Scientia Africana, Vol. 21 (No. 1), April, 2022. Pp 77-86 https://dx.doi.org/10.4314/sa.v21i1.7
© Faculty of Science, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

REMOVAL OF BTEX FROM REFINERY WASTE USING HDTMAC-MODIFIED OGWUTA SOURCE CLAY: ADSORPTION EQUILIBRIUM AND THERMODYNAMIC INCLINATIONS

Agha, I. I.[1], Ibezim-Ezeani, M. U.,[2] and Obi, C.[2]*
[1]Department of Chemistry, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria
[2]Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, P.M.B. 5323, Choba, Port Harcourt. Rivers State, Nigeria.
***Corresponding Author Email:**chidi.obi@uniport.edu.ng

Received: 01-03-2022
Accepted: 30-03-2022

ABSTRACT

The possible non-compliance of refineries to the demands of environmenteal protection laws has led to the discharge of poorly treated and contaminated wastewater to the environment. Carcinogenic compoiunds such as benzene, toluene, ethylbenzene, and xylene (BTEX) find their way to the ecosystem. This study is aimed at investigating the isotherm and thermodynamics of the uptake of BTEX using hexadecytrimethylammonium chloride (HDTMAC)-modified natural Ogwuta clay. Batch adsorption process was used at different BTEX concentrations and at temperatures of 303^{o}K, 313^{o}K and 323^{o}K. Langmuir, Freundlich, Dubinin-Radushkevich (D-R), and Tempkin models were used to describe the process while changes in enthropy (ΔS), enthalpy (ΔH), and Gibbs free energy (ΔG) of the process were evaluated. The maximum monolayer coverage capacity (q_m) of 1.83, 0.92, 0.86 and 0.69 mg/g of BTEX was lower than the calculated values of 4.94, 2.64, 2.76 and 2.20 mg/g respectively, implying uptake of pollutants through other mechanisms. The Dubinin-Radushkevich monolayer coverage range of 0.81-2.66 mg/g agreed with the monolayer coverage of the Langmuir model but with energy less than 1 kJ/mol. Freundlich adsorption intensities for BTEX were 1.64, 1.41, 1.11 and 1.22 respectively and R^2 values of not less than 0.99 for each pollutant showed that the model best fits the process. Results of the thermodynamic parameters showed that the process was more feasible at increased temperature, endothermic and lead to increased randomness at the solid-liquid interface. This study has presented hexadecyltrimethylammonium chloride-modified Ogwuta source clay as a veritable adsorbent for organic pollutant decontamination both from laboratory and real-life sources.

Keywords: BTEX**,** Batch reactor system, isotherm, adsorption, hexadecyltrimethylammonium chloride

INTRODUCTION

Refineries are plants engaged in complex multiple operations aimed at transforming crude oil into more useful products. Some of the operations such as light and heavy coking, cracking, desalting, cooling, stripping, etc heighten the demand for water i.e. making refineries larger comsumer of water relative to other industries. Pingping *et al*. (2018) found out that 1.9 gallons (7.19 L) of water are required to process 1 gallon (3.79 L) of crude thereby generating categories of waste water such as the desalter effluent, sour water, tank bottom draws and spent caustic. This wastewater gets contaminated in the course of operations due to contact with crude.

Mahdi *et al*. (2021) observed gross negligence to the demands of the environmental regulations on the management of petroleum refinery effluents (PRE) in most developing countries. Therefore, many of these industries discharge inadequately treated wastewater into the environment. This discharge allows for the introduction of pollutants such as heavy metals, synthetic materials, aromatic and polyaromatic hydrocarbons, to the environment which in most cases far exceed permissible limits (Obi and Woke, 2014). Netai *et al*. (2013) noted that phenols and some other aromatic compounds such as BTEX (benzene, toluene, ethylbenzene and xylene) are priority pollutants since exposure to them can cause cancer, irritation of mucosal membrane, disruption of liver, and kidney functions, etc in humans; creating an unpleasant taste and odour in drinking water. Thus a great deal of concern has been raised globally to remove these pollutants from refinery effluents in particular and other industrial effluents in general into the fragile ecosystem, and it has become obligatory for industries to properly treat their wastewater effluent to ensure safe disposal to the environment (Taghreed and Muftah, 2018).

