

Kinetics, Isotherms and Thermodynamics Modeling of PAHs Adsorptions onto Organo-Bentonite. (Part 2)

By

S. L. Abdullahi,* A. A. Audu* and N. K. A. Bakar[#]

Abstract

Polycyclic aromatic hydrocarbon (PAHs) is classified as persistent hazardous organic priority pollutants produced by anthropogenic as well as natural activities. The present study investigates the kinetics, isotherm, and thermodynamic behavior of five PAHs (fluorene, phenanthrene, anthracene, fluoranthene and benzo[k]fluoranthene) for their adsorption onto a Nigerian bentonite clay modified with hexadecylpyridinium bromide. Kinetic models of pseudo-first order (Lagergren) and pseudo-second order (Ho–McKay) were evaluated for the kinetic studies and intra-particle diffusion (Weber and Morris) model was applied for the adsorption mechanism. The results suggest the better applicability of pseudo-second order model (> 0.99) and the mechanism of the adsorption was found to be intra-particle diffusion with occurrence of some other mass transfer mechanisms. Among the isotherms, Langmuir, Freundlich and Temkin models were used for the equilibrium studies, Langmuir isotherm models exhibited the best fit (> 0.80). The calculated values of R_L and n were between 0-1 and $n > 1$ respectively, indicating the favorability of the adsorption process. The thermodynamic parameters: Gibb's free energy change, ΔG was found to be negative, indicating that the adsorption process was spontaneous and feasible. The positive values of the enthalpy ΔH and entropy ΔS changes indicate the endothermic nature of the adsorption process and increase in the degree of randomness at the solid–liquid interface as well as good affinity of PAHs towards the adsorbents.

Keywords: PAHs, kinetic models, equilibrium isotherms, thermodynamic parameters

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic organic compounds comprising of two or more benzene rings made up of hydrogen and carbon atoms without heteroatoms or substituents^{1,2}. The pollution of water bodies by petroleum is a consequence of civilization and growing need for energy. In most cases, petroleum-related pollution are associated with port activities and outflow of urban and industrial wastewater contaminated with petroleum and its derivatives.³ Most PAHs released to the environment are believed to originate from pyrogenic

* Department of Pure and Industrial Chemistry, Bayero University Kano, Nigeria.
slabdullahi39@gmail.com

* aaaudu.chm@buk.edu.ng

[#] Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia,
kartini@um.edu.my

¹ Albayati, T.M. and Kalash K.R. (2019). Polycyclic aromatic hydrocarbons adsorption from wastewater using different types of prepared mesoporous materials MCM-41in batch and fixed bed column. *Process Safety and Environmental Protection*. <https://doi.org/10.1016/j.psep.2019.11.007>

² Hąc-Wydro, K., Połec, K., Broniatowski, M., (2019). The impact of selected Polycyclic Aromatic Hydrocarbons (PAHs) on the morphology, stability and relaxation of ternary lipid monolayers imitating soil bacteria membrane. *J. Mol. Liq.* 276, 409–416.

³ Mustapha, H.I (2018). Treatment of Petroleum Refinery Wastewater with Constructed Wetlands. Thesis

and petrogenic sources such as volcanic eruptions, pyrolysis of organic matter, emissions from power plants and petroleum spills, use of fossil fuel, petrochemical, coal mining and coking industries⁴. They are ubiquitous in the environment and occur in various aquatic systems such as influent and effluent from wastewater treatment plants, groundwater, surface waters or seawater as a result of natural and anthropogenic activities.⁵ Sixteen types of PAHs have been classified as priority pollutants by the US Environmental Protection Agency (US EPA) and the European Union (EU) due to their mutagenic, teratogenic and carcinogenic effects. Short and long-terms health exposures of humans to PAHs can lead to eye irritation, nausea, vomiting, diarrhea and an increased risk of developing cancer in a variety of organs and tissues.⁶ The main routes of exposure to these compounds include inhalation of ambient air and indoor air, ingestion of food contaminated with PAHs and dermal contact from both occupational and non-occupational settings.⁷ As such it becomes essential to remove these substances from the environment. Various authors have reported on the adsorption kinetics, isotherms and thermodynamic modeling for the adsorption of PAHs on different materials such as activated carbon,^{8,9,10} silica-based mesoporous materials,^{1,11,12} agricultural wastes¹³ and modified clay minerals.^{7,14,15}

