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Effect of the pre-selection of particle size range on the treatment of locally-sourced bentonite clay using aqueous acid and alkali solution

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ABSTRACT

The effect of the pre-selection of particle size range on the treatment of locally-sourced bentonite clay from logomani, North-Eastern Nigeria using aqueous acid and alkali solution has been studied. Characterization of the clay adsorbents was done via Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction analyses (XRD). The acid and alkali modified clay adsorbents were applied in the removal of methylene blue from aqueous media. The highest adsorbed amount (51.196mg/g) which represents 91.421% for the HCl-treated clay was obtained with the clay particle size range of < 63µm treated with 0.5M HCl. While on the other hand, the lowest adsorbed amount of 24.726mg/g which represents 44.154% for the HCl-treated clay was obtained with the clay particle size range of 106-125µm treated with 2.5M HCl. A similar trend was also observed for the H_2SO_4-treated clay in which case the highest value of Q_t (42.636mg/g)which represents 76.137% was obtained with particle size range of < 63µm treated with 0.5M H_2SO_4 and the lowest value of Q_t (24.632mg/g) which represents 43.986% with particle size range of 106-125µm treated with 2.5M H_2SO_4. Generally, the values for amount adsorbed Q_t, obtained for the clays treated with alkali solutions were higher. The optimum adsorptive capacity for the alkali-treated clay was 52.190mg/g, which represents 93.196%. This was obtained with the clay treated with 0.5M NaOH and the lowest, 43.713mg/g, which represents 78.059% which was obtained with the particle size range of 106-125µm. In general, the values for amount adsorbed Qt, obtained for the clay samples for which particle size was pre-selected prior to treatment were greater than the values for the unselected clay.

Keywords: Bentonite, Acid, Alkali, Fourier Transform Infrared Spetroscopy (FTIR), X-ray Diffraction (XRD), Methylene blue

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INTRODUCTION

Natural clay minerals are well known to mankind right from the dawn of civilization. As a result of their low cost, abundance in many parts of the world, high sorption properties and ion exchange ability, clay materials are attractive candidates as adsorbents [16].

Clays have received considerable attention especially as potential adsorbents environmental pollution remediation processes. There is a wide distribution of clay deposits in Africa, especially, Nigeria [2, 7, 8, and 12].

Clays whose basic clay mineral is montmorillonite are generally called bentonites [9]. Bentonite is usually formed from weathering of volcanic ash, most often in the presence of water.

Bentonites may be used as adsorbents both naturally and after some physico-chemical treatments using aqueous solutions of acid and alkali, ion exchange and heating. In their natural state, bentonites generally show mediocre decolorizing effect, hence the need for some form of modification. The most common chemical modifications of bentonites, used for both industrial and scientific purposes, are acid and alkali treatment. This consists of the treatment of clay with a mineral acid solution, usually HCl or H_2SO_4, or with an alkali solution, usually NaOH or Na_2CO_3. The main task is to obtain partly dissolved material of increased specific surface area, porosity and surface acidity or alkalinity as the case may be [13].

Acid treated bentonites are widely used in various fields, for example catalysts, catalyst supports in the chemical industry, and a component of carbonless copying papers as well as detergent in paper industry. In fact, the important applications of them are purification, decolorization and stabilization of vegetable oils in term of market consumption. They are able to remove undesirable colors by decreasing the levels of chlorophyll, carotene and other color bodies, to reduce traces of phospholipids and soap and to minimize the increasing of free fatty acid during bleaching.

Sodium bentonite is an important product manufactured from natural bentonite by treatment with alkali solution [28]. Nowadays, the application of Na–bentonite has been developed for extreme chemical processes such as adsorption, catalytic applications, drilling fluids, ceramic bodies, and nano-structure polymers.

Most research efforts in the area of chemical treatment of bentonites have focused on the concentration of the aqueous solution, temperature and may be pH of the solution. There is paucity of information in literature on the role of particle size prior to treatment on the adsorptive capacity of the modified bentonite.

This work therefore seeks to investigate the role of particle size of the starting bentonite clay on the chemical treatment with aqueous acid (HCl and H_2SO_4) and alkali solutions (NaOH and Na_2CO_3) as well as optimize both particle size and concentration of the acid and base used in the study.

EXPERIMENTAL SECTION

The bentonite clay used throughout this study was obtained from local mining sites at Logomani in Borno State. Logomani is precisely located at longitude 14° 01´E and latitude 12° 11´N in Dikwa Local Government Area. The clay was milled with Automatic milling machine and sieved with the various Endecotts Laboratory test sieves on Omron No 17748 (manual timer) sieve shaker.

