

# Investigation of Mixture Effects on the Adsorption Rates of Aromatics from Aqueous Solution on Clay and Sandy Soil

Ebuwa I Osagie\* and Owabor CN

School of Energy, Environment and Agric-food, Engineering Department, Cranfield University, Bedford, Bedfordshire, MK43 0AL, UK

## Abstract

The adsorption behavior of a mixture of two polycyclic aromatic hydrocarbons (PAHs); naphthalene and pyrene and one cyclic aromatic hydrocarbon using clay and sandy soil as adsorbents was examined under ambient conditions in this study. The adsorption from the aqueous solution was observed to be time dependent and the time taken to attain adsorption equilibrium for benzene, naphthalene and pyrene in the mixture were 22, 16 h, 18 and 14 h, and 26 and 18 h in clay and sandy soil, respectively. Among the tested kinetics model in this study, the pseudo-second order equation successfully predicted the adsorption. The rate of adsorption using the pseudo-second order rate expression for benzene, naphthalene and pyrene were 0.00096, 0.00072, 0.00092 min<sup>-1</sup> and 0.00091, 0.00080, 0.00090 min<sup>-1</sup> for clay and sandy soils respectively. These results suggest that benzene was more selectively adsorbed than naphthalene and pyrene in both clay and sandy soil.

**Keywords:** Benzene; Naphthalene; Pyrene; Adsorption isotherms; Adsorption kinetics; Clay; Sandy soil

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) such as benzene occur naturally in petroleum oil, coal and the burning of fuel. The activities of paper mills also release these compounds to the environment. The heavy dependence of these chemicals for economic development is one of the most adverse aspects of global industrialization. A direct consequence of the fast development of industrial activities is the amount and variety of chemical waste thrown into water resources [1]. The occurrence of large concentrations of toxic pollutants in wastewater has become an important environmental issue, in particular, in densely populated cities where the demand for water is very high. Polycyclic aromatic hydrocarbons (PAHs) and cyclic aromatic hydrocarbons constitute an important class of highly toxic and long persistent environmental pollutants. In recognition of their toxicity and high mobility in the environment the world.

Health Organization has recommended a limit for PAHs in drinking water [2]. The European Environmental Agency (EEA) also has included these compounds in its list of priority pollutants to be monitored in industrial effluents [3]. Faced with an increasing contamination of water resources, adsorption technology has become widely used in water treatment plants since it is well established and powerful technique due to its high depuration efficiency [4]. Powdered and granular activated carbon has been proven to be effective adsorbent in adsorption process due to their adequate porous and chemical features [5].

However, there have been attempts recently to exploit low cost material to remove organic and inorganic contaminants from wastewater due to the relatively high cost of activated carbons [6]. There has been an increasing interest in utilizing natural clay minerals for the removal of toxic metals, colours and some aromatic organic pollutants from aqueous solutions [7]. The abundance of natural clay in most continents of the world and its low cost make it a strong candidate as an adsorbent for the removal of many pollutants from wastewaters. The adsorption behavior of individual PAHs, namely, naphthalene and pyrene and a cyclic aromatic hydrocarbon such as benzene onto clay and sandy soil has been investigated. Adsorption of benzene

on different soils [7,8] adsorption of naphthalene on clay and sandy soils [9,10] and lastly, evaluation of pyrene on tropical soils [11-14]. However, no studies have been carried out to evaluate the adsorption behavior of the mixture of polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and pyrene and a cyclic hydrocarbon such as benzene using clay and sandy soils as adsorbents. Therefore, the aim of this study was to investigate the effect of the mixture of naphthalene, pyrene and benzene on the adsorption rates of naphthalene, pyrene and benzene using clay and sandy soil as adsorbents. The importance of this study was to explore the effect of the mixture on the sorption rates and to develop a viable and cheap technology for the removal of recalcitrant pollutants from the environment. The analysis of the kinetic modeling data obtained from the experiments provided the basis for the choice of a suitable mechanism for describing the adsorption process.

