

Multicomponent Adsorption of BTEX from Refinery Waste water Using Source Clay Modified with Hexadecyltrimethylammoniumchloride

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Abstract

Refinery waste water disposal is one of the most threatening health hazards in Nigeria and in large extent a contributor of global environmental deterioration. This study therefore, dwells on the investigation of the effects of the time, temperature, dosage, pH, and concentration on the removal of BTEX (Benzene, Toluene, Ethylbenzene and Xylene) from refinery waste water using source clay modified with HDTMAC surfactant. Source clay from Ugwu Nzu, in Unwana-Afikpo, Ebonyi State of Nigeria was modified using synthesized hexadecyltrimethylammoniumchloride (HDTMAC). The produced organophilic clay was used to remove BTEX (Benzene, Toluene, Ethylbenzene and Xylene) from Port Harcourt Refinery Company Eleme wastewater. The results showed that the modified clay was more efficient in the removal of Benzene with 92% adsorbed within the first 20 min while 80%, 75.3% and 78.7% respectively for Toluene, Ethylbenzene, and Xylene. The result also showed that a 400% increase in dosage led to only 25% increase in adsorption efficiency while increasing temperature of the adsorbate had a corresponding increase in adsorption. Above all, the result obtained from the use of Ogwuta clay after an elaborate study showed ability to remove contaminants from Port Harcourt Refinery Company Eleme waste water and as such may offer some outlets for utilization in many petrochemicals and allied industries based on its abundance, biodegradability, affordability and ecofriendly attributes.

Keywords: Hexadecanol, thionyl chloride, kaolin, BTEX, wastewater, adsorbate, HDTMAC

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I. Introduction

Petroleum refineries are industrial plants where (crude oil with limited use) is transformed into more useful components. It involves complex systems of multiple operations that depend on the desired products and the input crude. Many of the processes, such as cooling, boiling, stripping, washing, desalting, etc involve use of copious amount of water thereby making refineries large consumer of water relative to other industries. The processes generate categories of wastewater as desalter effluent, sour water, tank bottom draws and spent caustic. This wastewater gets contaminated in the course of operations due to contact with crude.

Evans (2011) observed that owing to the obsolete state of most of the process units, particularly in most developing countries, it is unlikely to achieve high efficiency. This does not exclude the wastewater management operation. Therefore, many industries discharge inadequately treated wastewater into the environment.

This discharge of wastewater, according to Obi and Woke, (2014) introduces pollutants to the environment which in most cases exceed the admissible sanitary standards of living. They identified the major pollutants to include heavy metals, synthetic materials, aromatic and poly aromatic hydrocarbons; etc. Netai *et al.*, (2013) noted that phenols and some other aromatic compounds such as BTEX (Benzene, Toluene, Ethylbenzene and Xylene) are priority pollutants.

Occasional haemorrhages in retina and conjunctiva, neuroretinal edema and papilledema, in addition to optic neuritis have been associated with benzene contacts (D'Andrea, 2018). Sidmara *et al.*, (2013) added that long term (about one year) exposure affects the bone marrows and can cause a decrease in red blood cells, leading to anaemia. Also, repeated or prolonged contact of BTEX with the skin leads to defatting of the skin thereby causing it to crack and peel. Consequently, removal of these contaminants from waste water has become a priority. In achieving this, the demands for chemical processes that are clean, energy efficient and intrinsically safe are on the increase. This tilts the objectives of most chemical industries towards achieving processes that are environmentally friendly, includes use of less hazardous and energy source with nearly zero waste generation. The global awareness of the environmental deterioration and health impact of some refinery

wastewater pollutants has caused wastewater treatment to receive greater attention (Kiursk *et al.*, 2011). This interest has led to the development of several treatment techniques, methods and means by researchers who posit that any technique has to agree with the wastewater properties. (Saad, 2015; Rashu and Monika, 2013; Obi and Woke, 2014).

Some undesirable organic pollutants according to Lidia *et al.*, (2017) can be removed from aqueous solutions through chemical precipitation, ion exchange, electrodeposition, solvent extraction, membrane separation, reverse osmosis and adsorption process. The development of low cost adsorbents with easy manipulation and regeneration for possible reuse has been an object of significant attention. Several types of materials such as activated carbon, carbonized maize tassels, banana pitch, cassava waste, coal and clay minerals have been researched to adsorb organic pollutants from aqueous solutions (Okoro and Abii, 2011).

