Removal of Polycyclic Aromatic Hydrocarbons (PAHs) from Spiked Aqueous Solutions and Synthetic Petroleum Refinery Wastewater Using Organo-bentonite (Part 1)

By

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are a group of priority pollutants that are persistent, ubiquitous, and toxic, which are released to the environment through natural and anthropogenic sources. The effectiveness of bentonite clay modified with hexadecyl pyridinium bromide has been explored for the removal of five PAHs, fluorene, phenanthrene, anthracene, fluoranthene and benzo[k]fluoranthene from spiked aqueous solutions and synthetic petroleum refinery wastewater. The studies were carried out using batch and fixed-bed column adsorption methods. The effects of various experimental parameters such as pH, mass of sorbent, contact time and temperature on adsorption were evaluated in a series of batch experiments. The selected working parameters were then used in the fixed-bed column experiment. The removal efficiency of the adsorbent in the batch method ranged from (84 to 97 %) while for the fixed-bed column adsorption it ranged from (93 to 99 %). Removal of the PAHs from the synthetic petroleum refinery wastewater was higher (91 to 99 %) than that from spiked aqueous solutions (84 to 97 %). The adsorption affinities were related to the hydrophobicity of the PAHs as determined by their log Kow values which were in the order; benzo[k]fluoranthene > fluoranthene > anthracene > phenanthrene > fluorene.

Keywords: Adsorption, PAHs, hexadecyl pyridinium modified bentonite, synthetic petroleum refinery wastewater

Introduction

Industrialization is one of the major sources of hazardous pollutants into water bodies, especially in developing countries where untreated or partially treated industrial wastewater is discharged into the environment and posing considerable environmental challenges. Petroleum refineries also generate large volumes of effluent in the course of refining petroleum crude oil which are characterized by the presence of large quantities of crude oil products such as, polycyclic aromatic hydrocarbons (PAHs), phenols (creosols and xylenols), metals and their derivatives, ammonia, suspended solids, and sulphides.[1,2] Polycyclic aromatic hydrocarbons (PAHs) are compounds made up of only carbon and hydrogen atoms. Previous studies proved that PAHs are part of numerous organic contaminants that are ubiquitous, persistent, semi-volatile, and resistant to degradation. Furthermore, these pollutants have long transport

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potential and can remain in the environment for long periods of time[3, 4, 5]. Due to these properties, PAHs have been placed on the list of priority pollutants by the United States Environmental Protection Agency (US-EPA) and the European Environment Agency[6]. PAHs are generated by natural as well as anthropogenic activities such as industrialization and urbanization through atmospheric fallouts, industrial discharges, transportation, biomass burning, tobacco smoking, waste incineration, wastewater from petrochemical plants, combustion of coal, petrol, gas and wood, forest fires, volcanic eruptions, and natural oil seeps[7]. PAHs are widely distributed throughout the environment due to their ability to travel over long distances and in any media and have been detected in different media including sediments[8,9], water,[10,11] wastewater[12,13] as well as aquatic organisms[14,15]. The environmentally significant PAHs are those that contain two (e.g., naphthalene $C_{10}H_8$; MW = 128.17 g/mol) to seven benzene rings (e.g., coronene $C_{24}H_{12}$; MW = 300.36 g/mol) bonded in linear, angular of cluster arrangements[3]. There are more than a hundred known PAHs, of which sixteen (16) are actively monitored and regulated strictly by the USEPA as priority PAHs, based on their potential carcinogenic, mutagenic and teratogenic effects on organisms, including human beings. These include acenaphthene, benzo[ghi]perylene, chrysene, acenaphthylene, benz[a] anthracene, benzo[b]fluoranthene, anthracene, benzo[k]fluoranthene, benzo[a]pyrene, fluoranthene, Indeno[1,2,3- cd]pyrene, naphthalene, phenanthrene, dibenz[a,h]anthracene, fluorene, and

