diffusion model equation given as (*Akpomie and Dawodu 2015*):

$$ln(1-F) = -K_{fd} t + D \quad (17)$$

Where F is the fractional attainment of equilibrium, (F = q_t/q_e) and K_{fd} (mg g^{-1} min^{-1}) is the film diffusion adsorption rate constant. A linear plot of ln($1 – F$) versus t with zero intercept would suggest that the adsorption is solely controlled by diffusion through the liquid film surrounding the adsorbent. Also, the occurrence of the intercept indicates that film diffusion is not the only diffusion mechanism. The R^2 values obtained for MB on both adsorbents were very high (> 0.94) which confirmed that film diffusion mechanism is the major mechanism of the sorption process and this corroborated the deduction of the Bangham's kinetic rate equation.

Thermodynamic analysis

A decrease in the adsorption on both adsorbents with increase in temperature from 300-323K was obtained (**Figure 6**). This suggests that the process is exothermic in nature. The observed trend may be due to the tendency of MB ions to escape from the solid phase to the bulk phase with an increase in temperature.

Thermodynamic parameters such as free energy change (ΔG$^\circ$), enthalpy change (ΔH$^\circ$) and entropy change (ΔS$^\circ$) were evaluated to examine the spontaneity, feasibility and heat change of the sorption process. The following thermodynamic equations were applied (*Liang et al. 2010*):

$$\Delta G^o = -RTlnK_c \tag{18}$$

$$lnK_c = (\Delta H^o / RT) + (\Delta S^o / R) \tag{19}$$

Where K_c is the equilibrium constant, $T(K)$ is the absolute temperature and R (8.314 J mol^{-1} K^{-1}) is the ideal gas constant (**Table 4**).

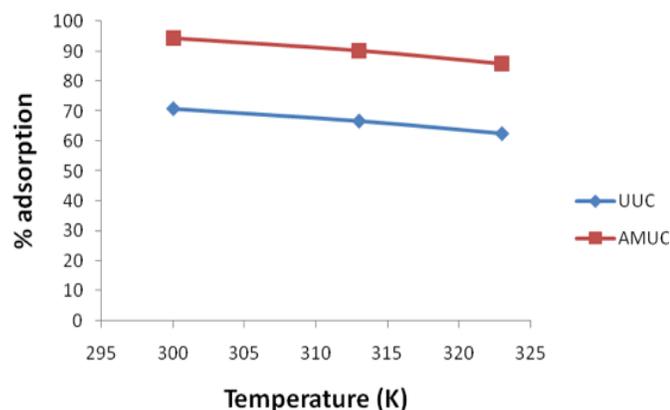Table 4. Thermodynamic model parameters for the adsorption of methylene blue.

Thermodynamic parameters	UUC	AMUC
300K (ΔG$^\circ$) (KJ/mol)	-2.227	-7.045
313K (ΔG$^\circ$) (KJ/mol)	-1.819	-5.776
323K (ΔG$^\circ$) (KJ/mol)	-1.383	-4.830
ΔH$^\circ$ (KJ/mol)	-13.12	-35.958
ΔS$^\circ$ (J/mol K)	-36.29	-96.36

Negative values of ΔH$^\circ$ were obtained for the sorption of MB on both adsorbents, which indicates an exothermic adsorption process and supports the decrease in adsorption with temperature recorded (**Figure 6**). A decrease in randomness at the solid/solution interface was indicated by the negative values of ΔS$^\circ$ and the low values suggest that no remarkable change in entropy occurred (*Liang et al. 2010*). Furthermore, negative ΔG$^\circ$ values obtained at all temperatures indicate that the sorption process is spontaneous and feasible. The values of ΔH$^\circ$ from 2.1-20.9 kJ mol^{-1} and 80-200 kJ mol^{-1} correspond to physisorption and chemisorptions, respectively (*Akpomie and Dawodu 2014*). The absolute values of ΔH$^\circ$ for UUC and AMUC are 13.128 and 35.958 kJ mol^{-1}, respectively, which indicate that MB adsorption on UUC is a physical one, while that on AMUC corresponds to a physicochemical sorption process rather than a purely physical or chemical one (**Table 4**). Similar result was also obtained on the sorption of MB on montmorillonite obtained from Turkey (*Fil et al. 2012*). It is clearly seen that despite the best fit presented by the PSO model which would have easily been concluded to be chemisorptions, the value of ΔH$^\circ$ showed no value within the chemisorptions range of 80-200 kJ mol^{-1} but rather a physical and physicochemical adsorption process. A more accurate deduction of the mechanism would be enhanced by considering desorption of the MB molecules already loaded on the adsorbents.