## Materials and Methods

### Preparation of the adsorbent

The clay and sandy soil samples used in this study were obtained from Ikpoba River, Benin City, Edo State, Nigeria. On collection, the clay and sandy soil samples were kept separately in a black polythene bags and stored in a refrigerator to ensure the prevalence of anaerobic conditions. Pretreatment of the samples was carried out by removing stones and other heavy particles. A 220 µm mesh was used to remove the large non-clay fractions from the clay. A 2.5 mm mesh was used to sieve the sandy soil. The soils were dried overnight at 383 K in a vacuum oven and stored in an air tight container covered with a black polythene bag prior to the adsorption experiments.

\*Corresponding author: Ebuwa I Osagie, School of Energy, Environment and Agric-food, Engineering Department, Cranfield University, Bedford, Bedfordshire, MK43 0AL, UK, E-mail: [e.i.osagie@cranfield.ac.uk](mailto:e.i.osagie@cranfield.ac.uk)

Received September 27, 2015; Accepted September 29, 2015; Published November 07, 2015

Citation: Osagie EI, Owabor CN (2015) Investigation of Mixture Effects on the Adsorption Rates of Aromatics from Aqueous Solution on Clay and Sandy Soil. Chem Sci J 6: 112. doi:10.4172/2150-3494.1000112

Copyright: © 2015 Osagie EI, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

## Soil sample extraction

Ten gram (10 g) of the clay soil sample was measured and added to a beaker containing 40 ml of a solvent made up of 50% acetone and 50% dichloromethane. The clay soil solvent mixture was then placed in a sonicator for about 20 minutes to heat it to 70°C. To the soil-solvent mixture, 10 g of anhydrous sodium sulphate was added and then shaken gently to obtain a clear extract. The content of the beaker was separated leaving only soil in the beaker. The extracted solvent was poured into a conical flask and then put into a rotary evaporator. After evaporation for some minutes, the conical flask was withdrawn from the evaporator and 2 ml of solvent was measured with a pipette and put into vial bottle for analysis using a capillary column Gas Chromatogram equipped with a flame ionization detector. The same procedure was repeated for the sandy soil sample.

## Removal of PAHs and benzene from clay and sandy soil

The samples (clay and sandy soil) were washed with distilled water by a process involving agitation and dissolution. The soil samples were soaked in distilled water for two days while continuously stirring using a manual stirrer so as to remove all contaminants. The mixture was drained using a micro sieve and continuously flushed with distilled water several times. The mixture was then allowed to drain completely and put into a furnace to get heated up at a high temperature to dry the sample. It was subsequently allowed to cool naturally in open air. The sample was then analysed using a Gas Chromatogram equipped with a flame ionization detector. Results of the analysis showed that there were no naphthalene, pyrene and benzene after washing the samples. The clay and sandy soil samples were then analysed for their physico-chemical properties such as moisture content, pH, specific gravity, bulk density, surface area, particle density and porosity. The results are shown in Table 1.

The adsorbates; benzene, naphthalene and pyrene were supplied by a Chemical Laboratory in Benin City, Edo State, Nigeria. The distilled water used for sample preparation, dilution and solution was obtained from the Department of Chemical Engineering, University of Benin, Benin City, Edo State, Nigeria.

## Adsorption kinetics experiments

The rates of adsorption by the samples (clay and sandy soil) were determined from the uptake levels of the mixture of the two PAHs and benzene from aqueous solution in batch experiments before and after contact until adsorption equilibrium was attained in the clay and sandy soil. For each experiment, 100 mL of the mixture of naphthalene, benzene and pyrene with different initial concentrations (50-250 mg/l) was placed in a tightly corked 1000 ml flask at room temperature. The slurry suspensions were sampled at intervals of 2 hours and UV Spectrophotometer was used for sample analysis. The UV spectrophotometer was set to the various wavelengths of naphthalene, benzene and pyrene which are 244 nm, 229 nm and 373 nm, respectively and the equilibrium time for each wavelength was

	Clay	Sandy soil
pH	5.5	9.0
Moisture content (%)	52	27
Bulk density (g/cm <sup>3</sup> )	1.624	1.192
Surface area (mg/g)	4.102	3.077
Porosity (%)	14	9
Particle density (g/ml)	2.782	3.324

Table 1: Characteristics of natural clay and sandy soil (Physico-chemical analysis).

performed by the adsorption on clay and sandy soil, respectively. This was done for all five samples.

