

# **Original Research Article**

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

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### **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.

*Keywords: Adsorption, Kinetics, BTEX, Kaolinite, Ultisols, Oxisol, Organo-clay*

## 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.

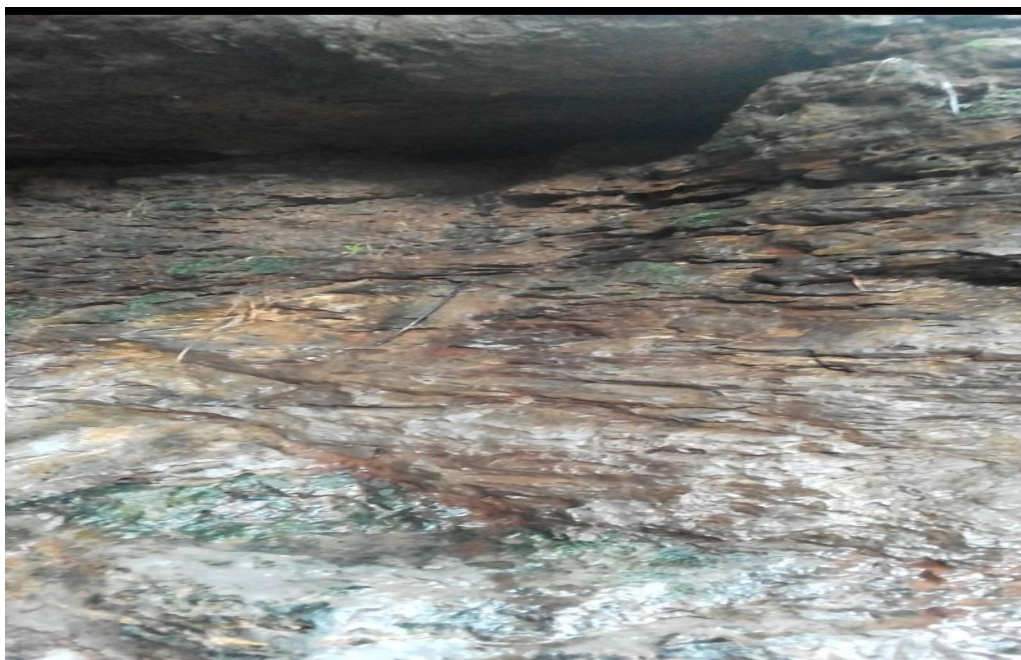
Experimental studies have been reported on technologies such as membrane separation, reverse osmosis, chemical oxidation, biological treatment, air stripping, and adsorption that can achieve substantial removal of organic pollutants from industrial wastewater [10-13].

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].

The clay deposit (majorly kaolinite in Plate 1) in Ehugbo (Afikpo), the South Eastern part of Nigeria on latitude  $6^{\circ} 06' 93''$  N and longitude  $8^{\circ} 19' 94''$  E (Figure 1) has been idle and the investigations on it by Agha and Obi [26] and Agha et al. [25, 27] have really exposed the physical and chemical properties of the clay. Kaolinite clay mineral is the major component of ultisols and oxisols soils.

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).