Over the years, several methods have been adopted in an attempt to remove organic contaminants from aqueous phase. They include; chemical precipitation, ion exchange, electrodeposition, solvent extraction, membrane separation, reverse osmosis and adsorption process. Gopinathan et *al.* (2017) remarked that in general, adsorption is a far less energy-intensive unit operation. Consequently, 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).

Hexadecyltrimethylammonium chloride (HDTMAC) is an eco-begnin cationic surfactant emanating from the organic chloride group of cetytrimethylammonium (Inya *et al.*, 2021). It is a quaternary ammonium salt with molecular formula $C_{19}H_{42}N.Cl$ and highly soluble in aqueous phase.

Clays are layered phyllosilicates with very small particle size of less 2 µm. Structurally, they have a net negative charge due to the isomorphous substitution of silicon ion by aluminum ion in the tetrahedral layers or likely substitution of aluminum ion by magnesium ion. Thus, cations such as sodium, potassium and calcium may be attracted to the mineral surface to neutralize the layer charge (Ivana *et al.,* 2014). This underscores the hydrophilicity of clay and reduces its application in an organic medium. To improve its

Scientia Africanca, Vol. 21 (No. 1), April, 2022. Pp 77-86 https://dx.doi.org/10.4314/sa.v21i1.7
© Faculty of Science, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

application, clays are modified with suitable organic surfactants (Leyva-Ramos *et al*., 2021; Padmaja *et al*., 2018, Bhattacharyya and Mandof, 2014). Hence, the need for the modification of Ogwuta Source clay situated at Iyi Ogo Afikpo, Ebonyi State for real-life application.

In this work, adsorption thermodynamics of refinery wastewater BTEX unto natural Ogwuta clay modified with hexadecyltrimethylammonium chloride (HDTMAC) was investigated considering the significance of adsorption isotherm in wastewater treatment as it provides valuable insights into the application of design.

MATERIALS AND METHOD

All the chemicals used for the purpose of this work were of analytical grade. A 0.1 M HCl and 0.1 M 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 (AR, 3130). The hexadecyltrimethylammonium chloride clay was crushed with an iron roller to fine particle sizes. These clay particles were sieved through a 63 µm sized mesh and stored in a glass bottle.

Adsorption Process

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 showed the following initial concentrations of 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 aid of a magnetic stirrer, the mixture was stirred until equilibrium reached. The suspension was filtered and the filtrate was analysed by GC-MS. The adsorption capacity of BTEX in the solid, q_e (mg/g), was evaluated using the expression:

Adsorption Capacity (q_e)

$$= \frac{(C_o - C_e)}{M} \times V \qquad (1)$$

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.

Adsorption Isotherm Studies

To describe the relationship between the amounts of BTEX molecules adsorbed on the HDTMAC-modified ogwuta clay, the following isotherm models were employed to provide insight into sorption mechanism, surface properties, and the affinity of pollutants.

Temkin Model: This was employed to explain possible indirect chemical interaction between the adsorbate and the adsorbent. It assumes that the fall in energy as the process continues is linear rather than logarithmic within intermediate concentrations. The linear form of the equation is expressed as:

$$q_e = \frac{RT}{b}\ln K_T + \frac{RT}{b}\ln C_e \qquad (2)$$

Where, values of the constants K_T, provides the information about the binding energy and b, is a measure of the heat of adsorption.

Langmuir Model: This model gives the fractional coverage on an adsorbent at constant temperature. It assumes uniform energy of adsorption on the surface of the adsorbent. The equation for this analysis is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_e} \qquad (3)$$

Where, q_m is the monolayer uptake capacity, K_L is Langmuir constant related to intensity of adsorption, and other parameters remain as decribed above.