## Adsorption kinetics models

The adsorption kinetics which describes the mechanism of the adsorption process in a given system were determined in this study using pseudo-first model as described by ref. [15] and pseudo-second order model [16].

## Results and Discussion

The results of the experimentation and computation of the kinetic modeling of the adsorption of the mixture of benzene, naphthalene and pyrene in clay and sandy soil are presented below. The potential for the two adsorbents to adsorb the solutes have been exploited. The analysis of the predictions from the kinetic modeling data obtained from the experiments provided the basis for the choice of the applicable and suitable mechanism for describing the adsorption process.

## Equilibrium time for adsorption

In Figures 1-3, show the results of the adsorption times to reach equilibrium for benzene, naphthalene and pyrene in the mixture concentration. The adsorption results showed that equilibrium was attained in 22 and 16 h for benzene in clay and sandy soil, respectively. There was a steady adsorption of benzene by the two different adsorbents. Similarly, for naphthalene it took 18 h and 14 h to reach equilibrium in clay and sandy soil, respectively. There was also a steady adsorption of naphthalene by the two different adsorbents. In the case of pyrene it took 26 h and 18 h to reach equilibrium in clay and sandy soil, respectively. There was a steady adsorption of pyrene by two different adsorbents. From the equilibrium times, sandy soil was observed to reach equilibrium faster than clay for all of the contaminant solutes used in this study. This can be attributed to the large pore spaces, intra-porous nature of sandy soil and its high permeability [17].

The adsorption times to reach equilibrium without the mixture for the three polycyclic aromatic hydrocarbons were for benzene 32 and 22 h; naphthalene, 26 and 20 h, while for pyrene it was 34 and 28 h in clay and sandy soil, respectively. It was observed that it took a shorter time to reach equilibrium for the mixture concentration. Therefore, the effect of the mixture concentration was to reduce the times to reach equilibrium for the three aromatic hydrocarbons (PAHs).

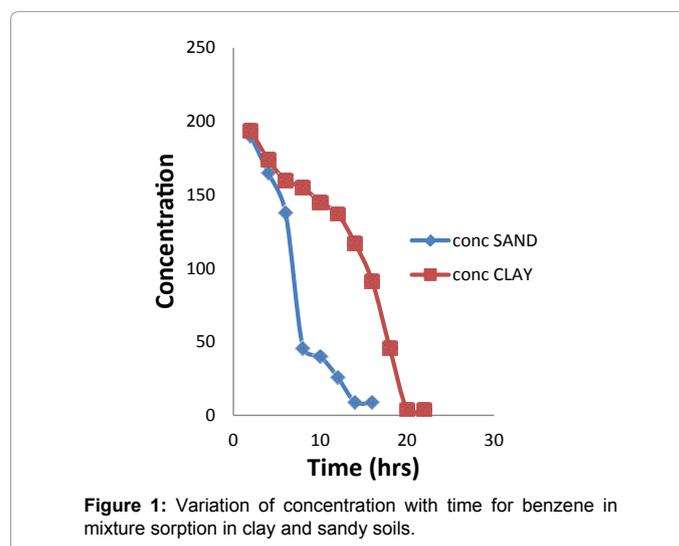


Figure 1: Variation of concentration with time for benzene in mixture sorption in clay and sandy soils.