Clay minerals are naturally occurring materials composed of fine-grained phyllosilicates (minerals which show plasticity through a variable range of water content, trapped in the mineral structure by polar attractions). They are any group of hydrous aluminum silicates with a layer structure and very small particle size. They have a high surface area, are non toxic and are low in cost with high efficacy in adsorption of pollutants from aqueous solutions (Neeraj and Chandraa, 2021). Natural clays are inherently hydrophilic due to the hydration of organic cations in its active sites. This makes it ineffective in the removal of organic substances such as BTEX that is non polar and non ionic. Therefore, to enhance its applicability, natural clays are modified using cationic surfactants.

Studies, on the removal of BTEX using surfactant-modified clay have been conducted, (Carvalho *et al.*, 2012, Nourmoradi *et al.*, 2012, Fabiola *et al.*, 2014, Egbuchunam *et al.*, 2016). However, investigation on the applicability of Ogwuta clay (one of the largest clay deposits in the Southeastern Nigeria), have not been reported. Therefore, in this study, source clay of predominantly kaolin mineral, was modified with hexadecyltrimethylammoniumchloride (HDTMAC) surfactant and used to remove BTEX from Port Harcourt refinery wastewater.

II. Materials and Methods

2.1 Materials

All the chemicals used were of analytical grade and the following processes were carried out. A 0.1M HCl and 0.1M NaOH stock solutions were used to adjust the pH of samples. The concentration of the sample before and after sorption was measured using Agilent 6890N Gas Chromatography. A (AR, 3130) weighing balance was used to determine the weight of samples.

2.1.1. Stock Collection

Wastewater stock sample was collected from the observation tank of Port Harcourt Refining Company (PHRC), Eleme using BIG bottles, transported and stored in the laboratory for use.

2.1.2. Sample Collection and Preparation

The clay sample was collected from its natural deposit 12 cm below earth surface in Unwana, Afikpo North Local Government Area of Ebonyi State, Nigeria. The collected materials were brought to the laboratory in polythene bags. The sample was sun - dried for 2 – 3 days at a temperature between 28^oC and 32^oC. Observed impurities found on the clay sample were removed by hand picking. The sample was further oven- dried at 105^oC for 2 hrs using BTOV 1423 oven, and subsequently crushed with an Iron roller to fine particle sizes. These clay particles were sieved into 63 µm size using Stainless Steel Drum Sieve and stored in a glass bottle.



Plate 1. Ugwu Nzu clay deposit

2.2. Methods

2.2.1. Synthesis of hexadecyltrimethylammoniumchloride (HDTMAC) Surfactant

The synthesis was done in line with the method described by Asdani *et al.* (2017). The process involved the preparation of hexadecylchloride intermediate from hexadecanol and thionyl chloride and subsequently used in the synthesis of hexadecyltrimethylammonium chloride. A 1.0 M hexadecanol was prepared by dissolving 23.5 g in 1000 cm³ ether and 1.0 M sulphurous dichloride was prepared by making up 7.3 cm³ to 1.0 dm³ using ether. 500 ml each were mixed in a flask and refluxed for 24 hrs at 60°C. The condenser was removed and shaken for another two hours before being allowed to cool at 10°C for 24 hrs. 11.2 cm³ of trimethylamine was further added and refluxed for another 24 hrs at 60°C. The slightly yellow liquid mixture was cooled overnight and stored in a bottle.

