Enhancing adsorption capacity of clay and application in dye removal from waste water

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ABSTRACT

Natural clay has been considered as a potential absorbent for removing pollutants from water and waste water. Nonetheless, the effective application of clay for water treatment is limited due to small surface area and presence of net negative surface charge, leading to it low adsorption capacity. The absorption capacity was boosted via intercalation of CaO derived from snail shell (SS). The methylene blue sorption potential, PZC, and the surface area of unmodified clay sample were substantially enhanced by the intercalation process. The process of sorption of MB from solution was analyzed using five different isotherm models (Langmuir, Freundlich, Temkin, Harkins-Jura, and Halsey isotherm equations). The value of the Langmuir monolayer sorption capacity q_m (mg/g) increased from 50.12 to 88.71, PZC values increased from 4.50 to 7.40, and the surface area (m^2/g) value increased from 27 m^2/g to 123 m^2/g after the intercalation process. The experimental data were fitted into two kinetic models: Lagergren pseudo-first order and the chemisorptions pseudo-second order. It was observed that chemisorptions pseudo-second order kinetic model described the sorption process with high coefficients of determination (r2) better than pseudo first other kinetic models. The modification caused no change in the clay surficial microstructure but increased the lattice spacing of the clay framework.

Keywords: Snail shell; Methylene blue; Natural clay; Langmuir; Freundlich; Temkin; Halsey and Harkins-Jura isotherm equations

1. INTRODUCTION

The recent leap in industrial and technological advancement at a global pedestal brought with it the introduction of pollutants of diverse nature into water bodies. Dyes and organic compounds are among such pollutants. These organic-based contaminants are either oxidized to simple nontoxic substances or are degraded to give obnoxious and non biodegradable products. Dyes are chemical compounds that absorb certain wavelength of light and reflect others, which account for the highly colored nature of wastewaters from industries that use dyes in their operations. Color interferes with the transmission of light into water bodies, thereby retarding photosynthesis and a possible disruption of the food chain in the ecosystem.

Some dyes have been found to act as substrate for metal ions and may import contamination by heavy metals [1]. It has also been reported that many dyes and pigments have toxic as well as carcinogenic, mutagenic, and tetratogenic effects on aquatic life as well as humans [2,3]. The removal of dyes and organics in an economic fashion remains an important problem, although a number of successive systems have been developed with the adsorption technique [4]. Adsorption has been found to be superior to most other wastewater treatment techniques in terms of initial cost, simplicity of design, ease of operation, and insensitivity to toxic substances [5]. Adsorption, as a wastewater treatment process, exploits the ability of some solids to concentrate certain substances to form a solution onto their surface. Activated carbon has been the most favored sorbent in the adsorption process but the high cost and tedious procedure for its preparation and regeneration has engendered the search for low-cost potential sorbents. In the search for potential low-cost sorbents for pollutant attenuation in an aqueous medium, a number of materials have been investigated for their ability for pollutant attenuation. Amongst them are peat, [6] bark and woodchips, [7] lignite, [8] industrial waste, [9-12] and fortified.

In recent time, interest in the use of biosorbents, as inexpensive sorbents, has continued to grow and their potentiality is being extensively investigated. Biosorbents of plant origin are mainly cellulosic in nature. The unique ability of these cellulosic sorbents to bind pollutants has been attributed to the presence of various polar functional groups, which can attract and sequester the ionized pollutants. Batch adsorption studies have been the conventional method of assessing the sorption capacity of low-cost, nonconventional sorbents in the removal of pollutants. Batch adsorption experiments are used easily in the laboratory for the treatment of a small volume of effluents, but are less convenient to use on an industrial scale, where large volumes of wastewater are continuously generated.

Industrial utilization of sorbents screened using batch adsorption studies usually involves fixed bed sorption. In fixed bed, the sorbate is continuously in contact with a given quantity of fresh sorbent, thus providing the required concentration gradient between sorbent and sorbate for sorption. Fixed-bed sorption of pollutants involves percolation of wastewater through one type or another of percolator material. During the transit of the wastewater through the percolator, the wastewater is purified by a physicochemical process. Natural clay minerals are low-cost materials due to their abundance in most continents of the world and possess a layered structure which can act as host materials with high sorption properties. Although clays themselves possess the high adsorption capabilities, the modification of their structure can successfully improve their capabilities [13].

The shell of African land snail (SS) is being proposed to be used as a precursor for the derivation of the CaO to be used for the intercalation because of the chemical and mineralogical assemblage. SS has the same basic construction as other Molluscan shells and consists three layers whose basic building block is aragonite [14-15]. In the present study, naturally occurring tropical clay was modified by intercalation of CaO derived from the shell of African land snail (Achatina achatina), and characterized.

The ability of the modified clay was tested against unmodified clay in methylene blue removal from aqua system in a batch adsorption process. Sorption process data were obtained via equilibrium isotherm analysis and kinetic studies. Process variables were optimized by method of continuous variations and the effects of the sorbate uptake on the sorbent surface microstructure and crystalline were investigated via SEM and XRD analysis of the spent and virgin sorbents.

2. MATERIALS AND METHODS

2. 1. Snail shell preparation

The snail shell was washed thoroughly in tap water before drying in the oven between 103-105 °C. It was then crushed with the aid of mortar and pestle and ground using laboratory grinding machine. The snail shell was finally sieved using standard sieve of known mesh size (100 µm).

2. 2. Sorbent Modification and Characterization

The natural clay used for this study was obtained from Agbede, Etsako L.G. Area, Edo State. The clay was modified with CaO derived from snail shell as described by [16] (Figure 1) thus: 20 g of clay, previously sieved with a standard laboratory sieve of 425 µ was dispersed in 300 ml of 2.0M NaOH and the temperature of the reaction mixture was maintained at 90 °C for 4 hours. Calcium chloride ($CaCl_2$) was prepared from snail shell by dispersing 20 g of snail shell into a (9:1) H_2O: HCl. The base activated clay was dispersed into 150 ml of $CaCl_2$ aqueous solution prepared from snail shell. The whole mixture was stirred and allowed to stand for 24 hours. The settled mixture was decanted and 300 ml of 0.1 M NaOH aqueous solution was added slowly to the residue and left for some hours to settle.
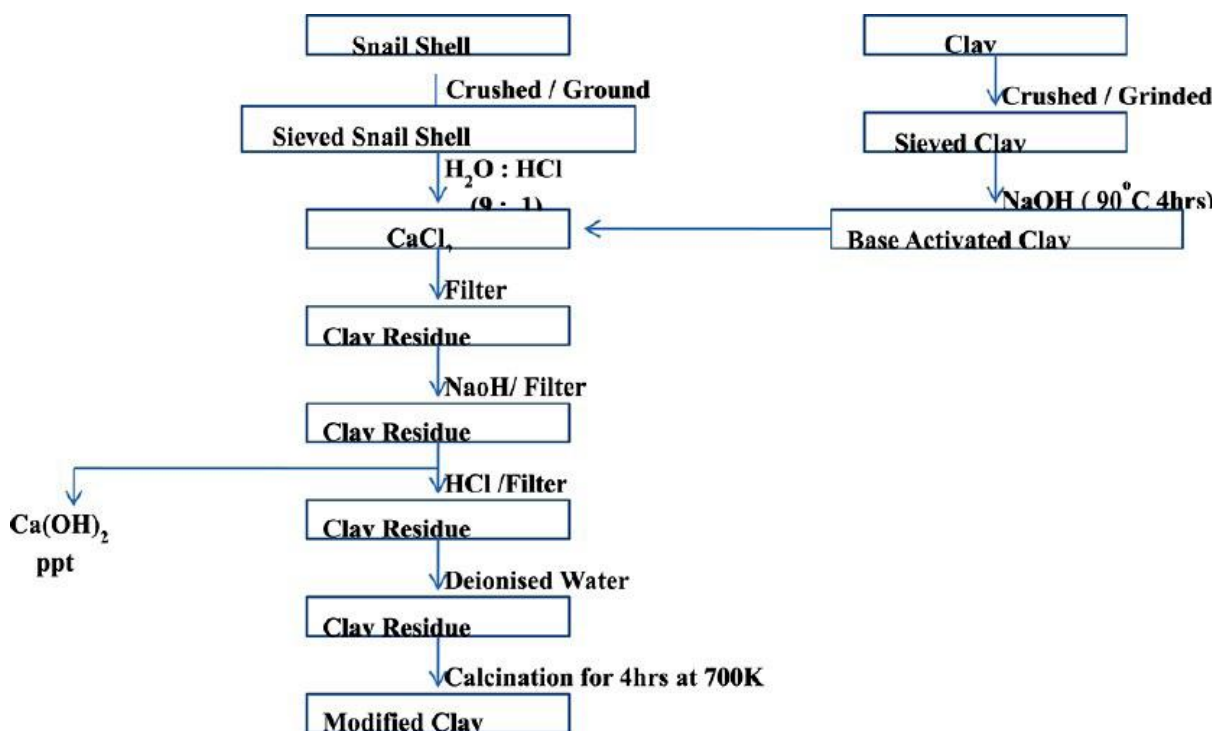