Freundlich Model: The Freundlich isotherm model was employed to describe multilayer adsorption on a heterogeneous adsorbent surface. The model is described by:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (4)$$

Where, the values of the constants, K_F (Lg^{-1}) which indicates the adsorption capacity and measures the favourability of adsorption, and $\frac{1}{n}$shows the extent of adsorption intensity.

Dubinin-Radushkevich Model: This model was applied to categorize adsorption process into physical, chemical or ion exchange (Morunmradi, 2012). The linear form of the expression is as follows:

$$\ln q_e = \ln q_m - \beta_\varepsilon{}^2 \qquad (5)$$

Where, q_m(mg/g) is the theoretical sorption capacity, β (kJ/mol) is related to the mean adsorption energy, and ε (Polanyi Potential) is equal to:

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \qquad (6)$$

The mean adsorption energy E is related to β by:

$$E = \frac{1}{\sqrt{2\beta}} \qquad (7)$$

The energy value specifies the type of adsorption process. For E< 8 $kJmol^{-1}$, the process is physical. If $8 < E < 16$ $kJmol^{-1}$, the process occurred through ion exchange. While for E>16 $kJmol^{-1}$, the process involves chemical interaction (Dada *et al.*, 2012).

Thermodynamic Evaluations

The thermodynamic studies were investigated by carrying out the effect of temperature on the adsorption of BTEX unto HDTMA-modified Ogwuta source clay at 30°C, 40°C and 50°C respectively. The thermodynamic parameters of changes in enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS) were calculated using the following equations (Nourmoradi *et al.*, 2013):

$$K = \frac{q_e}{C_e} \qquad (8)$$

Scientia Africana, Vol. 21 (No. 1), April, 2022. Pp 77-86 https://dx.doi.org/10.4314/sa.v21i1.7
© Faculty of Science, University of Port Harcourt, Printed in Nigeria ISSN 1118 – 1931

$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$ (9)

$\Delta G = \Delta H - T\Delta S$ (10)

Where, K is the distribution coefficient and is related to the Langmuir constant $K_L = (\frac{q_e}{C_e})$ which is dimensional with common units (L/g) (Hong. *et al.*, 2009), C_e is the equilibrium concentration (mg/L) and R the universal gas constant ($8.314 Jmol^{-1}K^{-1}$).

RESULTS AND DISCUSSION

Temkin Analysis

The result obtained by plotting q_e against $\ln C_e$ was presented in Table 1. As can be seen, the binding energy K_T (L/g) for benzene, toluene, ethylbenzene, and xylene were 0.869, 0.756, 0.802 and 0.712 respectively. With high b > 0 values of 355.41, 687.64, 550.88 and 839.00 J/mol respectively for BTEX and coefficient of correlation of over 0.98 for each of the pollutant, which suggests that the process involves chemical interaction (Nimibofa *et al*., 2017).

Langmuir Analysis

The total monolayer capacity of the adsorbent, q_m and the Langmuir constant K_L, obtained from the slope and intercept of a plot of $\frac{C_e}{q_e}$ against C_e was presented in Table 1. The equilibrium parameter, $R_L = \frac{1}{1+(1+K_L C_e)}$, a dimensionless quantity related to the separation factor was also presented in Table 1. Given that R_L reveals the adsorption nature of being unfavourable ($R_L > 1$), linear ($R_L = 1$), and favourable ($0 < R_L < 1$ or irreversible ($R_L = 0$)) (Davoud *et al.*, 2017). The values of BTEX lying between 0.174 - 0.287 show that adsorption process was favourable. However, the maximum monolayer coverage capacity q_{max} of 1.83, 0.92, 0.86 and 0.69 mg/g for BTEX was lower than the calculated equilibrium capacity values of 4.94, 2.64, 2.76 and 2.20 mg/g respectively. This difference, according to Dada *et al.*, (2012) may have been due to further uptake of pollutants by other mechanisms.