⁴Mojiri, A., John, L. Z., Akiyoshi, O., Noriatsu, O., Tomonori K. (2019). Comprehensive review of polycyclic aromatic hydrocarbons in water sources, their effects and treatments. *Science of the Total Environment* 696; 133971

⁵ Lamichhane, Shanti K.C. Bal Krishna, Ranjan Sarukkalige (2016). Polycyclic aromatic hydrocarbons (PAHs) removal by sorption: A review. *Chemosphere* 148, 336-353

⁶ Lawal, A. T. (2017); Polycyclic aromatic hydrocarbons. A review. *Cogent Environmental Science* (2017), 3: 1339841 <https://doi.org/10.1080/23311843.2017.1339841>

⁷ Hedayati, M. (2018). Removal of Polycyclic Aromatic Hydrocarbon from Deionized Water & Landfill Leachate by using Modified Clinoptilolites. Thesis.

⁸ Wu, Z., Sun, Z., Liu, P. Li, Q., Yanga, R. and Xia Y. (2020). Competitive adsorption of naphthalene and phenanthrene on walnut shell based activated carbon and the verification via theoretical calculation. *RSC Adv.*, 10, 10703–10714 | 10703.

⁹ Gupta, H. and Singh, S. (2018). Kinetics and thermodynamics of phenanthrene adsorption from water on orange rind activated carbon. *Environmental Technology & Innovation* 10, 208–214

¹⁰ Zheng, X., Lin, H., Tao, Y., Zhang, H., (2018). Selective adsorption of phenanthrene dissolved in Tween 80 solution using activated carbon derived from walnut shells, *Chemosphere*. doi: 10.1016/j.chemosphere.2018.06.025

¹¹ Vidal, C. B., Allen, L. B., Cícero P. M., Ari C.A. de Lima, Francisco S. D., Luiz. C.G. V., Pierre B.A. F., Ronaldo F. N. (2011); Adsorption of polycyclic aromatic hydrocarbons from aqueous solutions by modified periodic mesoporous organosilica. *Journal of Colloid and Interface Science*, 357; 466–473

¹² Balati, A., Shahbazi, A., Amini, M.M., Hashemi, S.H., (2015). Adsorption of polycyclic aromatic hydrocarbons from wastewater by using silica-based organic-inorganic nanohybrid material. *J. Water Reuse Desalin.* 5, 50.

¹³Younis, S. A., El-Gendy, N. S. Waleed I. E. & Yasser M. M. (2014): Kinetic, isotherm, and thermodynamic studies of polycyclic aromatic hydrocarbons biosorption from petroleum refinery wastewater using spent waste biomass. *Desalination and Water Treatment*, DOI: 10.1080/19443994.2014.964331

¹⁴ Cobas, M., Ferreira, L., Sanromán, M.A., Pazos, M., (2014). Assessment of sepiolite as a low-cost adsorbent for phenanthrene and pyrene removal: kinetic and equilibrium studies. *Ecol. Eng.* 70, 287-294.

¹⁵ Kaya, E.M.O., Ozcan, A.S., Gok, O., Ozcan, A., (2013). Adsorption kinetics and isotherm parameters of naphthalene onto natural- and chemically modified bentonite from aqueous solutions. *Adsorption* 19 (2-4), 879-888.

Adsorption of PAHs (fluorene, phenanthrene, anthracene, fluoranthene and benzo[k]fluoranthene) on hexadecyl pyridinium-modified bentonite (HDP-PK) has been reported in Part One of this paper; but the extensive study involving equilibrium, kinetics and thermodynamics has not been reported. Therefore, the aim of this study is to investigate the equilibrium, kinetics and thermodynamics parameters for the adsorption of the five PAHs on the adsorbent HDP-PK.

Materials and methods

Materials

PAHs Standards; fluorene (FLO), anthracene (ANT), phenanthrene (PHE), fluoranthene (FLA) and benzo[k]fluoranthene (BkF) of 99 % purity manufactured by Sigma–Aldrich (Schnelldorf, Germany). HPLC-grade n-hexane, methanol, acetonitrile, dichloromethane (DCM), acetone were obtained from Merck (Darmstadt, Germany). All other chemical reagents were of analytical grade and were used without further purification. Milli-Q Ultrapure water was used throughout the study.

