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Adsorption of Spill Crude Oil from Aqueous Solution Using Organo Modified Bentonite Clay

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Abstract

The study of the adsorption of crude oil from aqueous solution using organ modified bentonite clay. The primary objective of the study is to develop organ modified bentonite clay adsorbent, to characterize and to study the adsorption efficiency of the develop adsorbent in adsorption of crude oil from aqueous solution. The XRD, SEM/EDX and FTIR analysis, shows that the crystal structure of the organ modified bentonite clay comprises mainly quarts and albite with small amounts of microcline silicates and found that the organ modified bentonite clay were remarkably altered by forming more holes and cracks with more exfoliated, loose, and curled layers for oxalic acid pretreated organomodified bentonite clay and confirm the intercalation alkylammonium in the interlayer of galleries of the bentonite clay. The adsorption study shows maximum removal of 97.518% at 60 min, maximum removal of 98.050% at 75 °C, maximum removal of 94.681% at 2g and maximum removal at a pH of 9 of crude oil from contaminated water use the produce acid pretreated organ modified clay. Therefore, pretreatment of organ modified clay with organic acid such as oxalic acid could improve the adsorption capacity of organ modified bentonite clay. The results show that organ modified bentonite clay is a promising technology adsorbent for the removal of crude oil from contaminated wastewater.

Keywords: *Bentonite, Oxalic Acid, SEM/EDX, FTIR, XRD*

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Background to the Study

Over the years, global population growth and industrialization have led to release of different contaminants into environment, which in most cases are toxic even in trace levels. As a result, environmental pollution has become a prime concern for industrial and developing countries, particularly water pollution. Water is increasingly being polluted by anthropogenic activities including urbanization, population growth, poor land use, agricultural activities and oil spillage which has led to rapid degradation of surface and ground water quality. Of these sources of pollution, oil spillage remains a serious concern especially with increase in crude oil processing facilities in oil producing regions of the world. The elimination of these contaminants from water resources is usually done to reduce their amounts down to a safe level (Foroutan, Zareipour and Mohammadi, 2018). Crude oil contamination affected both aquatic and terrestrial ecosystems with serious environmental consequences on human health and aquatic life. Major environmental contamination may occur due to accidental losses associated with extraction or transportation, or even intentional discharge by illegal refineries and illegal refinery wastewater (Vollaard, 2017). These activities have increased the threat of oil pollution to the environment and subsequently concomitant discharged into the natural environment has resulted in major ecological problem throughout the world.

Crude oil comprises of complex mixture that often contains toxic organic pollutants that are hazardous to human and environmental health (Foroutan *et al.*, 2018; Linan *et al.*, 2018). The problem of removing pollutants from water is an important process and is becoming more important with the growing industrial refinery and illegal refinery activities particularly in the Niger Delta region of Nigeria (Osin, Yu and Lin, 2017). Though crude oil can be generally removed from wastewater by means of conventional methods such as physical or chemical methods, however, these methods are usually expensive and difficult to maintain, even with advanced technologies (Linan *et al.*, 2018). Particularly, physical method, such as sorption is considered a simple and suitable strategy for crude oil removal in polluted effluents because of its high efficiency, easy handling, and economical feasibility (Na, Xiaoli, Shitao, Huaqin and Lei, 2018). Other technologies have been used for the removal of pollutant from wastewater which includes membrane processes and biological materials. These techniques are very expensive and economically unfavorable or technically complicated, and are used only in special cases of wastewater treatment. Relatively a new green technology for the treatment of industrial wastewater was adsorption of crude oil from aqueous solutions by using natural material. Adsorption process using natural material has been proved to be an excellent way to treat industrial waste effluents, offering significant advantages like the low cost, availability, profitability, easy operation and efficiency (Guptaa and Babua, 2006). Thus, the preparations of adsorbent from natural material is motivated by cost considerations (relatively cheaper), local generation in countries such as Nigeria and effectiveness in crude oil removal from waste effluents.

Over the past decades the removal of various toxic substances such as crude oil from water and wastewater has been of primary interest to many researchers around the globe (Auta and Hameed, 2014; Uddin, 2017; Momina *et al.*, 2018). Materials used as adsorbent in removing crude oil from aqueous solution are limited due to high production cost, as a result, clay materials have been found to be good adsorbent alternatives over the years with bentonite gaining more interest (Hokkanen *et al.*, 2018, Foroutan *et al.*, 2018). Bentonite have proven to be efficient in removing many toxic material particularly metal ions and organic contaminants from an aqueous solution (Uddin, 2017; Foroutan *et al.*, 2018; Hokkanen *et al.*, 2018; Momina *et al.*, 2018). However, its ability to absorb organic molecules such as crude oil constituent is very low and the active site of bentonite is not uniform, so a solution is needed to improve its adsorption performance.