Freundlich Analysis

The sorption bond between pollutant and adsorbent would be relatively strong if n values obtained were greater than 1 (Nournmradi *et al.*, 2013). By extension, the value measures the extent of fitness of the model to the adsorption process. Therefore the n values of 1.64, 1.41, 1.11 and 1.22 respectively for BTEX showed that they were suitably adsorbed by HDTMAC-modified ogwuta source clay. This agrees with the observation made by Sharmasarkar *et al.* (2000) in the removal of BTEX using montmorillonite organoclays. The measure of the favourability was determined by the value of K_F. Favourable values lie between 1 - 20 Lg^{-1} (Nimibofa *et al.*, 2017). Therefore with the values of K_F in Table 1 lying between 4.31 and 10.6 shows that the model favours and fits the process.

Dubinin-Radushkevich Analysis

The values of the D-R parameters for the adsorption of BTEX onto HDTMAC-modified clay were presented in Table 1. The q_m range of 0.81 - 2.66 mg/g agreed with the monolayer coverage of the Langmuir values as well as mean adsorption energy less than 1 $kJmol^{-1}$. This process showed that the three models of Langmuir, Freundlich, and D-R were favored. However, the values of the regression coefficient (R^2) showed that Freundlich's model best fits the experimental data.

Table 1: Parameters for Langmuir, Freundlich, D-R and Temkin isotherm models for adsorption of BTEX using HDTMAC-clay

Isotherm	Parameter	Adsorbate			
		Benzene	Toluene	Ethylbenzene	Xylene
Langmuir	K_L	0.335	0.530	0.344	0.507
	q_{max}	1.83	0.92	0.86	0.69
	R^2	0.985	0.997	0.982	0.994
	R_L	0.174	0.207	0.287	0.263
Freundlich	K_F	10.6	4.71	8.67	4.31
	n	1.64	1.41	1.11	1.22
	R^2	0.998	0.997	0.998	0.999
D-R	q_m	2.16	1.08	1.07	0.81
	E($kJmol^{-1}$)	0.41	0.71	0.41	0.50
	R^2	0.912	0.889	0.898	0.917
Temkin	b_T	355.41	687.64	550.08	839.10
	K_T	0.869	0.756	0.802	0.712
	R^2	0.990	0..997	0.993	0.998

Thermodynamic Analysis

The values of the thermodynamic parameters were obtained from the plot of lnK versus $\frac{1}{T}$, with the entropy change ($Jmol^{-1}K^{-1}$) obtained from the intercept and the change in enthalpy ($Jmol^{-1}$) obtained from the slope as shown in Figures 1-4 and Table 2. The negative values of the change in Gibbs free energy $(\Delta G)$for temperatures of 303, 313 and 323 K for the removal of BTEX using HDTMAC-Clay showed that the adsorption process was thermodynamically feasible as well as spontaneous (Nourmoradi *et al.*, 2012; 2013, Konggidinata *et al.*, 2017). The values of ΔG for benzene adsorption were found to decrease from -531 $Jmol^{-1}$ at 303 K to -407 $Jmol^{-1}$ at 323 K which indicates that the adsorption process became more feasible at higher temperatures (Nourmoradi *et al.* 2017; Kumar *et al.*, 2016). The calculated values for change in enthalpy ΔH for the BTEX were all positive, which indicates that the process was endothermic. Also the positive values of entropy ΔS of 177.2, 95.9, 91.6 and 85.6 $Jmol^{-1}K^{-1}$ of BTEX reflect the affinity of organic contaminants and the increasing randomness at the solid-liquid interface.