Figure 1. Flow chart for clay modification.

The filtrate of the settled mixture was decanted and the obtained powder was rinsed with 0.01 M HCl aqueous solution which removed the excess calcium hydroxide ($Ca(OH)_2$) precipitated on the outer surface of the clay. After settling the filtrate was decanted away and

the residue was further washed with deionized water until the filtrate is neutral to litmus paper. Then the sample was calcined for 4 hours in the muffles furnace at a temperature of 700 K.

The CaO modified (CIC) and unmodified natural (UNC) clay samples were characterized thus: specific surface area was determined using the method of [17] the point zero charge (PZC) was determined by solid addition method [18], the surface microstructure was determined by scanning electron microscope and the crystalline was determined by X-ray diffract gram.

2. 3. Sorbate Preparation

MB ($C_{16}H_{18}CN_3S$), the model basic dye, used in the present study is a monovalent cationic dye. It is classified in dye classification as C.I Basic Blue 9; C.I. Solvent blue 8; C.I.52015. It has a molecular weight of 373.90. A stock solution of 1000 mg/l of MB was prepared by dissolving an appropriate quantity of MB in a 1 dm^3 of deionized water. The working solution was prepared by diluting the stock solution with deionized water to give the appropriate concentration of the working solutions. The concentration of the dye was measured using UV–visible spectrophotometer at a wavelength corresponding to the maximum absorbance for the dye solution (λmax = 661 nm).

2. 4. Dye Quantification.

The MB concentrations in the aqueous solutions were quantified by the determination of the absorbance at the characteristic wavelength using a double beam UV/visible spectrophotometer. Standard solutions of the dye were taken, and the absorbances were determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to the maximum absorbance (λmax) 661 nm, as determined from this plot, was noted and the wavelength was used for the preparation of the calibration curve used in the present studies.

2. 5. Sorption Isotherm Studies

The sorption isotherm capacity was investigated by contacting 0.1 g of the modified and unmodified clay with 50ml of the working solution of varying concentrations (25, 50, 100, 150, 200 and 300 mg/L) and agitated for a period of two hours using magnetic stirrer. The experiment was conducted at ambient temperature and agitation speed of 200 rpm. The residual MB in the aqueous medium was determined using a UV/visible spectrophotometer. The amount of MB sorbed per unit mass of the clay (q in mg/g) was calculated using the mass balance procedure:

$$q_t = \frac{V(C_o - C_f)}{M}$$

where q_t is the amount of sorbate sorbed per gram (g) of adsorbent (mg/g), C_o is the initial concentration of MB (mg/l), C_f is the final residual MB concentration (mg/l), and m is the mass of clay (mg).

2. 6. Kinetic Sorption Process

The kinetics of the sorption of MB on clay were studied by carrying out a set of sorption experiments in which the effects of initial sorbate concentration were studied at constant temperature, and monitoring the amount of dye sorbed over time.

The effects of initial concentration on the kinetics of the sorption process were investigated at different initial MB concentrations ((25, 50, 100, 150, 200 and 300 mg/L) and constant agitation speed (200 rpm) in a thermostatic water bath at fixed time intervals (5, 10, 20, 30, 60, 90, 120, 180 and 240 min).

The residual MB in the aqueous medium was determined over time using a UV/visible spectrophotometer at the λ_{max} of the dye.

3. RESULTS AND DISCUSSIONS

The CaO modification of the clay framework produced a material (CIC) whose PZC value (7.40) was greater than that of the unmodified clay (UNC) (4.50). Values of PZC that ranged between 3.0 and 7.5 have been reported for kaolinite [19,20]. The estimated PZC values of 4.50 and 7.40 for both UNC and CIC are within the range of values reported in literature for kaolinite samples.

The higher value of the PZC obtained for the CIC could be ascribed to the presence of the CaO, within the clay framework, which possibly modified the surface charge of the clay. The results of the specific surface area of the UNC and CIC showed that the CIC had higher specific surface area (123 m^2/g) than that of the UNC (27 m^2/g). The higher specific surface area of the CIC could be ascribed to the CaO modification of the clay which opened up the silicate layers and the pores.

The results of the SEM analysis of the UNC and CIC are presented in Figure 2 **a** and **b**. Both samples are made up of discrete particles of irregular size and shape and no distinct transformation in the surficial microstructure of the CIC could be deciphered. The XRD analysis of the UNC showed that the material is crystalline and some prominent peaks (degree) synonymous with kaolinite 12.46, 20.12, 24.99, 35.15, 36.03, 36.96, 37.85, 38.66, 40.99, 45.79, 54.62, and 55.12 were identified (Figure 3 **a** and **b**).

The CIC retained some of the prominent kaolin peaks but more peaks were introduced between the 2θ values of 20° and 30° and a slight increase in the basal spacing (>3 nm) of the lattice structure was observed. In the UNC, the d-spacing of the different 2θ values were mainly below 3 nm. The new found peaks and the broad increase in the d-spacing values were ascribed to the intercalation of the CaO in the CIC.

