

## Research paper

## Concentration-dependent and simultaneous sorption and desorption of pyrene and fluorene on major soil minerals in sub-Saharan Africa

Paul N. Diagboya<sup>a,\*</sup>, Bamidele I. Olu-Owolabi<sup>b</sup>, Ezekiel D. Dikio<sup>a</sup>, Kayode O. Adebowale<sup>b</sup><sup>a</sup> Department of Chemistry, Vaal University of Technology, Vanderbijlpark, South Africa<sup>b</sup> Department of Chemistry, University of Ibadan, Ibadan, Nigeria

## ARTICLE INFO

## Keywords:

Polycyclic aromatic hydrocarbons (PAHs)  
Competitive sorption  
Tropical soils  
Soil minerals  
Agro-ecological zone  
Nigeria

## ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) sorption-desorption in soils, as influenced by soils' physicochemical conditions, control the extent of PAHs translocation, persistence and bioavailability. Though mono-PAHs sorption on soils reports abound, co-occurrence of PAHs in the environment is common and affects individual PAHs sorption characteristics competitively or cooperatively. Besides, most reports were not on sub-Saharan soils. Hence, the batch experiments to study simultaneous sorption-desorption of pyrene and fluorene on five soils, with varying minerals contents, from different sub-Saharan agro-ecological zones. Sorption was concentration dependent and increased as concentration. There was higher preference for pyrene, though lower sorption than in mono-PAHs solutions. Irrespective of competition, soil organic matter ( $\geq 4.5\%$ ) caused high pyrene sorption similar to mono-PAHs sorption. At 25 °C, pyrene had lower hysteresis in simultaneous desorption compared to mono-PAHs, while higher hysteresis was observed in fluorene for all soils. Simultaneous sorption was higher at 40 than 25 °C and higher hysteresis exhibited as temperature increased in contrast to desorption at 25 °C. Isotherm model studies showed that simultaneous sorption of both PAHs were on heterogeneous surfaces and are composites of several linear and non-linear isotherms. Ultimately, soil constituents, PAHs concentration, competition for sorption sites, size and structural relationship play vital roles in simultaneous sorption on these soils. Risk of environmental contamination is higher for fluorene than pyrene during co-occurrence and likely so in the warmer and low organic matter soils of northern sub-Sahara.

## 1. Introduction

Understanding the fate of polycyclic aromatic hydrocarbons (PAHs) in soil is of paramount importance because of soils' roles in global development issues such as food security and global burden of disease. Several PAHs are known to be toxic, some being mutagenic and/or carcinogenic to biota; and thus they have been classified as priority pollutants (ATSDR, 1995; USEPA, 2007; Joseph-Ezra et al., 2014; Javadi et al., 2017). Natural co-occurrence of organic pollutants especially PAHs in the soil environment is ubiquitous but has been enormously supplemented by recent anthropogenic activities resulting in unprecedented soil pollution levels (Lee and Kim, 2002; USEPA, 2007; Pan and Xing, 2010; Olu-Owolabi et al., 2017). In soil, various physical and chemical processes determine the fate of pollutants (Hwang and Cutright, 2002; Teixeira et al., 2011; Diagboya et al., 2015; Mokwenye et al., 2016). Among these processes, sorption is relatively the most studied because data obtained can give valuable information on suitable remediation strategies for the polluted soils (Sparks, 2003; Olu-Owolabi et al., 2015).

Although PAHs are among the most intensively studied pollutants around the world (White and Pignatello, 1999; Zhao et al., 2001; Javier Rivas et al., 2008; Changchaivong and Khaodhiar, 2009; An et al., 2010; Guo et al., 2010; Haftka et al., 2010; Nasser and Mingelgrin, 2012; Biswas et al., 2015; Adesina et al., 2017), there is dearth of information concerning their fate on tropical sub-Saharan soils. This is vital because PAHs fate in soils depends on their interactions with the soil components as well as the prevailing conditions in the soil environment. This implies that PAHs may exhibit different characteristics in different soils formed from different parent materials under different environmental conditions (Hwang and Cutright, 2002; Huang et al., 2003; Olu-Owolabi et al., 2014; Diagboya et al., 2016). Since soils from the various agro-ecological zones (AEZs) of sub-Sahara Africa vary extensively in physical and chemical properties due to different soil forming parent materials and the prevailing environmental conditions (temperature, moisture, and biota), PAHs sorption studies on these soils are worthwhile.

Sorption and desorption of pyrene and fluorene on soils from the various AEZs of sub-Sahara Africa have been reported earlier (Olu-

\* Corresponding author.

E-mail address: [pauldn2@yahoo.com](mailto:pauldn2@yahoo.com) (P.N. Diagboya).

Owolabi et al., 2014, 2015). These studies were carried with mono-PAHs solutions and cannot be used to predict the behaviour of these PAHs when they co-occur as contaminants in soil. Understanding the behaviour of co-occurring PAHs in soil is necessary because PAHs are released into the environment as a mix rather than individual compounds, and the sorption characteristics of the individual PAHs can be modified by the presence of other PAHs (Hwang and Cutright, 2002). Hence, the purpose of this study was to determine the simultaneous sorption characteristics of pyrene and fluorene when both co-occur as contaminants in soils using five soils from different sub-Saharan AEZs. The sorption characteristics were evaluated by determining the effects of PAHs concentration and environmental temperature. The data were analyzed and modeled using various sorption isotherm models as well as compared with sorption characteristics of both PAHs obtained from mono-PAHs sorption experiments.

## 2. Materials and methods

### 2.1. Soil sampling, characterization and PAHs solutions preparations

The soil samples used in this study were collected from major sub-

Saharan AEZs (Fig. 1a). Five representative surface soils (0–30 cm) samples were obtained from locations relatively free from anthropogenic activities. These were air-dried, crushed gently and sieved through a 230-mesh size sieve and the fine fractions retained for the sorption study. The soils' pH values in milipore ultra-pure water and 1.0 M KCl (ratio 1:1), particle size, organic matter, metals (oxides, exchangeable and trace), and soil mineralogy were determined following the methods earlier described in Olu-Owolabi et al. (2014, 2015, 2016) (Supporting Information, SM 1).