Methods

Adsorption Kinetics and Equilibrium Studies

Kinetics Studies

Adsorption kinetics study was performed to determine the time required to achieve equilibrium during the adsorption process¹⁶. For the kinetic experiments 10 mL of 1 mg L⁻¹ PAHs aqueous solution was mixed with 10 mg of the adsorbent (HDP-PK) in an Erlenmeyer flask (25 mL) sealed with PVC film and placed on an orbital shaker at 150 rpm with variations of time (30–1800 minutes). Samples were withdrawn during shaking at preset time intervals. The adsorbent was removed by filtration, the filtrate was extracted with DCM using Liquid-Liquid Extraction (LLE) procedure;¹⁷ and the extract was analyzed by GC-FID¹⁸.

The adsorption capacity, expressed as the amount of PAH adsorbed per unit mass of the adsorbent q_e (mg/g)^{1,8}, was calculated by the following equation.

$$q_e = \frac{(C_o - C_e)V}{m} \dots \dots \dots (Eq. 1)$$

where, q_e , C_o , and C_e , are the amount of PAH adsorbed (mg/g) at equilibrium, initial and equilibrium concentration of the PAHs solution (mg/L) respectively. V is the volume (L) of the solution in the flask and m (g) is the mass of the adsorbent.

The kinetic models of pseudo-first-order (Eq. 2); pseudo-second-order (Eq. 3) and intraparticle diffusion (Weber and Morris) (Eq. 4) were used to evaluate the kinetic rate and the mechanisms involved in the adsorption process. In addition, linear regression was used to determine the best-fitting model (R^2).

¹⁶ Inyinbor A.A., Adekola F.A, and Olatunji, G.A (2016); Kinetics, isotherms and thermodynamic modeling of liquid phase adsorption of Rhodamine B dye onto *Raphia hook* Erie fruit epicarp. *Water Resources and Industry* 15; 14–27

¹⁷ Nkansah, M. A., Christy, A. A., Barth, T. & Francis, G.W. (2012); The use of lightweight expanded clay aggregate (LECA) as sorbent for PAHs removal from water. *Journal of Hazardous Materials*, 217-218: 360- 365;

¹⁸ Yakout, S.M.& Daifullah, A.A.M. (2013); Removal of selected polycyclic aromatic hydrocarbons from aqueous solution onto various adsorbent materials. *Desalination and Water Treatment*, 51:34-36, 6711-6718, DOI: 10.1080/19443994.2013.769916

$$\text{Log } (q_e - q_t) = \text{log } q_e - \frac{k_1}{2.303} t \quad \dots \text{Eq. 2 (pseudo-first order)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \dots \dots \dots \text{Eq. 3 (pseudo-second order)}$$

where q_e and q_t are the amounts of PAHs adsorbed (mg/g) at equilibrium and at time t (min), respectively, k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the rate constants for the pseudo-first-order and pseudo-second-order kinetic models respectively. Linear graphs are obtained from plots of $\log (q_e - q_t)$ and t/q_t against t respectively. Values of k_1 , k_2 and q_e can be calculated from the slope and intercepts of the plots.

$$q_t = k_f t^{0.5} + c \quad \dots \dots \dots \text{Eq. 4 (intra-particle diffusion)}$$

where, c (mg g^{-1}) is the intercept and a constant related to boundary layer thickness, large intercept suggests great boundary layer effect, k_f is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1}$).

A plot of q_t versus $t^{0.5}$ can give a linear or multilinear in shape, suggesting that intraparticle diffusion is involved in the adsorption process, or two or more steps govern the adsorption process, which may be operating simultaneously. However, if a linear graph is obtained and the plot passes through the origin then intraparticle diffusion is said to be the only rate-controlling step.⁷