The ionic radius of Ca^{2+} is 0.99 Å, whereas the single bond covalent radius of Ca^{2+} is 1.74 Å. Consequently, the hydrated form of the Ca−O bond length is 1.74 Å for the case of $(Ca(OH_2))$. The smaller size of Ca^{2+} can in principle explain the minimal increase in the basal spacing. Reduction in phyllosilicate basal spacing by addition of Fe^{3+} has been reported by [16] who attributed this effect to strong attractive forces between iron and the silicate sheets of montmorillonite.
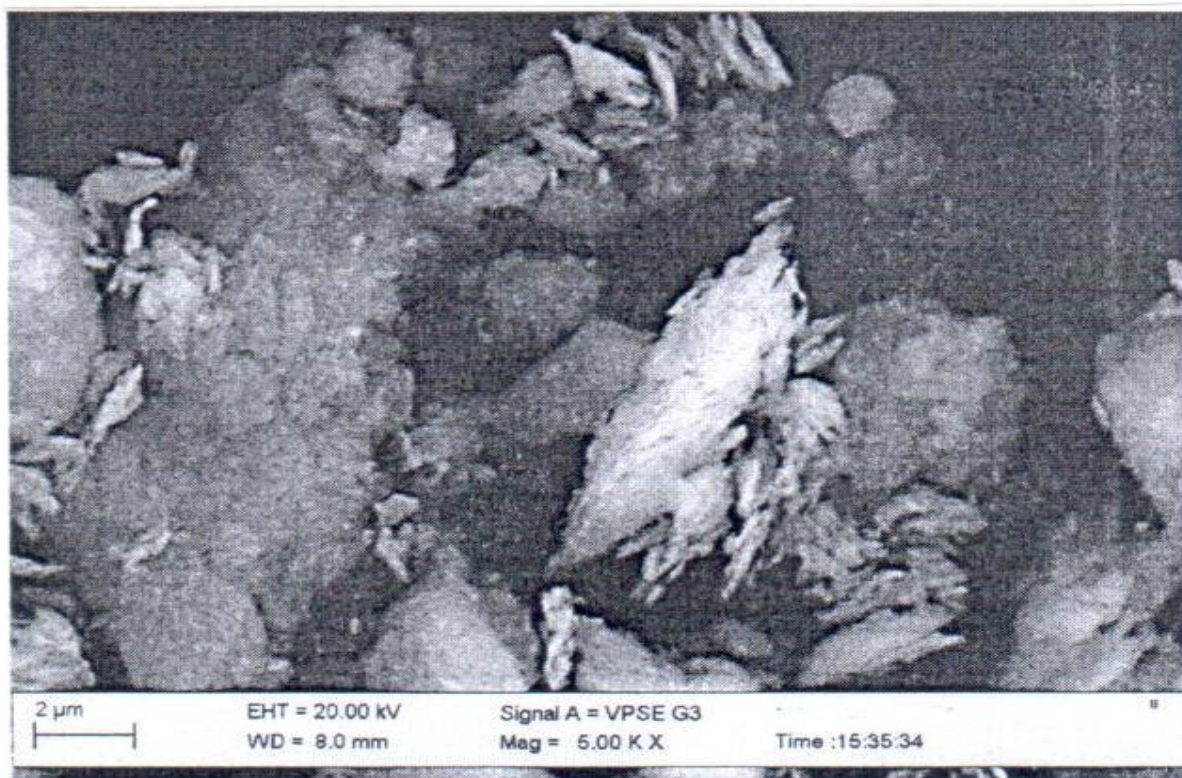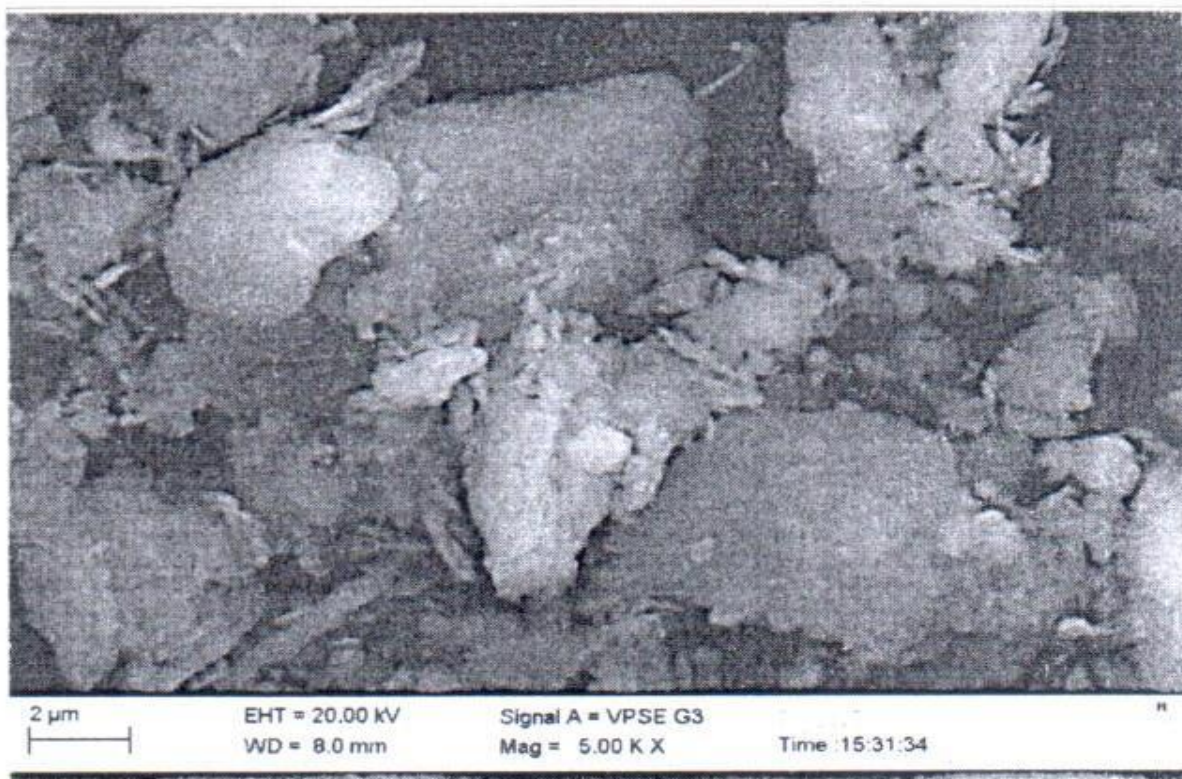
Fig. 2a. Result of SEM analysis of unmodified clay.
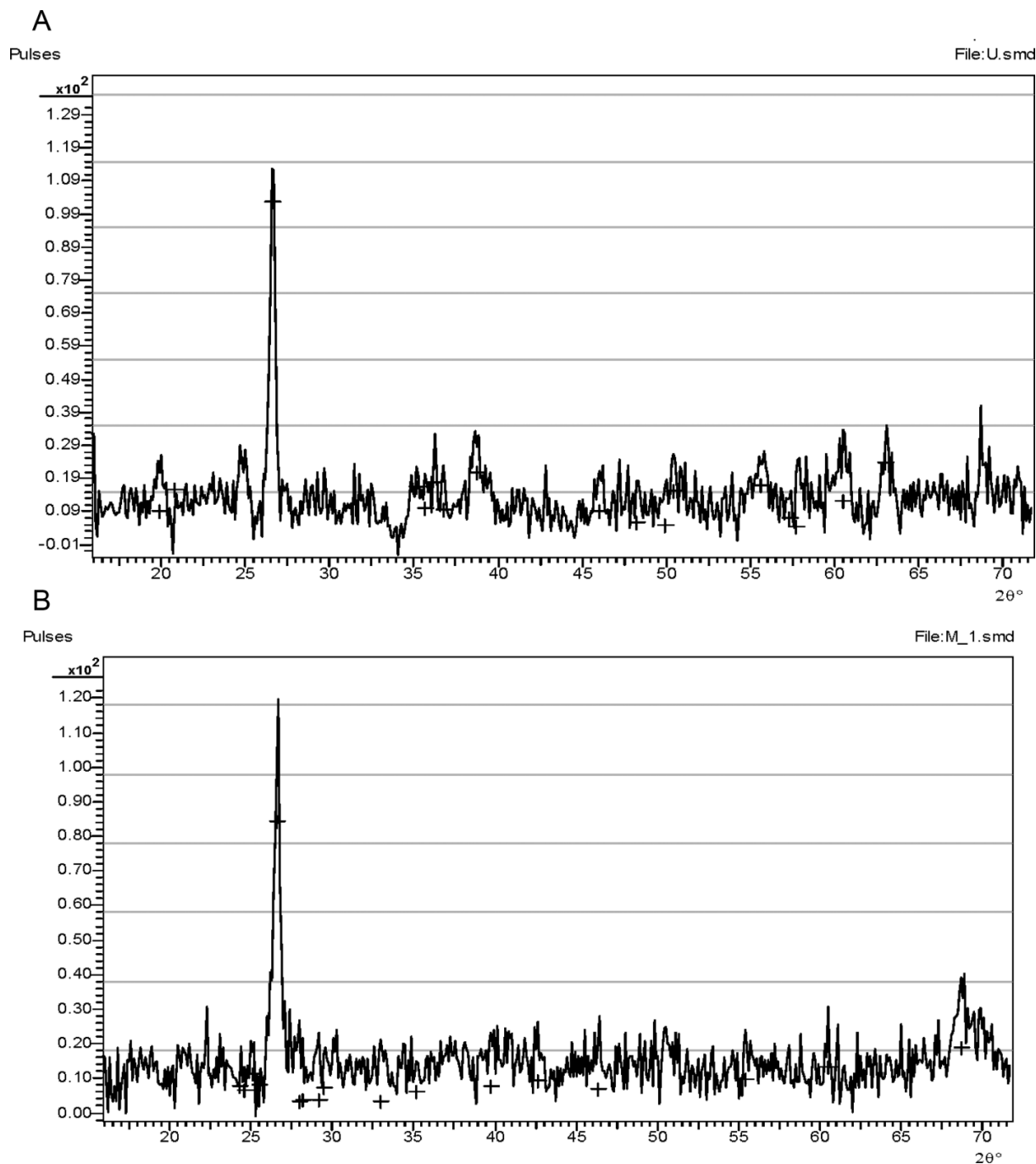