Stock solutions (1000 µg/L each) of pyrene and fluorene were prepared separately in 20% v/v acetonitrile/milipore ultra-pure water and 10% v/v methanol/milipore ultra-pure water, respectively. The working solutions of 100 µg/L each were prepared from the stocks separately in 5% v/v acetonitrile/milipore ultra-pure water and 5% v/v methanol/milipore ultra-pure water, respectively (solubility of both PAHs in water at 25 °C are 135 and 1992 µg/L, respectively). The background electrolyte and biocide used to eliminate microbial degradation for these preparations were 0.005 M CaCl<sub>2</sub> and 0.01 M NaN<sub>3</sub>, respectively.

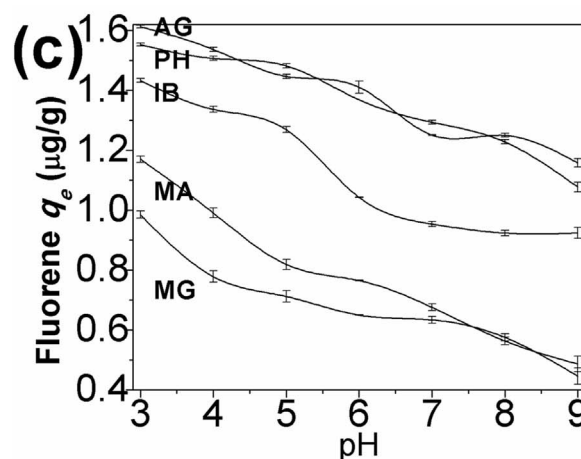
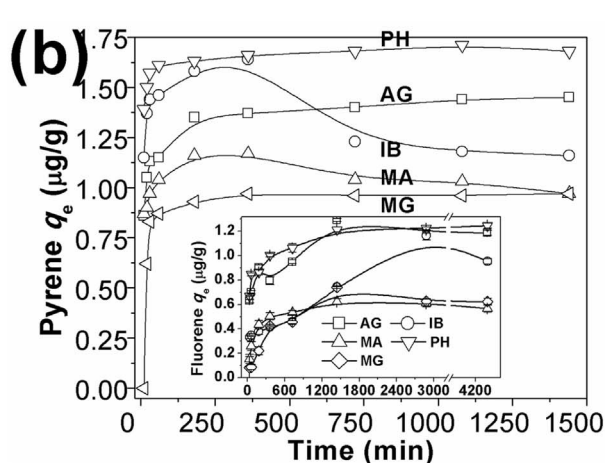
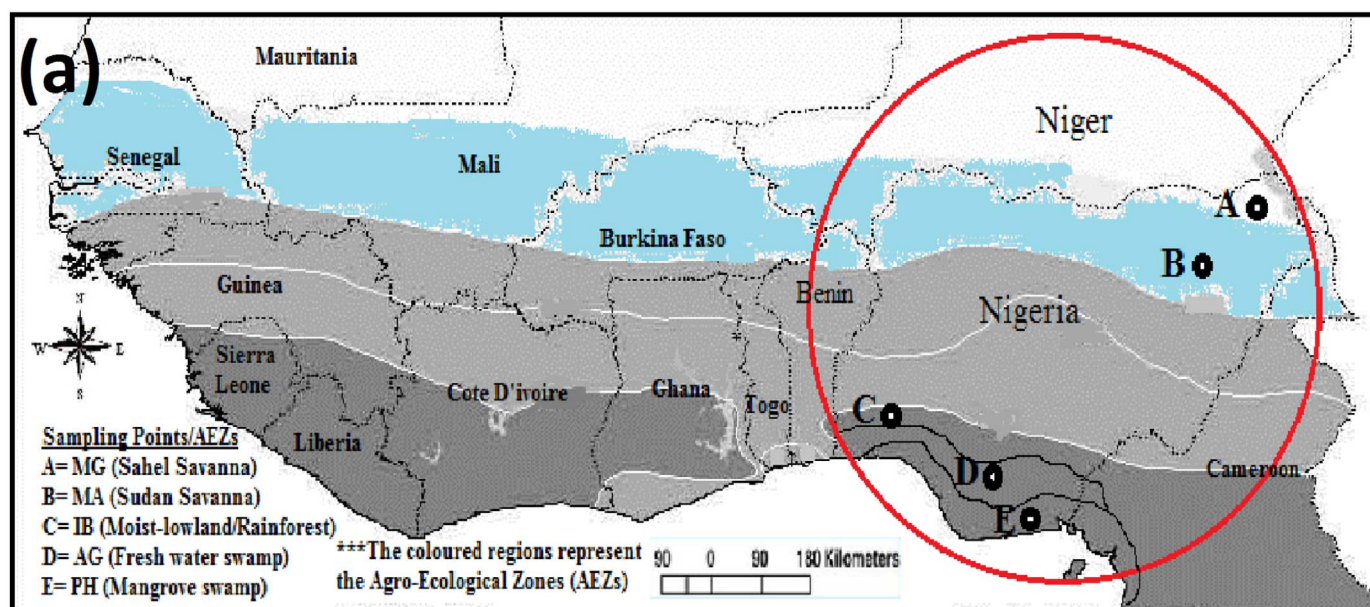


Fig. 1. (a) Sampling locations within the major AEZs (shaded areas) of sub-Saharan West Africa; (b) effect of time on pyrene sorption (Insert: fluorene); (c) effect of pH on fluorene sorption.