The adsorption capacity of bentonite can be increased through its modification into organoclay as a functional material for crude oil adsorption. Modification of bentonite clay for improved crude oil adsorption can be achieved using organic cations such as Hexadecyltrimethylammonium (HDTMA) cations and cetyltrimethylammonium bromide (CTMAB). Several studies have been reported on the use of organomodified bentonite in the adsorption of many toxic material particularly metal ions (Jović-Jovičić *et al.*, 2010; Arellano-Cárdenas *et al.*, 2013; Aroke *et al.*, 2015; Bounab *et al.*, 2017) However, no studies have been in relevant current extant literature on the adsorption of crude oil from aqueous solution using organomodified bentonite clay. It is against this background that this study seeks to investigate the adsorption of crude oil from aqueous solution using organo modified bentonite clay. This study aims to investigate the adsorption of crude oil from aqueous solution using organomodified bentonite clay. The objectives are development of organomodified bentonite clay adsorbent, characterization of the developed organomodified bentonite clay adsorbent and adsorption study of the developed adsorbent in adsorption of crude oil from aqueous solution.

Methodology

Materials

The waste effluent used for the adsorption study was collected from Ejama-Ebubu, Eleme LGA in Rivers State while the bentonite clay was obtained from Ngalda, Yobe State. The organomodified bentonite clay was prepared from Cetyl-N,N,N Trimethyl Amminium Bromide (CTMABr) selected as a modifying agent purchased from Loba Chemie PVT Ltd. Oxalic acid used for pretreatment was obtained from Kermel. All chemical used were of analytical grade.

Sample Pretreatment

Two samples were prepared by pretreatment with deionized water and the other pretreated with oxalic acid solution. For the first sample, 200g of bentonite clay was measured into a 1-liter beaker. 500 mL of deionized water was measured and added to the clay material in the beaker at room temperature. The mixture was stirred continuously at 900 rpm for 30 min to form two layers (a settle able heavier particulate layer and a colloidal suspension which is the bentonite clay). The suspended layer was carefully and completely decanted after which the colloidal layer was recovered. The supernatant was decanted and the bentonite clay washed thoroughly with distilled water to remove traces of impurities. The impurity free bentonite clay was recovered and oven dried at 100 °C to obtain dried bentonite clay samples. The dried bentonite clay was grounded, sieved to 450 μm mesh size and after which it was kept in a closed container ready for use in the preparation of organomodified bentonite clay adsorbent.

In the second sample, 200g of bentonite clay was measured into a 1-liter beaker. 2 mol/L Oxalic (126.06 g/L Oxalic Acid) solutions were prepared using deionized water. 500 mL of the prepared Oxalic Acid solution was measured and added to the raw bentonite clay material in the beaker at room temperature. The mixture was stirred continuously at 900 rpm for 30 min to form two layers (a settle able heavier particulate layer and a colloidal suspension which is the acid treated bentonite clay). The suspended layer was carefully and completely decanted after which the colloidal layer was recovered. The supernatant was decanted and the acid treated bentonite clay washed thoroughly with distilled water until the pH is almost neutral. The Oxalic Acid treated bentonite clay was recovered and oven dried at 100 oC for 30 min to obtain dried bentonite clay samples. The dried Oxalic Acid treated bentonite was grounded to 450 μm mesh size and after which it was kept in a closed container ready for use in the preparation of organomodified bentonite clay adsorbent.

Preparation of Organo Clay Adsorbent

200g of deionized water treated bentonite clay was measured and dispersed into 1-liter deionized water. The mixture was stirred thoroughly at 900 rpm for 20 min and then left to settle. A measured quantity (69.25g) of CTMABr equivalent to prepared 0.190 mol/L of CTMABr solution was added to the treated bentonite clay mixture. The mixture was stirred thoroughly at 900 rpm for 20 min and left to settle for 24 hr at room temperature. After 24 hr, the CTMABr modified bentonite clay products was washed with deionized water to remove excess surfactants, filtered and dried at $60 \pm 5\ ^{\circ}C$ till constant weight is achieved. The dried the CTMABr modified bentonite clay products was stored at room temperature for the characterization and adsorption study. The same procedure was repeated using Oxalic acid treated bentonite clay tagged as Acid-CTMABr sample.

Characterization of Organo Clay Adsorbent

The prepared adsorbent was characterized using FTIR to determine the functional group organoclay adsorbent, SEM/EDS to examine the surface morphology and elemental mapping of the produced organoclay adsorbent and XRD to examine the crystal structure of the organoclay adsorbent.

Batch Adsorption Study

The aqueous solutions of the crude oil contaminated water were used for the adsorption study. The effect of initial concentration (0.05 – 3 mg/L), temperature (25 – 75 °C), Dosage (0.5 – 3 g), contact time (10 – 60 min) and pH (4 – 10) wer investigated using batch adsorption study. Adsorption experiments were conducted in a batch mode to obtain equilibrium data. A measured quantity of the adsorbent (organomodified bentonite) was contacted with 40 mL of the aqueous solution in glass-stoppered tubes. The glass tubes was then be shaken at room temperature until the equilibrium condition is attained. At the predetermined equilibrium time, the liquid and the solid phases were separated. Samples of supernatant were taken and the concentration of unabsorbed crude oil in the organo modified adsorbent samples would be calculated using the equation 3.1.