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pyrene[3,6,8,16]. PAHs differ in their behavior, distribution in the environment, and their effects on biological systems, all these depend on their physical and chemical characteristics, such as the number of aromatic rings (structure), water solubility, vapor pressure and their molecular weight.[3,5]. Due to their carcinogenic, mutagenic, and teratogenic potentials, it is therefore prudent to remove them from the environment. Removal of PAHs from the environment can be performed through biological, chemical, and physical processes, which include coagulation[17,18], flocculation[18], chemical oxidation[19], membrane filtration[20,21], ultrafiltration[22], reverse osmosis[23], phytoremediation[24], chemical precipitation[25], photocatalytic degradation[26], and adsorption.[27,28]However these methods are energy intensive, expensive and generate byproducts that are often toxic to both humans and the environment. In the case of removing PAHs from aqueous systems, it has been reported that adsorption is one of the simplest, most efficient, cost effective, quickest, and broadly applicable method among other types of remediation technologies[3,5]. Among several materials used as adsorbents, activated carbons (ACs) have been employed for decades in wastewater treatment operations for the removal of different types of emerging compounds, PAHs included, but their use is sometimes restricted

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due to high cost[27,28,29]. This has resulted in attempts by various workers to prepare low cost alternatives for pollution control. The use of adsorbents such as agricultural wastes[30,31], mesoporous materials[16,32], graphene[33,34] and clay minerals[35,36,37,38] (bentonite, sepiolite, zeolite, clinoptilolites, montmorillonite) and their modified forms have been considered as alternatives. The aim of this study is to investigate the adsorption features of modified Nigerian bentonite clay samples obtained from Potiskum, Yobe State for the removal of fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA) and benzo[k]fluoranthene (BkF) from aqueous solution and synthetic petroleum refinery wastewater samples using batch and fixed-bed column adsorption processes. The modification of the clay using hexadecylpyridinium bromide surfactant and subsequent characterization has been described elsewhere.[39] The current effort is to determine the effect of various experimental conditions such as contact time, adsorbent dose, pH, initial PAHs concentration and temperature on the adsorption properties of the compounds.

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 was obtained from Merck (Darmstadt, Germany). All other chemical reagents were of

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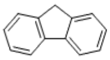
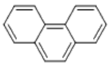
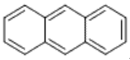
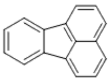
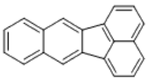
analytical grade and were used without further purification. Milli-Q Ultrapure water was used throughout the study.

Methods

Table 1: Chemical Structures and selected physical properties of the 16 USEPA Priority PAHs[40, 41]

PAH	Chemical name & structure	MF	MW (g/mol)	Bp (ºC)	Mp (ºC)	Vp (mmHg) at 25 ºC	S_{H2O} (mg/L) at 25 ºC	Log K_{ow}
(FLO)	 Fluorene	$C_{13}H_{10}$	166.22	298	111-114	$7.1x10^{-4}$	1.98	4.18
(PHE)	 Phenanthrene	$C_{14}H_{10}$	178.23	340	98-100	$9.6x10^{-4}$	1.15	4.57
(ANT)	 Anthracene	$C_{14}H_{10}$	178.23	340	215	$1.7x10^{-5}$	0.075	4.54
(FLA)	 Fluoranthene	$C_{16}H_{10}$	202.25	384	109	$5.0x10^{-6}$	0.206	5.22
(BkF)	 Benzo[k]fluoranthene	$C_{20}H_{12}$	252.31	480	215-217	$5.1x10^{-7}$	0.0008	6.00

Standard and working solutions

The PAHs stock standard solution (1000 mgL^{-1}) containing the five PAHs was prepared according to EPA Method 610[42], by dissolving 0.01 g of each PAH in a 25 cm^3 beaker with 2 cm^3 acetonitrile and transferred to a 10 cm^3 volumetric flask and its volume made to the mark. The resulting standard solutions were transferred into Teflon-sealed screw cap 15 cm^3 amber bottles and stored at 4 °C protected from light before further use. The working standard solutions containing all the analytes (5 PAHs) were freshly prepared by dilution of the stock solutions with the ultrapure water immediately prior to use.