**Table 1a**  
Physicochemical properties of the soil samples (Olu-Owolabi et al., 2015).

Soil	*AEZ	Sampling coordinate	pH water	pH 1 N KCl	EA	*OM (%)	Particle size analysis (%)			Oxides (wt%)	
							*Sand	*Silt	*Clay	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
Agbor (AG)	Fresh water swamp	6° 11' 36" E; 6° 15' 06" N	6.29	5.39	0.10	5.26	83.80	15.44	0.76	1.54	2.78
Port Harcourt (PH)	Mangrove swamp	6° 59' 55" E; 4° 47' 21" N	7.66	7.24	0.06	5.29	68.04	30.50	1.45	1.09	2.96
Ibadan (IB)	Moist-lowland/Rainforest	3° 54' 00" E; 7° 26' 30" N	6.57	5.88	0.08	4.68	69.94	16.44	13.63	3.71	3.18
Maiduguri (MA)	Sudan SV*	13° 09' 42" E; 11° 50' 36" N	6.67	5.21	0.02	1.67	70.44	28.89	0.67	0.99	2.23
Monguno (MG)	Sahel SV*	13° 36' 51" E; 12° 40' 14" N	8.40	7.59	0.12	0.18	82.24	17.25	0.50	0.93	1.50

\*AEZ – Agroecological zone; SV\* – savanna; \*OM – Organic matter; EA – Exchange acidity; % sand (> 20 µm); % silt (2–20 µm); % clay (< 2 µm).

## 2.2. Sorption studies

### 2.2.1. Non-simultaneous sorption of pyrene and fluorene

Sorption experiments were carried by adding 10 mL of 100 µg/L (except where otherwise stated) of pyrene or fluorene solution into brown glass vials containing 0.50 g of the soil sample and these were tightly sealed with Teflon lined screw caps. Aluminum foil was used to wrap the vials to minimize possible losses by photochemical decomposition. The vials were equilibrated in the dark by shaking horizontally at 100 rpm in a temperature (25 °C) controlled shaker. For the effect of time, the vials were incubated from 10 to 1440 min (10–4320 min for fluorene sorption). Equilibrium studies and effect of temperature were investigated in the concentration range of 20–100 µg/L at 25 and 40 °C. All experiments were done at the ambient soil pH except the effect of pH which was carried out from pH 3 to 9 using 100 µg/L of each PAHs separately. After the equilibrium experiments, PAHs desorption studies were carried out immediately by thoroughly decanting the supernatant solution and replacing with a fresh 5% v/v acetonitrile/milipore ultra-pure water (5% v/v methanol/milipore ultra-pure water for fluorene) background solution containing no PAHs. These were incubated for 1440 min (4320 min for fluorene), centrifuged and PAHs concentration determined. Control experiments without soil samples were carried out to account for possible losses due to volatilization and sorption onto the vials walls (and these were found to be negligible). All experiments were replicated and the averages of the data have been used for computation.

### 2.2.2. Simultaneous sorption and desorption of pyrene and fluorene

Simultaneous sorption of pyrene and fluorene were carried out using 0.50 g soil aliquot and equi-concentrations of pyrene and fluorene solutions ranging from 20 to 100 µg/L. The sorption experiments were incubated for 2880 min (this time was enough for both PAHs to attain equilibrium) and at two temperatures: 25 and 40 °C. After each sorption, desorption experiments (as described above) were also carried out at both temperatures. The experiments were carried out in replicates.

### 2.2.3. Determination of pyrene and fluorene in solution

After each incubation period, the vials were centrifuged at 4000 rpm for 20 min, and the concentrations of pyrene in various solutions determined by Perkin Elmer fluorescence spectroscopy (model LS 55) using the synchronized scan at a wavelength difference ( $\Delta\lambda$ ) of

36 nm and scanning from 300 to 400 nm with scanning speed of 500 nm/min. The synchronous peak at 335 nm was used to monitor pyrene sorption. Fluorene was determined by using the synchronized scan at a wavelength difference ( $\Delta\lambda$ ) of 45 nm and scanning from 200 to 350 nm with scanning speed of 1000 nm/min. The synchronous peak at 264 nm was used to monitor fluorene sorption.

## 2.3. Data treatment

The concentrations of pyrene or fluorene removed from solution were calculated from the initial ( $C_0$ ) and final ( $C_e$ ) concentrations in solutions using  $q_e = (C_0 - C_e)V/m$ , where  $q_e$ ,  $V$  and  $m$  are the amount of PAHs sorbed (µg/g), volume of the solution (mL) and mass (g) of sample, respectively (Okoli et al., 2017).

The sorption data were explained using three adsorption isotherm models (Langmuir, 1916, Freundlich, 1906, and the Weber et al. (1992) distributed reactivity model); as well as the thermodynamic parameters – standard free energy ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) (SM 2).

## 3. Results and discussion

### 3.1. Soil properties

The physicochemical properties of the soils are shown in Tables 1a and 1b, SM (Fig. 1 and Table 1). Olu-Owolabi et al. (2014, 2015, 2016) have described these soils in detail. However, brief descriptions are given here. The soils were mainly neutral (6.0–7.5) except for MG which was alkaline (8.4). Organic matter (OM) was relatively high (Fagbami and Shogunle, 1995) except for MA and MG soils which were described as medium and very low, respectively. AG and PH had the highest SOM contents. The mineralogical compositions (Table 1b, SM Fig. 1) showed that the soils' main minerals are aragonite, calcite, dolomite, gibbsite, hematite, kaolinite, quartz, and siderite, with quartz being the most common mineral followed by the Al oxide mineral – gibbsite. Small quantities of 2:1 expansive clay minerals, montmorillonite and illite, were observed in MA and MG, respectively. The soils were classified texturally as sandy loam (PH, IB, and MA) and loamy sand (AG and MG) (Soil Survey Staff, 2006). Olu-Owolabi et al. (2014) have attributed these variations in the properties to the different ambient environmental conditions (vegetation, temperature, topography,

**Table 1b**  
The mineralogical compositions of the soils (Olu-Owolabi et al., 2015).

Soil	Mineral (%)										
	Aragonite	Calcite	Dolomite	Gibbsite	Goethite	Hematite	Illite	Kaolinite	Montmorillonite	Quartz	Siderite
AG	2.49	5.37	8.70	23.49	–	1.58	–	0.68	–	57.69	–
PH	6.53	7.40	10.69	4.61	–	0.88	–	1.48	–	68.41	–
IB	15.14	0.52	4.17	51.04	5.15	–	–	2.18	–	21.33	0.47
MA	9.89	2.37	11.72	3.48	–	2.19	–	4.62	0.14	63.21	2.38
MG	14.38	4.48	8.19	12.67	–	2.15	36.89	1.28	–	19.96	–

rainfall, climate, soil forming minerals, biotic influence, etc.) obtainable in the sampling AEZs.