Results and Discussion

XRD Analysis of the Produced Organo modified Clay (Acid-CTMABr)

The crystal structure of the synthesis Acid-CTMABr organo modified bentonite clay was characterized by XRD. Figure 1 presents the XRD pattern of the Acid-CTMABr organo modified bentonite clay. It can be seen that the diffraction peak at 2θ angle of 26.67° was the typical diffraction peak of albite and quartz and shows that the treated the Acid-CTMABr organomodified bentonite clay mainly crystalline silica of quartz and albite. From the XRD analysis, the basal spacing of the Acid-CTMABr organo modified bentonite clay at 2θ angle of 26.67° was 3.343 Å, indicating the 1 0 1 plane of quartz. Also, the peak at 2θ angle of 20.89° was typical of quartz and microcline. The basal spacing of the Acid-CTMABr organo modified bentonite clay at 2θ angle of 20.89° was 3.189 Å, indicating the 0 0 2 plane of albite (Zhang *et al.*, 2019). From Figure 1, it can be seen from the diffractograms that the crystal structure comprises mainly of quarts and albite with the highest intensity of 21803 count and small amounts of microcline with the highest intensity of 4859 count. Meaning that the quarts and albite content of the Acid-CTMABr organomodified bentonite clay is higher than microcline content. In addition, the higher basal spacing in the presence of the quaternary salt (CTMABr) is known to facilitate the intercalation of the organo modified bentonite clay.

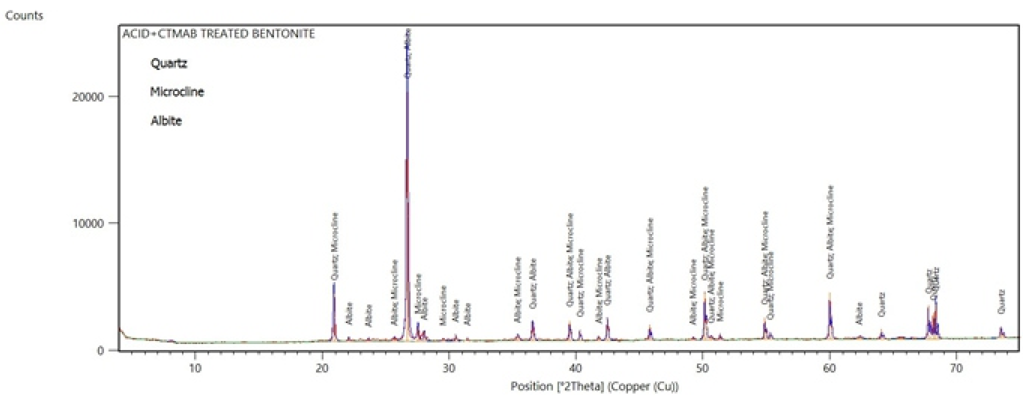

Figure 1: XRD analysis of acid pretreated organomodified bentonite clay

SEM/EDX Analysis of the Synthesis Organo modified Clay

The morphology of both Acid-CTMABr and CTMABr organomodified bentonite clay was studied using SEM/EDX analysis. The SEM imaging was used to study the surface morphology and pore development of the synthesis Acid-CTMABr and CTMABr organomodified bentonite clay while EDX was used to study the elemental map of the synthesis Acid-CTMABr and CTMABr organomodified bentonite clay. Figure 2 shows the SEM image of the synthesis Acid-CTMABr and CTMABr organo modified bentonite clay at magnifications of 500 with macro and mesoporous. Figure 2 (a) and (b) shows that both CTMABr and Acid-CTMABr organomodified bentonite clay are large particles. The surface of CTMABr organo modified bentonite clay was relatively flat and smooth; a regular and compact stacked lamellar structure was observed with slightly thicker lamellae and fewer pores. However, the particle size and structure of Acid-CTMABr organomodified bentonite clay were remarkably altered by forming more holes and cracks with more exfoliated, loose, and curled layers. The view from the side shows that there is a certain distance between the layers, accompanied by some sharp edges, and there are more fine particles between the layers. The surface morphology directly affects the adsorption capacity for organic pollutants such as crude oil. The surface morphology of Acid-CTMABr organomodified bentonite clay shows that oxalic acid pretreatment of the bentonite clay has impact on the surface morphology of the synthesis organomodified bentonite clay. The structure of bAcid-CTMABr organomodified bentonite clay showed favorable channels and voids for adsorbing oil.