Preparation of Synthetic Petroleum Refinery Wastewater (SPRW)

Synthetic petroleum wastewater with physicochemical characteristics of petroleum refinery effluents from the Malaysian Oil Refining Company Sdn Bhd was prepared similar to the method described by[43, 44] with some modifications, whereby 1 cm^3 each of petrol, diesel and engine oil was pipetted and dissolved in a mixture of methanol: dichloromethane (DCM) (50:50 v/v). The mixture was thoroughly shaken to make a homogeneous solution using VTX-3000L model Mixer. One hundred microliter (100 µL) of the mixture was further diluted 10-fold with

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methanol and transferred into 100 cm^3 volumetric flask containing the lake water and the volume was made to the mark after mixing thoroughly again with the mixer.

Batch Adsorption Experiments

For the batch experiments, aqueous solution of PAHs (fluorene, phenanthrene, anthracene, fluoranthene and benzo[k]fluoranthene) was prepared by spiking 10 µL of 1000 mg/L stock standard solution containing all the 5 PAHs into 10 mL of ultrapure water. The 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 for 24 h and at 30 ± 1 ºC. Effects of experimental parameters: pH (2-11), adsorbent dosage (10-100 mg), contact time (30–1800 min), concentration (0.02, 1.5, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 mg/L) and temperature (303, 313 and 323 K) were studied. The desired pH was adjusted with 0.01 M HCl and 0.01 M NaOH using pH meter (Model Ella Instrument). In studying each parameter, the other parameters were kept fixed. For each batch, a blank containing only ultrapure water and the adsorbent (HDP-PK) was performed[45].

After agitation in all the experiments, the adsorbent was separated from the solution by paper filtration, then the filtrate was extracted with DCM using Liquid-Liquid Extraction (LLE) procedure[46]. The PAHs residual concentration in the solution after sorption was analyzed by gas chromatography (Agilent Technologies 7683 series), equipped with a splitless injector and flame ionization detector (GC–FID)[31] A HP-5 silica fused capillary column (30 m × 0.32 mm inner diameter × 0.25 µm film thickness) was used with nitrogen (purity 99.999 %) as the carrier gas. The removal efficiency (% R) and the adsorption capacity (qe) of the adsorbent (HDP-PK) were calculated using Equations (1) and (2), respectively.

$$\% R = \frac{Co-Ce}{Co} \; X\, 100 \ldots\ldots\ldots.. (1)$$

where % R, Co, and Ce, are the removal efficiency of the PAHs, the initial and equilibrium concentrations (mg L^{-1}) of the PAHs in the solution, respectively. V is the volume (L) of the solution in the flask and m (g) is the mass of adsorbent.

Fixed-Bed Column Experiment

A fixed-bed column was prepared by packing 10.0 mg of HDP-PK adsorbent into an empty cartridge (6 mL polypropylene syringe). Upper and lower frits were placed at each end of the cartridge to hold the packing material in place. The samples were pumped vertically upward continuously through the columns using a peristaltic pump (Masterflex, Tubing L/S 13, 14, 16 and 25) Model 77202-50 (USA) at a flow rate of 1 mL/minute. Parameters selected for the batch method; pH 7, temperature 30 °C and concentration of 1.0 mg/L were applied. The flow of the samples from the column was halted when a volume of 10 mL of the effluent was collected. The effluent solution collected was then extracted with DCM using LLE technique and analyzed by GC-FID.

Results and Discussion

Batch Adsorption

The efficiency of HDP-PK adsorbent for the removal of the five PAHs is shown in (Fig. 1) whereby about 85, 88, 92, 88 and 96 % of fluorene, phenanthrene, anthracene, fluoranthene

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and benzo[k] fluoranthene respectively were removed. The removal was in the order; benzo[k] fluoranthene > fluoranthene > anthracene > phenanthrene > fluorene which could be due to the hydrophobicity and molecular structure of the compounds which can be related to the n-octanol/water partition coefficient (log K_{ow} values: Flo 4.18, Phe 4.57, Ant 4.54, Fla 5.22 and BkF 6.00). It is reported that the solubility of PAHs in water decreases almost linearly with increasing molecular weight and that heavy molecular weight PAHs are readily adsorbed on particles[18,47], hence the above trend was observed. This is also in accordance with what had been reported, by other researchers.[35,43,45]