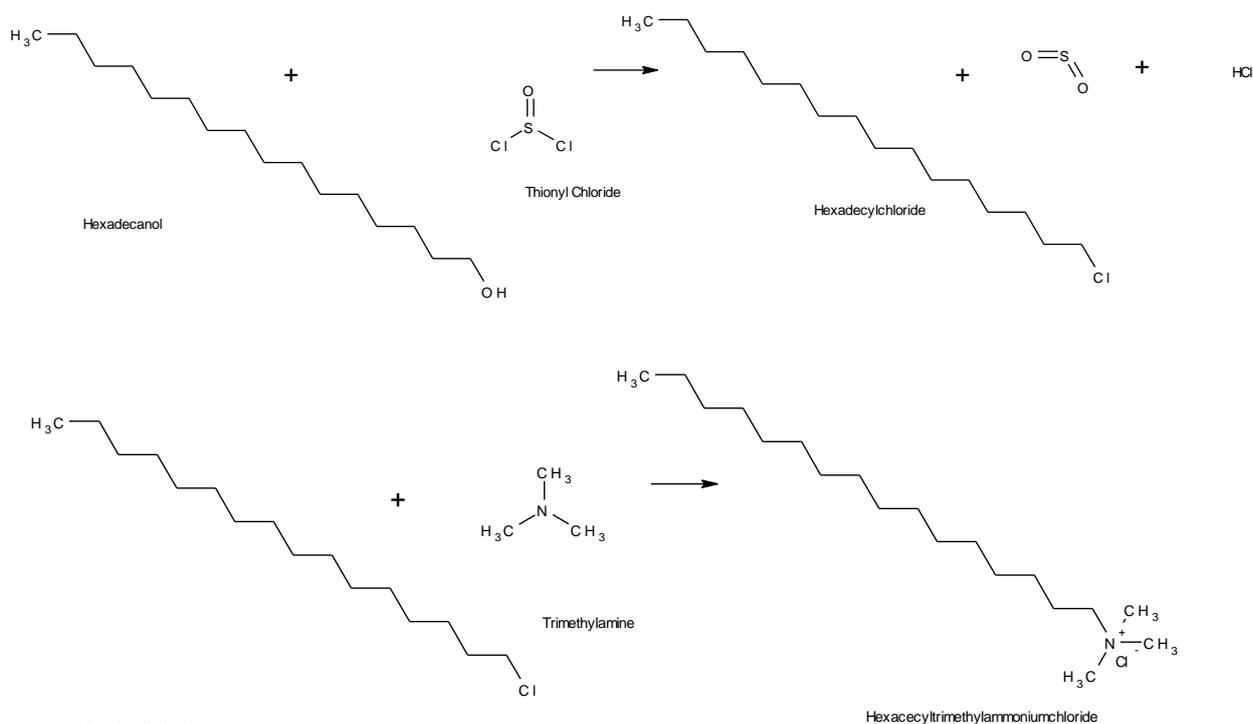


Figure 1. Reaction equations for the synthesis

2.2.2 Organophilization of Source Clay

According to Shirin *et al.* (2012), A 20 g of clay was dispersed in a 2 L capacity beaker containing 1000 ml of water for 90 min at a rotation of 250 rotations per minute and at 80°C. A solution containing 10 g of HDTMA chloride with 4.2 ml concentrated HCl in 500 ml hot distilled water was subsequently added and allowed to mix for another 90 min at the same rotation after which the solid was filtered using a vacuum filtration apparatus. The modified clay was oven-dried for 24 hrs at 80°C, ground into powder using mortar and pestle, labelled and then stored in a desiccator.

2.3. Adsorption Tests

All adsorption tests (except the one for the effect of temperature on the adsorption) were carried out at room temperature. Batch adsorption process was employed using 250 ml conical flasks to access the adsorption efficiency of the HDTMAC-modified clay. Results of the refinery wastewater show the following initial concentrations: 20.38 ppm benzene, 11.13 ppm ethylbenzene, 13.17 ppm toluene and 9.56 ppm xylene. It was used without further treatment. A 0.2 g of the organoclay was added to 50 ml of BTEX wastewater solution and by the help of a magnetic stirrer, the mixture was stirred until equilibrium reached. The suspension was filtered and the filtrate was analysed by GC-MS. The percentage removal of BTEX from the solution and their uptake in the solid, q_e (mg/g), were calculated using the following expressions:

$$\% \text{BTEX removal} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$\text{Adsorption capacity } (q_e) = \frac{(C_o - C_e)V}{m} \quad (2)$$

Where, C_o is the initial BTEX concentration (mg/L), C_e is the concentration (mg/L) at any time t , V is the volume (L) of the solution and m is the mass (g) of the adsorbent.

2.3.1. Effect of pH

To determine the effect of pH, the tests were carried out using wastewater adjusted to pH values of 2-12 with the aid of 0.1M NaOH and 0.1M HCl stock solutions.

2.3.2. Effect of Adsorbent Mass

The effect of adsorbent mass was investigated using the following masses of the adsorbent; 0.2 g, 0.4 g, 0.6 g and 0.8 g. This was done at a constant pH of 6.