Fig. 2b. Result of SEM analysis of modified clay.

Figure 3. (**a**) XRD analysis of the UNC, (**b**) XRD analysis of the CIC.

3. 1. Equilibrium isotherm studies

The equilibrium relationship between the concentration of the MB in the fluid phase and the MB in the clay at a given temperature was studied. The results obtained were analyzed using 5 different isotherm equations (i.e. Langmuir, Freundlich, Temkin, Halsey and Harkins–Jura isotherm equations). In order to understand the mechanism of MB adsorption on clay, the experimental data were fitted to the aforementioned equilibrium isotherm equations and the different isotherm parameters, obtained from the different plots, are presented in Table 1 and

2. An error function is required to evaluate the fitness of each isotherm equation to the experimental data obtained from the optimization process employed. In the present study the linear coefficient of determinations, r^2, was used. The values of the linear correlation, r^2, of each isotherm equation, when fitted to the experimental data obtained from the sorption of MB by modified and unmodified clay are presented in Table 2 **a** and **b**. The highest values of r^2 were obtained when the experimental data were fitted into Freundlich and Halsey isotherm equations (0.999) for modified clay while unmodified clay are 0.971 and 0.987. The description of the sorption of MB on clay by the Freundlich isotherm equations is a pointer to the heterogeneity of the surface with a non-uniform distribution of heat of adsorption over the surface of the clay, while the Halsey isotherm fitting is an indication of the heteroporosity of the surface and the multilayer adsorption nature of the MB on clay.

Table 1. Equilibrium Isotherm Parameters of sorption of MB on modified clay.

Langmuir Isotherm parameters			Freundlich Isotherm parameters			Temkin Isotherm	Harkins-Jura Isotherm	Halsey Isotherm
q_m (mg/g)	K_L(1/mg)	r^2	K_f (1/g)	1/n	r^2	$B_1 = 9.878$ K_T(1/mg)=31.84 $r^2 = 0.8567$	A=11.72 B=0.62 r^2=0.7629	N=1.3752 K=163.5 r^2=0.999
88.71	1.4523	0.8352	60.75	0.9788	0.999			

Table 2. Equilibrium Isotherm Parameters of sorption of MB on unmodified clay.

Langmuir Isotherm parameters			Freundlich Isotherm parameters			Temkin Isotherm	Harkins-Jura Isotherm	Halsey Isotherm
q_m (mg/g)	K_L(1/mg)	r^2	Kf (1/g)	1/n	r^2	$B_1 = 8.845$ K_T(1/mg)=37.79 $r^2 = 0.8156$	A=10.65 B=0.61 r^2=0.7532	n=0.9863 K=146.6 r^2=0.987
50.12	0.9674	0.8116	32.51	1.3572	0.971			

The maximum adsorption value, qm(mg/g), obtained in the present study was compared with those of other sorbents for MB adsorption (Table 3). The results of this comparison showed that clay has great potential as a sorbent for MB adsorption in water systems and can compete favourably with other sorbents that have been studied by other researchers.

Table 3. Comparison of the Langmuir sorption capacity (qm in mg/g) of different sorbents for MB.

Adsorbents	q_m (mg/g)	References
Unmodified clay	50.12	Present Study
Modified clay	88.71	Present study
RSS	82.64	Oladoja et al, 2008
Cereal chaff	20.30	Han et al., 2006
Rice husk	40.60	Vadivelan and Kumar, 2005

Mansonia sawdust	28.89	Ofomaja, 2008
Castor seed shell	158.73	Oladoja et al., 2008
Raw beech sawdust	9.78	Batzias and Sidiras, 2004

3. 2. Kinetics of the sorption process

Initial sorbate concentration: The initial methylene blue concentration was studied to observe if the initial concentration of sorbate would have an influence on the sorption process. In the range of MB concentration studied, the uptake of the MB was rapid in the first 2 min. The rapid uptake then gave way to a much slower adsorption, which became constant at 30 min (Figure 4 and 5).

This initial rapid uptake can be attributed to the concentration gradient created at the start of the adsorption process between solute concentration in solution and that at the clay surface. As the dye loading increases this gradient reduces and gives way to slower uptake. The kinetic studies of a sorption process are paramount because the data obtained from such studies are necessary to understand the variables that influence the sorption of solutes.

The results can also be used to determine the equilibrium time and the rate of adsorption can be used to develop predictive models for column experiments. Owing to these facts, Lagergren pseudo-first order and the chemisorptions pseudo-second order [6] were employed to study the concentration-time profile features of the sorption processes.
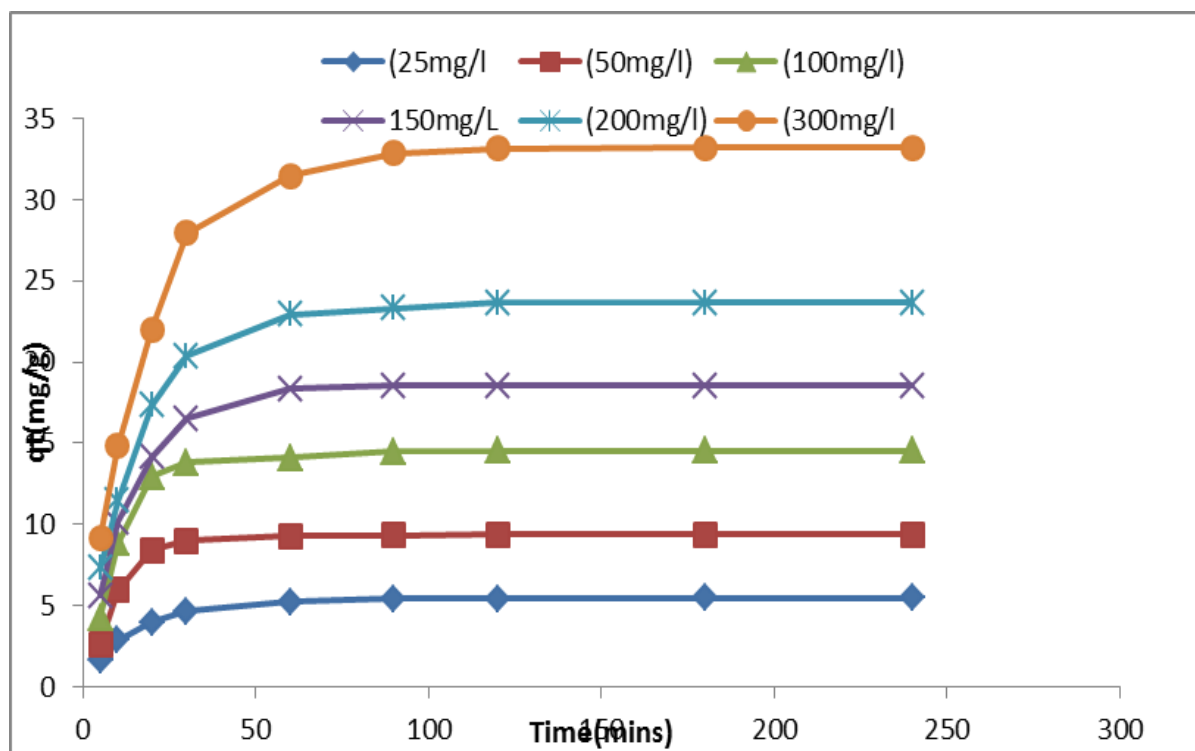

