

Original Research Article

Kinetic Viewpoint of BTEX Removal Using Ehugbo-Nigerian Kaolinite Clay Modified with Hexadecyltrimethylammonium Chloride (HDTMAC)

ABSTRACT

Aim: Refinery wastes have been regarded as a consortium of majorly organic pollutants and improper management metamorphose to the distortion of human and environmental domains. In this study, the efficiency of hexadecyltrimethylammonium chloride (HDTMAC)-modified Ogwuta kaolinite clay in the removal of benzene, toluene, ethyl benzene and xylene (BTEX) from refinery wastewater was evaluated.

Methodology: Batch adsorption process was employed in the evaluation. The initial and final concentrations determined using Gas Chromatography-Mass Spectrometer (GC-MS) at different time intervals of 10, 20, 30, 40 and 60 min. Pseudo-first order, pseudo-second order, and intra-particle diffusion kinetic models were employed to analyze experimental data generated.

Results: Results showed that 92.0, 80.0, 75.3 and 78.7% removal efficiencies of benzene, toluene, ethyl benzene, and xylene were achieved within 20 min. The result further revealed that pseudo-second order kinetic model fitted best with R-squared values of 0.999 for each of the hydrocarbon pollutants. The calculated equilibrium capacity of 5.00, 2.722, 3.14 and 2.31 mg/g were approximately equal to that generated experimentally. This study reveals that pseudo-second order rate constant was nearly proportional to the size and structure of the monocyclic

hydrocarbon pollutants with removal efficiency in the order of benzene = toluene > xylene > ethyl benzene.

Conclusion: This study has revealed that modified kaolinite clay can serve as a veritable option for the removal of BTEX and other organic pollutants from both wastewaters and other sources.

Future Scope of Study: This study recommends that further work on adsorption and desorption with respect to other inorganic and organic pollutants should be carried out using the product and hence, the findings obtained will form a blue-print in environmental regulation formulations and policies.

Keywords: Adsorption, BTEX, Kaolinite, Kinetics, Organo-clay, Soil

1. INTRODUCTION

The excessive use of water due to the complex modes of operations involved in refining crude oil makes refineries the largest consumer of water among chemical industries. The water is used largely by the oil processing industries on cooling and steam generation [1].

Petroleum refinery and petrochemical plants extensively generate toxic organic pollutants and persistent organic polluted water [2, 3].

According to the World Health Organization (WHO), the permissible limits of BTEX in potential portable water are less than 0.8 mg/L [4]. Kong et al. [5] observed that refineries in the Gulf of Mexico and Indonesia discharged wastewater containing benzene ranging from 2.3 mg/L to 2.8 mg/L, representing 230-280 times in excess of the limit for benzene, and this is attributed to the drawbacks associated with the process systems. These limitations according to Kirkeleit et al. [6], is not linked to the obsolete state of most process lines of refineries in the developing countries.

Fengsheng et al. [7] reported that the components of BTEX are toxic and carcinogenic. However, low level exposure can be associated to rapid sperm mutation, cardiovascular disorders, respiratory abnormalities, dizziness, etc. [8]. In addition, ingestion was among the factors identified to harm human immune system with other health impacts such as leukemia and anemia [9]. This underscores the imperativeness of the removal of BTEX from wastewater of refineries in particular and other chemical industries in general.

Experimental studies have been reported on technologies such as membrane separation, reverse osmosis, chemical oxidation, biological treatment, air stripping, and adsorption that can achieve substantial removal of organic pollutants from industrial wastewater [10-13].

Adsorption technique has been singled out as one of the best decontamination foundations for the removal of pollutants (inorganic, organic, etc.) from wastewaters, polluted soils, air, etc. arising from the possibility of using readily available and thermally stable materials [14-16]. Extensively, many of such materials including activated carbon and clay are commonly used [17-20]. However, the exorbitant cost of regeneration of activated carbon increases the preference for clay [21, 14].

Clay minerals are composed of layered structures which allow the accumulation of substances (gaseous, solids, and liquids) at the surface during pollution investigations [22]. The isomorphous substitution of metal ions in clay has inherently made it hydrophilic and this property limits its application in aqueous organic medium with non-polar compounds such as BTEX. The valorization process using quaternary ammonium salts has transformed clay into organophilic matrix suitable for the decontamination of organic pollutants [17, 23]. "This enhancement increases the inter-laminar distance or basal spacing of d_{100} plane and modifies the surface properties" (24, 25).

Momina and Suzylawati [26] reported that "the recovery/regeneration techniques enhance the adsorption and retention potential of spent low-cost adsorbents and reflects on the future prospects for their use in wastewater treatment". The authors further highlighted that the recovery process is seamless, cheap, and eco-benign depending on the method adopted.