Scientia Africana, Vol. 21 (No. 1), April, 2022. Pp 77-86 *https://dx.doi.org/10.4314/sa.v21i1.7*
© Faculty of Science, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

Table 2: Thermodynamic parameters for BTEX removal using HDTMAC-Clay

	ΔS (Jmol^{-1}K^{-1})	ΔH (Jmol^{-1})	ΔG(Jmol^{-1}) 303 K	313 K	323 K
B	177.2	53151.4	-531.0	-2302.8	-4074.5
T	95.90	29182.2	-112.2	-847.2	-1806.6
E	91.60	27619.1	-141.8	-1058.0	-1974.2
X	85.60	26322.1	-385.3	-470.7	-1326.0

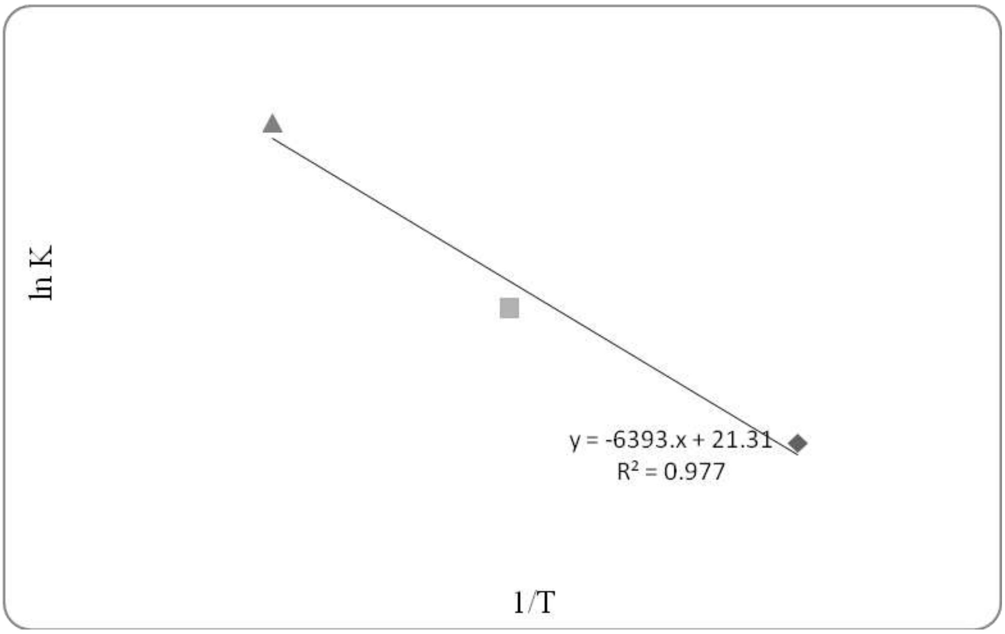

Figure 1: Plots of lnk versus 1/T for effect of temperature on benzene uptake

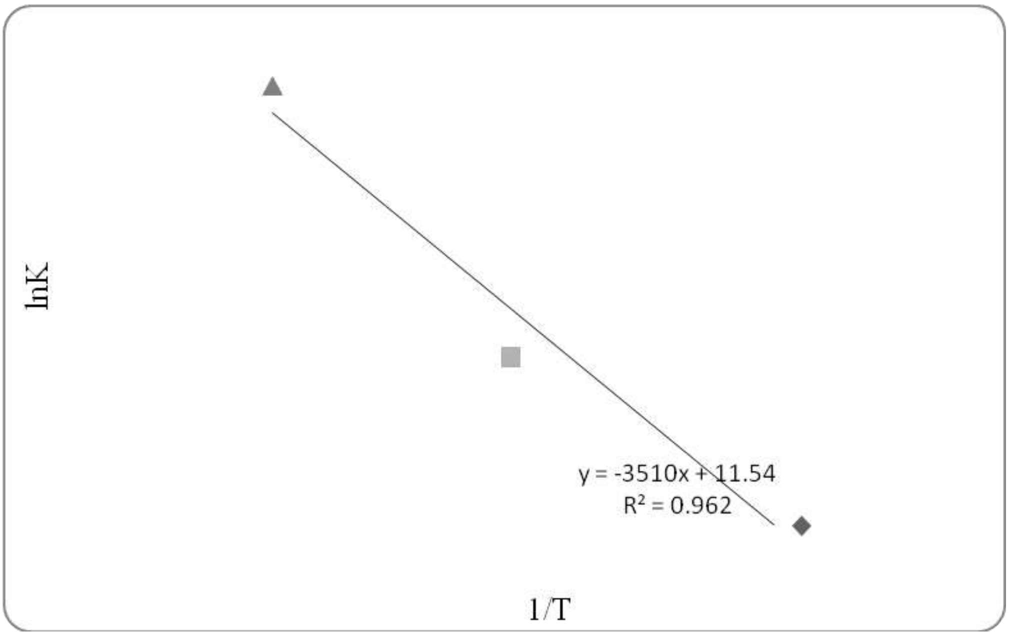

Figure 2: Plots of lnk versus 1/T for effect of temperature on toluene uptake

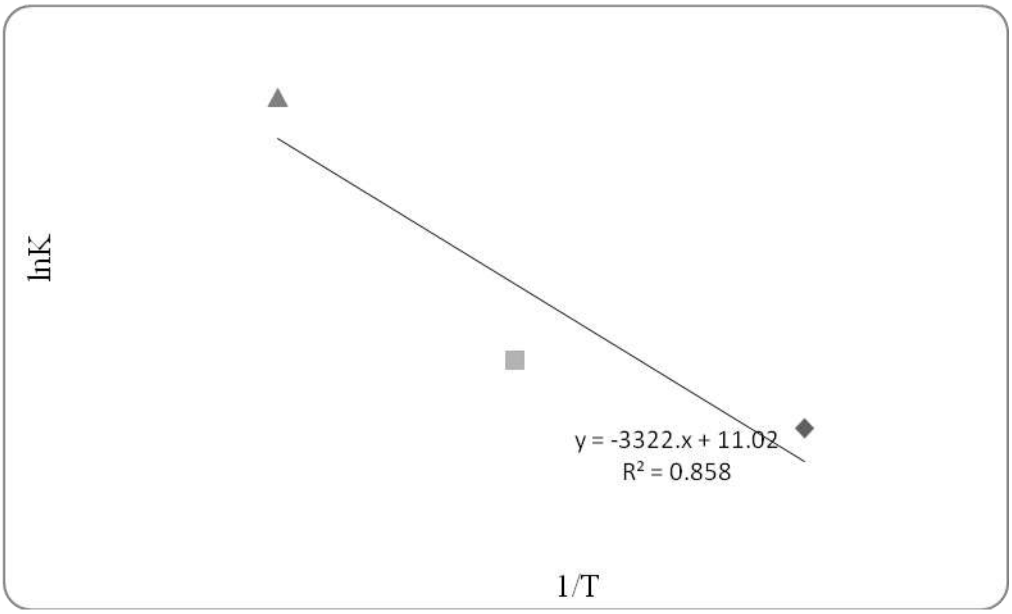

Figure 3: Plots of lnk versus 1/T for effect of temperature on ethylbenzene uptake