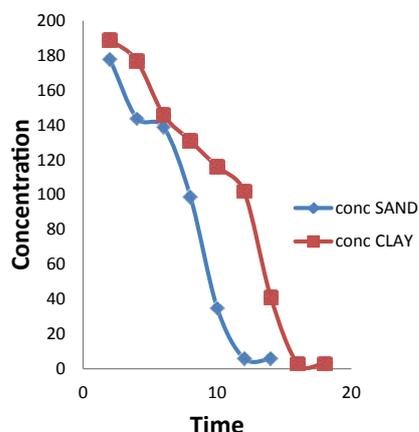


Figure 2: Variation of concentration with time for naphthalene in mixture sorption in clay and sandy soils.

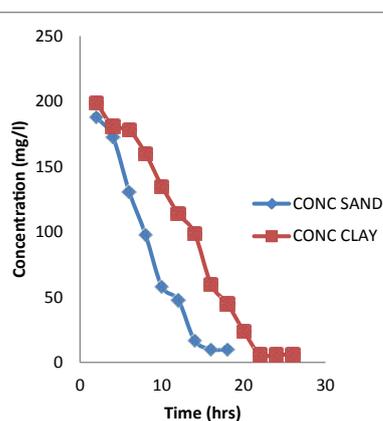


Figure 3: Variation of concentration with time for Pyrene in mixture sorption in clay and sandy soils.

### Adsorption mechanism

The adsorption kinetics of the mixture of two polycyclic aromatic hydrocarbons; naphthalene and pyrene and one cyclic aromatic hydrocarbon, benzene onto clay and sandy soil was evaluated using different models such as pseudo-first order and pseudo-second order models shown in Figures 1-6. Fitting the adsorption experimental data of these models, various parameters were calculated and shown in Tables 2 and 3. The reaction rate constant predicted for the adsorption kinetics by the pseudo-first order is characterized by negative rate constants. These plots are shown in Figures 7-9. Thus, the pseudo-first order model did not give good fits for the clay and sandy adsorbents. The adsorption kinetics data best fitted the pseudo-second order kinetic model for the mixture concentration. Thus, the pseudo-second order model best described the mechanism of adsorption of the mixture of benzene, naphthalene and pyrene.

However, the results indicated that the data were not strongly correlated as the correlation coefficient values were low, ranging from 0.5174 to 0.6058 in clay and from 0.4674 to 0.7115 for sandy soil. The correlation coefficients obtained from the pseudo-second order model for the contaminant solutes were consistent for both clay and sandy soil. This further affirms the suitability of the model. The data were

more strongly correlated during the adsorption of each contaminant solute [8].

The rate of adsorption using the pseudo-second order rate expression for benzene, naphthalene and pyrene in the mixture concentration were 0.00096, 0.00072, 0.00092  $\text{min}^{-1}$  and 0.00091, 0.00080, 0.00090  $\text{min}^{-1}$  for clay and sandy soil, respectively. These results suggest that benzene was more selectively adsorbed than naphthalene and pyrene in both clay and sandy soil [8,18,19] showed that the rate of adsorption for benzene, naphthalene and pyrene when they were adsorbed separately were 0.00083, 0.00069 and 0.00088  $\text{min}^{-1}$  and 0.00019, 0.00023 and 0.00085  $\text{min}^{-1}$  for clay and sandy soil, respectively. These results imply that the effect of the mixture concentration was to slow the rate of adsorption process compared to the reaction rate constant when the contaminant solutes were adsorbed separately [20].

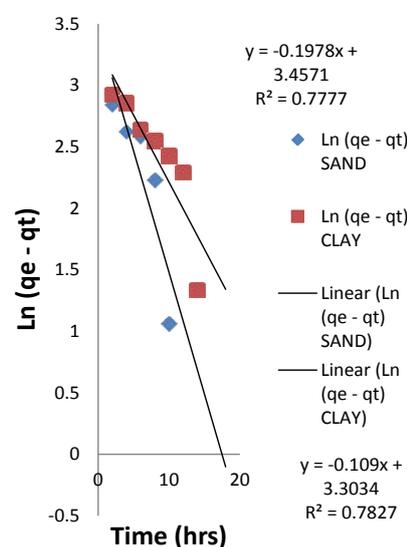


Figure 4: Pseudo-first order kinetic data plot for Naphthalene in mixture sorption with clay and sandy soil samples.