### 3.2. Non-simultaneous sorption studies of pyrene and fluorene

In order to have a better comprehension of the behaviour of both pyrene and fluorene in a simultaneous sorption scenario, it is vital to understand the individual sorption characteristics of both PAHs on these soils used for the study; hence, the preliminary non-simultaneous sorption of the individual PAHs. Results (Fig. 1b and insert) showed that equilibrium fluorene sorption on these soils were attained within 1440 min except for PH soil which attained equilibrium in 2880 min. This variation in equilibria was attributed to the sorption characteristics of individual soils' constituents such as mineralogy and organic matter. For instance, soils containing high amounts of non-expansive minerals, such as kaolinite, quartz and gibbsite, are likely to attain equilibrium faster than those with more expansive soils minerals. This is because adsorption occurs faster on surface sites than on pores or partitions within expansive soils. This finding is in line with other studies which show that fluorene sorption equilibrium on soils does not occur at any specific time but is dependent on soil constituent (Kohl and Rice, 1999; Chilom et al., 2005). Generally, pyrene sorption was relatively faster in attaining equilibrium at 180 min except for MA and IB soils which attained equilibrium at 720 min. Studies by Cottin and Merlin (2007) and Teixeira et al. (2011) have reported similar trends on pyrene sorption on soils. Since the rate of sorption in soils may be related to its bio-availability, it implies that fluorene will be more available during the initial 48 h of release to these soils than pyrene.

The aqueous pH is an important parameter because of its influence on soil constituents and properties which are responsible for the sorption of these hydrophobic PAHs (An et al., 2010). The changes in pyrene and fluorene sorption as the soil solution pH increased are as shown in Fig. 1c (and SM Fig. 2a). It was noticed that higher pyrene and fluorene sorption occurred at lower pH and sorption decreased continuously with increase in pH from 3 to 9. This trend was similar for these soils irrespective of the soil properties, but the amounts of PAHs sorbed at any particular pH varied in proportion to the quantity of surface hydrophobic sites on the soils' minerals and organic matter. Similar findings were earlier reported (Zeledon-Toruno et al., 2007; An et al., 2010) for these PAHs. The higher PAHs sorption at low pH values was ascribed to increased protonation and reduced polarity of charged soil surface sites on the organic matter and clay minerals at lower pH. This resulted in the surface becoming more hydrophobic with enhanced affinity for these uncharged and hydrophobic PAHs possibly via  $\pi$ - $\pi$  interactions. However, as pH increased there was a corresponding decrease in hydrophobicity and increase in ionization hence, the reduced sorption.

Equilibrium sorption study, which gave details of the sorbate–sorbative relationship at equilibrium, showed that both PAHs sorption were concentration dependent and increased with increase in concentration (Fig. 2a; SM Fig. 2b). The result was attributed to presence of expansive minerals in these soils such as Montmorillonite and Illite, as well as the carbonate minerals (aragonite, calcite, siderite, and dolomite). This trend may be due to the fact that when the soils' external surface film and internal pores transports of each PAHs are equal, the trans-boundary movements between the external surface film and internal pores will not be significantly permissible; however, increasing concentration will re-initiate the trans-boundary movement of the PAHs and thus sorption will then be concentration dependent (Site, 2001). Another highly plausible reason is that the increased of the PAHs in solution led to increased occurrence of multi-layer adsorption due to  $\pi$ - $\pi$  interactions (Olu-Owolabi et al., 2015).

Increasing the solution temperature from 25 to 40 °C led to significant reduction in the sorption of both PAHs (Fig. 2b; SM Fig. 2c); implying that higher temperature did not favour sorption. Generally, sorption of hydrophobic organics decrease with increasing temperature

(Site, 2001). This is because their surface adsorption process usually occurs via weak hydrophobic forces (requiring low sorption heat) of interaction between the soil adsorption sites and their molecules. These weak hydrophobic forces are easily broken. Hence, as temperature increased, it resulted in higher kinetic energy and consequently increased solubility and mobility of these PAHs away from the sorption sites (Haftka et al., 2010; Shu et al., 2010).

Desorption studies demonstrated that the extent of desorption was proportional to the quantity of PAHs sorbed on the soil (Fig. 2c–f; SM Figs. 3–4); the amount of PAHs desorbed was inversely proportional to the concentration and temperature. Often, 'hysteresis' (delayed reversibility) was observed (Site, 2001) especially for soils with higher organic matter content. Hysteresis is important because lower desorption signifies a lowered chemical activity of the sorbed chemical and consequently decreased toxicity of the chemical (Huang et al., 2003). A reason for this hysteresis may be the entrapment of PAHs molecules within the pores of the various soil mineral compartments and organic matrices (Site, 2001; Huang et al., 2003).