Pretreatment of the raw bentonite

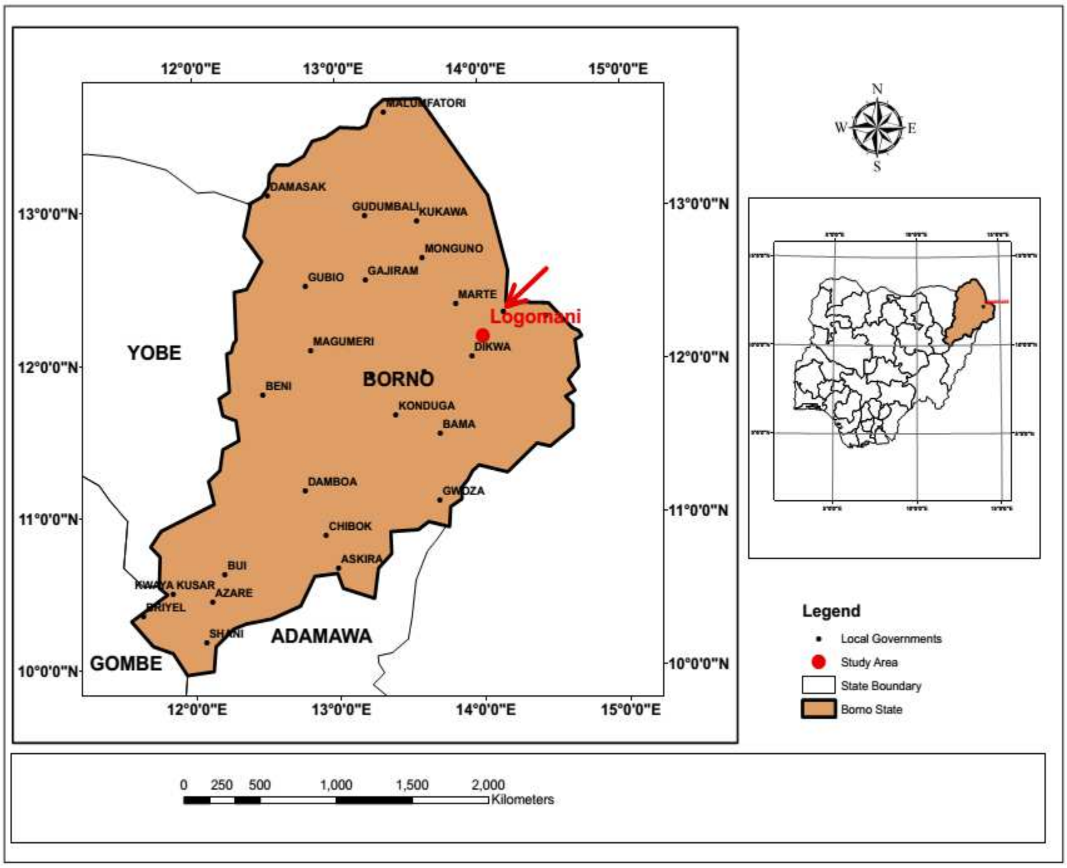
The clay sample is dispersed in the deionized water contained in a 20 liter plastic bucket. The dispersed clay is stirred vigorously and allowed to settle. The upper layer which consists of insoluble impurities and plant particles are sieved-off. The process of stirring and sieving-off is repeated with the lower layer until it becomes free from suspended particles. The dispersed clay is then allowed to settle for 24 hrs to allow the sedimentation process since different clay particle sizes are present. The top layer was collected via decantation and the remainder was washed with deionized water, allowed to settle for 24 hrs (for further sedimentation) and decanted to collect the top layer.

All reagents and chemicals used in the study were of analytical grade and were used without further purification.

The prepared clay is dried in an oven at 105°C for 6hrs, pulverized and screened into the following particle size ranges: 106–125 μm (0.106-0.125mm), 63–106 μm (0.063-0.106mm) and less than 63 μm (0.063mm). The prepared powders were further dried in an oven at 105°C for 4hrs and placed in a dessicator prior to use.

The following procedure was used, based on method of Valenzuela Diaz and Souza Santos [26]. 70 grams of the ground clay (dry basis, 105°C) were placed in a 0.5 litre round bottom flask heated by an electrical mantle; 300ml (0.5, 1.0, 1.5, 2.0, 2.5M) of mineral acid solutions were added. The dry acid/clay ratio (w/w) were 0.16 (300ml of 1M HCl include 3.7g/100ml so, dry acid/clay ratio =11.1g / 70g ≈ 0.16) 0.48, and 0.8 respectively. Thermometer, stirrer and reflux condenser were attached to the flask. The temperature was maintained at 100°C for 2hours with constant stirring. While hot, the clay suspension was transferred to a 2 litre beaker and washed by decantation with deionized water until it is acid free (tested with litmus paper). The pH was determined by pH meter and adjusted to 3.5-4.0. The acid treated clay was filtered in a Büchner funnel, dried at 105°C at 3 hours and reground 100% below

38μm (0.038mm) mesh using porcelain mortar and pestle to avoid contamination of samples and stored in a dessicator prior to the batch adsorption studies.



Study map showing area where clay samples were collected

For the alkali treatment, the above procedure was repeated, this time with following concentrations 0.5, 1.0, 1.5, 2.0 and 2.5M of NaOH and Na_2CO_3 respectively.

Methylene blue was used adsorbate for the batch adsorption studies. Strong adsorption onto solids and high solubility in water informed the choice of MB. A stock solution of MB was prepared by dissolving its 1 g in 1000 ml distilled water. The stock solution was diluted accordingly to obtain solutions of desired concentrations which were made fresh at the start of each experiment. All dye stock solutions were kept in amber-coloured bottles.

The cation exchange capacity of the bentonite was determined by the methylene blue (MB) test. The MB test is a method based on the principle of replacing original cations at the external and internal structure of the clay minerals by organic molecules. Maximum absorption of methylene blue corresponded to complete exchange of the inorganic ions by the organic ions is used to estimate the cation exchange capacity.

Fourier transform infrared spectroscopic analysis (FTIR) was carried-out on treated and untreated samples to determine the chemical bonds and their changes during the treatment process. The mineralogical analysis of treated and treated samples was determined by X-ray diffraction (XRD) analysis.