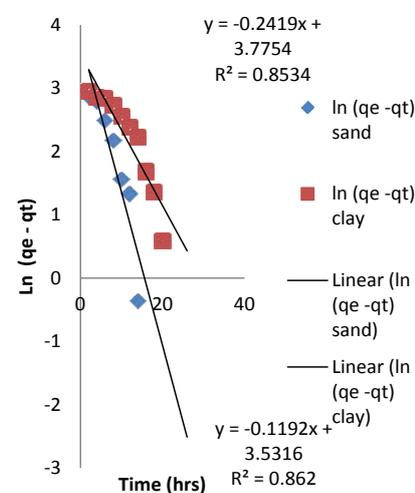


Figure 5: Pseudo-first order kinetic data plot for Pyrene in mixture sorption with clay and sandy soil samples.

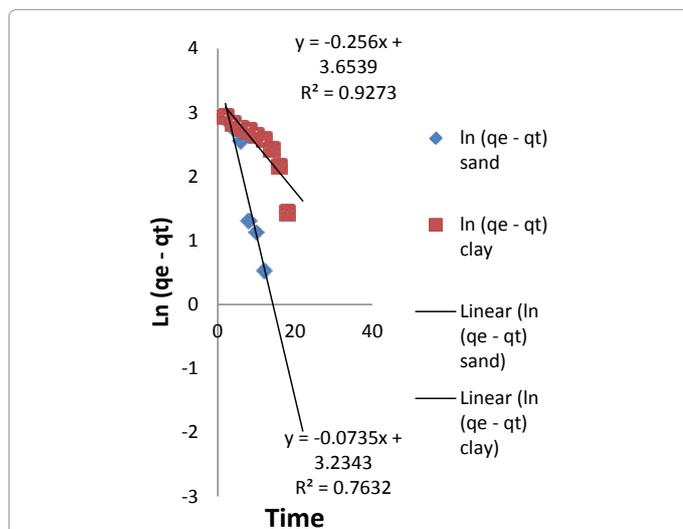


Figure 6: Pseudo-first order kinetic data plot for Benzene in mixture sorption with clay and sandy soil samples.

Kinetic Models	Parameters	Benzene	Naphthalene	Pyrene
Pseudo-first order	$k_1$	0.0735	0.1090	-0.1192
	$q_e$	1715	20.11	1715
	$R^2$	0.7632	0.7770	0.8620
Pseudo-second order	$k_2$	0.00096	0.00072	0.00088
	$q_e$	43.29	53.76	39.06
	$R^2$	0.5952	0.5174	0.6058

Table 2: Kinetic Parameters and Correlation Coefficient ( $R^2$ ) Values for the Adsorption of Benzene, Naphthalene and Pyrene in Mixture Sorption in Clay.

Kinetic Models	Parameters	Benzene	Naphthalene	Pyrene
Pseudo-first order	$k_1$	0.9273	0.1978	0.2419
	$q_e$	45071	28.65	45071
	$R^2$	0.9273	0.7827	0.8534
Pseudo-second order	$k_2$	0.00091	0.00080	0.00085
	$q_e$	56.82	32.15	44.05
	$R^2$	0.6732	0.4674	0.7115

Table 3: Pseudo-first order kinetic data plot for Benzene in mixture sorption with clay and sandy soil samples.