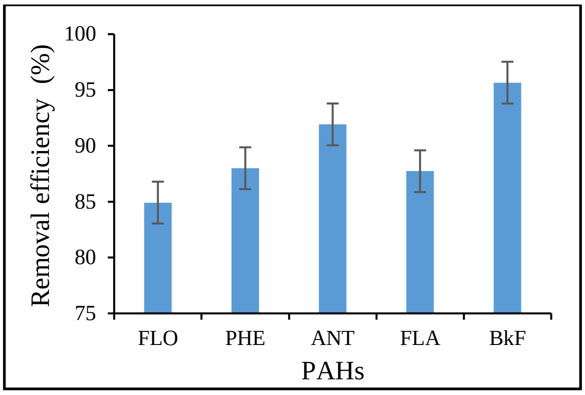

Fig. 1: Efficiency of HDP-PK Adsorbent for Removal of PAHs

For the investigation of pH effects on the adsorbent efficiency for the five PAHs removal, the results are presented in (Fig. 2). It can be observed that each PAH behaves differently at different pH values, for instance the maximum percentage removal for fluorene, anthracene, and benzo[k] fluoranthene occurred at pH 9, fluoranthene at pH 4 and 9 while phenanthrene at pH11 with values > 93 %. All the five PAHs were efficiently removed in such a way that at each of the pH values used (2-11), there was over 90 % removal. This shows that variation of pH has no significant influence on the adsorption of PAHs onto different media. Similar observations have been made by researchers.[28,32] Consequently, pH 7 was selected for the continuation of the adsorption studies carried out since it is within the pH range of some wastewater, Petroleum refinery wastewater (6.5-9.5) included.[48]

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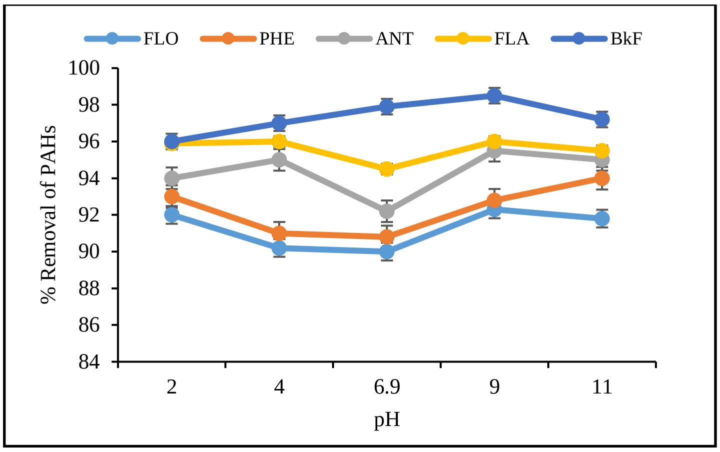

Fig. 2: Percent Removal of PAHs on HDP-PK at Different pH (2, 4, 6.9, 9 and 11)

Upon varying the masses of HDP-PK from 10-100 mg the percent removal of the five PAHs increased from 95.60 to 99.90 % (Fig. 3). This could be attributed to the large surface area (binding sites) available on the adsorbent[16]. More than 99 % of the five PAHs were adsorbed on 100 mg of the adsorbent though, even at low dosage (10 mg), removal of the PAHs was higher than 93 %. Similar results have been reported whereby increase in sorption increased with mass of sorbent.[16,35,45,46,49]