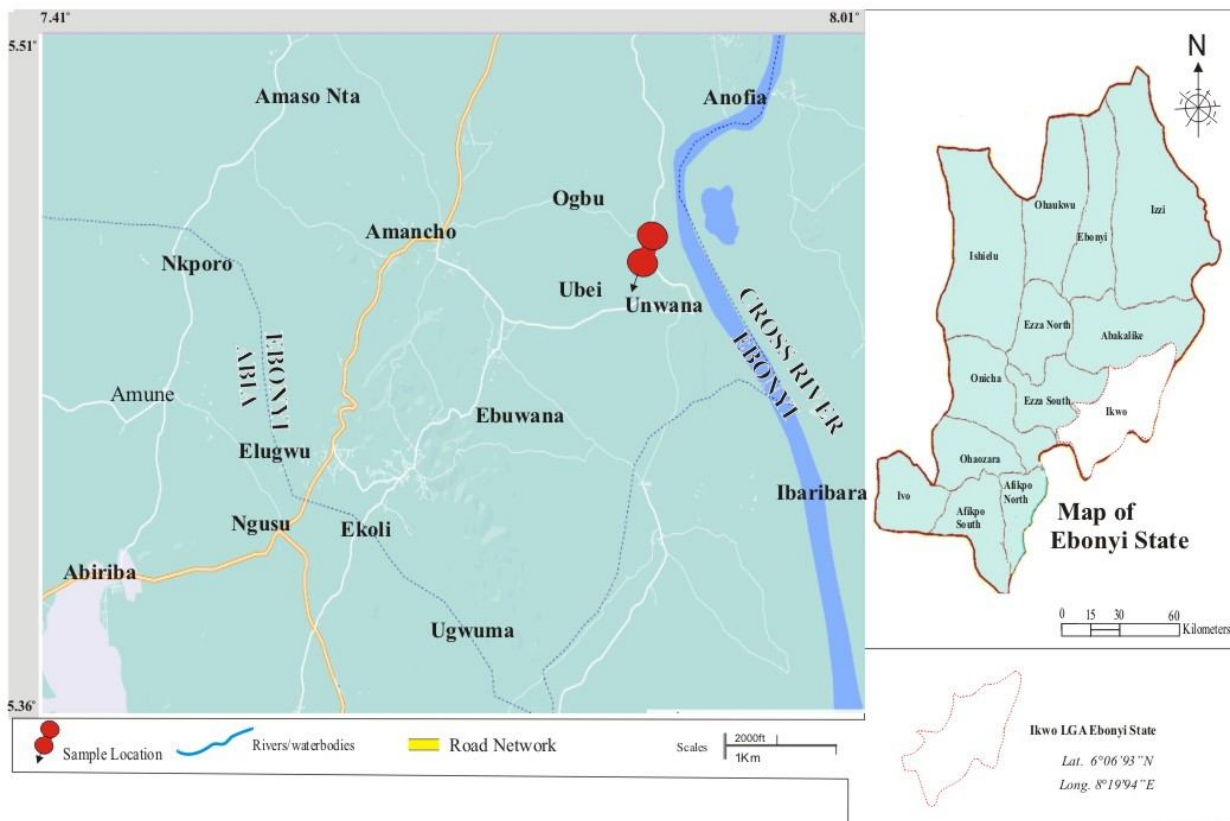


**Plate 1. Ogwuta clay deposit**

## **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  $\mu\text{m}$  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 [28, 29].

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  $k_1$  ( $\text{min}^{-1}$ ) 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 [30]:

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

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 [31].

$$h = q_e^2 K_2 \quad (6)$$

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 [32].

### 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. [33] 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 20<sup>th</sup> and 40<sup>th</sup> 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. [31], 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. [34] and Ozdemir et al. [35]. 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 [36]. 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.