Batch Adsorption Study

Adsorption experiments were carried out batch wise. A specific amount of adsorbent (10mg) was added to dark amber glass bottles of 120 mL capacity containing 70 mL of 8mg/dm^3 MB solution. The bottles were subsequently capped and placed on a mechanical shaker (Griffin, UK) and shaken for 60 minutes. After adsorption,

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the solution was centrifuged at 2500 rpm for 5minutes. The residual dye concentrations of each solution were determined by measuring their characteristic absorbance using UV-Vis spectrophotometer (Jenway, 6505) at a wavelength of maximum absorbance (660 nm). The absorbance is then converted to concentration using the calibration curve. The amount of adsorbed MB at any time, Q_t (mg/g), was calculated using Eq. 1; and the removal efficiency by Eq. 2.

$$Q_t = \frac{(C_o - C_t)}{m} \times V \quad \text{mg/g} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

$$R_e = \frac{(C_o - C_t)}{C_o} \times 100 \quad \% \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where,
C_o = initial concentration, mg/ dm^3
C_t = concentration at time t, mg/ dm^3
V =volume of adsorbate solution, dm^3
m = mass of adsorbent, g
R_e = removal efficiency, %
Q_t = amount adsorbed, mg/g

RESULTS AND DISCUSSION

XRF Characterization

XRF analysis was performed to ascertain the chemical compositions of the minerals present in the clay sample. The data given in Table 1 below show that the alumina and silica oxide are present in major quantities with percentage content of 21.268% and 62.687% respectively, while other minerals are present in trace amounts; thus confirming that the original clay sample is an aluminosilicate. Also, the values obtained for alumina and silica oxide are in agreement with those obtained by other workers for bentonitic clays; 14% and 68.20% [28], 15.12% and 65.24% [27] and 14.41% and 65.13% [11] for alumina and silica oxide respectively in each case. According to Murray [15], the theoretical composition without the interlayer material is SiO_2, 66.7% and Al_2O_3, 28.3%. The results from the XRF analysis also show a Na_2O content of 0.159% and CaO content of 1.727%. The higher percentage of Ca as compared to Na confirms that the sample is a calcium bentonite.

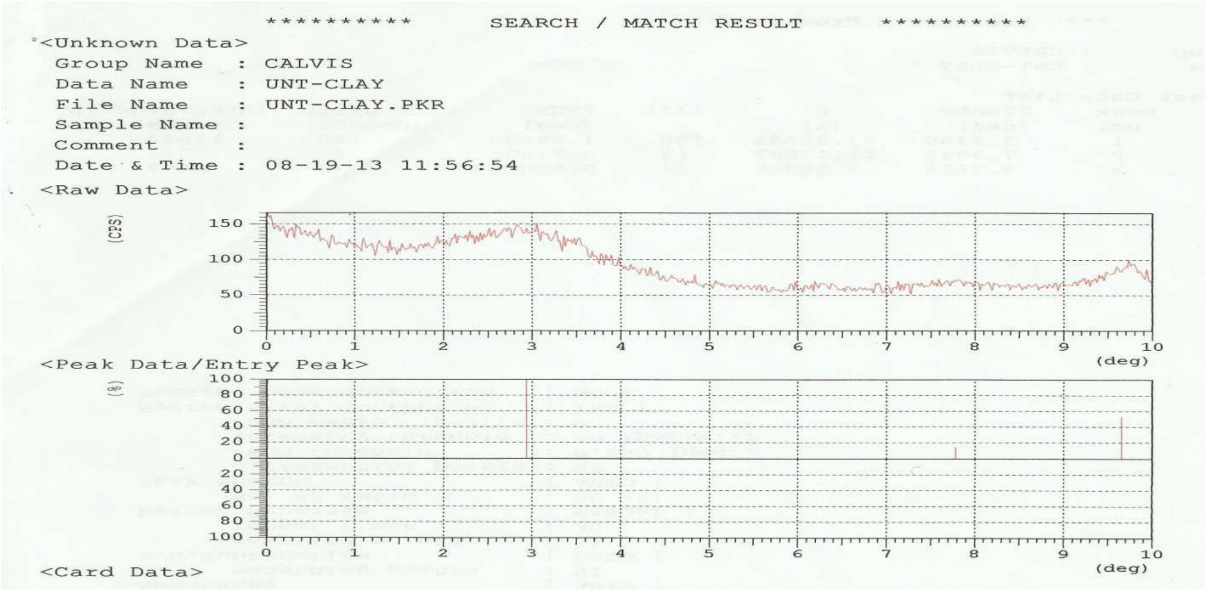
Table 1: Chemical composition of the original clay sample

Element	Content, %
Na_2O	0.159
MgO	1.480
Al_2O_3	21.268
SiO_2	62.687
P_2O_5	0.071
SO_3	0.216
Cl	0.009
K_2O	1.101
CaO	1.727
TiO_2	1.613
Cr_2O_3	0.018
Mn_2O_3	0.124
Fe_2O_3	0.949
ZnO	0.010
SrO	0.025

XRD Characterization

The low angle XRD pattern of the clay sample showed a broad peak appearing at approximately $2\theta = 3°$ which is characteristic of montmorillonites and a basal spacing d(001) value of 11.176Å characteristic of calcium montmorillonites [27].

The occurrence of a peak before 2θ = 10 ° is representative of the basal distance (d_{001}) for smectite clays. This peak tends to be intense, which enables their detection even in small quantities [5, 21, 25, and 27].