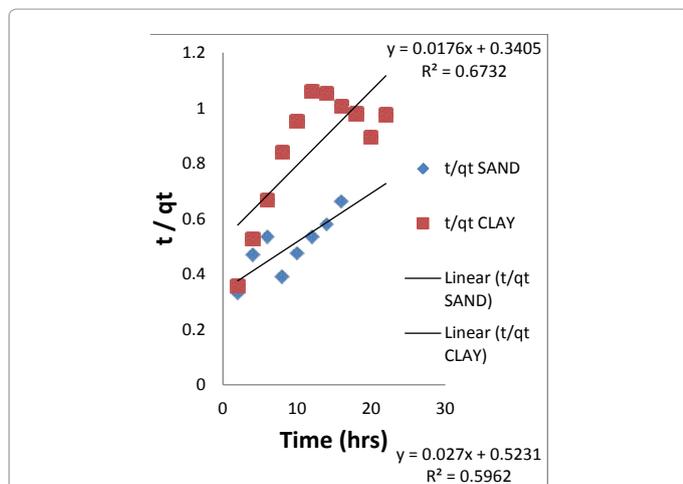


Figure 7: Pseudo-second order kinetics plot for adsorption of benzene in mixture sorption on clay and sandy soil.

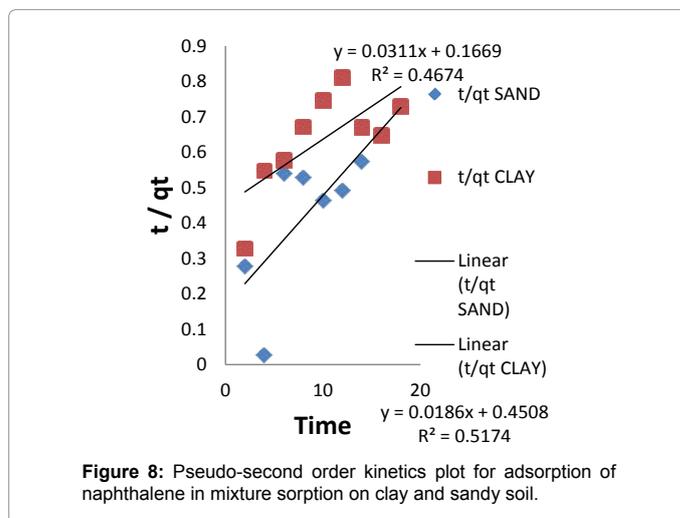


Figure 8: Pseudo-second order kinetics plot for adsorption of naphthalene in mixture sorption on clay and sandy soil.

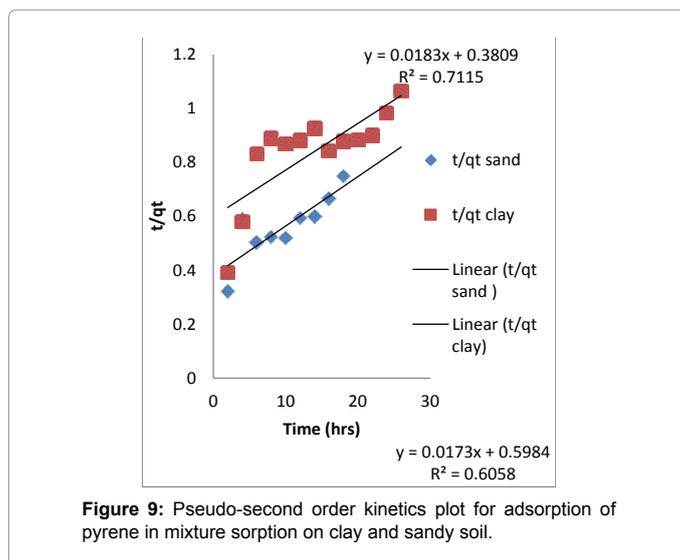


Figure 9: Pseudo-second order kinetics plot for adsorption of pyrene in mixture sorption on clay and sandy soil.

## Conclusion

The adsorption behavior of the mixture of two polycyclic aromatic hydrocarbons (PAHs); naphthalene and pyrene and one cyclic aromatic hydrocarbon, benzene on clay and sandy soil has been investigated. The study showed that adsorption of the mixture occurred in the different adsorbents. Equilibrium was attained faster in the sandy soil than clay. This is due to the higher permeability of sandy soil. The kinetic model of the pseudo-second equation has been successfully applied to predict the adsorption mechanism of the mixture concentration. The negative rate constant of adsorption determined in the pseudo-first order equation suggested that this model cannot be adapted to describe the kinetics of the mixture concentration. The present findings suggest that clay and sandy soil may be used as inexpensive and effective biosorbent without treatment or any modification for the removal of a mixture of naphthalene and pyrene (PAHs) and benzene from aqueous solution.