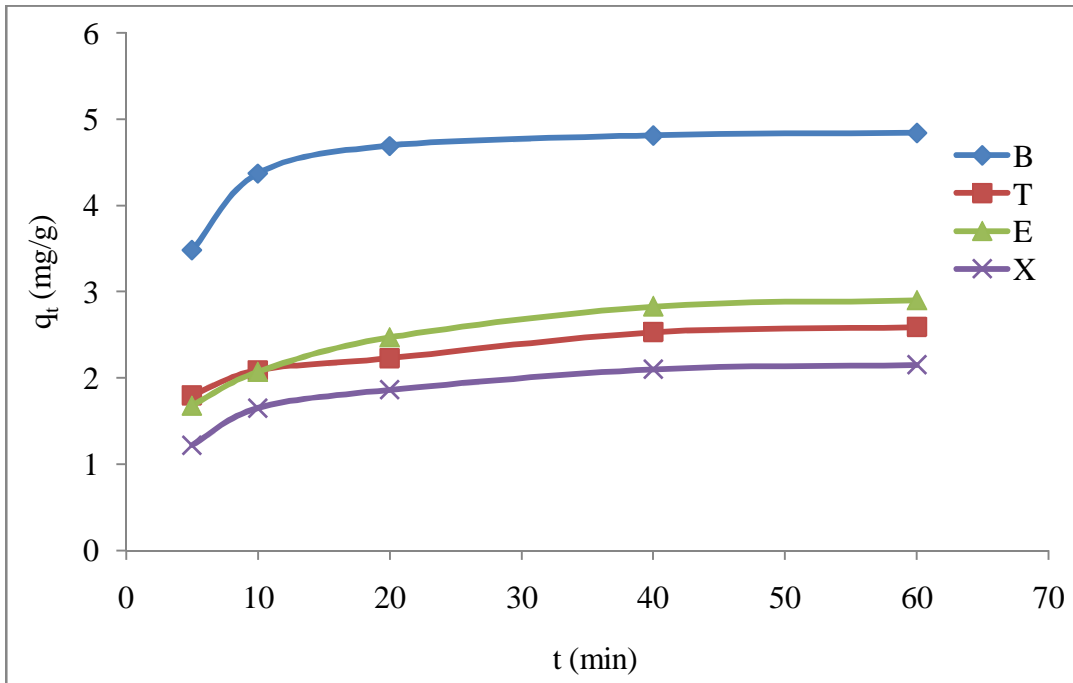


Fig. 2. Plots of adsorption capacity (mg/g) versus time

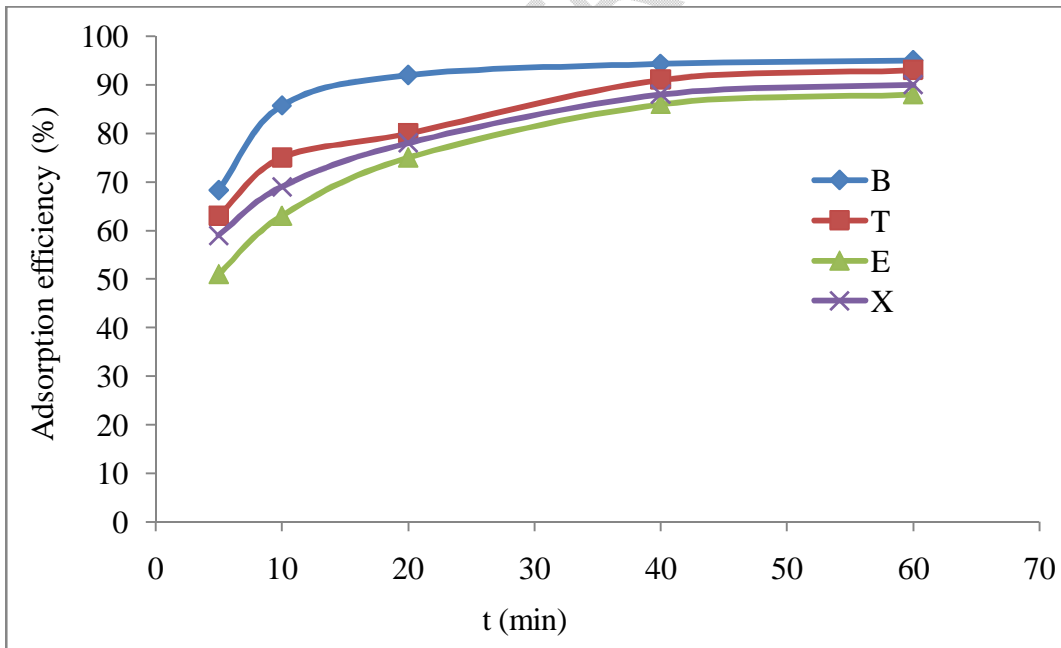


Fig. 3. Removal efficiency (%) versus time

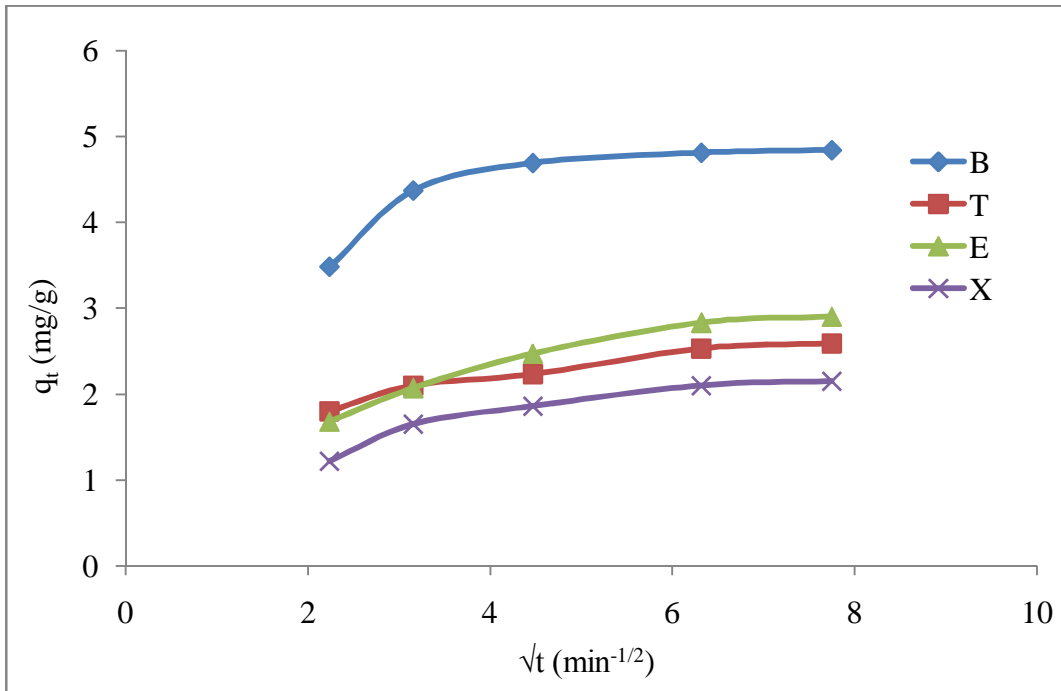


Fig. 4. Intra-particle plot of  $q_t$  versus  $\sqrt{t}$

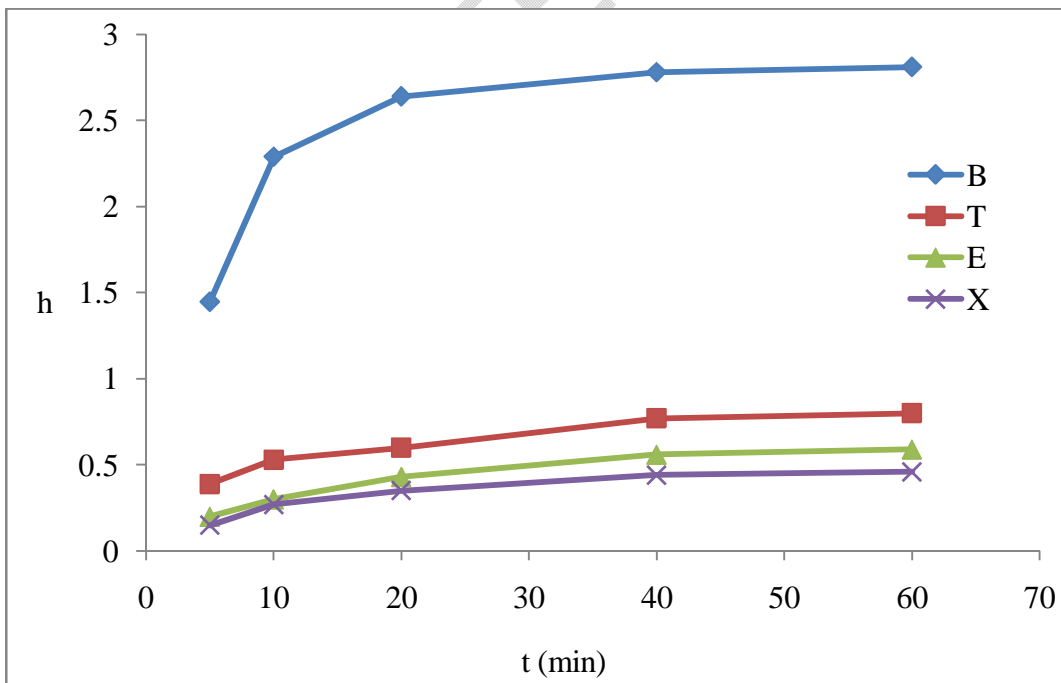


Fig. 5. Plots of initial adsorption rate ( $h$ ) versus  $t$

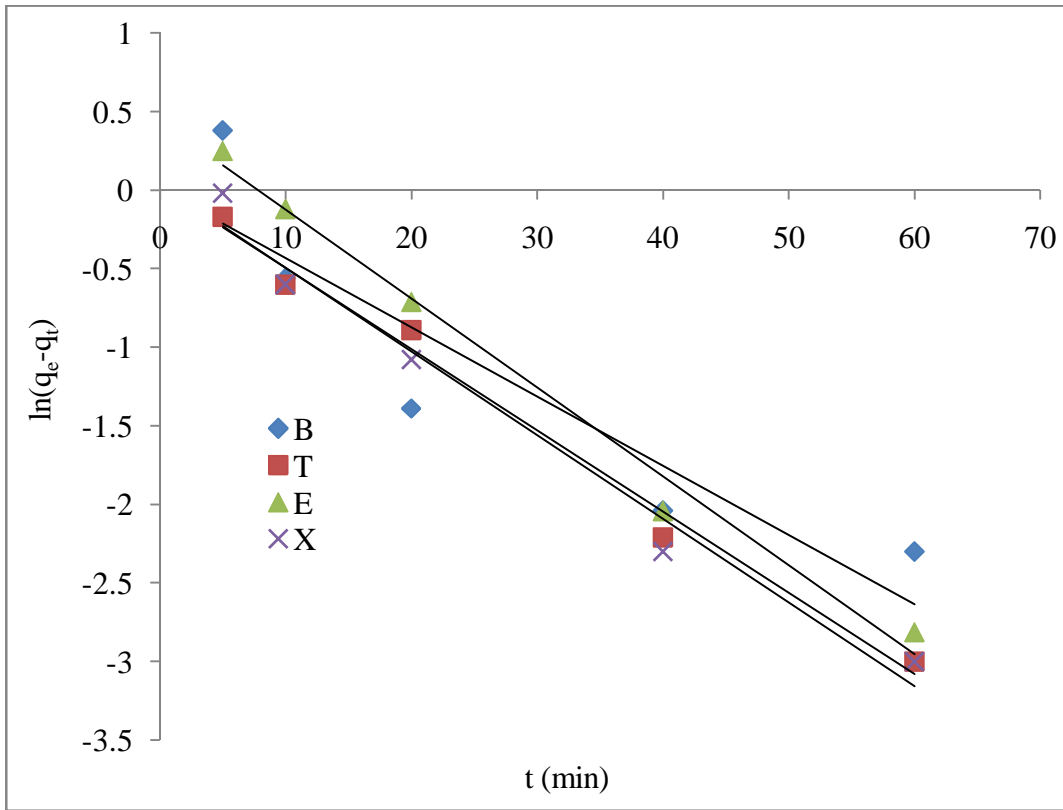


Fig. 6. First-order kinetic plots of  $\ln(q_e - q_t)$  versus  $t$

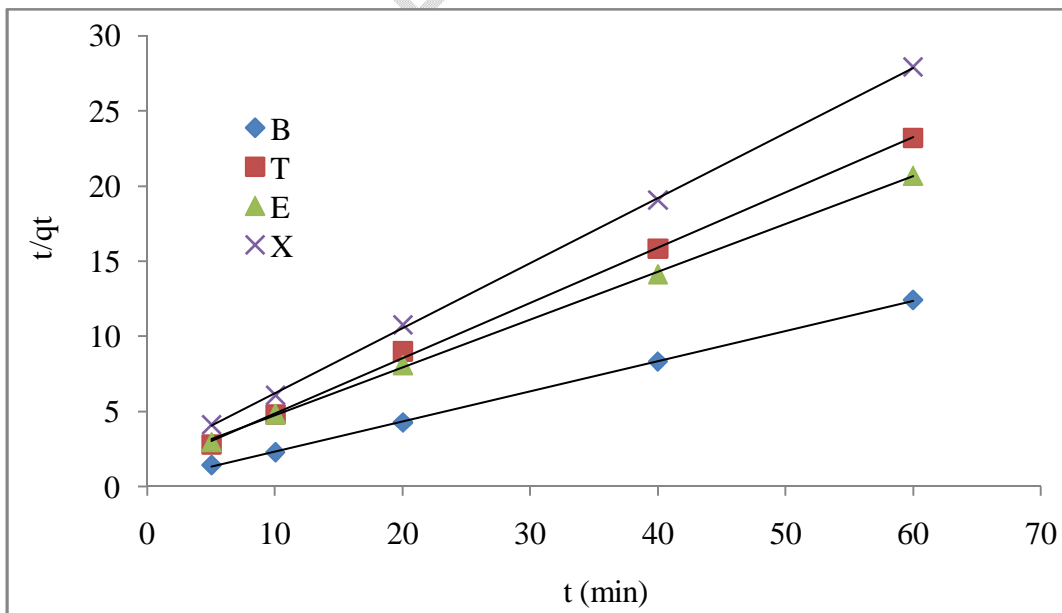