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  Sample Name  :
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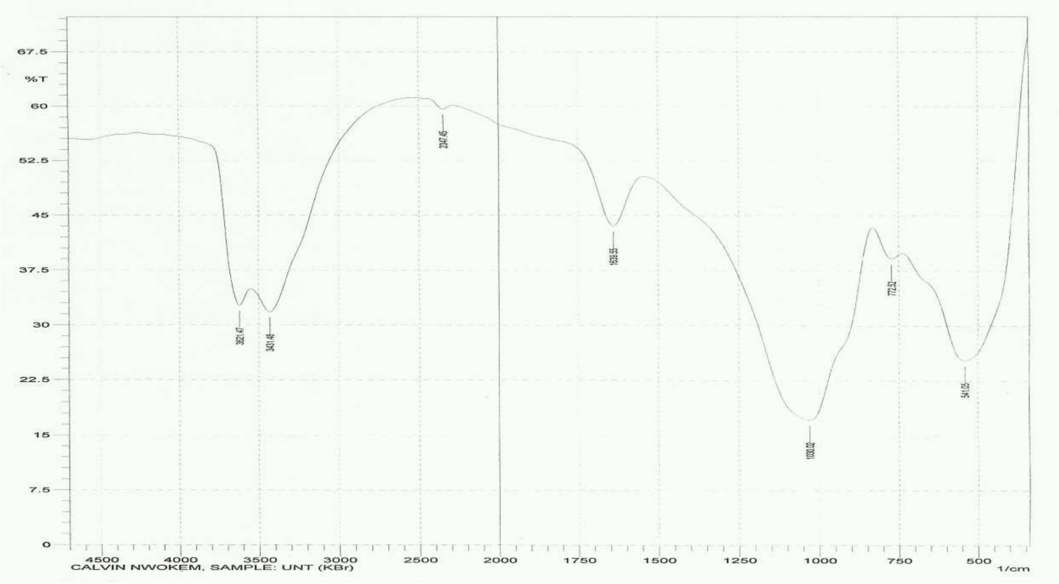
X-ray Diffractogram of the Original/untreated Clay



FTIR spectrum of the original/untreated clay sample

Table 1: Amount absorbed by the various adsorbents

	HCl			H_2SO_4			NaOH			Na_2CO_3		
	Q_t, mg/g			Q_t, mg/g			Q_t, mg/g			Q_t, mg/g		
Conc.	< 63 µm	63-106 µm	106-125 µm	< 63 µm	63-106 µm	106-125 µm	<63 µm	63-106 µm	106-125 µm	<63 µm	63-106 µm	106-125 µm
0.5M	51.196	45.908	41.982	42.636	38.929	32.333	51.823	52.190	50.337	51.058	50.337	48.333
1.0M	47.229	41.75	34.609	41.206	30.902	27.533	49.301	49.833	48.648	49.110	48.482	46.795
1.5M	44.668	34.173	28.489	40.101	28.558	25.529	48.538	48.907	47.691	47.691	47.446	45.731
2.0M	40.320	30.902	26.813	37.144	28.517	26.349	46.641	47.693	46.711	47.012	46.221	44.816
2.5M	38.403	28.558	24.726	33.437	27.372	24.632	45.458	46.615	45.365	46.807	45.365	43.713