The clay deposit (majorly kaolinite in Plate 1) in Ehugbo (Afikpo), the South Eastern part of Nigeria on latitude 6° 06' 93" N and longitude 8° 19' 94" E (Figure 1) has been idle and the investigations on it by Agha and Obi [27] and Agha et al. [25, 28] have really exposed the physical and chemical properties of the clay. Kaolinite clay mineral is the major component of ultisols and oxisols soils.

Adsorption isotherms play vital role in the assessment of the interaction between adsorbate (BTEX) and adsorbent (modified clay) and the optimum removal efficiency of the adsorbent. Owing to the good properties exhibited by this untapped natural clay during the base-line characterization [25, 27, 28], it is therefore pertinent to evaluate the adsorption kinetics (mechanism) to ascertain the extent of efficiency and effectiveness of the modified clay during the adsorption process.

Therefore, in this work, adsorption kinetics of refinery wastewater containing benzene, toluene, ethyl benzene, and xylene (BTEX) has been evaluated using Ogwuta kaolinite clay modified with hexadecyltrimethylammonium chloride (HDTMAC).

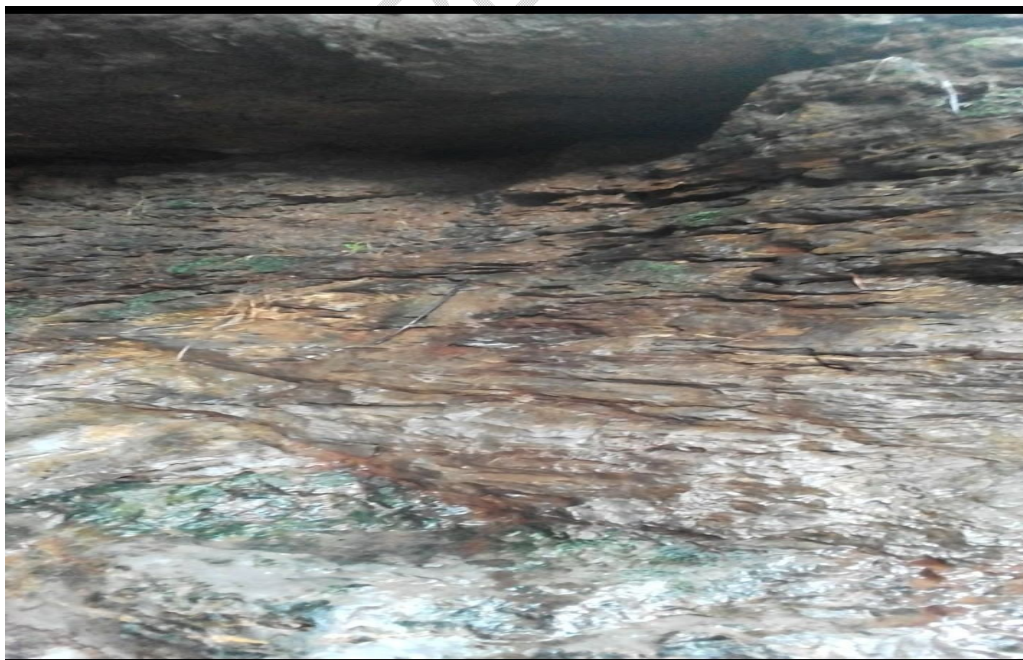


Plate 1. Ogwuta clay deposit

2. METHODOLOGY

2.1 Materials

All the chemicals used for the purpose of this work were of analytical grade. A 0.1M HCl and 0.1M NaOH stock solutions were used to adjust the pH of samples of the wastewater collected from the observation tank of Port Harcourt Refining Company (PHRC), Eleme using specialized bottles called “Bassey and God Investment” (BGI) to prevent evaporation given the volatility of the pollutants. The concentration of the sample before and after sorption was measured using Agilent 6890N Gas Chromatography. A weighing balance (AR3130) was used for weighing of samples. The hexadecyltrimethylammonium chloride clay [25] was crushed with an iron roller to fine particle sizes. These clay particles were sieved into 63 μm size and stored in a glass bottle.