2.3.3. Effect of Time

To determine the effect of time on the adsorption process, 0.2 g of adsorbent was used at different time interval of 10, 20, 30, 40 and 60 min

2.3.4 Effect of Concentration

Concentration effect experiment for the adsorption process was done at pH 8. A 25 ml each of wastewater stock was diluted by the addition of 25 ml, 50 ml, and 75 ml of deionized water thereby producing the initial, $\frac{1}{2}$, $\frac{1}{3}$ and $\frac{1}{4}$ respectively of the initial concentration of the wastewater sample. A 0.2 g of adsorbent was added to 50 ml of the diluted sample and stirred with magnetic stirrer at 250 rpm for 30 minutes

III. Results and Discussion

3.1 Effect of pH Change

The influence of hydrogen ion concentration of the adsorbent on BTEX removal from aqueous solution was assessed. As can be seen from Figure 1a and figure 1b, adsorption capacity (q_e) and efficiency did not change significantly as the pH was changed from 2 to 10. The maximum adsorption was observed at pH 8 and decrease slightly after wards. Eydi *et al.*, (2018) opined that this indifference of BTEX removal to change in the pH is attributed to the non- involvement of ion exchange in the process. However, Teng and To (2000) added that with the sign of the zeta potential at increasing pH, desorption at equilibrium tends to be favoured due to electrostatic repulsion on the surface of the adsorbent. Therefore, adsorption is better at the range $5 < \text{pH} < 10$.

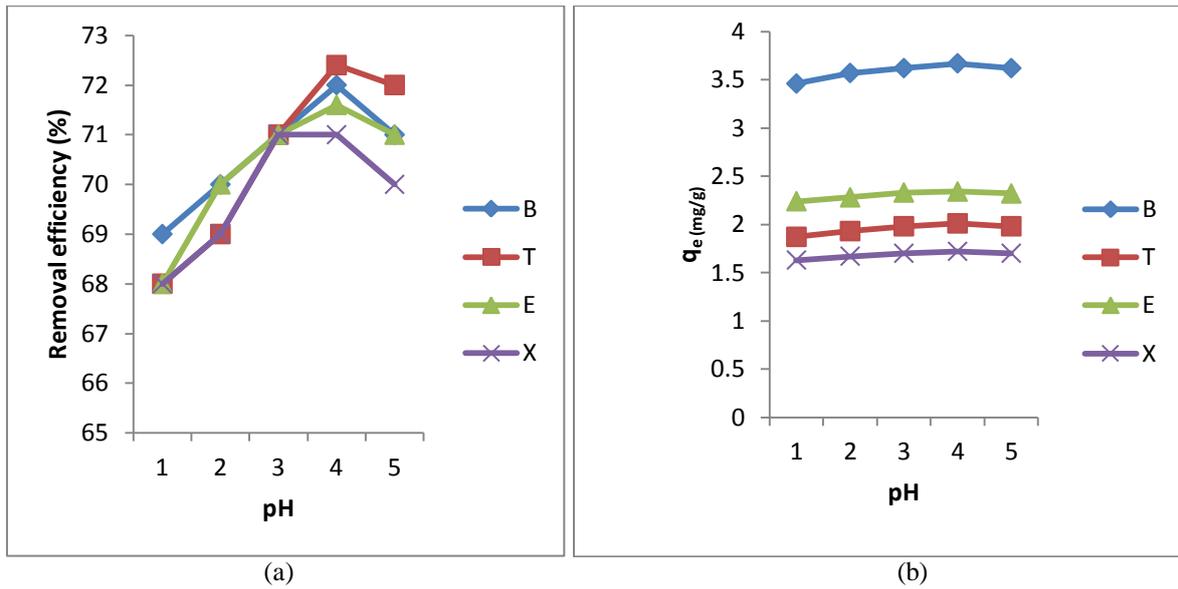
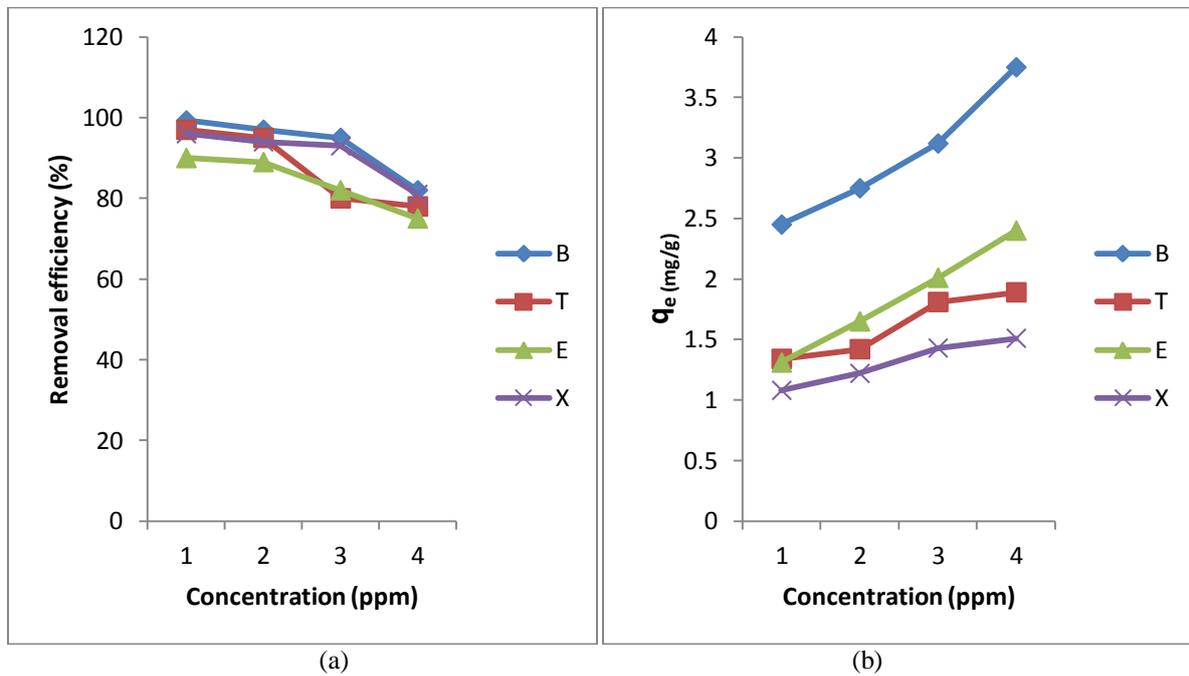