### 3.3. Simultaneous sorption and desorption of pyrene and fluorene

#### 3.3.1. Simultaneous equilibrium sorption of pyrene and fluorene

Simultaneous sorption curves of fluorene and pyrene (Fig. 3a–c; SM Fig. 5a–b) showed that the sorption of both PAHs were concentration dependent and increased with concentration. Comparing simultaneous sorption data with the single PAHs sorption (Fig. 3d–f; SM Fig. 5c–d), PAHs sorption from mono-PAHs solutions was higher than from the mixture solutions. The mineralogical compositions of the soils did not affect the competitive sorption process in any obvious manner. However, for soils with relatively higher organic matter contents – AG and PH, the sorption amounts of pyrene in the single and mixed PAHs solutions were not significantly different. This may be due to the high affinity of pyrene for organic matter on these soils as well as multi-layer adsorption on already adsorbed pyrene on the soils' surface.

However, simultaneous sorption of fluorene on the relatively higher organic matter soils (AG, IB and PH) was always lower than in mono-PAHs solutions. This trend has been attributed to the type of organic matter present in these soils – soft and hard organic matter (Weber et al., 1992). Soft organic matter are rich in aromatic functionalities while hard organic matter have far less aromatic functionalities. Soft organic matter with the abundance of aromatic functionalities may increase fluorene sorption by two suggested mechanisms: abundance of the aromatic functionalities can directly increase fluorene sorption via hydrophobic and  $\pi$ - $\pi$  interactions between benzene rings in the PAHs; and the formation of secondary PAHs layer on the already (initial) sorbed PAHs layer on the soil surface (multi-layer) (Xu et al., 2014). Considering the environmental conditions of the AG, IB and PH sampling sites at the sampling time, their organic matter were assumed to be the hard one with little aromatic functionalities. The size and structures of the PAHs are also important features that are believed to determine whether pyrene or fluorene is sorbed more. Though pyrene and fluorene have nearly similar molecular size, pyrene contains more aromatic benzene rings than fluorene (ratio 4:2) in its structure, and this unique difference affects the extent of their sorption. Fluorene thus has lower affinity for aromatic functionalities in soil as well as reduced capacity to form  $\pi$ - $\pi$  interactions than pyrene; hence, the reduced sorption.

Desorption results (Fig. 3a–b; SM Fig. 5a–c) showed that pyrene had lower hysteresis (higher desorption) in simultaneous desorption than mono-desorption for all soils. This observation was attributed to the idea that simultaneous sorption may leave more pyrene molecules loosely bound to the soil surfaces and vulnerable to easy desorption. However, the reverse case was observed for fluorene desorption from these soils—fluorene desorption was lower in simultaneous desorption than in mono-desorption for all soils. This result could mean that simultaneous sorption of pyrene along with fluorene on soils enhanced

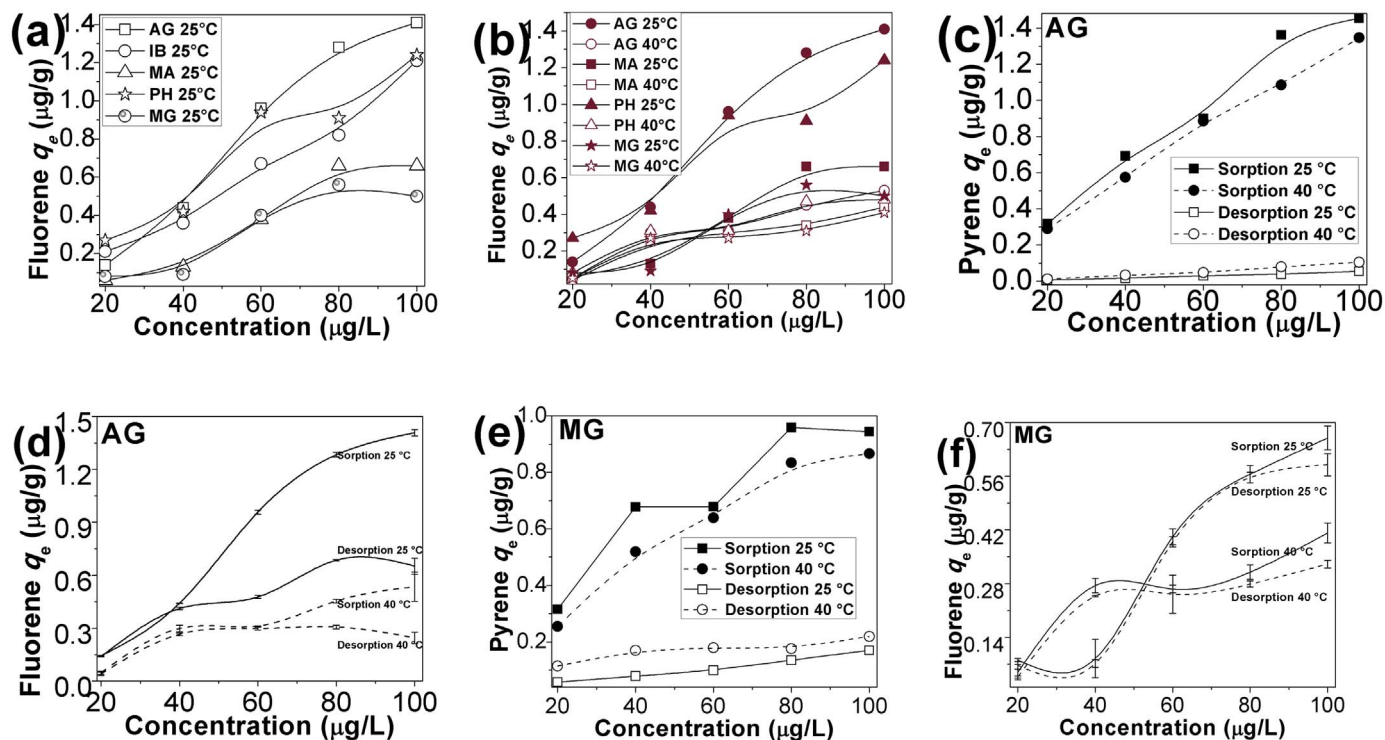


Fig. 2. Effects of (a) concentration, and (b) temperature on fluorene sorption; and sorption and desorption trends of (c) pyrene, (d) fluorene on AG soil, and (e) pyrene and (f) fluorene on MG soil.

the interaction between fluorene species in solution and other adsorbed surface molecules as well as the soil sorption surfaces (cooperative sorption). This enhancement is thought to be via hydrophobic and  $\pi$ - $\pi$  interactions. When this occurs, multi-layer adsorption is established on the soil surface (Xu et al., 2014).