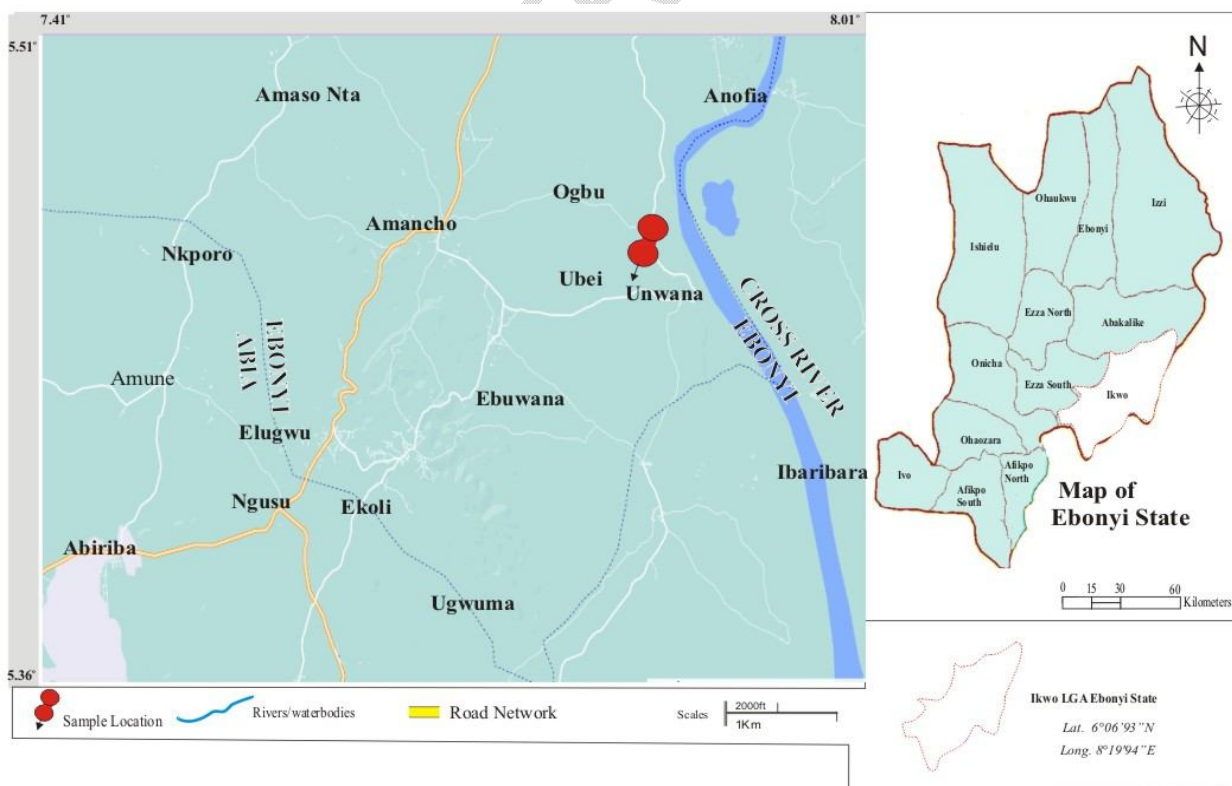


Fig. 1. Map showing the study area of interest

2.2 Batch Adsorption Experiments

Batch adsorption process was employed using 250 ml conical flasks to determine the adsorption efficiency of the HDTMAC-modified clay. Results of the refinery wastewater show the following initial concentrations: Benzene (20.38 ppm), ethylbenzene (11.13 ppm), toluene (13.17 ppm), and xylene (9.56 ppm). It was used without further treatment. A 0.2 g of the HDTMAC-modified kaolinite clay was added to 50 ml of BTEX wastewater solution maintained at pH 6 and 298 K and by the help of a magnetic stirrer, the mixture was stirred until equilibrium reached. The suspension was filtered and the supernatant analyzed using GC-MS. This was repeated at different time intervals of 10, 20, 30, 40 and 60 min. The adsorption capacity and removal efficiency of BTEX in the waste was evaluated using the expression:

$$\text{Adsorption Capacity } (q_e) = \frac{(C_o - C_e)V}{m} \quad (1)$$

$$\text{Removal efficiency } (\%) = \frac{(C_o - C_e)V}{m} \times 100 \quad (2)$$

Where, C_o is the initial BTEX concentration (mg/L), C_e is the concentration (mg/L) at equilibrium, V is the volume (L) of the solution and m is the mass (g) of the adsorbent. The concentration of the BTEX in the wastewater was varied by serial dilution.

2.3 Adsorption Kinetic Models

In order to identify the kinetic order and the rate-limiting step, the data generated from the experiment were processed using three (3) kinetic models [29, 30].

Firstly, the pseudo-first order kinetic model assumes sorption is followed by diffusion through the boundary layer and expressed as:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where, q_e and q_t are the amount of BTEX adsorbed (mg/g) using HDTMAC-kaolinite clay at equilibrium condition and at any other time (t) respectively while k_1 (min^{-1}) is the Lagergren

rate constant of the first order. k_1 and q_e were respectively obtained from the slope and intercept of a plot of $\ln(q_e - q_t)$ versus t .