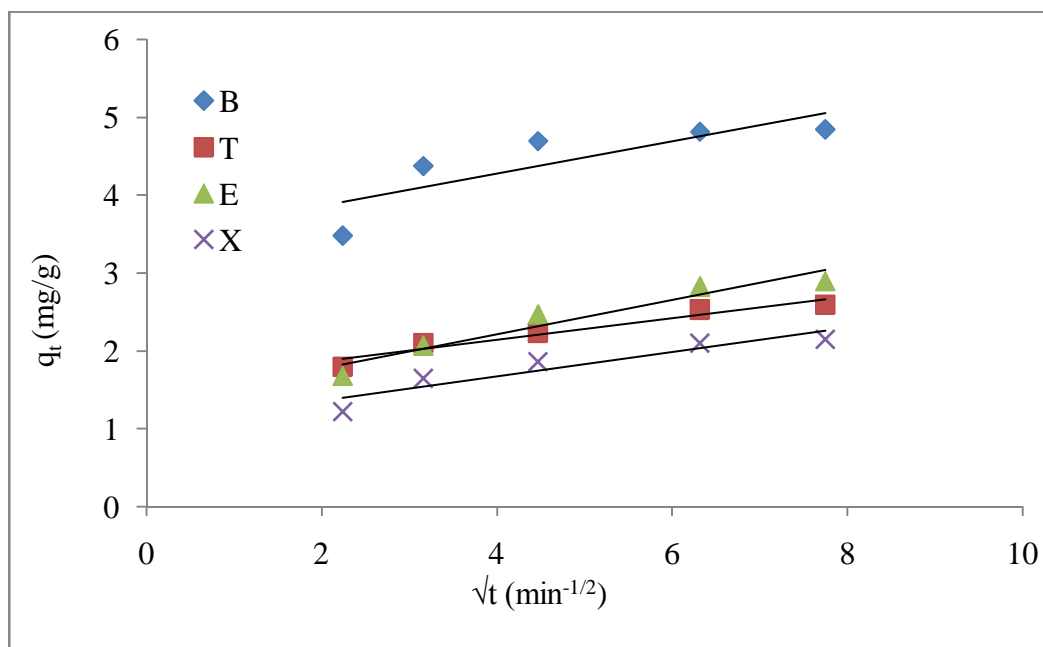


Fig. 7. Second-order kinetic plots of  $t/q_t$  versus  $t$



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

The results revealed that the 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. [37] and Sidmara et al. [38] 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. Benzene and toluene with lower molecular weight can better penetrate into the internal adsorption sites of the adsorbent compared with xylene and ethylbenzene with higher molecular weight

[39]. Also, the structure of the pollutants may affect the extent of steric hindrance arising from the activating agent on the organo-clay [40].

This mechanism showed that the interactions between BTEX and HDTMAC-kaolinite clay involved valence forces through sharing or exchange of electrons in the rate limiting step [41]. The process of uptake using the modified clay adsorbent followed a chemical sorption process [42]. However, it was clear from the sorption tests that it involved two-step mechanisms. The first step which was faster and took place within the first 20 min and the second step was slower and the rate determining step as evident in the kinetic evaluation.

#### **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 application of this natural clay will create another employment window for people in the locality.

#### **REFERENCES**

1. Taha A, Amani M. Water Chemistry in Oil and Gas Operations: Scales Properties and Composition. *Inter. J. Org. Chem.* 2019; 9(3): 23-36.
2. Su F, Lu C, Hu S. Adsorption of benzene, toluene, ethyl benzene and p-xylene by NaOC-oxidized carbon-nanotubes. *Coll. Surf. A: Physicochem. Eng. Aspects.* 2010; 353(1): 83-91.