The observed hysteresis for both PAHs might be linked to their sizes.

Assuming that all desorbed PAHs molecules were from the multi-layer on the soil surfaces, then one can argue that pyrene might desorb easily when compared with fluorene because the magnitude of hydrophobic and  $\pi$ - $\pi$  interactions holding both molecules in place in a multi-layer position will be more effective for a relatively smaller molecule such as fluorene. Thus, the lower fluorene desorption or higher hysteresis after

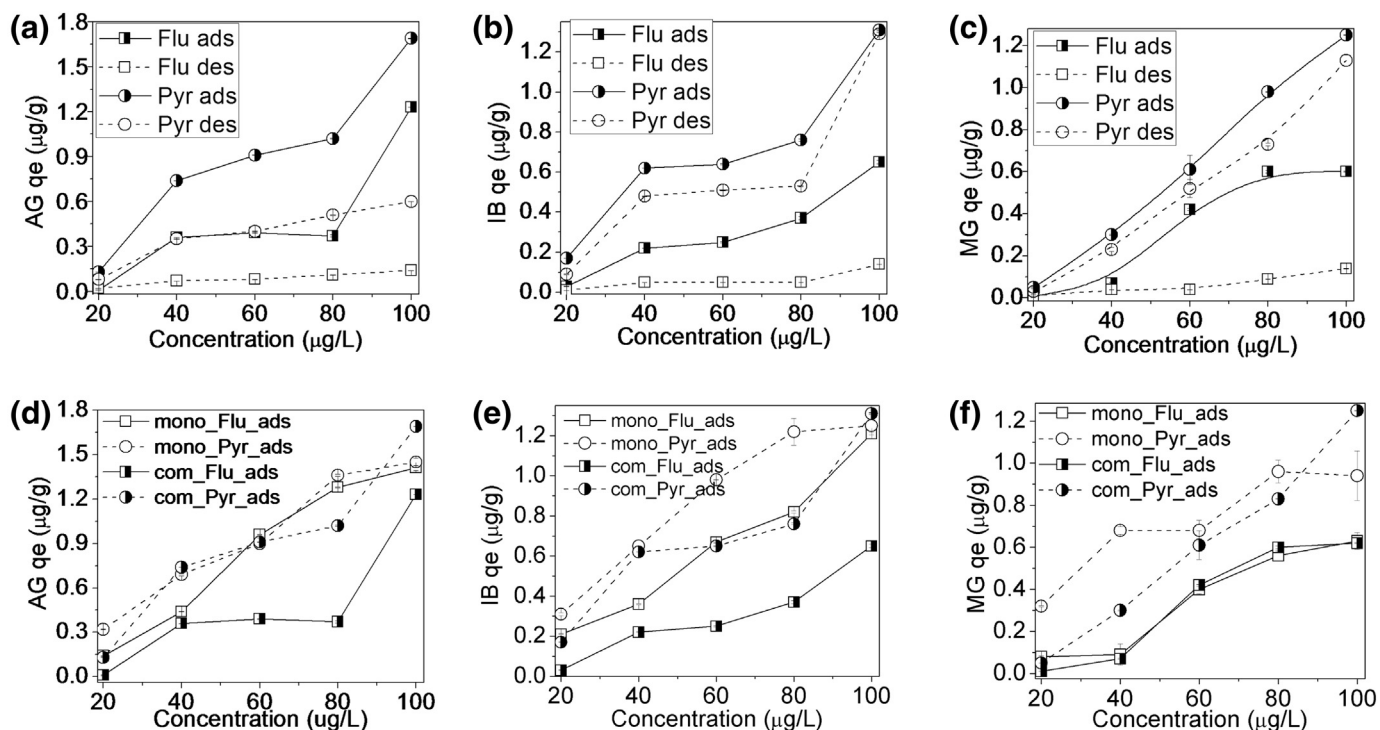


Fig. 3. Simultaneous sorption and desorption trends on (a) AG, (b) IB and (c) MG soils; comparison of the sorption trends for single and simultaneous studies on (a) AG, (b) IB and (c) MG soils.