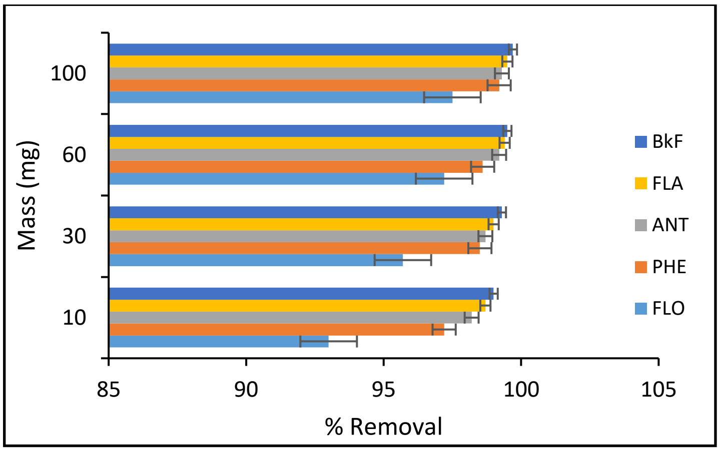

Fig. 3: Effect of Sorbent Mass on PAHs Adsorption

The results of the effect of contact time are shown in (Fig.4) whereby sorption increased with increase in contact time until an optimum point was reached. More than 50 % of all the five PAHs (fluorene, phenanthrene, anthracene, fluoranthene and benzo[k]fluoranthene) were adsorbed from the solution by HDP-PK within the first 2 hours as 51.8, 58.8, 60.4, 67.2 and 69.4 % respectively. Adsorption was observed to reach equilibrium for each PAH at different time from the 6th to the 12th hour (benzo[k] fluoranthene – fluorene). No significant change was observed with increase in time up to 28 h. Fluorene was less removed at the maximum sorption time (12 h) than phenanthrene, anthracene, fluoranthene and benzo[k] fluoranthene.

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[49] 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,

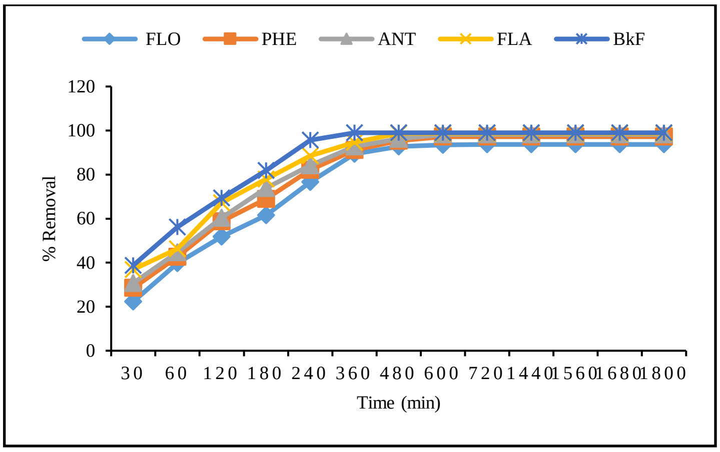

Fig. 4: Effect of Contact Time on PAH Adsorption on HDP-PK

Increase in adsorption of all the five PAHs was observed as the temperature of the system increased from 303 to 323 K (Fig. 5), this indicates that adsorption of the PAHs on HDP-PK was endothermic. Furthermore, the PAHs adsorption onto HDP-PK ranked in the following order: BkF > FLA > ANT > PHE > FLO. Similar endothermic nature of adsorption has been observed by[43,45,50]

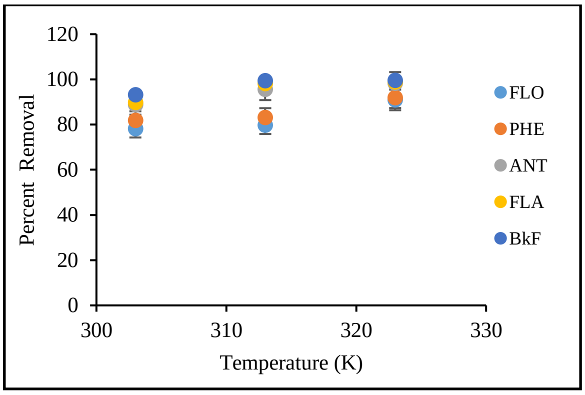

Fig. 5: Effect of Temperature on PAHs Adsorption

Fixed-Bed Column (FBC) Adsorption

The results for the fixed-bed column adsorption process are presented in (Fig. 10) which shows high percentage removal of all the five PAHs > 93 % from the two water samples (PAHs spiked aqueous solution (PSAS) and synthetic petroleum refinery wastewater (SPRW). The removal of the PAHs was higher from the SPRW, which could be due to higher concentration of the PAHs in the sample.