Secondly, the experimental data were analyzed using a pseudo-second order Lagergren equation expressed as follows [31]:

$$\frac{dq_e}{dq_t} = k_2(q_e - q_t)^2 \quad (4)$$

Where, q_e and q_t are the amounts of BTEX, in mg/g at equilibrium and at time (t) in min respectively while k_2 is the second order rate constant in $\text{gmg}^{-1}\text{min}^{-1}$. Integrating between $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, equation (4) after conversion to its linear form becomes;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

A plot of $\frac{t}{q_t}$ against t gave a straight-line graph with slope equal to $1/q_e$. The values of k_2 and q_e were calculated from the intercept and slope respectively. A factor, h , with unit $\text{mgg}^{-1}\text{min}^{-1}$ measures the initial sorption rate as time approaches zero [32].

$$h = q_e^2 k_2 \quad (6)$$

Finally, the intra-particle diffusion (IPD) equation as expressed in equation (7) was also adopted to investigate the rate limiting step during the uptake of BTEX.

$$q_t = k_{id}\sqrt{t} + C \quad (7)$$

Where, k_{id} is the rate constant for intra-particle diffusion in $\text{mgg}^{-1}\text{min}^{-1}$, obtained from a linear plot of q_t versus \sqrt{t} . The intercept C , measures the boundary thickness. That is, the greater the value of C , the greater the boundary effect. By implication, if the line passes through the origin, the intra-particle diffusion constitutes the rate-limiting step [33].

3. RESULTS AND DISCUSSION

The effect of time on the adsorption capacity and efficiency as presented in Figures 2 and 3 showed that as the time increased, adsorption of BTEX using HDTMAC-modified kaolinite clay increased proportionally. This observation according to Netai et al. [34] may have been due to the increased number of vacant sites on the adsorbent. One notable observation was

that adsorption capacity jumped to 5.00, 2.23, 2.47 and 1.86 mg/g representing 92.0, 80.0, 75.3 and 78.7% removal efficiencies of benzene, toluene, ethyl benzene and xylene within the first 20 min. However, between 20th and 40th min, the capacity increment was marginal. Also, from the plots of the non-linear intra-particle diffusion model and the initial adsorption rate (h) in Figures 4 and 5, two-line segments were evident. According to Daniela et al. [32], “the first segment was associated with film diffusion followed by intra-particle diffusion into the porous structure of the modified clay”. Similar patterns were reported for metal ions by Nan et al. [35] and Ozdemir et al. [36]. “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” [37]. However, further increment in adsorption arose from the penetration of pollutant to the inner active sites of the HDTMAC-modified kaolinite clay.

Table 1. Parameters of the kinetic models obtained from this study

Pollutant	First-order				Second-order					IPD		
	k_1	q_e (Exp)	q_e (Cal)	R^2	k_2	q_e (Exp)	q_e (Cal)	R^2	h	k_{id}	C	R^2
B	0.04	5.00	1.00	0.829	0.12	4.94	5.00	0.999	0.59	0.21	3.44	0.684
T	0.05	2.64	1.02	0.988	0.12	2.64	2.72	0.999	0.32	0.14	1.58	0.939
E	0.06	2.96	1.56	0.988	0.07	2.96	3.14	0.999	0.21	0.22	1.32	0.927
X	0.05	2.20	1.04	0.979	0.10	2.20	2.31	0.999	0.22	0.16	1.04	0.874

*IPD stands for intra-particle diffusion

The plots of the pseudo-first order, pseudo-second order Lagergren equations, and linear presentation of intra-particle diffusion kinetic models of the analyses of the experimental data were represented in Figures 6-8 while the parameters of the models were outlined in Table 1.