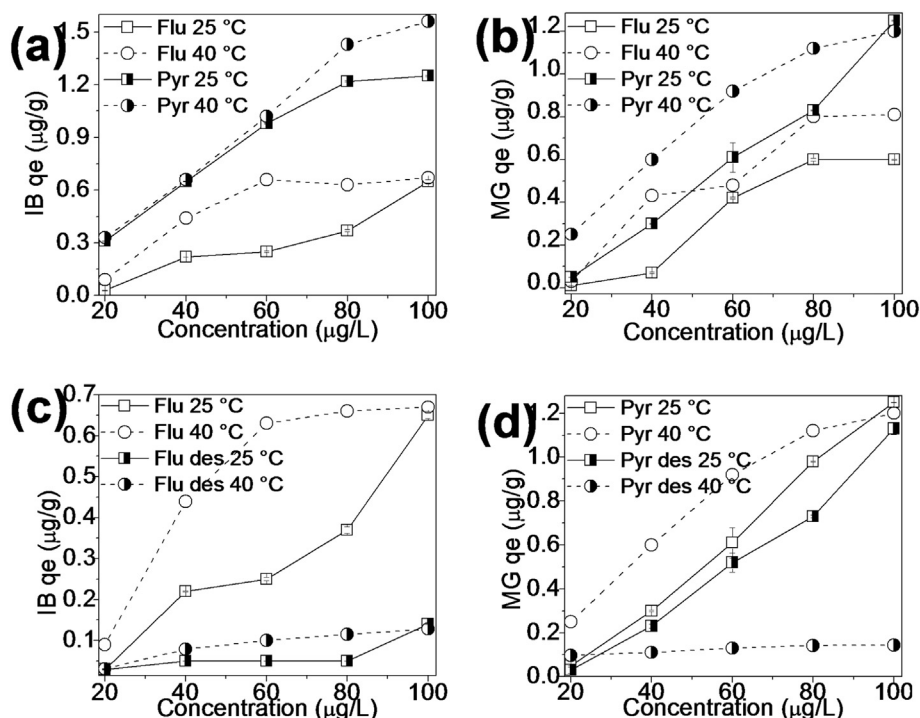


Fig. 4. Effect of temperature on simultaneous PAHs sorption on (a) IB and (b) MG soils; effect of temperature on the simultaneous PAHs sorption and desorption on (c) IB and (d) MG soils.

simultaneous sorption.

3.3.2. Effect of temperature on the simultaneous sorption of pyrene and fluorene

The effect of temperature results (Fig. 4a–b; SM Fig. 6a–c) showed that the sorption of both PAHs were higher at 40 °C than at 25 °C. This contrasts the results obtained for PAHs sorption from mono-PAHs solutions where increase in temperature led to decrease in sorption. A major reason adduced for this trend was that increase in temperature increases PAHs solubility as well as the entropy. Since film diffusion is a rate limiting step in the initial fast phase of PAHs sorption on soils as observed from the intra-particle diffusion kinetics model (Olu-Owolabi et al., 2014, 2015), increase in entropy might have enhanced film diffusion which resulted in trans-boundary movement of PAHs as well as multi-layer adsorption via  $\pi$ - $\pi$  stacking of the PAHs on one another at the soil surface. Hence, increase in temperature resulted in  $\pi$ - $\pi$  stacking of the PAHs leading to cooperative sorption between pyrene and fluorene. Similar observations have been noted in the report of Javier Rivas et al. (2008) and Xu et al. (2014) on sorption of PAHs from PAHs mixture solutions. In contrast to mono-PAHs sorption, this might not be the case due to higher degree of freedom in mono-PAHs solutions.

Desorption experiments carried out at both temperatures (Fig. 4c–d; SM Fig. 7a–h) showed that fluorene desorption were very low (high hysteresis) at these temperatures. High hysteresis was also observed for pyrene at the higher temperature studied, but lower hysteresis at reduced temperature. The high hysteresis for fluorene sorption on these soils may be attributed to the fact that  $\pi$ - $\pi$  interactions were very effective for the removal of PAHs from solution. Bearing in mind that the medium used for desorption was hydrophilic, it was assumed that these hydrophobic PAHs would rather prefer to remain in their hydrophobic associations on the surfaces as well as within pores of the soils rather than go into a hydrophilic solution; hence, the high hysteresis. This is in consonance with the idea of cooperative sorption between pyrene and fluorene at higher temperature. The reason above could be adduced for pyrene desorption at 40 °C. However, hysteresis was lower at 25 °C, and this may be attributed to the fewer amounts of hydrophobic interactions, especially  $\pi$ - $\pi$  stacking, that occurs at lower temperatures. Since the contributory energies associated with holding the PAHs together on

these soil sorbents were smaller at lower than higher temperatures, and pyrene being a larger molecule than fluorene, then the high pyrene desorption becomes reasonable.

3.3.3. Simultaneous sorption isotherm models

The Langmuir and Freundlich adsorption isotherm models were used to evaluate the generated simultaneous sorption data of fluorene and pyrene on the whole soils at 25 °C (Table 2). Values of the correlation coefficients ( $r^2$ ) and the estimated maximum sorption capacities ( $Q_0$ ) suggested that the Langmuir isotherm could not describe the sorption of these PAHs from a multi-PAHs solution. Nearly similar results were observed with the Freundlich isotherm, but a closer examination of the Freundlich isotherm parameters indicated that the sorption on these soils tended towards the Freundlich type isotherm (small  $n$  values and relatively higher  $r^2$  values). This may be attributed to the heterogeneous nature of soils and the affinity of hydrophobic

Table 2 Simultaneous sorption isotherm parameters of fluorene and pyrene.

Soil	Langmuir sorption model			Freundlich sorption model			Distributed reactivity model (DRM)	
	$Q_0$ (µg/g)	$B$	$r^2$	$q_e$ (µg/g)	$N$	$r^2$	$q_{T(l+n)}$ (µg/g)	$r^2$
Fluorene sorption								
AG	0.049	0.019	0.365	0.45	2.29	0.613	1.23	0.958
IB	0.436	0.008	0.494	0.55	1.39	0.941	0.65	0.973
MA	1.15	0.005	0.262	0.54	1.11	0.940	0.61	0.987
PH	0.941	0.052	0.475	0.64	0.75	0.668	1.44	0.984
MG	0.070	0.015	0.658	0.90	2.31	0.868	0.60	0.999
Pyrene sorption								
AG	2.00	0.014	0.020	0.61	1.05	0.211	1.69	0.997
IB	1.97	0.017	0.145	0.76	0.88	0.662	1.31	0.985
MA	0.05	0.016	0.324	0.30	2.28	0.504	1.08	0.991
PH	1.50	0.021	0.056	0.62	1.28	0.326	1.74	0.991
MG	0.01	5.614	0.108	0.86	0.99	0.205	0.83	0.999

$q_{T(l+n)}$  (µg/g) – Total linear (l) and non-linear (nl) sorption, its values are exactly equal to the experimental  $q_e$  values.