Desorption/ Adsorbent reuse

Ethanol and DW were used as eluents in this study because a good desorbing agent must be cheap, effective, and must not damage the adsorbent. Also, a previous study has showed ethanol to be very effective in desorption of MB molecules (*Sarici-Ozdemir 2012*). Furthermore, in order to clarify the physical or chemical mechanism of the adsorption process, it should be understood that if a reasonable amount of the adsorbate is desorbed by the use of DW only, the process is more likely a physisorption and high percentage desorption would be achieved by the use of a strong eluent. However, for chemisorptions an

Figure 6. Effect of temperature on the adsorption of methylene blue on the adsorbents.

insignificant or negligible amount of the adsorbate would be desorbed using DW alone and desorption can only be significantly achieved using strong eluents. This is due to the greater binding force between the adsorbate and adsorbent in chemisorptions than physisorption. From the results of desorption of MB from UUC and AMUC, using DW only, a desorption of 34% and 25% were obtained while higher amounts of 79.3% and 71% were achieved using ethanol. This result supported and further clarified that the adsorption of MB molecules on the adsorbents were based on physisorption mechanism despite the good fit obtained from the PSO model. Again the lower desorption from AMUC accounted for the physicochemical process stated earlier. Therefore, in the case of discrepancy in the classification of adsorption mechanism as physisorptions or chemisorptions arising from the PSO and enthalpy changes, clarity could be achieved by considering the desorption process. The higher percentage desorption of MB from UUC than AMUC could be attributed to the lower ΔH° value of the former.

It was observed that after the initial adsorption before desorption, a steady decrease in the percentage adsorption of MB on the adsorbents after each cycle was recorded (**Figure 7**). This decrease was due to the progressive weight loss of the adsorbents during washing after each cycle of experiment and the inability of all adsorbed MB to be removed from the active sites of the adsorbents during desorption. This led to a decrease in the number of active sites available for MB sorption after each cycle of experiment. However, the result proved the reusability of both adsorbents in the sorption of MB in which effective washing techniques could be developed to reduce the weight loss thereby increasing the adsorption potential during reuse.
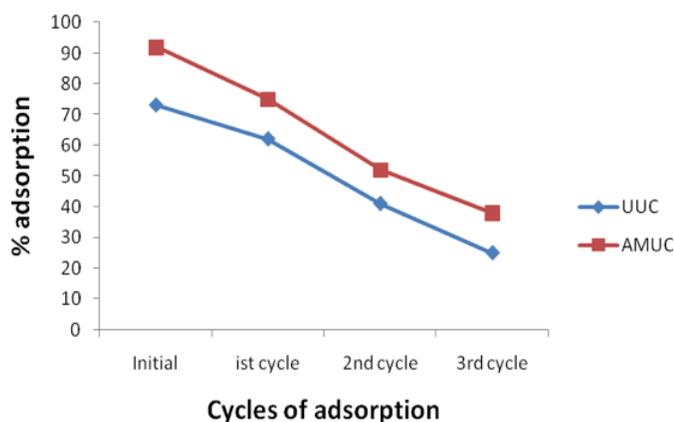

Figure 7. Percentage adsorption of methylene blue by the adsorbents after three cycles of desorption/adsorption experiments.

CONCLUSIONS AND RECOMMENDATIONS

The montmorillonite as an adsorbent of Nigerian origin was found to have good adsorption potential for methylene blue from solution. Acid modification of the clay enhanced further its adsorption capacity for MB. Interestingly, the adsorbents used in this study were found to have better adsorption potentials than most adsorbents in literature and can be utilized as effective low cost adsorbents to solve the problem of dye pollution of wastewaters from industries.

It is highly recommended to use the abundance of montmorillonite clay present in Nigeria for removal of toxic methylene blue from contaminated effluents in order to reduce the harmful effect on the environment and solve the problem of high cost activated carbon adsorbents.

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