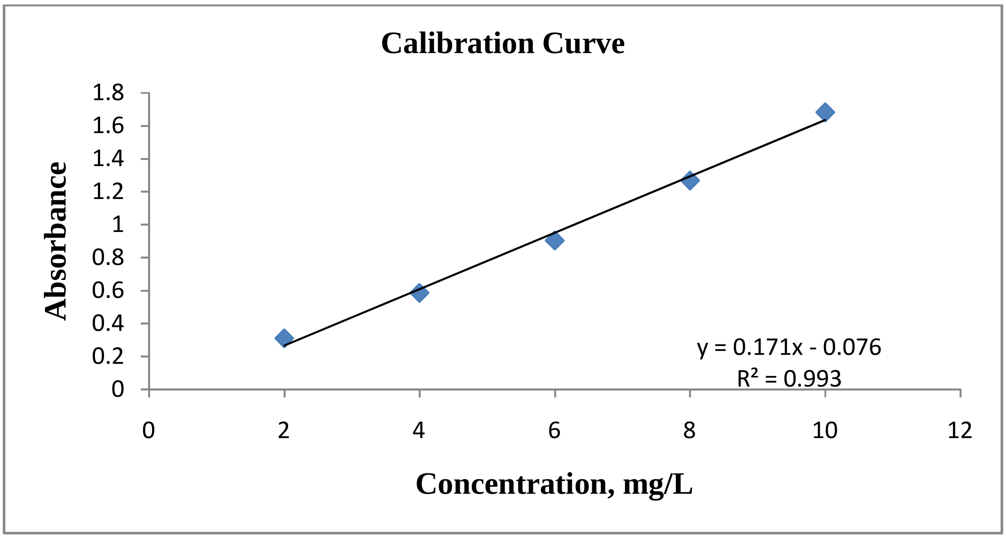


Figure 1: Calibration curve of methylene blue

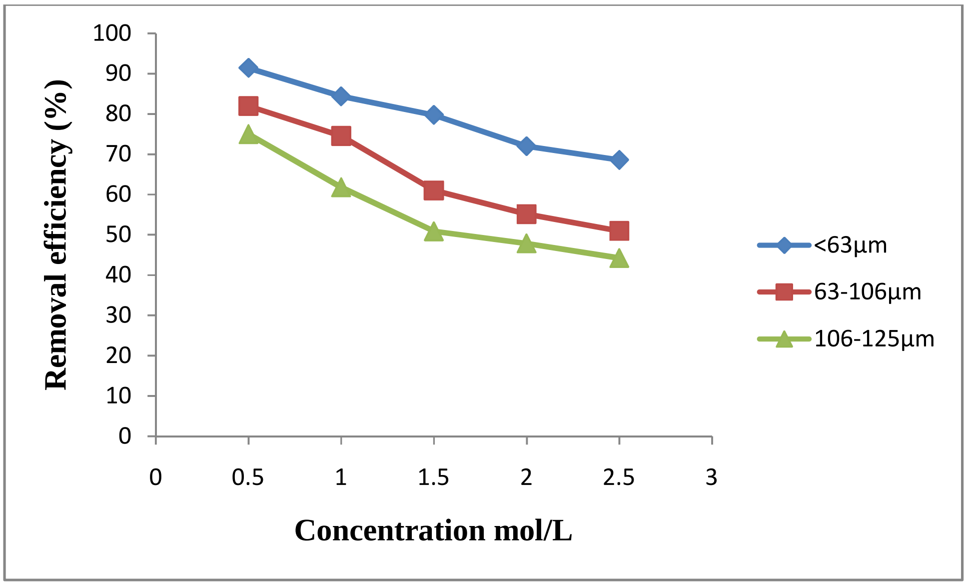


Figure 2: Removal efficiency-concentration plots for HCl-treated bentonite clay for the various particle sizes

It can be seen from Figure 2 that as the concentration of the acid solution increased from 0.5 to 2.5M, there was a decrease in the removal efficiency of the adsorbent. Also, the removal efficiency decreases as the selected particle size range prior to treatment with the HCl increased from <63, to 106-125µm. The highest value of adsorbed amount (Q_t), 51.196mg/g (see Table 1) for the HCl-treated clay was obtained with the clay particle size range of < 63µm treated with 0.5M HCl. While, the lowest adsorbed amount, Q_t, of 24.726mg/g for the HCl-treated clay was obtained with the clay particle size range of 106-125µm treated with 2.5M HCl.

A similar trend is observed on treatment of the clay sample with aqueous H_2SO_4 solution. It can be seen from Figure 3 that as the concentration of the acid solution increased from 0.5 to 2.5M, there was a decrease in the removal efficiency of the adsorbent. Also, the removal efficiency decreases as the selected particle size range prior to treatment with the H_2SO_4 increased from <63, to 106-125µm. The highest value of adsorbed amount Q_t, 42.636mg/g (Table 1) was obtained with particle size range of < 63µm treated with 0.5M H_2SO_4 and the lowest value of Q_t (24.632mg/g) with particle size range of 106-125µm treated with 2.5M H_2SO_4.

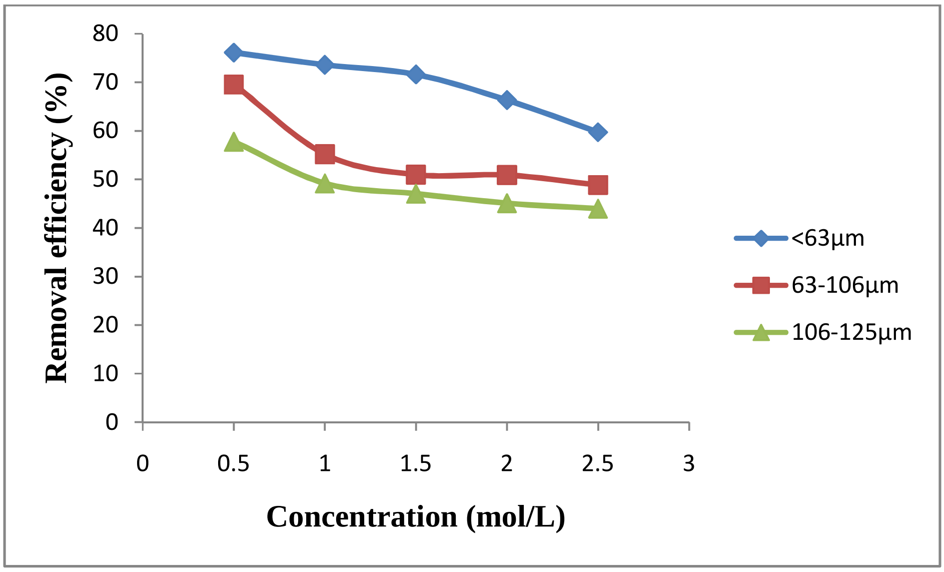


Figure 3: Removal efficiency-concentration plots for H_2SO_4-treated bentonite clay for the various particle sizes