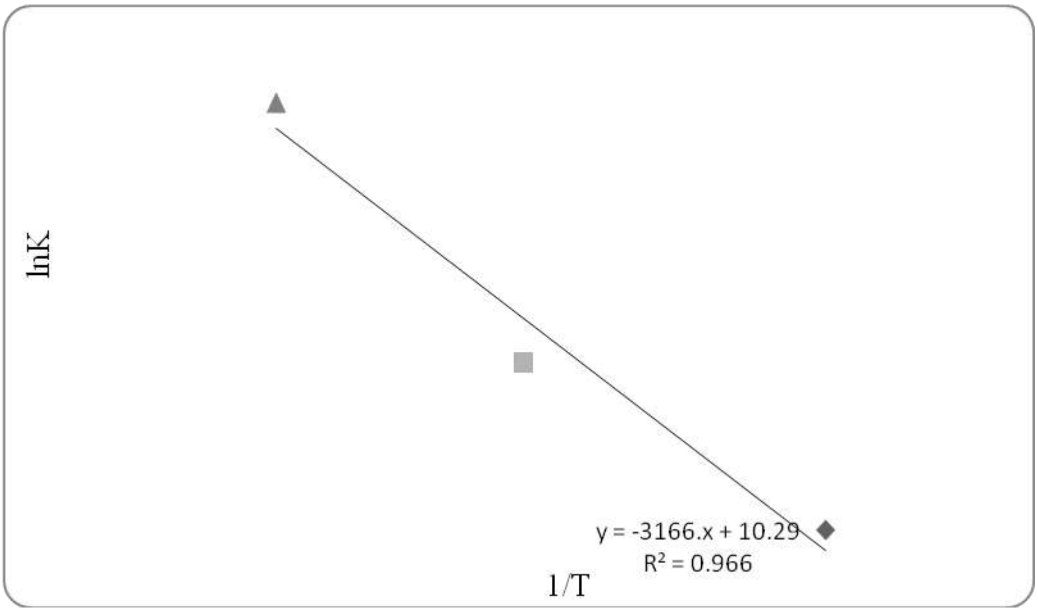

Figure 4: Plots of lnk versus 1/T for effect of temperature on xylene uptake

CONCLUSION

The removal of BTEX from refinery wastewater was carried out using hexadecyltrimethylammonium chloride modified Ogwuta source clay. Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin adsorption models were adopted to understand the pollutant-adsorbent interface interactions. The Temkin constants suggest some degree of chemical interaction as much as the D-R values agreed with the Langmuir theoretical monolayer coverage capacity. However, the values are at variance with the experimental data and the energy of adsorption was found to be less than 1 kJ/mol. The Freundlich model with R-squared value for each

Scientia Africana, Vol. 21 (No. 1), April, 2022. Pp 77-86 https://dx.doi.org/10.4314/sa.v21i1.7
© Faculty of Science, University of Port Harcourt, Printed in Nigeria ISSN 1118 – 1931

of the pollutant not less than 0.999 was found to be the best fit for the process. The changes in enthalpy and Gibbs free energy showed that the adsorption process was endothermically favorable and spontaneous. Hence, this study has presented hexadecyltrimethylammonium chloride modified Ogwuta source clay as a veritable adsorbent for organic pollutant decontamination both from laboratory and real-life sources.

Conflicts of Interest

The authors declare that no conflict of interest(s) exist.

REFERENCES

Bhattacharya, S., & Mandof, A. (2014). Studies on preparation and analysis of organoclay nanoparticles. *Research Journal of Engineering Sciences, 3*(3), 10-16.

Hong, S., Wen, C., He, J., Gan, F., & Ho, Y. S. (2009). Adsorption Thermodynamics of Methylene Blue unto Bentonite. *Journal of Hazardous Materials, 167*; 630-633.

Agha, I. I., Ibezim-Ezeani, M. U., & Obi, C. (2021): Physicochemical Properties of Organophilic Clay Developed Using Hexadecyltrimethylammonium Chloride (HDTMAC) Modifier. *International Research Journal of Pure & Applied Chemistry, 22*(9): 20-30. Doi: 10.9734/IRJPAC/2021/v22i930431

Kumar, G., Sen, S., & Bhattacharyya K. G. (2016). Adsorption of Crystal Violet on Raw and Acid-treated Montmorrilinite K10 in Aqueous Suspension. *Journal of Environmental Management,171*; 1-10.

Mahdi, N. R., Ali, J. J., & Abdulaziz, J. A. (2021). Treatment of Petroleum Refinery Effluent and Wastewater in Iraq: A Review. *Material Science Engineering, 1058*. Doi: 10.1088/1757-899x/1058/1/012072

Taghreed, A., & Muftah, E. (2018). Organic Contaminants in Refinery wastewater: Characteriztion and Novel Approach for Biotreatment; Recent Insights in Petroleum Science and Engineering. Doi: 10.5772/intechopen.72206

Gopinathan, R., Bhowal, C., & Galapati C. (2017). Thermodynamic study of some basic dyes adsorption from aqueous solution on activated carbon and new correlations. *Journal of Chemical Thermodynamics, 107*; 182-188.