2.2.1.2 Equilibrium Studies

Adsorption isotherm describes distribution of adsorbate molecules between the liquid and the solid phase (adsorbent)¹⁹. In the adsorption isotherms experiments, 10 mg of the adsorbent and 10 mL of the PAHs aqueous solution were also used, but this time the solution concentrations were varied in the range of 0.02–5.0 mg L^{-1} . After agitation for 8 h, the mixture was treated as in the kinetic experiments. Linear forms of the three most commonly used models namely; Langmuir, Freundlich and Temkin isotherm models were used to analyze the experimental data. The Langmuir Isotherm assumes a surface with homogeneous binding sites, no interactions between adsorbed species, equivalent sorption and activation energies.¹⁰ Mathematically it is expressed as in Eq. 5

$$\frac{C_e}{q_e} = \frac{1}{q_m} k_L + \frac{C_e}{q_m} \quad \text{or} \quad \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m} k_L * \frac{1}{C_e} \quad \dots \dots \dots \text{Eq. 5}$$

where C_e is the equilibrium concentration of adsorbate in the solution (mg L^{-1}); q_e the amount of adsorbate adsorbed on the adsorbent at equilibrium (mg g^{-1}); q_m the monolayer adsorption capacity (mg g^{-1}) and k_L is the Langmuir adsorption equilibrium constant (L mg^{-1}), which is related to the energy of adsorption. A plot of $C_e/(q_e)$ Vs C_e gives a straight line with a slope and intercept of $\frac{1}{q_{max}}$ and $\frac{1}{q_{max} k_L}$ respectively.

A dimensionless equilibrium parameter (R_L) which explains the favorability of adsorption process; can be calculated using constant k_L and the initial concentration Co as expressed in (Eq. 6)

$$R_L = \frac{1}{1 + k_L * Co} \quad \dots \dots \dots \text{Eq. 6}$$

If $0 < R_L < 1$, the adsorption process is favorable. If $R_L = 1$, the process is linear, the adsorption process is unfavorable if $R_L > 1$ and it is irreversible if $R_L = 0$.

¹⁹ Lamichhane, S., (2017). Improve the Efficiency of Constructed Wetlands in Removing Polycyclic Aromatic Hydrocarbons (PAH) From Storm Water. PhD Thesis. Curtin University, Australia

The Freundlich Isotherm demonstrates a multilayer adsorption involving surface heterogeneity with non-uniform distribution of adsorption heat and affinities over the sorbent surface.¹⁹ It can be represented mathematically as

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \dots\dots\dots \text{Eq. 7}$$

where q_e (mg/g) is the amount adsorbed, C_e = equilibrium aqueous concentration (mg/L), k_F (mg/g) and $1/n$ are the Freundlich constants related to sorption capacity and intensity, respectively. A plot of $\ln q_e$ against $\ln C_e$ yields a straight-line graph. The slope and intercept of the plot will give $\frac{1}{n}$ and $\ln k_F$ respectively and hence the values of n and k_F can be obtained.

If the values of n are within the range of (1–10) the adsorption process is favorable.^{15,18,20}

Temkin Isotherm assumes that the heat of adsorption of all the molecules in a layer decreases linearly with the surface coverage of the adsorbent and the adsorption is characterized by uniform distribution of binding energies¹². The mathematical expression of the equation is as follows;

$$q_e = B \ln A_T + B \ln C_e, \dots\dots\dots \text{Eq. 8}$$

$$B = \frac{RT}{b} \dots\dots\dots \text{Eq. 9}$$

where q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium, C_e (mg/L) is concentration of adsorbate in solution at equilibrium, b (Jmol^{-1}) is Temkin constant which is related to the heat of adsorption and A_T is Temkin isotherm constant (Lg^{-1}), T is the absolute temperature (K), R is the gas constant ($8.314 \text{ Jmol}^{-1} \text{ K}$). The constants (B and A_T) can be determined from the slopes (B) and intercepts ($B \ln A_T$) of a plot of q_e against

$\ln C_e$,

Effects of temperature on the adsorption of PAHs onto HDP-PK was studied. The thermodynamic parameters that explain the feasibility, spontaneity and the nature of adsorbate-adsorbent interactions (ΔG° , ΔH° and ΔS°) were calculated using the Van't Hoff equation in the mathematical relations below.^{1,9,10}

$$\Delta G = -RT \ln K_e \dots\dots\dots \text{Eq. 10}$$

$$K_e = \frac{q_e}{C_e} \dots\dots\dots \text{Eq. 11}$$

$$\ln K_e = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots \text{Eq. 12}$$

$$\Delta G = R \Delta H - T \Delta S \dots\dots\dots \text{Eq. 13}$$

where T is the temperature in Kelvin, R is the gas constant and K_e can be obtained from q_e/C_e .