Figure 1: (a) Plot of removal efficiency versus pH. (b) Plots of adsorption capacity versus pH



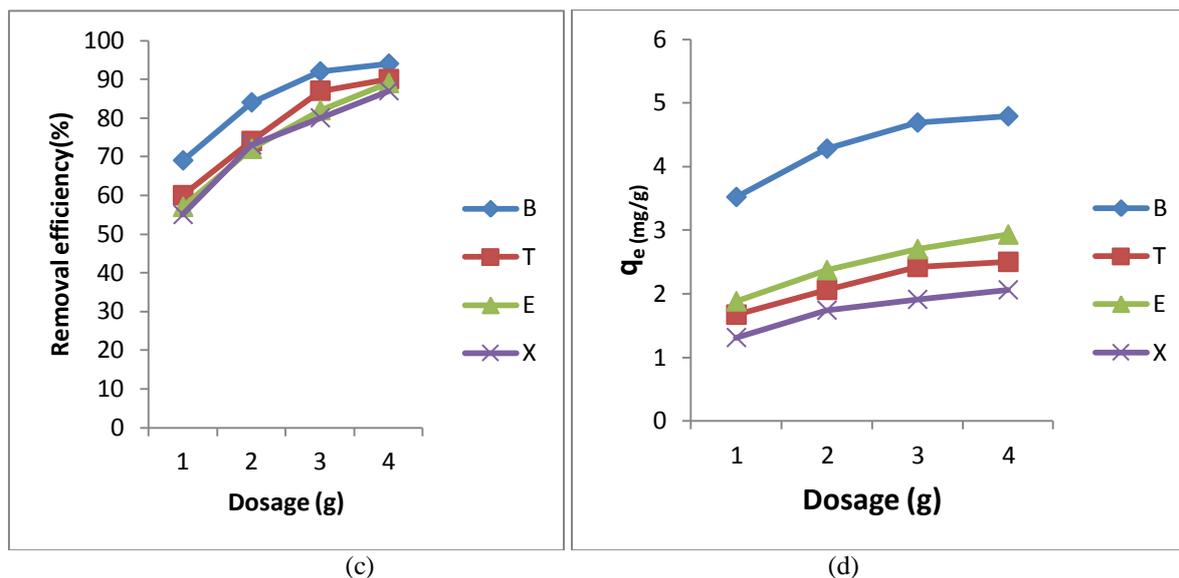


Figure 2: (a) effect of concentration on removal efficiency. (b) Effect of concentration on adsorption capacity. (c) Effect of adsorbent dosage on removal efficiency. (d) Effect of dosage on adsorption capacity