3. Mahal J, Abhradeep M, Partha SG, Ashok KG. A review on treatment of petroleum refinery and petrochemical plant wastewater: A special emphasis on constructed wetlands. *J. Environ. Manage.* 2020; 272: 111057.
4. World Health Organization (W.H.O), Guidelines for Drinking-Water Quality. World Health Organization, Geneva, 2004.
5. Kong H, Mat H, Azizi M, Yunus C. Batch adsorptive removal of BTEX from aqueous solution: A review. *Proceedings of the Third International Conference on Separation Technology. Adv. Eng. Res.* 2020; 200: 303-318.
6. Kirkeleit J, Riise T, Bråtveit M, Moen BE. *The Ann. Occ. Hyg.* 50(2), (2006), 123-129.
7. Fengsheng S, Chungsyng L, Kelvin RJ, Sukai H. Kinetics, Thermodynamics, and Regeneration of BTEX Adsorption in Aqueous Solutions via NaOCl-Oxidized Carbon Nanotubes. *Environanotechnol.* 2010, 71-97.
8. Ashley LB, Carol FK, Theo C. New Look at BTEX: Are Ambient Levels a Problem? *Environ. Sci. Technol.* 2015; 49: 5261-5276.
9. Rostami R, Fazlzadeh M, Babaei-Pouya A, Abazari M, Rastgho L, Ghasemi R, Saranjam B. Exposure to BTEX concentration and the related health risk assessment in printing and copying centers. *Environ. Sci. Pollut. Res. Int.* 2021; 28(24): 31195-31206.
10. Fu F, Wang Q. Removal of heavy metal ions from wastewater: A Review. *J. Environ. Manage.* 2011; 92: 407-418.
11. Makhatini TP, Rathilal S. Modeling competitive BTEX compounds removal from industrial wastewater in packed-bed columns using polystyrenic Resin. *J. Water Reuse Desal.* 2018; 8(3): 372-385.
12. Apemiye MA, Obi C, Okoye IP. Equilibrium dynamics of m-xylene removal from aqueous solution by organoclay. *Iranian J. Sci. Technol. Trans. A: Sci.* 2019; 43(1): 119-125.
13. Xidong D, Dongdong P, Yuan Z, Zhenkun H, Hanglong W, Yugang C. Investigation into the adsorption of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> on kaolinite clay. *Arab. J. Chem.* 2022; 15(3): 103665.

14. Kalebaila KK, Kenneth JM, Misheck M. Selected adsorbents for removal of contaminants from wastewater: Towards engineering clay minerals. *Open J. Appl. Sci.* 2018; 8(8): 355-369.
15. Siyal AA, Shamsuddin MR, Low A, Rabat NE. A review on recent developments in the adsorption of surfactants from wastewater. *J. Environ. Manage.* 2020; 254: 109797.
16. Khader EH, Mohammed JJ, Mughaffari N. Removal of organic pollutant from produced water by batch adsorption treatment. *Clean Technol. Environ. Policy.* 2021.
17. Abdelrahman MA, Shifa MRS, Rem J, Mona HG, Mustafa SN, Abdelbaki B, Samer A. Adsorption of organic pollutants by natural and modified clays: A comprehensive review. *Sep. Pur. Technol.* 2019; 228: 115719.
18. Blachnio M, Derylo-Marczewska A, Charmas B, Zienkiewicz-Strzalka M, Bogatyrov V, Galaburda M. Activated Carbon from Agricultural Wastes for Adsorption of Organic Pollutants. *Molecules.* 2020; 25(21): 5105.
19. Barakan S, Aghazadeh V. The advantages of clay mineral modification methods for enhancing adsorption efficiency in wastewater treatment: A review. *Environ. Sci. Pollut. Res.* 2021; 28: 2572-2599.
20. Sakhile K, Sarkar JP, Gupta P et al. Removal of Major Pollutants from Petroleum Wastewater by Adsorption with Activated Carbon Derived from Date Seed in an Inverse Fluidized Bed. *Arab. J. Sci. Eng.* 2022.
21. Nourmoradi H, Khiadani M, Nikaem M. Removal of benzene, toluene, ethyl benzene and xylene from aqueous solutions using montmorillonite modified with nonionic surfactants: Equilibrium, kinetic and thermodynamic study. *Chem. Eng. J.* 2012; 191: 341-348.
22. Katarzyna W, Piotr R, Wojciech S. Application of clay minerals and their derivatives in adsorption from gaseous phase. *Appl. Clay Sci.* 2019; 215: 106323.