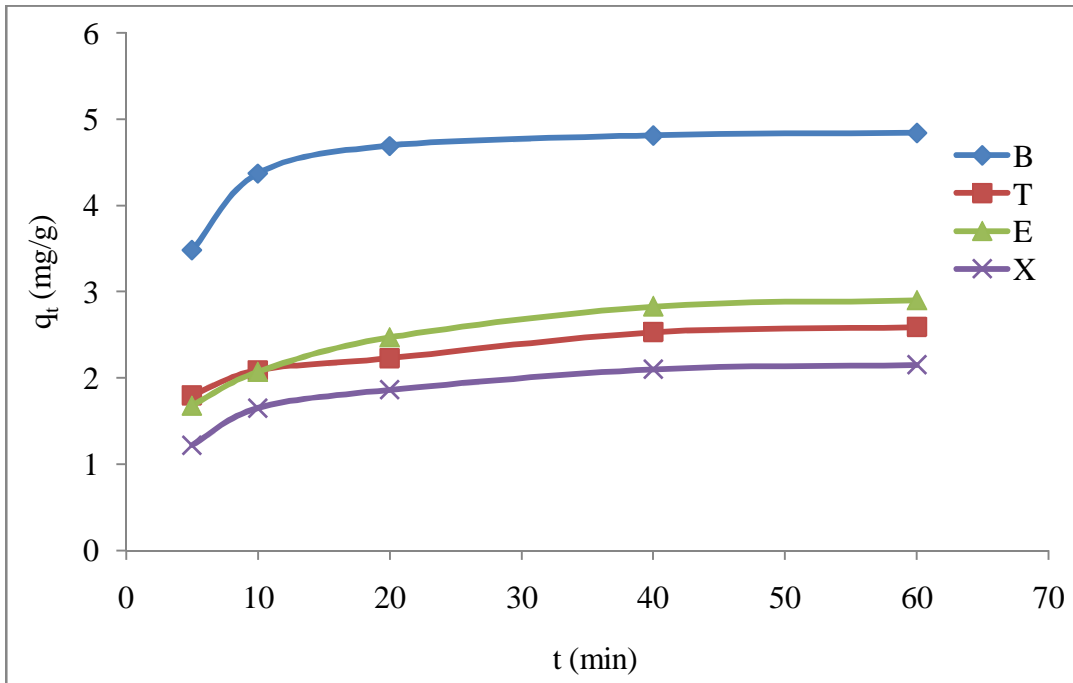


Fig. 2. Plots of adsorption capacity (mg/g) versus time

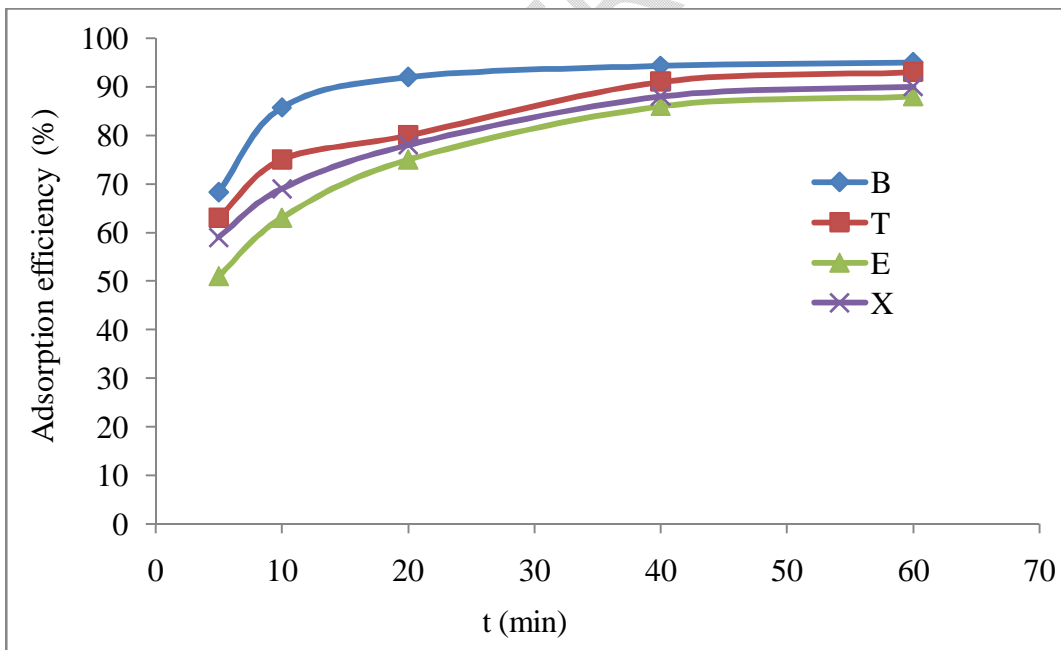


Fig. 3. Removal efficiency (%) versus time

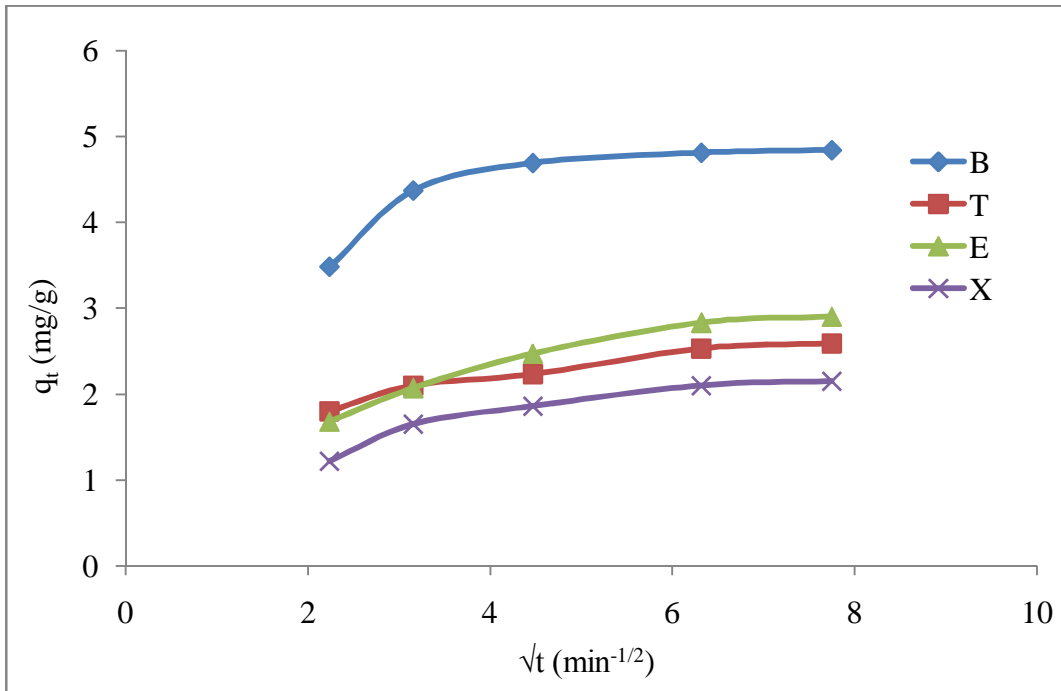


Fig. 4. Intra-particle plot of q_t versus \sqrt{t}

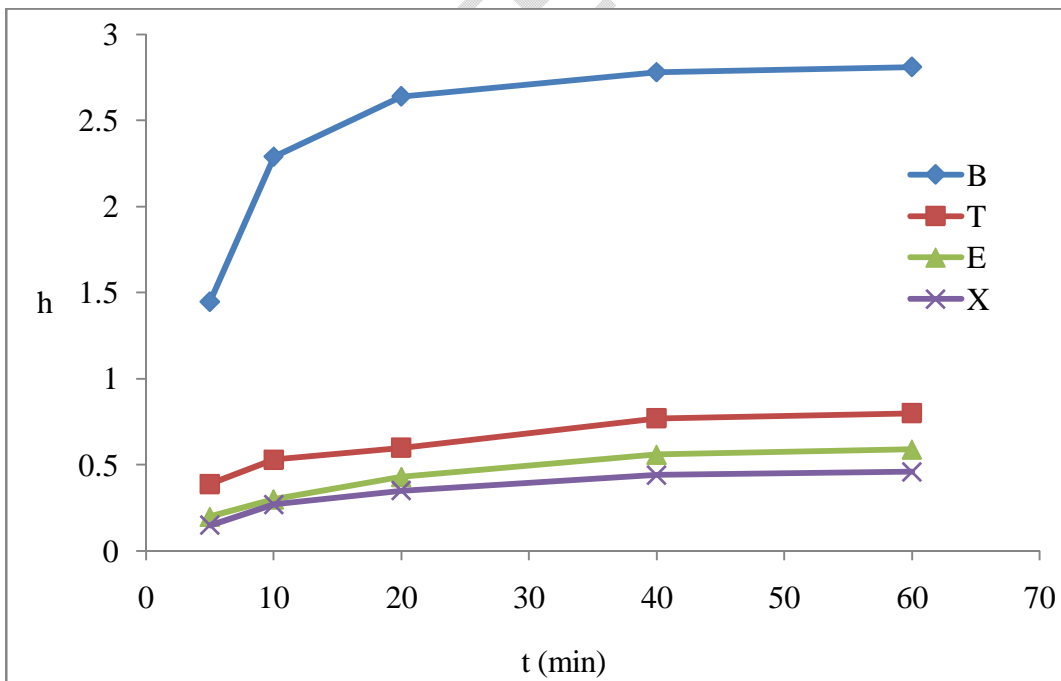


Fig. 5. Plots of initial adsorption rate (h) versus t

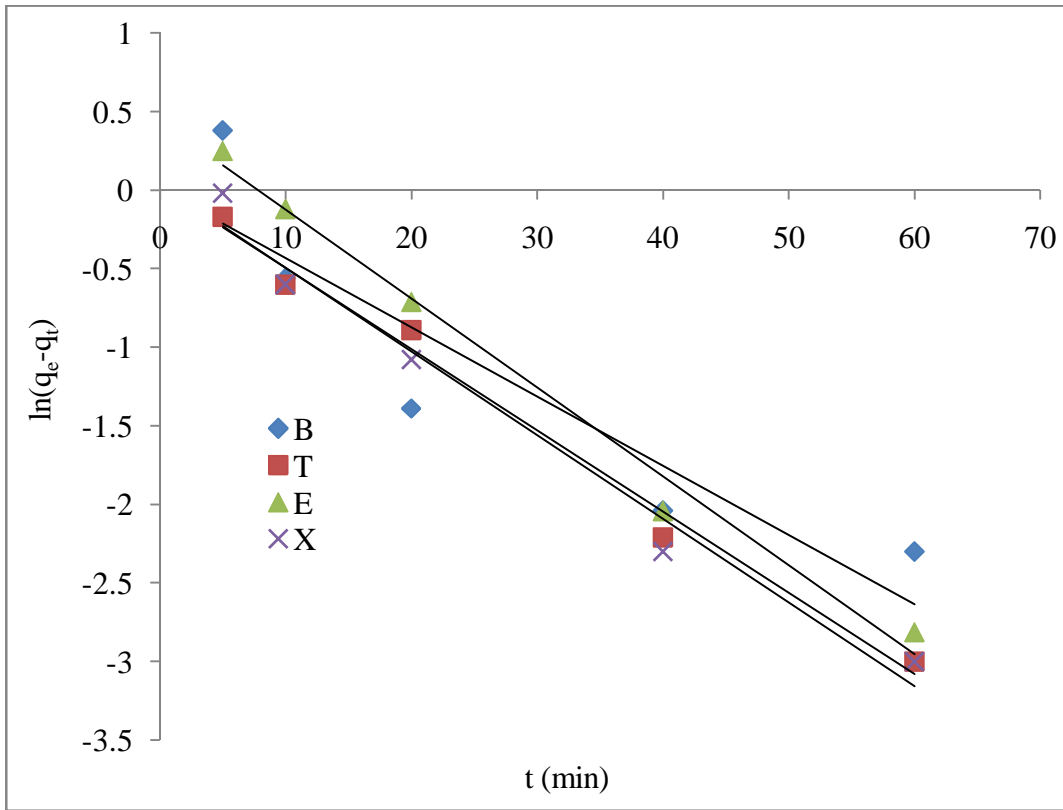


Fig. 6. First-order kinetic plots of $\ln(q_e - q_t)$ versus t

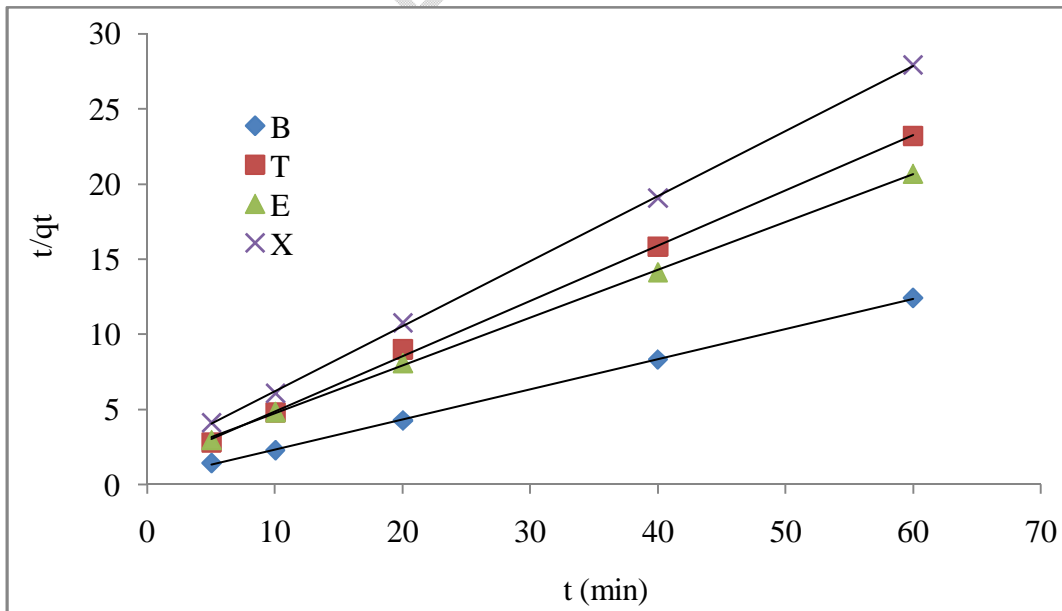


Fig. 7. Second-order kinetic plots of t/q_t versus t

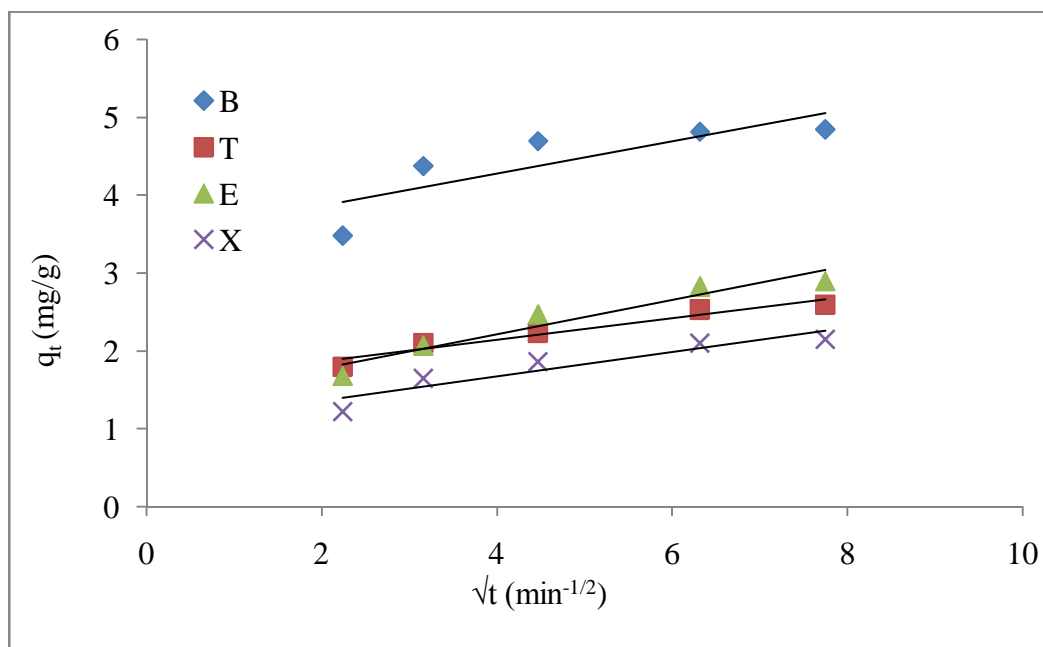


Figure 8: Linear plots of q_t versus \sqrt{t}

The results of the kinetic modeling showed that pseudo first-order and the intraparticle diffusion though not relatively suitable for this process revealed