The enthalpy ΔH (KJ/Mol) and entropy ΔS (kJ/Mol/K) were calculated from the slope ($-\Delta H/R$) and intercept ($\Delta S/R$) of the linear plot of $\ln (K_e)$ vs. $1/T$, respectively and ΔG was calculated from Eq. (13) above.

Results and Discussion

Adsorption Studies

Kinetics Modelling

Table 1 shows the results of the adsorption kinetics parameters (pseudo-first-order, pseudo-second-order and Weber and Morris models) for the PAHs adsorption onto HDP- PK.

²⁰Desta, M.B. (2013); Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (*Eragrostis tef*) Agricultural Waste. *Journal of Thermodynamics* <http://dx.doi.org/10.1155/2013/375830>

Figs. (1a & b) show the plots of pseudo-first order and pseudo-second order kinetic models.

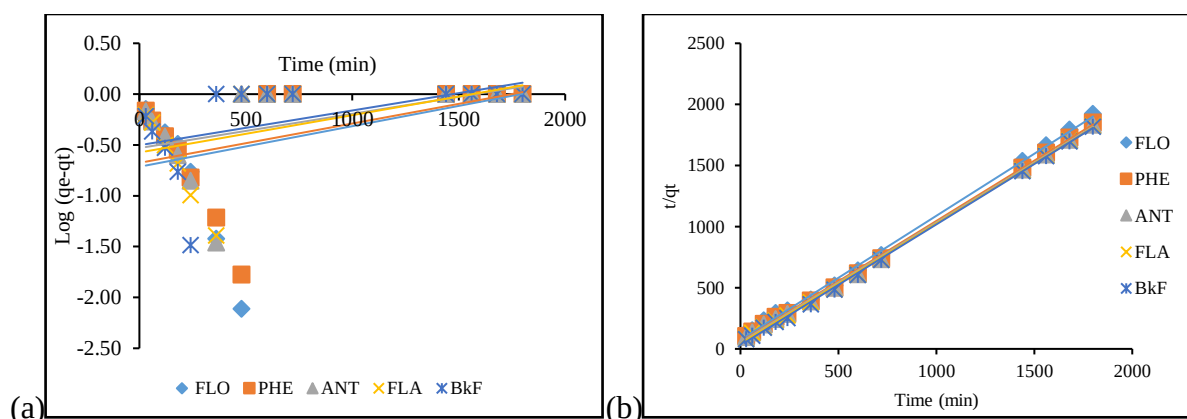


Fig. 1: (a) Pseudo-first-order kinetic studies (b) Pseudo-second-order kinetic studies

It was observed from the plots that pseudo-first-order model did not fit well for the whole range of contact time since the R^2 values ranged between (0.090 – 0.212) as shown in Table 1. In addition, the theoretical q_e values derived from the pseudo-first-order kinetic model did not correspond to the calculated values (q_c) indicating that the model did not fit well.

The experimental data for the adsorption of the five PAHs on HDP-PK, fitted very well with the pseudo-second-order kinetic model as shown in (Fig. 1b) with high correlation coefficients ($R^2 > 0.998$). Furthermore this model indicated a good agreement between the experimental (q_e) and the calculated (q_c) adsorption capacities. This suggests that the adsorption rate of PAHs is dependent on the availability of the adsorption sites.⁸

Table 1: Adsorption kinetic parameters for the sorption of PAHs onto HDP-PK

Parameter	FLO	PHE	ANT	FLA	BkF
q_e (mg g ⁻¹)	0.937	0.972	0.982	0.987	0.99
Pseudo-first-order					
q_c (mg g ⁻¹)	0.193	0.211	0.295	0.267	0.315
k_1 (min ⁻¹)	0.001	0.001	0.001	0.001	0.001
R^2	0.164	0.210	0.249	0.287	0.260
Pseudo-second-order					
q_c (mg g ⁻¹)	0.985	1.013	1.020	1.017	1.012
k_2 (g mg ⁻¹ min)	0.013	0.017	0.019	0.025	0.034
R^2	0.998	0.999	0.999	0.999	0.999
Weber and Morris					
k (mg g ⁻¹ min ⁻¹)	0.055	0.053	0.051	0.047	0.041
c (mg g ⁻¹)	0.381	0.439	0.467	0.523	0.583
R^2	0.752	0.749	0.737	0.702	0.642