Figure 4. Time variation of MB sorption on unmodified clay at different initial MB concentrations.
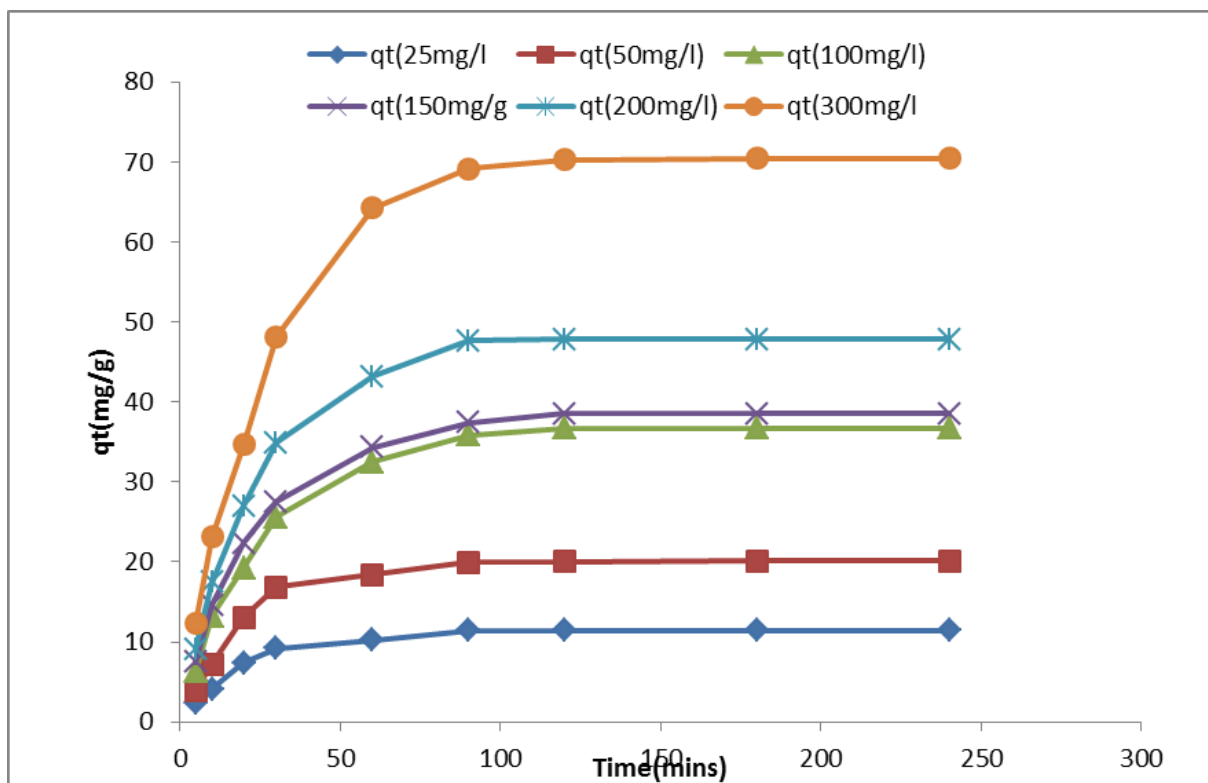
Figure 5. Time variation of MB sorption on modified clay at different initial MB concentrations.
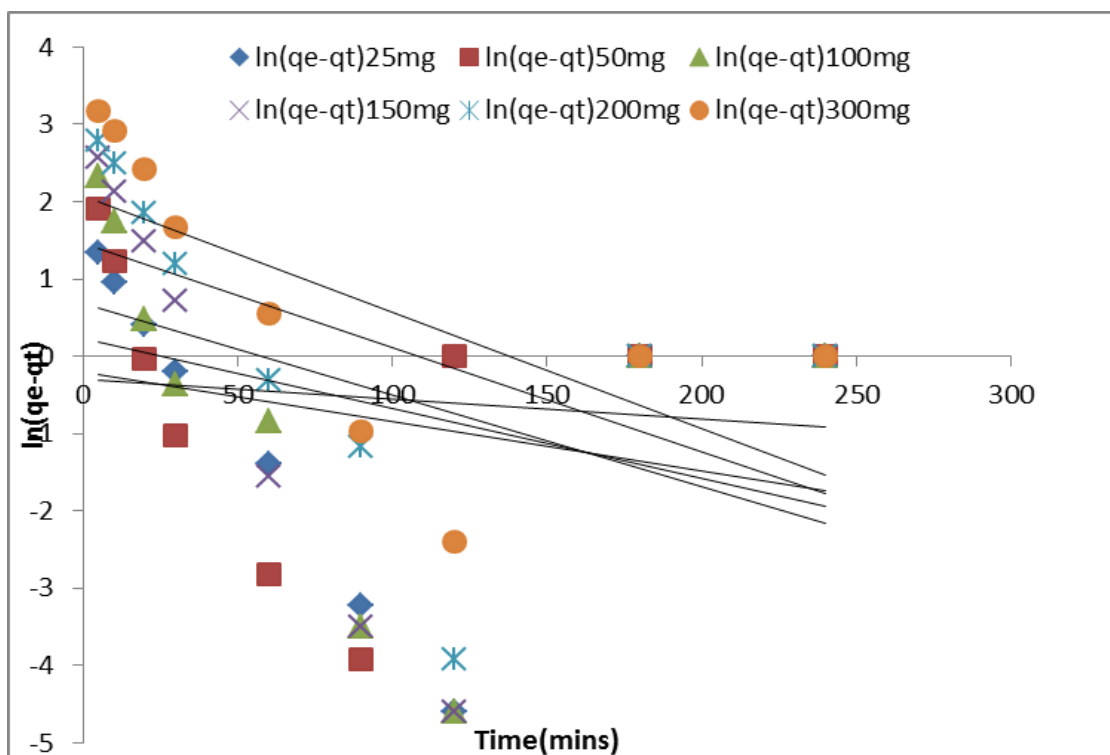