that the boundary thickness (C) and equilibrium uptake capacity (q_e) of benzene was higher than the other pollutants buttressing the conclusion that benzene was preferentially removed with respect to molecular size than others. Therefore, pseudo second-order kinetic model best fits the experimental data generated with the correlation coefficient (R^2) of 0.999 for each of the pollutants. The result further revealed a strong correlation between the experimental data and pseudo second-order kinetic model at different times. The calculated equilibrium pollutant uptake was in a strong agreement with the experimental value as in the case of benzene. This corresponds with the assertions of Poliana et al. [38] and Sidmara et al. [39] that all kinetic curves adhered to pseudo second-order model after respectively investigating the removal of hydrocarbons from aqueous solution using bentonite organo-clay and the adsorption of toluene on natural and organo-clay. The values of the pseudo-second order parameters listed in Table 1 showed that the rate constant k_2 ($\text{gmg}^{-1}\text{min}^{-1}$) follow the order of benzene = toluene > xylene > ethylbenzene. This pattern, in conjunction with the initial

adsorption rate (h) values may be attributed to the molecular weight and structure of the pollutants [40, 41].

This mechanism showed that the interactions between BTEX and HDTMAC-kaolinite clay was evident in the rate limiting step [42, 43]. However, it was clear from the adsorption tests that a two-step mechanism was involved. The first step which was faster, took place within the first 20 min and the second step which was slower form the rate determining step.

4. CONCLUSION

Batch adsorption removal of BTEX from Port Harcourt Refinery wastewater at different time intervals showed that more than 75% of each of the pollutants was taken up within the first 20 min with benzene having the highest initial adsorption capacity and removal efficiency. Pseudo-second order model showed best fit and the rate constant was nearly proportional to the size and structure of the monocyclic hydrocarbon pollutants. Hence, this modified clay can serve as a veritable option for the removal of BTEX and other organic pollutants from both wastewaters and other sources. The study reveals that the immediate exploration and exploitation of this natural clay will create another employment window for people in the locality.

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