[50] Gupta H. (2015). Removal of Phenanthrene from Water Using Activated Carbon Developed from Orange Rind. *International Journal of Scientific Research in Environmental Sciences*, 3(7), pp. 0248-0255.

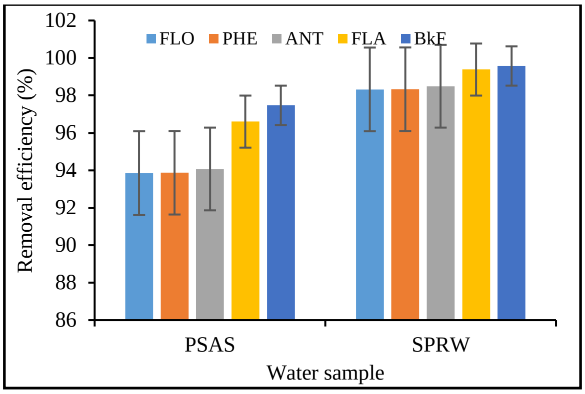

Fig 10: Fixed-Bed Column Adsorption Efficiency for PAHs Removal from Spiked Aqueous Solution and Synthetic Petroleum Refinery Wastewater.

Upon comparing the two adsorption processes, batch and fixed-bed column (Fig. 11), the fixed-bed column adsorption provided highest PAHs removal in both water samples (93 - 99 %) over the batch process (84 – 97 %), which could be due to the fact that in fixed-bed system the adsorbate is flowing continuously through the adsorbent bed at constant rate without disturbances from mechanical agitation.[51]

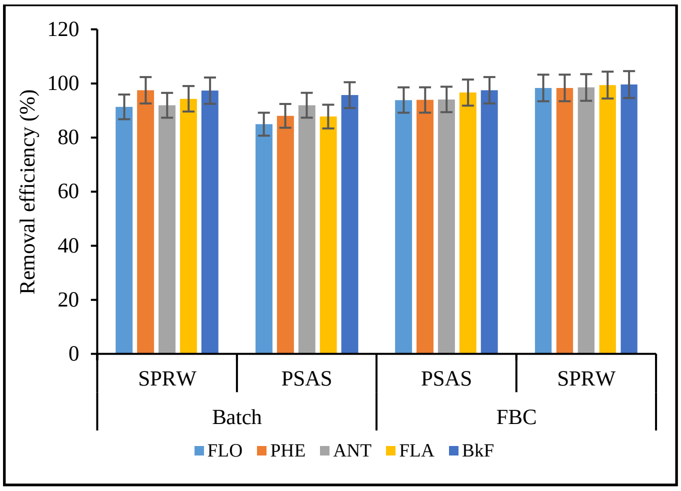

Fig. 11: Removal Efficiency (%) of HDP-PK for PAHs Adsorption using Batch and Column Adsorptions from PSAS and SPRW samples

Conclusion

The adsorption potential of HDP-PK was investigated for the adsorption of five PAHs from aqueous solution and synthetic petroleum refinery wastewater using batch and fixed-bed column adsorption experiments. Both the batch and column adsorption experiments showed that HDP-PK could effectively remove PAHs from water and synthetic petroleum refinery wastewater. The removal efficiency for the PAHs was in the order of BkF > FLA > ANT > PHE > FLO. Fixed-bed column removed substantial amounts of the PAHs (> 93 %) more than the batch process (> 83 %) in the two water samples. The study highlighted that HDP-PK can

[51]Patel, H. (2019). Fixed-bed column adsorption study: a comprehensive review *Applied Water Science*, 9:45. https://doi.org/10.1007/s13201-019-0927-7

be used as a potential adsorbent for the removal of PAHs from aqueous and synthetic wastewater systems using both the batch and column adsorption processes.

Recommendation

It is recommended that the parameters of breakthrough and column dynamic models be tested for the fixed-bed column adsorption of the five PAHs on HDP-PK adsorbents.

Acknowledgments

One of the authors, S. L. Abdullahi acknowledges with appreciation, the financial support of the Tertiary Educational Trust Fund of Nigeria (TETFUND).