Padmaja, M., Bhavani, R., Pamila, R. (2018). Adsorption of cadmium from aqueous solutions using low cost materials: A review. *International Journal of Engineering and Technology,7*(4.2); 26-29.

Leyva-Ramos, R., Jacobo-Auara, A., & Marinez-Costa, J. I. (2021). Organoclays: Fundamentals and applications for removing toxic pollutants from water solution. In: Moreno-piraja J, C., Giraldo-Gutierrez L., Gomez-Granadoz F. (eds) Porous Materials. Springer, *Cham.*, Doi. Org/10.1007/978-3-030-65991-2_13.

Pingpung, S., Amgad E., Micheal W., Jeonghoo, H., & Robert J. H. (2018). Estimation of US refinery water consumption and allocation to refinery products. *Fuel, 221*; 542-557.

Dada, A. O., Olalekan, P. A., and Olatunya, A. (2012). Langmuir, Freundlich Temkin and Dubinin-Radushkevich isotherm studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. *Journal of Applied Chemistry*, *3*(1); 38-45

Davoud B., Ferdps L., Hossein A., & Ali J. (2017). Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of ampicillin unto montmorillonite nanoparticles. *Journal of Pharmaceutical Research International*, *20*(2); 1-9.

Ivana, S., Stanisa, S., Ivan, S., & Dragoljub, G. (2014). Industrial application of clay and clay minerals. Earth Sciences in the 21st Century, Nova Science Publishers Inc. New York.

Kongjidinataa, M. I., Cjao, B., Lian, Q., Subramaniam, R., Zappi, M., 7 Gang, D. D. (2017). Equilibrium, kinetic and thermodynamic studies for adsorption of BTEX unto ordered mesoporous carbon (OMC). *Journal of Hazardous Materials,336*; 249-259.

Netai, M., Lydia, C., David, S., & Mathew, M. (2013). Adsorption of phenol from aqueous solution using carbonized maize tassels. *British Journal of Applied Sciences and Technology,3*(3); 649-661.

Nimibofa, A., Augustus, N., & Donbebe, W. (2017). Modelling and interpretation of adsorption isotherms. *Journal of Chemistry, 2017*; 67-77.

Nourmoradi, H., Avospour, M., Ghasiemian, N., Heidari, M., Moradnejedi, K., & Mohammadi, F. (2017). Surfactant modified montmorillonite as a low cost adsorbent for 4-Chlorophenol: Equilibrium, kinetic and thermodynamic study. *Journal of Taiwan Institute of Chemical Engineering*, *59*; 244 -251.

Nourmoradi, H., Khiadani, M., & Nikaeen, M. (2013). Multi-component adsorption of benzene, toluene, ethylbenzene, and xylene from aqueous solutions by Montmorillonite modified with tetradecyl trimethyl ammonium bromide. *Journal of Chemistry, 2013*(1-4); 1-10.

Nourmoradi, H., Khiadani, M., & Nikaeem M. (2012). Removal of benzene, toluene, ethylbenzene and xylene from aqueous solutions using montmorillonite modified with nonionic surfactants: Equilibrium, kinetic and thermodynamic study. *Chemical Engineering Journal, 191*; 341-348.

Obi, C., & Woke, J. (2014). The removal of phenol from aqueous solution by *Colocaciaesculenta* araesia Linn Schott. *Journal of Soil Science and Environmental Management*, *3*(6); 50-58.

Okoro, I. A & Abii, T. (2011). Sorption models of cadmium (II) ion onto edible fruit wastes. *American Journal of Scientific and Industrial Research, 2*(3), 386-390.

Sharmasarkar, S., Haynes, W., & Vance G. (2000). BTEX sorption by montmorillonite organoclays. *Water, Air and Soil Pollution, 19*(1-4); 257-273.