Figure 6. Pseudo-first order plot of sorption of MB on unmodified clay at varying initial MB concentrations.
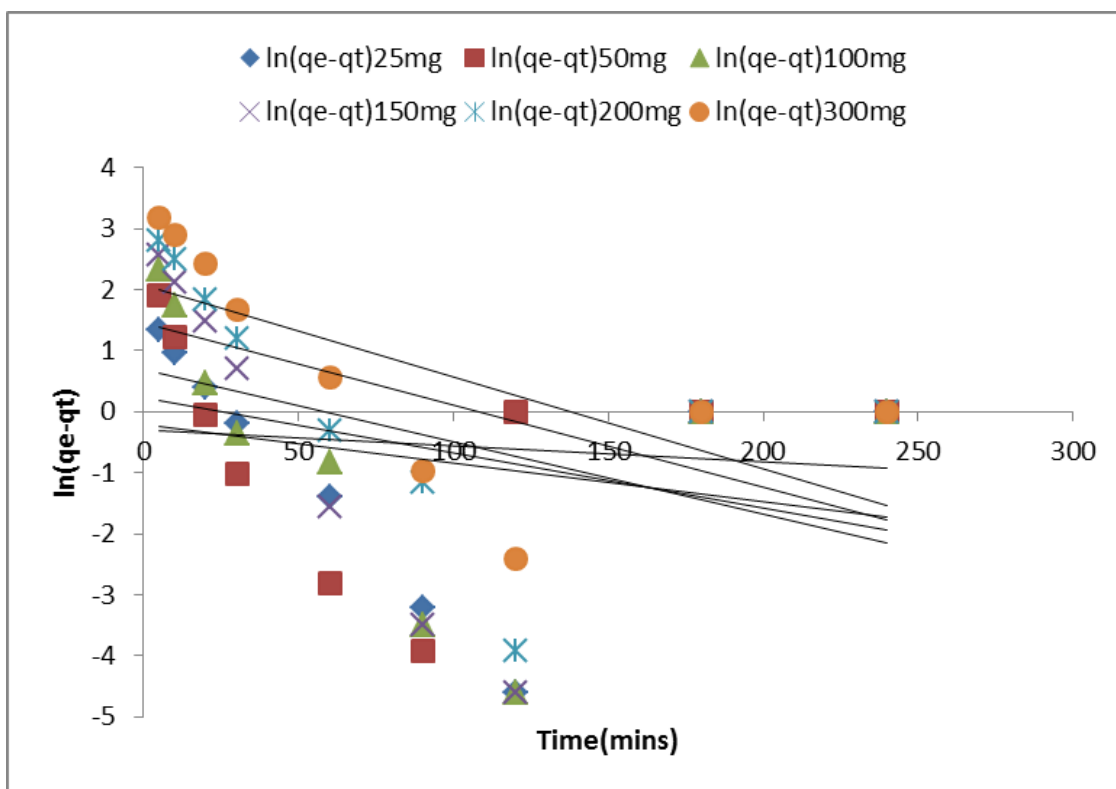
Figure 7. Pseudo-first order plot of sorption of MB on modified clay at varying initial MB concentrations.

The results presented in Figure 6 and 7 were obtained when the data obtained from the sorption experiment were analyzed with the Lagergren pseudo-first order kinetic model. The values of ln(qe-qt) were plotted against time. The linearity of the plots was not very high for both unmodified and modified clay (unmodified clay $r^2 = 0.014 – 0.436$ while modified clay $r^2 = 0.560 – 0.654$). The first order rate constant for unmodified clay ranged between 7.0×10^{-3} and 16.0×10^{-3} while that of modified clay ranged between 9.0×10^{-3} and 29.0×10^{-3}. Owing to the low linearity of the plots obtained from this study the chemisorptions pseudo second order kinetic model was also used to test the data obtained from the same studies.

The pseudo-second order kinetic model considers the rate-limiting step as the formation of a chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent. In contrast to the other kinetic models, it predicts the behaviour over the whole range of studies supporting a pseudo-second order equation and is in agreement with chemisorptions being the rate controlling step [6]. The plot of t/qt against t for both modified and unmodified clay (Figure 8 and 9) yields very good straight lines. An inverse relationship was observed in the values of the overall pseudo-second order reaction rate (k_2) and initial MB concentration, while a direct relationship was noted between the initial reaction rate (h) and initial MB concentration. The initial sorption rate constant (h) was greatly affected by the increase in the initial concentration of MB (Table 5).

This was consistent with the observations reported by [19] for the biosorption of basic dyes by water hyacinth roots and H. verticillta [15] for basic dye biosorption by giant duckweed (Spirodella polyrrhiza). It was noted that variation in the initial concentration of MB did not affect the time in which equilibrium was attained.
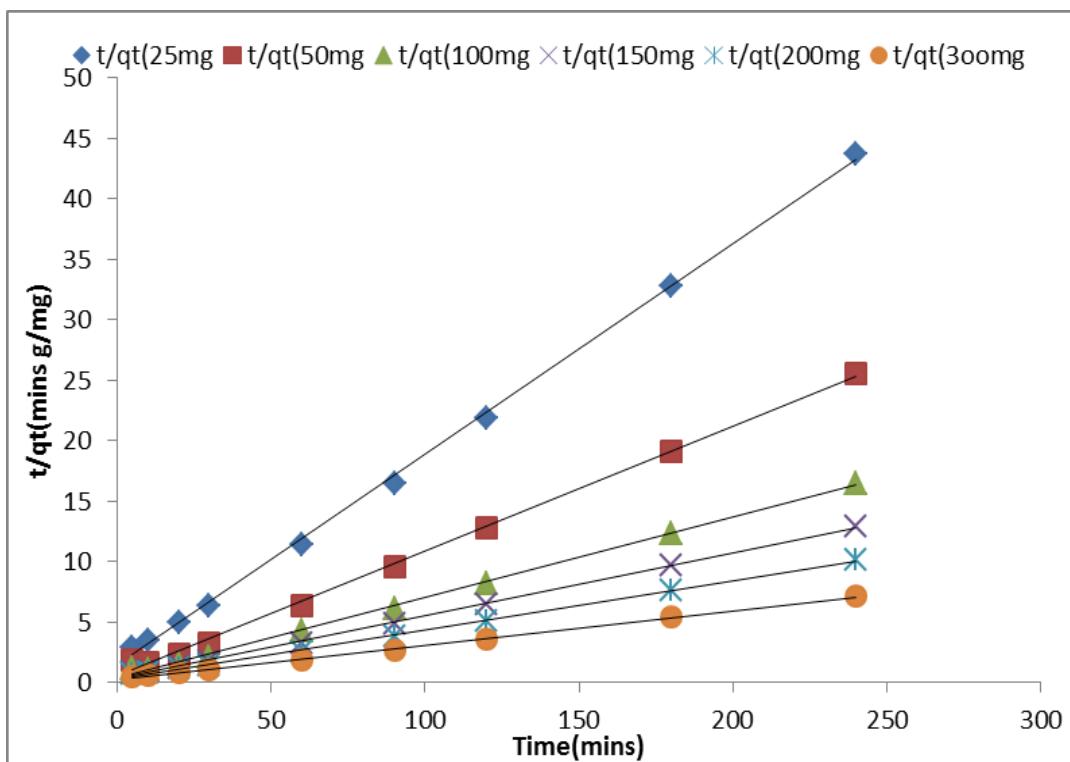
Figure 8. Pseudo-second order plot of sorption of MB on unmodified clay at varying initial MB concentrations.
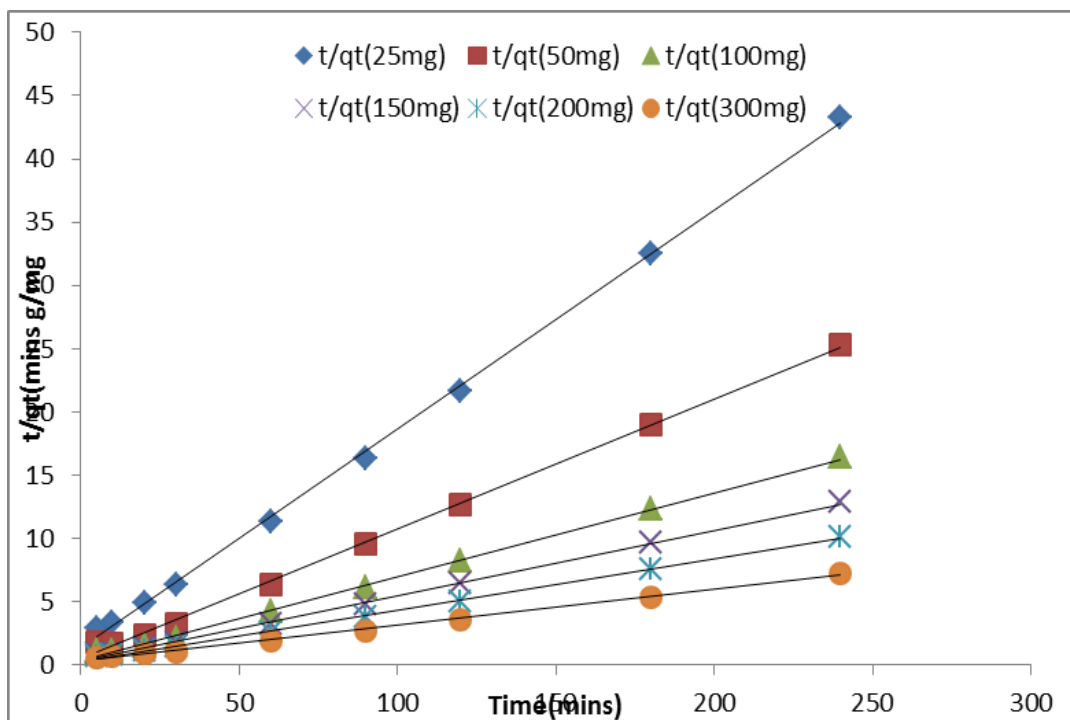