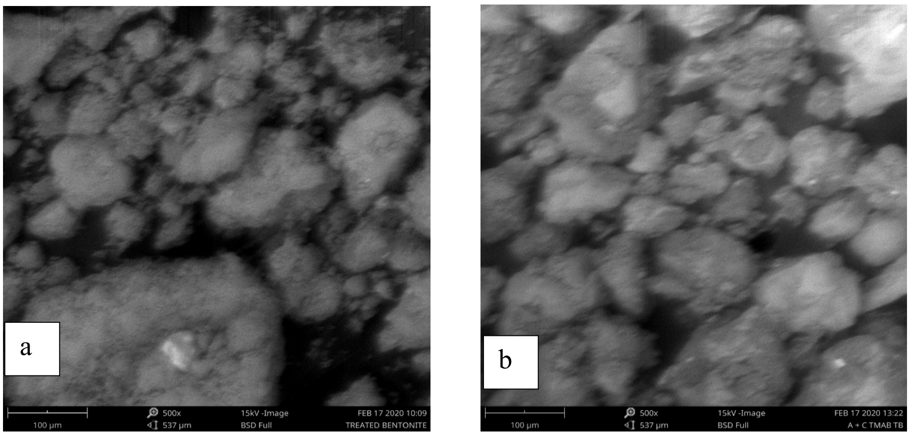

Figure 2: SEM image of (a) CTMABr organomodified bentonite and (b) Acid-CTMABr organomodified bentonite

The EDX analysis of the synthesis CTMABr and Acid-CTMABr organomodified bentonite clay was studied to determine the elemental mapping of the adsorbents (Scimeca *et al.*, 2018). Table 1 present the EDX results of the synthesis CTMABr and Acid-CTMABr organo modified bentonite clay. It was observed from the elemental analysis that the synthesis CTMABr contains 41.76% Si, 17.29% Al, 16.22% Fe, 7.26% K, 3.07% Ti, 1.9% Ag and 1.62% Ca while Acid-CTMABr contains 51.05% Si, 11.59% Al, 9.74% Fe, 7.18% K, 0.68% Ti, 4.3% Ag and 2.73% Ca. The high composition of Si and Al in both CTMABr and Acid-CTMABr organomodified bentonite clay further confirm the XRD result, that the synthesis adsorbents constitute primary aluminum silicate material. However, it was observed oxalic acid pretreated CTMABr organo modified bentonite clay has higher silicate content with lower alumna, Fe, K, Ti and Ag content. The reductions in acid pretreated CTMABr organomodified bentonite clay likely occurred as result of washing off of soluble salts of Al, Fe, K, Ti and Ag during the acid pretreatment with oxalic acid.

Table 1: EDX Analysis of the synthesis organo modified bentonite clay

Element Symbol	Element Name	CTMABr	Acid-CTMABr
Si	Silicon	41.76	51.05
Al	Aluminium	17.29	11.59
Fe	Iron	16.22	9.74
K	Potassium	7.26	7.18
Ti	Titanium	3.07	0.68
Ag	Silver	1.95	4.3
Y	Yttrium	1.78	2.03
Ca	Calcium	1.63	2.73
Zr	Zirconium	1.54	–
Cr	Chromium	1.44	–
Mg	Magnesium	1.34	1.11
Nb	Niobium	1.3	3.57
S	Sulfur	1.3	1.15
Cl	Chlorine	1.28	–
Na	Sodium	0.84	0.38
P	Phosphorus	0	2.17
V	Vanadium	–	0.68
C	Carbon	–	1.19
O	Oxygen	–	0.45
Mn	Manganese	–	0

Fourier Transform Infra-Red Analysis of the Synthesis Organomodified Clay

The FTIR is a measure of the quantitative and qualitative analysis of functional group of organic and inorganic samples in a material. The FTIR spectrum of the synthesis CTMABr and Acid-CTMABr organo modified bentonite clay are shown in Figure 3 and 4 respectively. It was observed that there was a change in the structural orderliness in the number and sharpness of peak with the oxalic acid pretreatment of the Acid-CTMABr organomodified bentonite clay (Figure 4) compared to that of CTMABr organo modified bentonite clay (Figure 4). It is known that the main infrared characteristic peaks of quartz, albite and microcline occur at 400 –1300 cm^{-1} (Ravisankar *et al.*, 2010; Zhang *et al*, 2019). In this range, there were similar bands in the range of 650 – 700 cm^{-1} in the CTMABr (689 cm^{-1}) and Acid-CTMABr (678 cm^{-1}) organo modified bentonite clay. This peaks indicat the presence of Si-O-Si bending vibration and the coupling between the O–Si–O deformation stretching (Wang *et al.*, 2015).