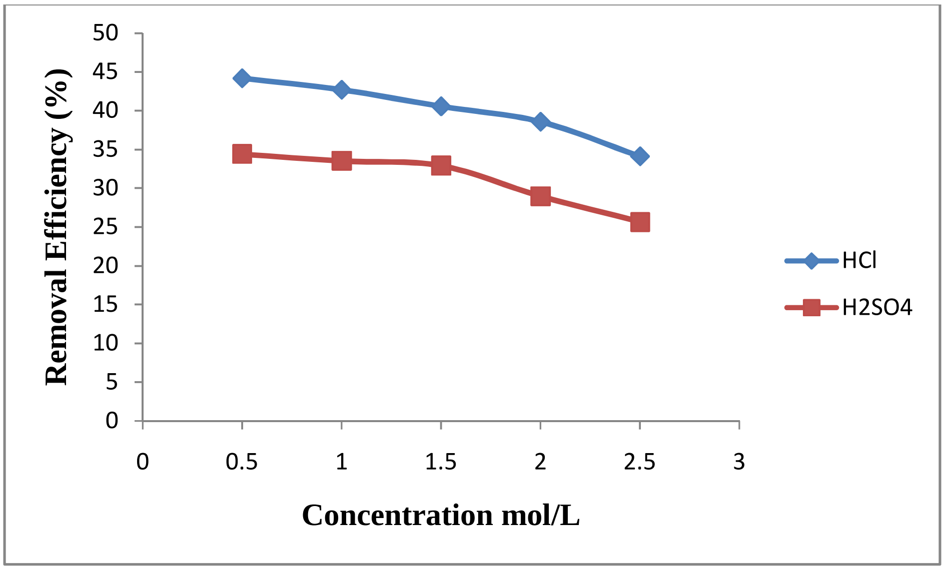


Figure 4: Removal efficiency-concentration plots for acid-treated bentonite clay for unselected particle sizes

From Figure 4, it can be seen that the trend observed in the acid-treated clays as observed in Figures 2 and 3 was maintained. As the concentration of the aqueous acid solution increased from 0.5 to 2.5M, there was a decrease in the removal efficiency of the adsorbent. Also it is observed that the values of removal efficiency obtained using the HCl-treated clay was higher than those obtained using the H_2SO_4-treated clay as was the case with the acid treated clay for which particle size range was selected prior to treatment. For the HCl-treated clay (particle size range not selected), the highest amount removed was 24.726mg/g with the 0.5M HCl, while the lowest was 34.104mg/g with 2.5M HCl. For the H_2SO_4-treated clay (particle size range not selected), the highest amount removed was 34.40mg/g with the 0.5M H_2SO_4, while the lowest was 25.66mg/g with 2.5M H_2SO_4.

It can be seen from Figure 5 that as the concentration of the alkali solution increased from 0.5 to 2.5M, there was a decrease in the removal efficiency of the adsorbent. Also, the removal efficiency decreased as the selected particle size range prior to treatment with the NaOH increased from <63, to 106-125µm. The highest value of adsorbed amount (Q_t), 52.190mg/g (Table 1) for the NaOH-treated clay was obtained with the clay particle size range of 63 -

106µm treated with 0.5M NaOH. While, the lowest adsorbed amount, Q_t, of 45.365mg/g for the NaOH-treated clay was obtained with the clay particle size range of 106-125µm treated with 2.5M NaOH.

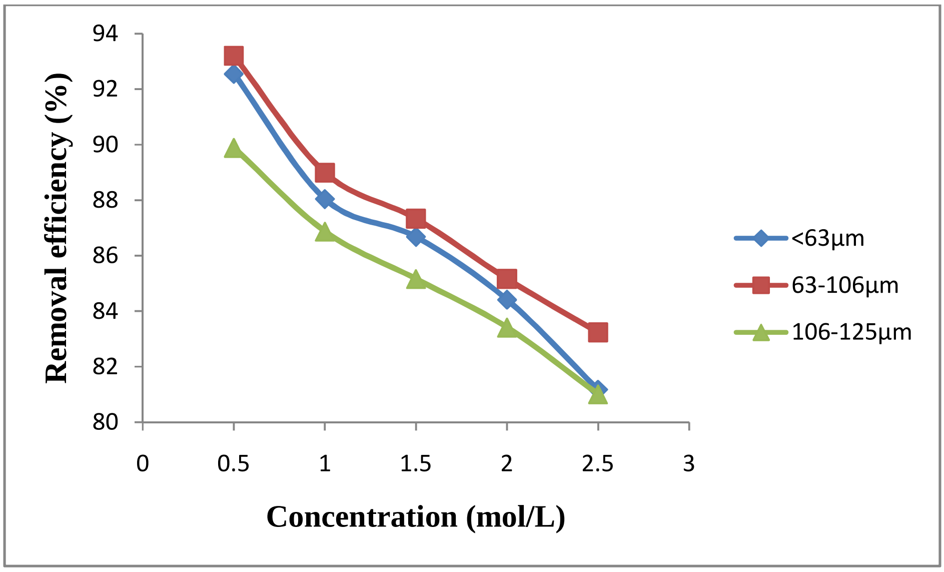


Figure 5: Removal efficiency-concentration plots for NaOH-treated bentonite clay for the various particle sizes