Figure 9. Pseudo-second order plot of sorption of MB on modified clay at varying initial MB concentrations.

The rapid uptake of dye indicates that the sorption process could be ion exchange in nature, where the cationic dye molecules bind with the various negatively charged organic functional groups present on the surface of the aquatic plants. Based on the results obtained from the analysis of the sorption data with pseudo second order kinetic model it can be suggested that the pseudo-second order kinetic model described the sorption of MB on both unmodified and modified clay better.

Table 4. Pseudo First Order Kinetic Parameters of the Sorption of MB by Unmodified and Modified Clay at Different Initial MB Concentration.

Initial conc. Mg/l	Unmodified clay				Modified clay			
	q_{exp}	q_{cal}	K_1	r^2	q_{exp}	q_{cal}	K_1	r^2
25	6.46	0.9082	0.007	0.070	21.43	5.225	0.009	0.560
50	10.37	0.8588	0.003	0..014	30.12	17.895	0.018	0.560
100	15.54	1.3586	0.009	0.111	46.74	17.895	0.018	0.560
150	18.23	2.4451	0.008	0.157	49.81	17.895	0.018	0.560
200	24.65	4.103	0.014	0.283	57.84	17.895	0.018	0.560
300	34.22	8.1125	0.016	0.436	80.45	35.158	0.029	0.654

Table 5. Pseudo Second Order Kinetic Parameters of the Sorption of MB by Unmodified and Modified Clay at Different Initial MB Concentration.

Initial conc. (mg/l)	Unmodified clay					Modified clay				
	q_{exp}	q_{cal}	K_2	H	r^2	q_{exp}	q_{cal}	K_2	h	r^2
25	6.46	6.73	0.0333	0.7947	0.997	21.43	13.5	0.0067	0.8447	0.999
50	10.37	10.709	0.0311	1.9526	0.997	30.12	23.22	0.0043	1.4359	0.998
100	15.54	16.152	0.0230	2.2255	0.996	46.74	42.667	0.0025	2.1247	0.998
150	18.23	21.032	0.0112	2.6327	0.997	49.81	45.752	0.0022	2.2352	0.998
200	24.65	28.027	0.0048	2.8273	0.995	57.84	53.632	0.0021	3.3041	0.994
300	34.22	36.714	0.0045	3.9626	0.997	80.45	84.333	0.0018	4.0606	0.998

3. 3. Determination of sorption mechanism by instrumental analysis

3. 3. 1. SEM analysis of spent sorbents

Comparison of the SEM image of both the virgin and spent sorbent (Fig. 10 and 11) showed that the uptake of phosphate by both sorbents caused no change in the surficial microstructure.
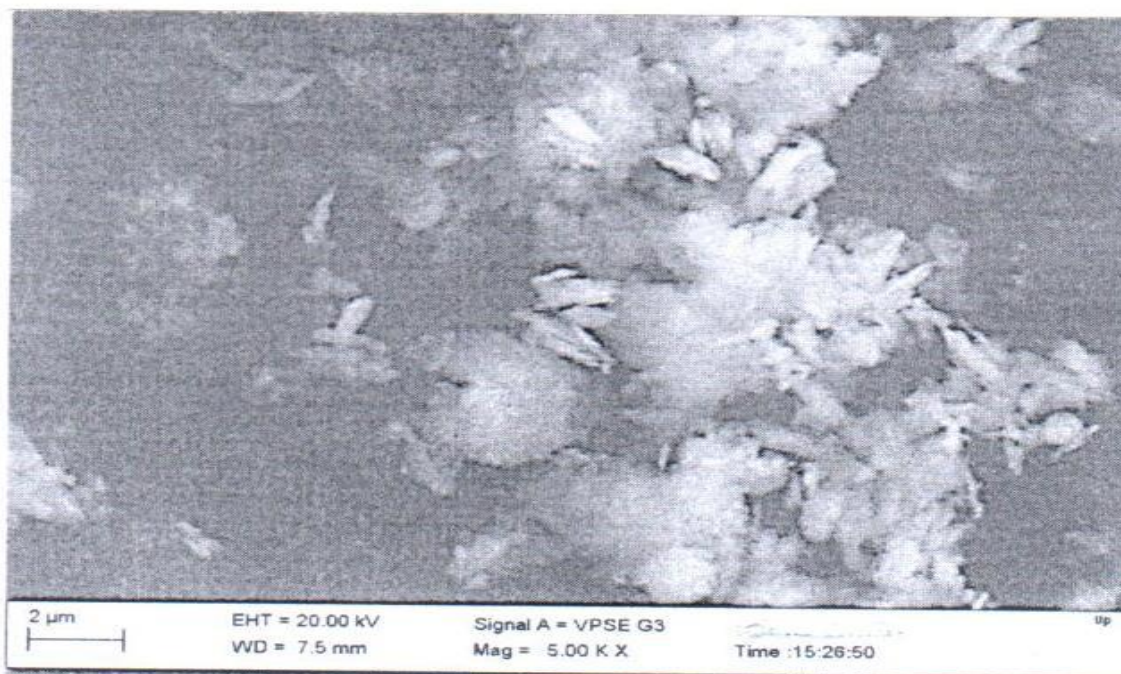