The band between 740 – 800 cm^{-1} indicated the Si-O-Al, particularly 775 cm^{-1} for CTMABr (Figure 4.3) and 779 cm^{-1} for Acid-CTMABr (Figure 4) and the band between 900 – 1100 cm^{-1}, particularly the peak at 909 cm^{-1} and 998 cm^{-1} for both CTMABr and Acid-CTMABr indicated Si-O symmetric bond stretching. The peak centered at 1707 cm^{-1} for CTMABr (Figure 3), and 1640 cm^{-1} for Acid-CTMABr (Figure 4) correspond to the bending and stretching vibrations of O-H and C–N group (Zhang *et al*, 2019). This meant that there were H-bonded hydroxyls and physically adsorbed water attached as well as amine presence on the organomodified bentonite clay surfaces. The band between 2800 – 3000 cm^{-1}, particularly 2855 cm^{-1} and 2922 cm^{-1} for CTMABr (Figure 3), and 2851 cm^{-1} and 2922 cm^{-1} for Acid-CTMABr (Figure 4), indicates C-H stretch for amine and methyl C=O for acid respectively. The bands located at 3697 cm^{-1} and 3623 cm^{-1} for CTMABr, and 3697 cm^{-1} and 3623 cm^{-1} for Acid-CTMABr are the typical indications of inner-surface hydroxyls (O-H) group and the one at 3623 is attributed to the stretching frequency of the internal hydroxyl groups and N-H amine group. These bands confirm the intercalation alkylammonium in the interlayer of galleries of the bentonite clay mineral (Mostofa *et al.*, 2015; Zhang *et al*, 2019).

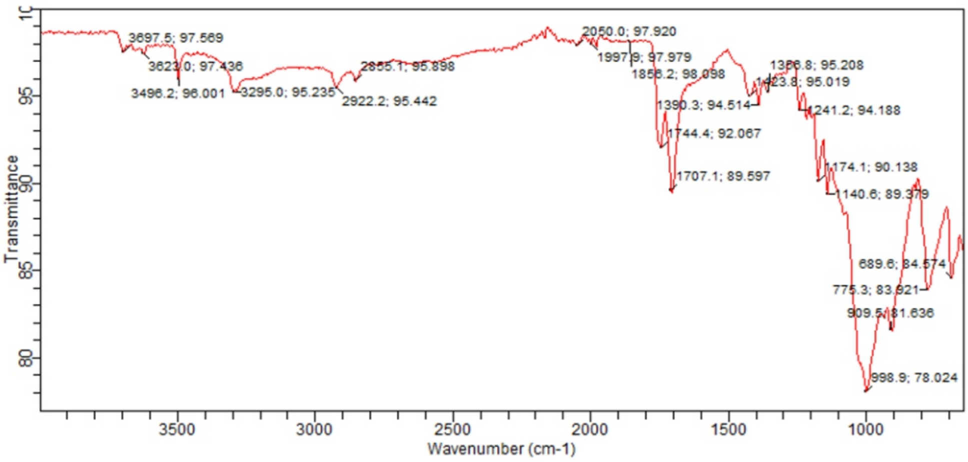

Figure 3: FTIR analysis of CTMABr organomodified bentonite clay

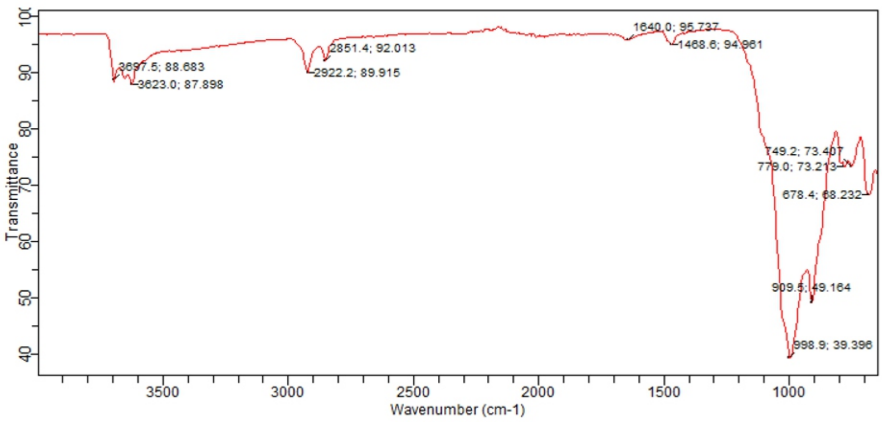

Figure 4: FTIR analysis of Acid-CTMABr organomodified bentonite clay

Adsorption Study

The synthesis CTMABr and Acid-CTMABr organomodified bentonite clay was utilized for the adsorption of crude oil from polluted water collected from Ejama-Ebubu, Eleme LGA in Rivers State. The initial concentration of crude oil in the polluted water was determined using Spectrophotometry analysis as 53.2075 mg/L which is comparable to **52.222 mg/L reported in literature (UNICEF, 2011)** and higher than acceptable for ground and surface water.

Adsorption study was investigated to determine the effect of contact time of the removal efficiency of CTMABr and Acid-CTMABr organo modified bentonite clay. Also, adsorption study was carried out to investigate the effect of temperature, adsorbent dosage, pH and concentration on the removal efficiency of the synthesis Acid-CTMABr organomodified bentonite clay.