Similarly, some researchers have reported that the adsorption kinetics of PAHs on various adsorbents such as, activated carbons,^{8,9,10,21} organo-clinoptilolites,⁷ silica-based organic–inorganic nano-hybrid material (NH₂-SBA-15),¹² plant residue based sorbent^{13,22,23}, sepiolite¹⁴, natural and chemically modified bentonite,^{15,24} mesoporous materials.^{1,11} were consistent with the pseudo-second-order kinetic model.

According to those authors, the pseudo-second-order kinetic model provided data that described adequately both fast and slow adsorption steps and assumed that the rate-controlling step could be associated with chemisorption or a combination of both physical and chemical sorption processes. The physical adsorption may be caused by the aromatic nature of the PAHs, probably combined with the hydrophobic (π – π dispersive) interaction and electron sharing mechanism that involved nitrogen with net positive charge on the head of the cationic surfactant.^{5,7,8,18,25}

In assessing the mechanism of the adsorption, the intra-particle diffusion model proposed by Weber and Morris, was used to investigate the mechanism. The Weber and Morris plots is as shown in (Fig. 2).

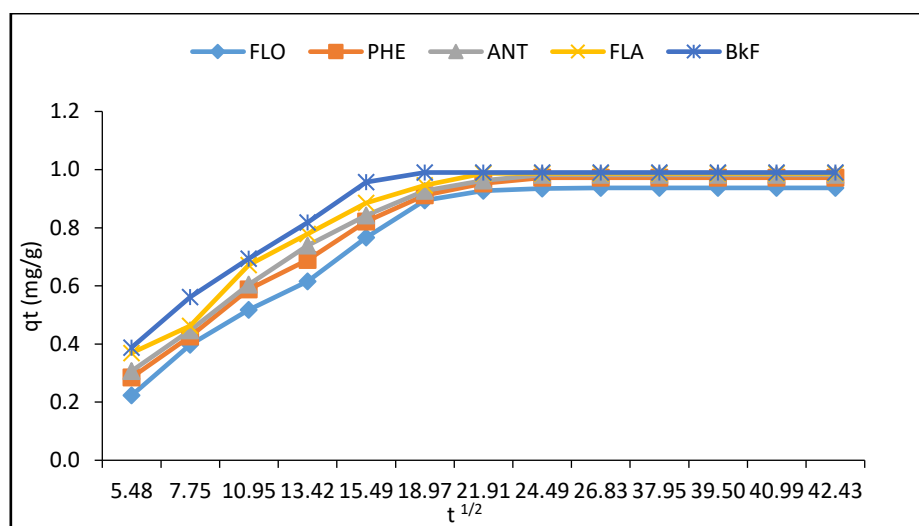


Fig. 2: Intraparticle-diffusion plot for the adsorption of the 5 PAHs on HDP-PK

²¹ Rad, R.M., Leila O., Hossein K.*, Farideh G., Hamed H., Rezvan A. L. and Kamal A. (2014). Adsorption of Polycyclic Aromatic Hydrocarbons on Activated Carbons: Kinetic and Isotherm Curve Modeling *Int. J. of Occup. Hyg.* 43-49.

²² Zhang, M., Li Heng X., Sang Soo L. & Yong Sik O. (2016) Sorption of Polycyclic aromatic hydrocarbons (PAHs) by dietary fiber extracted from wheat bran, *Chemical Speciation & Bioavailability*, 28:1-4, 13-17, DOI: 10.1080/09542299.2015.1136569.

²³ Xi, Z. and Baoliang Chen, B. (2014). Removal of polycyclic aromatic hydrocarbons from aqueous solution by raw and modified plant residue materials as biosorbents. *J. of Envi. Sci.* 26 (2014) 737–748

²⁴ Karaca, G., Baskaya, H.S., Tasdemir, Y., (2016). Removal of polycyclic aromatic hydrocarbons (PAHs) from inorganic clay mineral: bentonite. *Environ. Sci. Pollut. Res.* 23 (1), 242–252. <https://doi.org/10.1007/s11356-015-5676-z>.