3.2 Effect of Concentration

Figures 2a and 2b show how changes in the concentration affected BTEX uptake by the HDTMAC-modified clay. It can be observed that as the initial concentration of the adsorbate in the waste water was decreased by dilution from $\frac{1}{2}$ to $\frac{1}{4}$, the adsorption capacity decreased respectively from 3.72-2.45, 1.89-1.34, 2.14-1.31 and 1.51-1.08 mg/g for benzene, toluene, ethylbenzene and xylene. On the other hand, the removal efficiency increased as the concentration decreased as can be seen in figure 2b. This decrease according to Onwuka *et al.*, (2020) may be attributed to decrease in driving forces (van der Waal's) affecting BTEX compounds and active adsorption sites of the adsorbent. This could be possible due to the fact that solutions of the higher concentration tend to provide driving forces that can overcome mass transfer resistance between aqueous and solid phases (Mobashapour *et al.*, 2012). Also, but remotely, the increased adsorption at high concentration can be due to the possible creation of new active sites on the surface of the adsorbent (Nan *et al.*, 2011).

3.3 Effect of Dosage

The uptake of BTEX at different doses of HDTMAC-clay was also investigated and the result shown in Figures 2c and 2d. As evident in the Figures, following the increase in mass of the adsorbent from 0.2 g to 0.8 g, adsorption capacity (q_e) increased from 3.52 to 4.79 for benzene. This represented an increase of removal efficiency to 94% from 69% (Figure 2d). This 25% increase in removal efficiency was also observed for toluene, ethylbenzene and xylene. This is expected as increasing dosage makes available more adsorption sites and surfaces (Makhatini and Rhatilal, 2017). Also, 23% out of the 25% removal efficiency was observed after the second increase in adsorbent dose, making further removal only marginal as the dose was increased. This trend was also observed by Tadele and Fikiru (2020) when they assessed the removal of Basic Yellow (BY-28) dye from aqueous solution using Ethiopian Kaolin. However, it was also observed that increasing the dosage beyond 0.6 g did not give a corresponding increase in the adsorption.

3.4. Effect of Time

The effect of time on the adsorption capacity and removal efficiency as presented in Figures 3a and 3b revealed that as the time increased, adsorption of BTEX by HDTMAC-clay increased. This observation according to Netai *et al.*, (2013) may have been due to the increased number of vacant sites on the adsorbent. One notable observation was that adsorption capacity jumped to 4.69, 2.23, 2.47 and 1.86 mgg⁻¹ representing 92.0, 80.0, 75.3, and 78.7% respectively of benzene, toluene, ethylbenzene and xylene within the first 20 min. Between 20th and 40th min, the capacity increment was marginal. Also, from the graphical representation of the initial amount of adsorbate sorbed (Figures 3c), two line segments were evident. According to Daniela *et al.*, (2016), the first segment is usually associated with film diffusion and the second representing intraparticle diffusion into the porous structure of the clay. Similar pattern was reported for metal ions by Nan *et al.* (2011) and Ozdemir *et al.* (2009). The over 80% adsorption achieved within the first 40 min can be attributed to the initial accumulation of BTEX at the clay surface, thereby utilizing the relatively large surface area. As the surface binding sites were increasingly occupied, adsorption process was consequently slowed down (Iman *et*

al., 2014). Further increase in adsorption arose from the penetration of adsorbate to the inner active sites of the adsorbent.

Also, the effect of temperature on the adsorption of BTEX by HDTMAC-modified clay showed that as the temperature was increased from 30°C to 60°C, the adsorption equilibrium capacity increased (Fig 3d). This shows the process was endothermic (Thobeka and Suedesh, 2017).