Effect of Contact Time

The effect of contact time on the adsorptive properties of the CTMABr and Acid-CTMABr organo modified bentonite clay was investigate. Figure 5 (a) and (b) shows the effect of contact time on the percentage removal of crude oil pollutant from the waste effluent. The contact time was varied between 0 – 60 min (1 hr.). From Figure 5 (a) and (b), it was observed that the percentage removal of crude oil in the polluted water rise rapidly to 63.298% and 60.816% within 0 – 10 min for CTMABr and Acid-CTMABr organomodified bentonite clay respectively. However, from 10 – 40 min, it can be seen that the rate of crude oil removal from the polluted water slow down from 63.298 – 80.142% (Figure 5a) and 60.816 – 95.213% (Figure 5b) for CTMABr and Acid-CTMABr organo modified bentonite clay respectively. It can be seen that the Acid-CTMABr organomodified bentonite clay has higher removal efficiency than CTMABr organomodified bentonite clay. This indicates, that pretreatment of the bentonite clay with organic acid such as oxalic acid has could increase the adsorptive properties of the organo modified bentonite clay.

It could be inferred that equilibrium is reached at about 40min adsorption time. It was further observed that beyond 40 min, the adsorption rate of both CTMABr (Figure 5a) and Acid-CTMABr (Figure 5b) organo modified bentonite clay slow down significantly almost flatten from 40 – 60 min. Maximum removal of 86.170% and 97.518% was observed for CTMABr and Acid-CTMABr organomodified bentonite clay respectively at 60 min adsorption time. Hence, increase in contact time beyond 40 min does not have significant effect on the percentage removal of crude oil in polluted water. This showed that further increase in contact time above 40 min resulted in the adsorption sites getting saturated gradually and the uptake rate will be controlled by the rate at which the adsorbates (crude oil) is transported from the exterior to the interior sites of the organomodified bentonite clay adsorbent, thus, the adsorption became much slower (Talaat *et al.*, 2011). This shows that pretreatmen of organo modified clay with organic acid such as oxalic acid cold improved the adsorption capacity of organo modified bentonite clay. Therefore, in

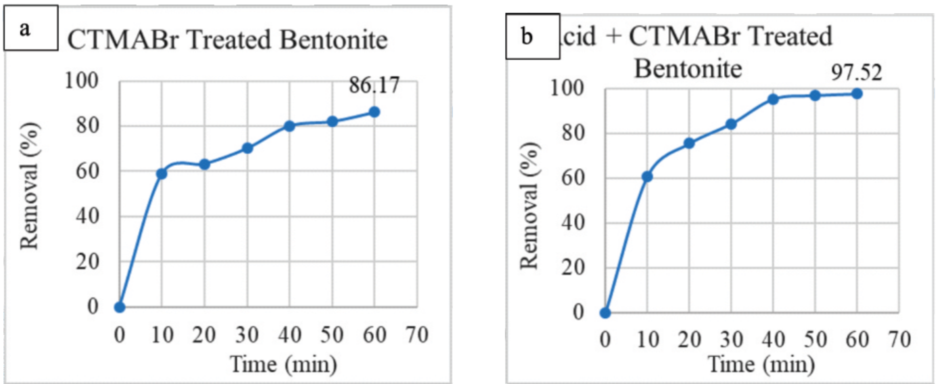

Figure 5: Effect of Contact Time on Adsorptive Properties of (a) CTMABr and (b) Acid-CTMABr organo modified bentonite clay

Effect of Temperature

The influence of temperature on the adsorptive properties of the synthesis Acid-CTMABr organo modified bentonite clay was investigated. Figure 6 shows the effect of temperature on the percentage removal of crude oil pollutant from the waste effluent. The temperature was varied between 25 – 75 °C at constant time of 40 min. It was observed that there was rapid increase in the percentage removal of crude oil to 86.702% at 45 °C. This could be attributed to the availability of sufficient adsorption site (Emam, 2013; El-Zahhar and Al-Hazmi, 2015). It can be seen that, from 45 – 75 °C, the rate of adsorption of crude oil into the pores of synthesis Acid-CTMABr organomodified bentonite clay was slow. This could be attributed to the fact that the adsorption site is almost filled up and saturated.

However, at 40 min constant time, maximum removal of 98.050% was reached at 75 °C. This indicates that increase in temperature result to increase in the percentage removal of crude oil from polluted water. This could be attributed to the fact that at higher temperature, the molecule of the crude oil gets lighter and could move freely and fast in to the pores of the Acid-CTMABr organomodified bentonite adsorbent. Hence, increase in temperature, increases adsorption capacity of Acid-CTMABr organo modified bentonite adsorbent.