²⁵ Eeshwarasinghe, D., Loganathan, P., Kalaruban M., Pratheep, D., S., Kandasamy, J. and Vigneswaran, S. (2018). Removing polycyclic aromatic hydrocarbons from water using granular activated carbon: kinetic and Equilibrium adsorption studies. *Environmental Science and Pollution Research*. <https://doi.org/10.1007/s11356-018-1518-0>

The multi-linearity of these plots confirmed that the sorption occurred in two phases of which one or any combination can be the rate-controlling mechanism: (i) external diffusion or boundary layer/film, followed by (ii) intraparticle diffusion in the inner porosity of the sorbents^{9,10}. In addition, the linear plots (first phase) did not pass through the origin, suggesting that intraparticle diffusion was involved in the adsorption process, though it was not the rate-limiting step, since the regression coefficients (R^2) ranged between 0.9713 to 0.9982. In the second phase, the fitting line deviated from the origin, indicating that the adsorption process is controlled by both external and intra-particle diffusion. Similar observation was reported for the adsorption of naphthalene and phenanthrene on walnut shell based activated carbon⁸ for the adsorption of phenanthrene on orange rind activated carbon⁹. It was also reported that the adsorption processes of PAHs on walnut shells^{8,10} and vehicular tyre²⁶ activated carbons were not solely controlled by intra-particle diffusion, but some other mass transfer mechanisms which occurred simultaneously.

Equilibrium Isotherms

From the plots of Langmuir, Freundlich and Temkin isotherm models, straight lines were obtained with various slopes and intercepts, which were used to calculate the parameters in the Table 2 below. The results appeared to be well represented by all the theoretical models tested, but the Langmuir model gave the highest R^2 values (0.801-1.000) over the other two models; Freundlich (0.638-0.966) and Temkin (0.586-0.831). In addition, the calculated R_L values which were less than 1, indicate that the adsorption process was favorable and also the interaction between the PAH molecules and the adsorbent may be due to chemical attraction. The values of n from the Freundlich equation were greater than 1, also showing the favorability of the adsorption process. As has been reported, the Langmuir isotherm showed the best fits for the experimental data at lower values of C_e , indicating that initially the adsorption process started as a monolayer phenomenon. However, it did not persist at higher concentration ranges when the adsorption sites became saturated and as such, the process turned to be multilayer. This gives the possibility of monolayer and heterolayer PAHs molecules formation on the adsorbent surface. Hence, this means that the adsorption mechanism was dominated by a combination of physical and chemical adsorption processes^{11,12,13}.

²⁶Gupta, H. and Gupta, B. (2016): Vehicular Tire as Potential Adsorbent for the Removal of Polycyclic Aromatic Hydrocarbons, Polycyclic Aromatic Compounds <http://dx.doi.org/10.1080/10406638.2016.1217890>

Table 2: Parameters of Langmuir, Freundlich, and Temkin isotherm models for PAHs Adsorption on HDP-PK

Isotherm	Parameter	FLO	PHE	ANT	FLA	BkF
Freundlich	K_F (mg/g)	0.094	0.027	0.009	0.029	0.005
	1/n	0.886	0.655	0.428	0.639	0.224
	n	1.129	1.528	2.335	1.566	4.47
	R²	0.681	0.954	0.638	0.896	0.966
Langmuir	K_L (L/mg)	0.345	0.091	0.031	0.101	0.006
	q_{max}	4.921	1.315	0.852	1.406	0.042
	R²	0.996	0.999	0.801	0.999	1
	R_L	0.39-0.99	0.71- 0.99	0.88-0.99	0.69-0.99	0.97-0.99
Temkin	B (J/mol)	4.15E+02	1.19E+02	7.25E+02	6.49E+02	5.29E+02
	A_T (L g⁻¹)	0.510	0.909	1.368	0.763	2.432
	R²	0.733	0.831	0.816	0.586	0.651

It has also been reported that the adsorption of aromatic hydrocarbons from water using several organoclays yielded a Langmuir-type isotherm²⁷. Similar results were obtained from other studies on PAHs adsorption from wastewater using different materials such as, spent waste biomass,¹³ orange rind activated carbon,²⁸ silica-based organic–inorganic nano-hybrid material (NH₂-SBA-15),¹² non-calcined mesoporous materials MCM-41¹ which have been found to fit well with the Langmuir isotherm model.