23. Perelomov L, Mandhieva S, Minkina T, Atroshchenko Y, Perelomov I, Bauer T, Pinsky D, Barakhov A. The synthesis of organoclays based on clay minerals with different structural expansion capacities. *Miner.* 2021; 11(7): 707-721.
24. Singla P, Mehta R, Upadhyay SN. Clay Modification by the Use of Organic Cations. *Green Sustain. Chem.* 2012; 2(1): 21-25.
25. Agha II, Ibezim-Ezeani MU, Obi C. Physicochemical properties of organophilic clay developed using hexadecyltrimethylammonium chloride (HDTMAC) modifier. *Inter. J. Pure Appl. Chem.* 2021; 22(9): 20-30.
26. Obi C, Agha II. Base-Line characterization of Unwana Ogwuta Cave (Iyi Ogo) new site clay in Afikpo, Ebonyi State. *Inter. J. Inn. Environ. Stud. Res.* 2016; 4(3):1-6.
27. Agha II, Ibezim-Ezeani MU, Obi C. Characterization of Ogwuta source clay using advanced analytical tools. *Asian J. Phys. Chem. Sci.* 2021; 9(4): 25-31.
28. Egbuchunam T, Obi G, Okieimen F, Tihminlioglu F. Removal of BTEX from aqueous solution using organo-kaolinite. *Inter. J. Appl. Environ. Sci.* 2016; 11(2): 505-513.
29. Farsouni EE, Shariati A, Khosravi-Nikou MR. Separation of BTEX compounds (benzene, toluene, ethylbenzene and xylenes) from aqueous solutions using adsorption process. *J. Disperse. Sci. Technol.* 2019; 40(3): 453-463.
30. Reza S, Vahid V, Mansuor Z, Akram V. Adsorption of AR18 by activated carbon from poplar wood; A kinetic and equilibrium Study. *E-J. Chem.* 2010; 7(1): 65-72.
31. Daniela S, Carmen Z, Marinela B. Kinetic modeling of dye sorption from aqueous solutions unto apple seed powder. *Cellulose Chem. Technol.* 2016; 50(9-10): 1085-1091.
32. Agnes P, Eliazar BN, Augustine EO. Intra-particle diffusion of Cr (VI) through biomass and magnetite coated biomass: A comparative kinetic and diffusion study. *South Afri. J. Chem. Eng.* 2020; 32: 39-55.
33. Netai M, Lydia C, David S, Mathew M. Adsorption of phenol from aqueous solution using carbonized maize tassels. *British J. Appl. Sci. Technol.* 2013; 3(3): 648-661.

- 34 Nan C, Zhenya Z, Chuanping F, Miao L, Rongzhi C, Norio S. Investigations on the batch and fixed-bed column performance of fluoride adsorption by Kanuma mud. *Desal.* 2011; 268(1-3): 76-82.
35. Ozdemir O, Turan M, Turan A, Egin A, Faki A. Analysis of Color Removal from textile wastewater in a fixed bed column system using surfactant-modified clay. *J. Hazard. Mater.* 2009; 166: 647-654.
36. Iman M, Esmail S, Ali L. Batch and fixed bed column performance of red mud for lead removal. *Canadian Chem. Trans.* 2014; 2(1): 83-96.
37. Poliana CB, Túlio CS, Cíntia AF, Carla EH, Lucienne LR. Removal of petroleum hydrocarbons from aqueous solution using sugarcane bagasse as adsorbent. *J. Hazard. Mater.* 2010; 175: 1106–1112.
38. Sidmara B, Maria F, Melissa G, Mauris C. Adsorption of toluene in batch in natural clay and organoclay. *Chem. Eng. Trans.* 2013; 32: 313-318.
39. Nourmoradi H, Khiadani M, Nikaeen M. Multi-component adsorption of benzene, toluene, ethylbenzene, and xylene from aqueous solutions by montmorillonite modified with tetradecyl trimethyl ammonium bromide. *J. Chem.* 2013.
40. Byungryul A. Cu (II) and As (V) adsorption kinetic characteristic of the multifunctional amino groups in chitosan. *Proc.* 2020; 8: 1194-1209.
41. Suzzoni A, Barre L, Kohler E, Levitz P, Michot LJ, M'Hamdi J. Interactions between kaolinite clay and AOT. *Coll. Surf. A: Physicochem. Eng. Aspects.* 2018; 556: 309-315.
42. Kajjumba GW, Emik S, Ongen A, Ozcan H, Aydin S. Modeling of adsorption kinetic processes-errors, theory and application. *Intechopen*, (2018).