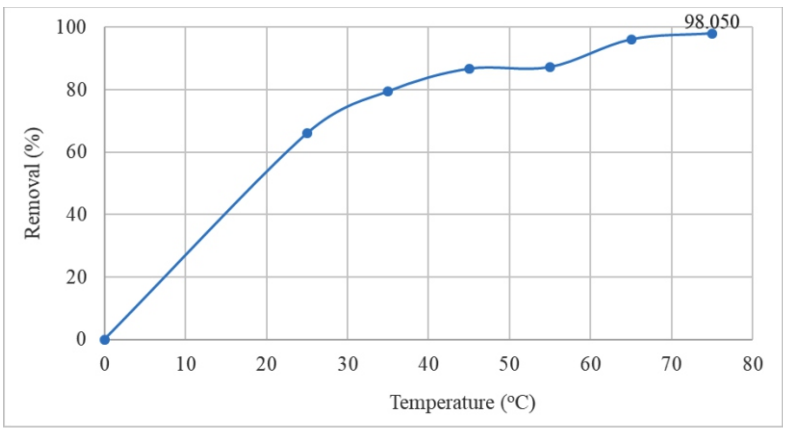

Figure 6 Effect of Temperature on Adsorptive Properties of Acid-CTMABr

Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorptive properties of the synthesis Acid-CTMABr organo modified bentonite clay was investigated. Figure 7 shows the effect of adsorbent dosage on the percentage removal of crude oil pollutant from the waste effluent. The adsorbent dosage was varied between 0.5 – 3g at constant time, initial concentration, pH and temperature. It was observed that, removal crude oil using the synthesis Acid-CTMABr organo modified bentonite clay increases rapidly to 44.681% at 0.5 g of adsorbent and then slowly to 49.113% at 1.0 g of adsorbent. Also, from rapid increase in the percentage removal of crude oil to 94.681% was observed as adsorbent dosage increases from 1 – 2g. This could be attributed to the high number of adsorption sites per unit mass of Acid-CTMABr organomodified bentonite clay adsorbent (Emam, 2013; El-Zahhar and Al-Hazmi, 2015).

However, increase in adsorbent dosage from 2 – 3g, does not have significant effect on the percentage removal of crude oil as the it only rises from 94.681% to 95.035%. Theis could be explained by the fact that, at low adsorbent dosage, the adsorption sites are diluted in the solution and available for interactions with crude oil from the polluted water while at high adsorbent dosage no significant removal due to possible aggregation of adsorbent in the polluted water (Emam, 2013; El-Zahhar and Al-Hazmi, 2015). Consequently, the availability of free adsorption sites is limited for removal of crude oil.

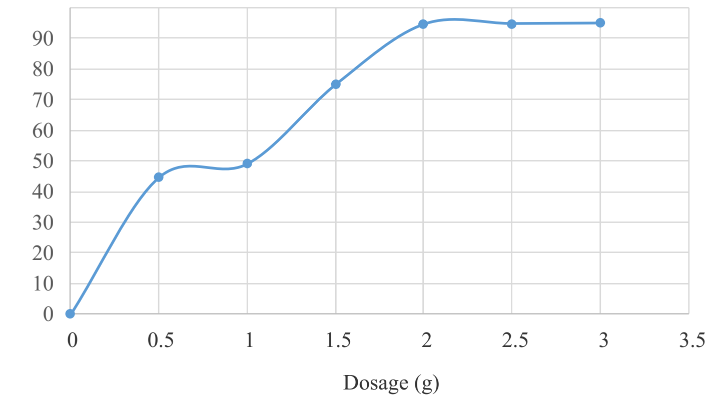

Figure 7 Effect of Adsorbent Dosage on Adsorptive Properties of Acid-CTMABr organomodified bentonite clay

Effect of pH

The influence of pH on the adsorptive properties of the synthesis Acid-CTMABr organomodified bentonite clay was also investigated. The pH of the solution is one of the significantly parameter when considering adsorption capacity from aqueous solution because, the pH of the aqueous solution controls the adsorption capacity due to its influence on the surface properties of the adsorbent (Emam, 2013). Figure 8 shows the effect of pH on the percentage removal of crude oil pollutant from the polluted. The pH was varied between 4 – 10 at constant time, initial concentration, dosage and temperature. It was observed that, the removal crude oil using the synthesis Acid-CTMABr organomodified bentonite clay increases rapidly and linearly to 85.461% as the pH increases from 4 – 9, and tends to decreases slightly to 85.106% as the pH increases to 10. The maximum removal occurred at of 9 (alkaline medium). The increase in crude oil percentage removal with increase in pH is attributed to the fact that the surface functional groups of the synthesis Acid-CTMABr organo modified bentonite clay ionizes resulting in greater retentive power towards the crude oil adsorbate (Emam, 2013; Aroke *et al.*, 2016).

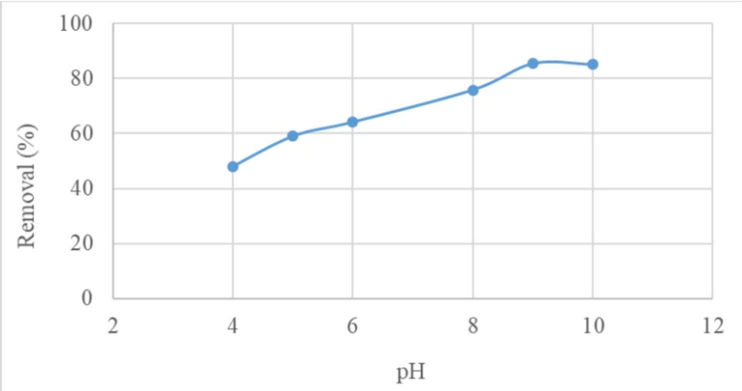

Figure 8 Effect of pH on Adsorptive Properties of Acid-CTMABr organomodified bentonite clay