Thermodynamic Studies

The thermodynamic parameters and correlation coefficients are summarized in Table 3 below. The adsorption enthalpy change (ΔH) values were positive, indicating that the adsorption of the five PAHs onto HDP-PK was endothermic in nature.

²⁷ Park, Y., Ayoko, G.A., Frost, R.L., (2011). Application of organoclays for the adsorption of recalcitrant organic molecules from aqueous media. *J. Colloid Interface Sci.* 354, 292e305.

²⁸

Table 3: Thermodynamics Properties of the Adsorption of PAHs on HDP-PK

PAH	ΔH (KJ/Mol)	ΔS (KJ/Mol/K)	ΔG (KJ/Mol)			
			303	313	323	R^2
FLO	37.518	0.132	-2.627	-3.952	-5.277	0.811
PHE	14.938	0.050	-0.302	-0.805	-1.308	0.892
ANT	200.841	0.677	-4.237	-11.005	-17.774	0.742
FLA	2.875	0.017	-2.164	-2.330	-2.496	0.982
BkF	37.483	0.149	-7.781	-9.275	-10.769	0.999

Also the positive values of the entropy change, ΔS ; suggested that there was an increase in the randomness at the solid–liquid interface during the adsorption process, reflecting good affinity of the adsorbents for the PAHs adsorption. The ΔG values were negative and decreased with increasing temperature, indicating that adsorption process was spontaneous in nature and that the adsorption of the PAHs on the HDP-PK was more favorable at higher temperatures. Similar results for endothermic adsorption were also observed on adsorption of Phenanthrene on orange rind activated carbon,⁹ new hybrid clay adsorbent [HYCA],²⁹ vehicular tire activated carbon [VTAC]²⁶, banana peel activated carbon,³⁰ silica-based organic–inorganic nano-hybrid material [NH₂-SBA-15],¹² spent waste biomass¹³ and magnetic graphene composite.³¹

Conclusion

The study investigated the kinetics, isotherms and thermodynamic parameters of HDP-PK efficiency for the adsorption of fluorene, phenanthrene, anthracene, fluoranthene and benzo[k]fluoranthene from aqueous solution. The kinetic data fitted well to pseudo-second order kinetic model with R^2 value (> 0.99) over pseudo-first order model, which had ($R^2 < 0.30$). Intra-particle diffusion model together with occurrence of some other mass transfer mechanisms described the mechanism for the adsorption of the five PAHs. The adsorption data were feasible with the Langmuir, Freundlich and Temkin models, but were better fitted to Langmuir model. The calculated values of R_L and n of the PAHs were between 0-1 and $n > 1$ respectively, indicating the favorability of the adsorption process. The thermodynamic parameters, the Gibb's free energy change, ΔG was found to be negative, indicating that the adsorption process was spontaneous and feasible. The positive values of the enthalpy ΔH and entropy ΔS changes indicate the endothermic nature of the adsorption

²⁹ Unuabonah1, E. I., Bamidele I. O., Leonard B. and Rolf-Alexander D. (2016) Adsorption of Polynuclear Aromatic Hydrocarbons from Aqueous Solution: Agrowaste-Modified Kaolinite vs Surfactant Modified Bentonite. *Bull. Chem. Soc. Ethiop.* 30(3), 369-376

³⁰ Gupta, H., Gupta, B., (2015): Adsorption of polycyclic aromatic hydrocarbons on banana peel activated carbon, *Desalination and Water Treatment*, <http://dx.doi.org/10.1080/19443994.2015.1029007>

³¹ Yang, X., Li, J., Wen, T., Ren, X., Huang, Y. & Wang, X. (2013) Adsorption of naphthalene and its derivatives on magnetic graphene composites and the mechanism investigation. *Coll. Surf. A* 422, 118–125.

process and increase in the degree of randomness at the solid–liquid interface; as well as good affinity of PAHs towards the adsorbent. It can be concluded that there is a good possibility of using HDP-PK as an adsorbent for the removal of PAHs from aqueous systems.

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