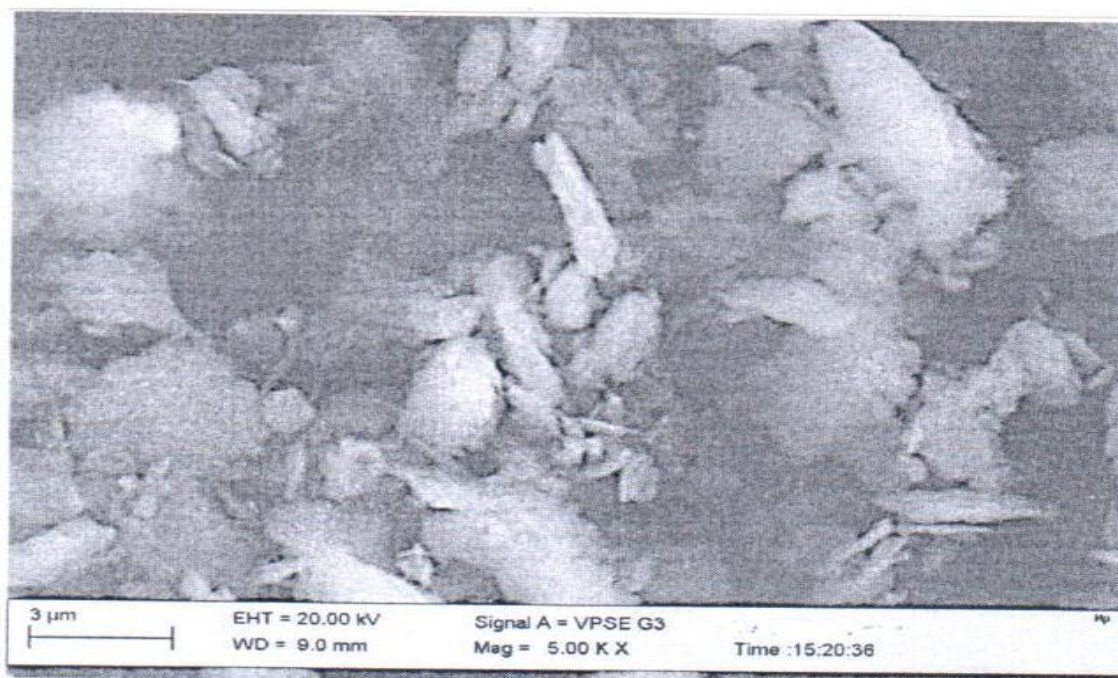**Fig. 10.** Result of SEM analysis of MB laden unmodified clay.

Fig. 11. Result of SEM analysis of MB laden modified clay.

3. 3. 2. XRD analysis of the spent sorbents

The XRD patterns of the virgin and phosphate laden sorbent (i.e. unmodified and modified clay) after phosphate uptake are compared in Fig. 12 **a** and **b**. The difference in crystallinity between the virgin and phosphate laden sorbent is pronounced. While the virgin sorbents exhibited fine and intense peaks characteristic of a crystallized material, the phosphate laden samples displayed poorly crystalline state with ill-defined peaks, especially in the unmodified sample. The lower crystallinity of phosphate laden sorbents could be ascribed to the surface complexation of phosphate moieties on the sorbents. Some authors attributed the poorly crystalline state of anion exchanged Layered Double Hydroxides to a disturbance in the stacking sequence of the layers caused essentially by anions adsorbed on the surface [20].
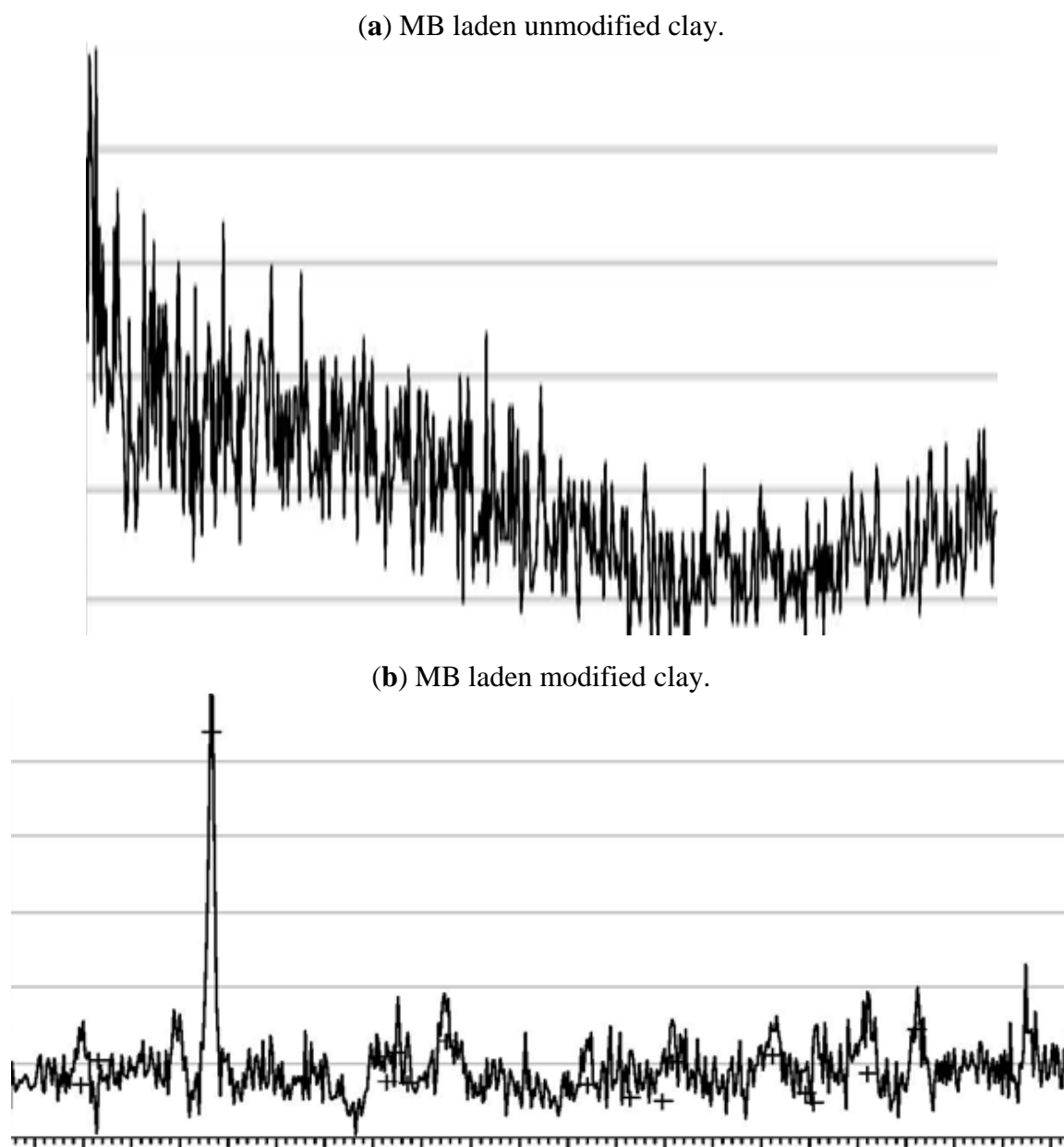
(**a**) MB laden unmodified clay.

(**b**) MB laden modified clay.

Fig. 12. Result of XRD analyis of MB laden unmodified clay and calcium intercalated clay.

4. CONCLUSIONS

The ability of unmodified and modified clay to abstract MB from aqueous solution was studied using equilibrium isotherm analysis. Langmuir, Freundlich, Temkin, Harkins-Jura, and Halsey isotherm equations were used to describe the sorption process. Freundlich and Halsey isotherm equations had the best correlations amongst all the isotherm equations used. This shows the heterogeneity of the surface of the clay and the multilayer adsorption nature of the MB on clay. The initial sorbate solution was found to affect the sorption process and the sorption process was found to follow the pseudo second order mechanism more than pseudo first order kinetic model.

The analysis of sorption mechanism by instrumental analysis (XRD and SEM) of both virgin and MB laden sorbents (unmodified and modified) revealed that MB sorption caused no change in the surficial microstructure of either sorbents but the crystallinity of the sorbents was considerably hindered due to the surface complexation of MB moieties on the sorbents.

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