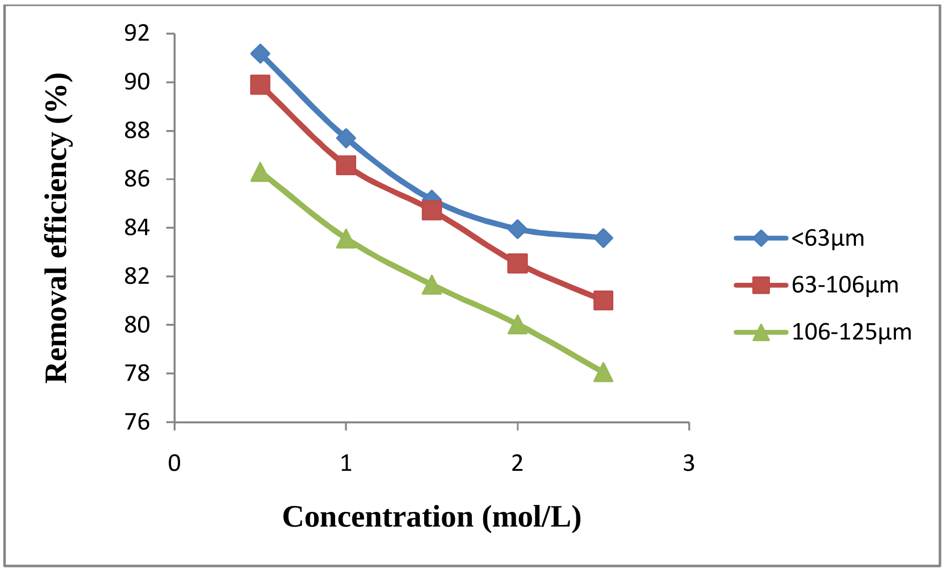


Figure 6: Removal efficiency-concentration plots for Na_2CO_3-treated bentonite clay for the various particle sizes

It can be seen from Figure 6 that as the concentration of the alkali solution increased from 0.5 to 2.5M, there was a decrease in the removal efficiency of the adsorbent. Also, the removal efficiency decreased as the selected particle size range prior to treatment with the Na_2CO_3 increased from <63, to 106-125µm. The highest value of adsorbed amount (Q_t), 52.058mg/g (Table 1) for the Na_2CO_3-treated clay was obtained with the clay particle size range of <63µm treated with 0.5M Na_2CO_3. While, the lowest adsorbed amount, Q_t, of 43.713mg/g for the Na_2CO_3-treated clay was obtained with the clay particle size range of 106-125µm treated with 2.5M Na_2CO_3.

From Figure 7, it can be seen that the trend observed in the acid-treated clays as observed in Figures 5 and 6 was maintained. As the concentration of the aqueous alkali solution increased from 0.5 to 2.5M, there was a decrease in the removal efficiency of the adsorbent. Also it is observed that the values of removal efficiency obtained using the

NaOH-treated clay was higher than those obtained using the Na_2CO_3-treated clay as was the case with the acid treated clay for which particle size range was selected prior to treatment. For the NaOH-treated clay (particle size range not selected), the highest amount removed was 47.53mg/g with the 0.5M NaOH, while the lowest was 38.403mg/g with 2.5M NaOH. For the Na_2CO_3-treated clay (particle size range not selected), the highest amount removed was 34.173mg/g with the 0.5M Na_2CO_3, while the lowest was 24.36mg/g with 2.5M Na_2CO_3.

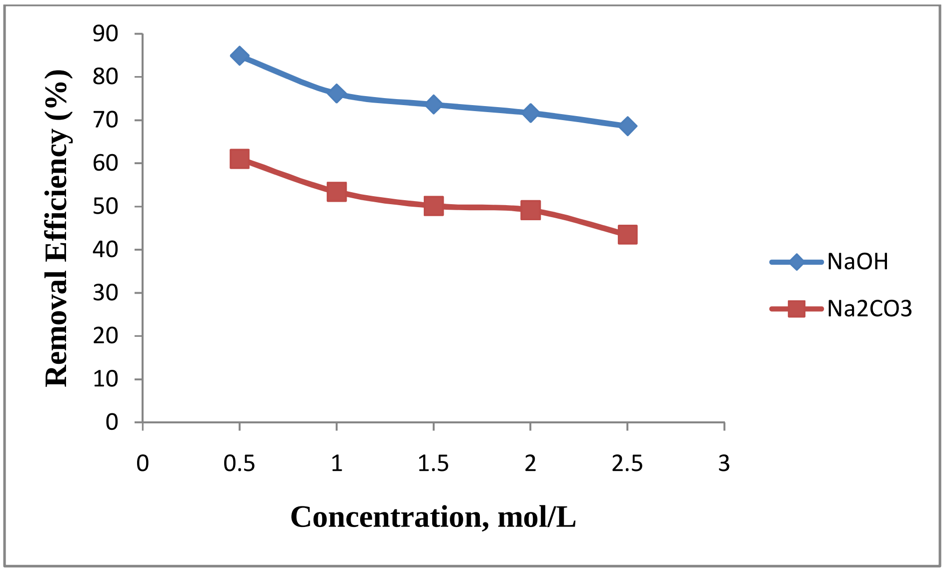


Figure 7: Removal efficiency-concentration plots for alkali-treated bentonite clay for unselected particle sizes

Effect of Acid treatment

This gradual decrease in adsorptive capacity with increasing particle size range as can also be seen in Figures 2– 4, can be explained by the fact that the smaller the clay particle size for a given mass of the clay, the more surface area is available for attack by aqueous solution used for treatment leading to the production of modified adsorbent with greater surface area (binding sites) and as a consequence the greater the number binding sites available to the adsorbate molecules.

In the same vein, the gradual decrease in adsorptive capacity observed with increasing acid concentration can be ascribed to increased attack on clay structure occasioned by the higher acid concentrations. Generally, the surface area of acid treated bentonite increases with increase in acid concentration until a maximum surface area is reached after which it gradually decreases [20]. The acid treatment of clays is a two-step procedure in which the splitting of particles within the octahedral sheet takes place. In the first step the exchangeable cations are replaced by protons (H^+). The second step involves the leaching of octahedral cations such as Al^{3+}, Mg^{2+} and Fe^{3+} from the octahedral and the tetrahedral sheets [22].