Effect of Initial Concentration

The effect of initial concentration on the adsorptive properties of the synthesis Acid-CTMABr organo modified bentonite clay was also investigated. The initial concentration of the solution has been found to impact adsorption capacity of adsorbent. Figure 9 shows the effect of initial concentration on the percentage removal of crude oil pollutant from the polluted. The initial concentration was varied from 0.05 – 0.30 mg/L at constant time, pH, dosage and temperature. It was observed that, the removal of crude oil using the synthesis Acid-CTMABr organomodified bentonite clay increases rapidly 62.589% at initial concentration of 0.05 mg/L and slightly to 62.766% as initial concentration increases from 0.05 – 0. 10 mg/L.

The high removal at the initial concentration of 0.5 mg/L could be attributed to the high number of adsorption sites available at the initial adsorption stage (Gandhi *et al.*, 2014). However, there was a slow rise in the percentage removal of crude oil to 83.511% as the initial concentration increases from 0.10 – 0.25 mg/L until it attains a maximum of 83.865% removal at 0.30 mg/L. This is because the adsorption sites become saturated gradually as initial concentration increases and the uptake rate will be controlled by the rate at which the adsorbates is transported from the exterior to the interior sites of the synthesis Acid-CTMABr organomodified bentonite clay adsorbent and as such, the adsorption became much slower (Talaat *et al.*, 2011). Hence, the number of free adsorption sites tends to decease, under this condition the removed amount of crude oil tends to reached equilibrium when no further uptake of the adsorbate would be observed.

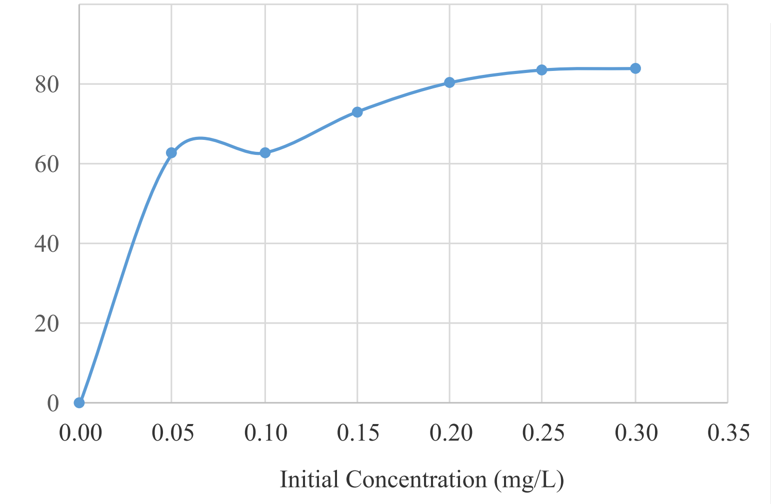

Figure 9 Effect of Initial Concentration on Adsorptive Properties of Acid-CTMABr organomodified bentonite clay

Conclusion

The development of organomodified bentonite clay using CTMABr was successful. The XRD analysis, shows that the crystal structure of id-CTMABr organomodified bentonite clay comprises mainly quarts and albite with the highest intensity and small amounts of microcline silicates. The SEM/EDX analysis also shows that the surface morphology of CTMABr organomodified bentonite clay was relatively flat and smooth with fewer pores while the particle size and structure of Acid-CTMABr organomodified bentonite clay were remarkably altered by forming more holes and cracks with more exfoliated, loose, and curled layers whereas, the high composition of Si and Al in both CTMABr and Acid-CTMABr organomodified bentonite clay further confirm the XRD result, that the synthesis adsorbents constitute primary aluminum silicate material. Furthermore, the FTIR analysis shows that the bands confirm the intercalation alkylammonium in the interlayer of galleries of the bentonite clay mineral in both CTMABr and Acid-CTMABr organomodified bentonite clay sample.

Adsorption study shows that increases in contact time increases the removal of crude oil from polluted water with a maximum removal of 86.170% and 97.518% for CTMABr and Acid-CTMABr organomodified bentonite clay respectively at 60 min adsorption time. Also, increases in temperature increases the removal of crude oil from polluted water with a maximum removal of 98.050% at 75 °C. Increase in adsorbent dosage increases the removal of crude oil with a maximum removal of 94.681% at 2g of adsorbent and maximum removal occurred in an alkaline medium at a pH of 9. Additionally, increase in initial concentration of crude oil conttaminat in water increases the removal of crude until it attains a maximum of 83.865% removal at 0.30 mg/L. Therefore, pretreatment of organomodified clay with organic acid such as oxalic acid cold improved the adsorption capacity of organomodified bentonite clay. The results show that organomodified bentonite clay is a promising technology adsorbent for the removal of crude oil from contaminated wastewater.

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