## Acknowledgements

The author is grateful to the Vice-Chancellor, University of Benin, Benin City, Edo State, Nigeria and Federal Government of Nigeria, Post-graduate Scholarship Board for financial support during the period of this project.

## References

1. Cabal B, Budinova T, Ania CO, Tsyntsarski B, Parra JB, et al. (2009) Adsorption of naphthalene from aqueous solution on activated carbons obtained from bean pods. *Journal of hazardous materials*. 161: 1150-1156.
2. World Health Organization (2006) Guidelines for the treatment of malaria. World Health Organization.
3. Loos R, Gawlik BM, Locoro G, Rimaviciute E, Contini S, et al. (2009) EU-wide survey of polar organic persistent pollutants in European river waters. *Environmental Pollution* 157: 561-568.
4. Bandosz TJ (2006) Activated carbon surfaces in environmental remediation. Academic Press.
5. Moreno-Castilla C (2004) Adsorption of organic molecules from aqueous solutions on carbon materials. *Carbon* 42: 83-94.
6. Aksu Z, Yener J (2001) A comparative adsorption/biosorption study of monochlorinated phenols onto various sorbents. *Waste Management* 21: 695-702.
7. Koh S, Dixon JB (2001) Preparation and application of organo-minerals as sorbents of phenol, benzene and toluene. *Applied Clay Science* 18: 111-122.
8. Osagie EI, Owabor CN (2015) Adsorption of Naphthalene on Clay and Sandy Soil from Aqueous Solution. *Advances in Chemical Engineering and Science* 5: 345.
9. Sands O, Shahalam A, Biouss A, Ayoub G, Acra A (1997) Competitive adsorption phenomena of petrochemicals-benzene, toluene, and xylene in hexane in fixed-beds. *Water, air and soil pollution* 95: 221-235.
10. Rogers RD, McFarlane JC, Cross AJ (1980) Adsorption and desorption of benzene in two soils and montmorillonite clay. *Environmental science & technology* 14: 457-460.
11. Hwang S, Ramirez N, Cutright T, Ju L (2003) The role of soil properties in pyrene sorption and desorption. *Water, air and soil pollution* 143: 65-80.
12. Hwang S, Cutright T (2002) The impact of contact time on pyrene sorptive behavior by a sandy-loam soil. *Environmental Pollution* 117: 371-378.
13. Teixeira SCG, Zioli RL, da Costa Marques, Mônica R, Pérez DV (2011) Study of pyrene adsorption on two Brazilian soils. *Water, Air & Soil Pollution* 219: 297-301.
14. Olu-Owolabi BI, Diagboya PN, Adebowale KO (2014) Evaluation of pyrene sorption-desorption on tropical soils. *Journal of environmental management* 137: 1-9.
15. Chang FC, Chang YC, Chen K, Tsai W, Shie J, et al. (2004) Adsorption of naphthalene on zeolite from aqueous solution. *Journal of colloid and interface science* 277: 29-34.
16. Ho Y (2006) Review of second-order models for adsorption systems. *Journal of hazardous materials* 136: 681-689.
17. Curry CW, Bennett RH, Hulbert MH, Curry KJ, Faas RW (2004) Comparative study of sand porosity and a technique for determining porosity of undisturbed marine sediment. *Marine Georesources and Geotechnology* 22: 231-252.
18. Osagie EI, Owabor C (2015) Adsorption of Pyrene from Aqueous Solution by Clay and Sandy Soil. *Advances in Chemical Engineering and Science* 5: 476-483.
19. Osagie E, Owabor CN (2015) Adsorption of Benzene in Batch System in Natural Clay and Sandy Soil. *Advances in Chemical Engineering and Science* 5: 352-361.
20. European Union (2000) EU Water Framework. Directive. Directive 2000/60/EC J L 327.