However, higher concentrations of acid solution brings about excessive leaching of Al^{3+}, which results in rupture of the lattice structure [4] and decrease in the surface area of the clay [26]. Optimum adsorptive capacity is not necessarily associated with maximum surface area. That is due to the fact that removal efficiency is not merely a physical adsorption process and other properties such as cation exchange capacity, as well as acidic and catalytic properties must be taken into account [6]. With moderate treatment conditions, especially acid concentration, only 25-30% of octahedral cations are removed, at same time, surface area and clay acidity increases [3].

Also, the lower values of Q_t obtained for the clay treated with H_2SO_4 as compared to those obtained for the clay treated with HCl is likely due to greater attack by H_2SO_4. Some workers (Hradil et al., 2002) reported that the dissolution rate (leaching) of kaolinite clay in 0.5M sulphuric acid at 25°C was approximately 3 times higher than in HCl of equivalent concentration.

The increase of adsorption capacity is usually due to the replacement of Al^{3+} or Fe^{2+} ions of bentonite by H^+ ion after HCl or H_2SO_4 acidification [24].

Acid activation affects mainly chemical composition of the octahedral layer, while the tetrahedral layer is less prone to it because of strong bonds among silicon and oxygen ions [1].

Increasing of specific surface area arises from the depletion of the cations from the interlayer and octahedral sheets of the smectite mineral, as well as dissolution of soluble impurities such as calcite and gypsum during acid treatment. It is also possible that a part of the specific surface area is associated with the amorphous silica phase formed by the slight destruction of the smectite [14]. Acid treatment changes the pore size distribution in that it brings about an increase in micropores, however, the pore size and number of micropores is independent of acid concentration [19].

Effect of Alkali treatment

Generally, the values for amount adsorbed Q_t, obtained for the clays (pre-selected particle size range) treated with alkali solutions are higher, the lowest being 43.713mg/g for the Na_2CO_3-treated clay which was obtained with the clay particle size range of 106-125µm treated with 2.5M Na_2CO_3; while the lowest value of Q_t for the acid treated clay, 24.632mg/g which was obtained with 2.5M H_2SO_4.

This clearly shows that the alkali-treated clays have better adsorptive abilities as compared to the acid-treated. Usually under alkali treatment, the dissolution processes affect mineral structures to a lesser extent, though formation of new mineral phases is a frequent phenomenon [23].

The decrease in adsorptive/removal capacity with increasing particle size range and increasing concentration of alkali solution is lower as compared to that observed in the case of acid treatment. This is clearly shown in the data in Table 1 as well as the steepness of the removal efficiency plots in Figures 5 and 6.

The optimum adsorptive capacity for the alkali-treated clay was 52.190mg/g. This was obtained with the clay treated with 0.5M NaOH. This result is in close agreement with the report by a group of workers [17]. They carried-out an investigation into the treatment of bentonite clay with varying concentrations of NaOH (1, 2, 3, and 4M). They reported a continuous drop in adsorptive activity as concentration of alkali used increases, with the 1M NaOH-treated giving optimum adsorptive activity.

For the alkali-treated clay (particle size range not selected), the highest amount removed was 47.53mg/g with the 0.5M NaOH, while the lowest was 24.416mg/g with 2.5M Na_2CO_3.

The difference in adsorptive abilities between the acid- and alkali-treated clays can be explained by the fact that acid treatment leads to a preponderance of H^+ ions on the clay thereby reducing the adsorption sites available to the dye cations, thereby leading to a decrease in the amount of dye cations that are eventually taken up. Methylene blue, a cationic dye gives positively charged ions when dissolved in water [18]. Treatment of the clay with acid solution leads to electrostatic repulsion between the dye ions and the edge groups with positive charge ($Si\text{-}OH^{2+}$) on the surface as follows:

$$-SiOH + H^+ \rightarrow -SiOH^{2+} + OH^-$$

However, upon treatment of the clay with alkaline solution, there is an increase in the negative charges present on the clay surface, due to the deprotonation of the surface hydroxyl site (M-OH), such as alumina and silica (Al-OH and SiOH). Therefore number of ionizable sites (adsorption sites) on clay surface increases. In this case the mechanism can be shown as follows:

$$-SiOH + OH^- \; -SiO^- + H_2O$$

$$-SiOH + Dye^+ \rightarrow -Si-O-Dye^+$$

The alkaline treatment of the clay increases the number of hydroxyl groups thus, increasing the number of negatively charge sites and enhancing the electrostatic attraction between dye and adsorbent surface.

CONCLUSION

The values for amount adsorbed Qt, obtained for the clay samples for which particle size was pre-selected prior to treatment were greater than the values for the unselected clay.

Generally, the values for amount adsorbed Q_t, obtained for the clays treated with alkali solutions are higher. The optimum adsorptive capacity for the alkali-treated clay was 52.190mg/g. This was obtained with the clay treated with 0.5M NaOH. Whereas the lowest amount adsorbed by the alkali-treated clay was 43.713mg/g, the lowest value of Q_t for the acid treated clay was 24.632mg/g. This clearly shows that the alkali-treated clays have better adsorptive abilities as compared to the acid-treated. Similar results were obtained with clay for which the particle size range was not pre-selected before treatment, as the alkali-treated samples had better adsorptive abilities as compared to the acid-treated.

Therefore, alkali-treated clays have better adsorptive abilities for the removal of methylene blue dye from aqueous solution than the acid-treated, whether the particle size range of the clay was selected prior to treatment or not.

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