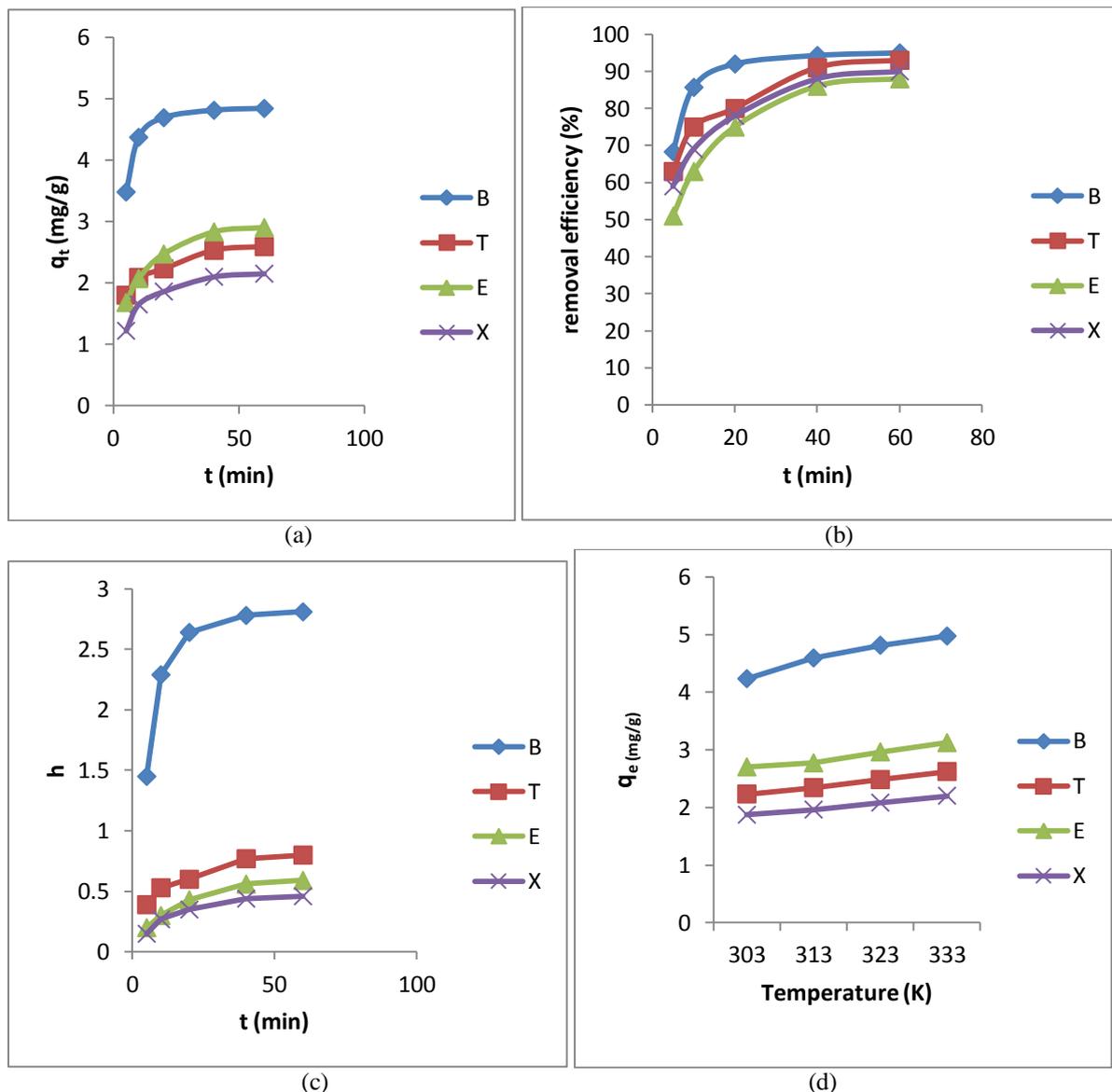


Figure3: (a) Plots of adsorption capacity with time. (b) Plots of removal efficiency with time. (c) Plots of initial adsorption rate (h) with time. (d) Plots of adsorption capacity (q_e) versus temperature (T)

IV. Conclusion

Organophilization of clay has been shown to increase its application. Source clay was modified using hexadecyltrimethylammoniumchloride (HDTMAC) and used to remove BTEX contaminants from refinery waste water. The effect of adsorbate pH and concentration, adsorbent mass, contact time and temperature on the adsorption process was investigated. The result showed that the process was time and temperature dependent with over 75% BTEX removed within the first 20 min. The amount adsorbed increased as the temperature increased. Therefore, Ogwuta clay shows increased application in removing phenyl-based contaminants from waste water when organophilized using quaternary ammonium surfactant. Above all, Ogwuta clay after an elaborate study showed ability to remove contaminants from refinery waste water may offer some outlets for utilization in many petrochemical and allied industries based on its abundance, biodegradable, affordability and ecofriendly attributes.

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