**Table 3**  
Comparison of pyrene and fluorene sorption on soils from different parts of the world.

PAH	Sorption quantity ( $\mu\text{g/g}$ )	Part of the world	Citation
Pyrene	0.82–1.94	South America	Teixeira et al., 2011
Pyrene	$\approx 0.7$ for soil organic matter	Europe	Cottin and Merlin, 2007
Pyrene	17–47	Asia	Sun and Yan, 2007
Pyrene	0.83–1.74	Sub-Sahara Africa	Present study
Fluorene	0.60–1.44	Sub-Sahara Africa	Present study
Fluorene	$\approx 0.1$	Europe	Weissenfels et al., 1992
Fluorene	$\approx 1.2$	North America	Kohl and Rice, 1999

PAHs towards other hydrophobic compounds, and the consequent formation of multi-layer adsorption.

Consequently, the Weber et al. (1992) distributed reactivity model (SM 2) was used to evaluate these data. The model describes sorption on heterogeneous system such as soil where different isotherm models are involved simultaneously and the final isotherm is a combination of all the models involved. The isotherm parameters obtained from the distributed reactivity model are also shown in Table 2. The  $r^2$  values (0.958–0.999) of fluorene and pyrene sorption suggested that the equilibrium sorption data were sufficiently described by the model. The estimated model  $q_e$  values were also significantly correlated with the experimental values. Hence, the simultaneous sorption isotherms of pyrene and fluorene on these soils were described as composite of several linear and non-linear isotherms, and hence the inability of the sorption data to fit into either the Langmuir or Freundlich type isotherms.

Comparison of pyrene and fluorene sorption on soils from different parts of the world (Table 3) has shown that sorption properties of different soils vary extensively and it depends on the inherent soil constituents.

### 3.3.4. Thermodynamics of the simultaneous sorption of pyrene and fluorene

Thermodynamics parameters (standard free energy –  $\Delta G^\circ$ , entropy change –  $\Delta S^\circ$ , and enthalpy change –  $\Delta H^\circ$ ) generated from the equilibrium experiments are shown in Table 4 for fluorene and pyrene. Values of  $\Delta G^\circ$  were all negative for pyrene and fluorene sorption at both temperatures. This indicates that the sorption of fluorene and pyrene on these soils were feasible and spontaneous. The  $\Delta S^\circ$  values were mainly negative and suggested that the adsorption of these PAHs species from solution led to a decrease in randomness as the sorption of both PAHs species proceeded towards equilibrium.

Calculated  $\Delta H^\circ$  values showed that the sorption of these PAHs were exothermic (negative). An exception to this is fluorene sorption on MA and PH soils which had small positive values. This may be attributed to

**Table 4**  
Thermodynamic parameters for the simultaneous sorption of fluorene and pyrene.

Soil	$\Delta H^\circ$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^\circ$ ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )	$\Delta G^\circ$ ( $\text{kJ mol}^{-1}$ )	
			298 K	313 K
<b>Fluorene sorption</b>				
AG	– 99.5	– 0.28	– 15.2	– 11.0
IB	– 26.2	– 0.04	– 13.8	– 13.1
MA	7.60	0.07	– 13.0	– 14.0
PH	18.5	0.10	– 10.2	– 11.7
MG	– 33.0	– 0.06	– 16.4	– 15.6
<b>Pyrene sorption</b>				
AG	– 22.6	– 0.04	– 10.5	– 9.90
IB	– 80.8	– 0.24	– 10.2	– 6.60
MA	– 125.6	– 0.37	– 15.9	– 10.4
PH	– 17.1	– 0.02	– 9.91	– 9.55
MG	– 123	– 0.37	– 13.8	– 8.31

minor errors associated with linear model calculations of the thermodynamic parameters which can become significant when dealing with low energy sorption surfaces (Olu-Owolabi et al., 2014). The magnitudes of the  $\Delta H^\circ$  values were in the range associated with the weak hydrophobic interactions such as the van der Waal's forces and  $\pi$ – $\pi$  interactions, and a strong indication that these forces were involved in the sorption of these PAHs species from solution (Haftka et al., 2010; Olu-Owolabi et al., 2014).

## 4. Conclusion

Simultaneous sorption of fluorene and pyrene showed that the sorption of both PAHs were concentration dependent and increased with concentration at 25 °C. However, PAHs sorption from mono-PAHs solution was higher than from the mixture solutions. High amount of organic matter in soils ( $\geq 4.5\%$ ) may lead to high amounts of PAHs sorption irrespective of competition. The various soils' minerals did not affect the competitive sorption process in any obvious manner. Similar to sorption from mono-PAHs solution, pyrene was more sorbed competitively than fluorene on these soils. Pyrene had lower hysteresis (higher desorption) in simultaneous desorption compared to mono-desorption, while higher hysteresis was observed in fluorene for simultaneous desorption for all soils.

In contrast to sorption from mono-PAHs solution, simultaneous sorption of both PAHs was higher at 40 °C than at 25 °C. Both PAHs exhibited lower desorption (higher hysteresis) as temperature increased in contrast to desorption at lower temperature. Equilibrium studies showed that the simultaneous sorption of pyrene and fluorene on these soils were on heterogeneous surfaces and the sorption isotherms were composites of several linear and non-linear isotherms. Thermodynamically, the sorption processes were feasible and spontaneous with decrease in randomness of solution PAHs as the sorption of the species proceeded towards equilibrium. Ultimately, soil constituents, concentrations of PAHs in solution, competition between PAHs for sorption sites, molecular size and the structural relationship between PAHs played vital roles in the simultaneous sorption of PAHs on these soils.

Environmentally, lower simultaneous PAHs sorption and low hysteresis from soils with low organic matter contents may imply higher risks of both PAHs being present in the soil water solution, and subsequent contamination of the aquifer. Hence, in the environment, these PAHs especially fluorene, is likely to cause environmental pollution and/or reach the aquifer faster in the warmer and low organic matter soils of the northern sub-Sahara Africa than the cooler and relatively high organic matter containing soils of the south.

## Acknowledgment

We acknowledge the supports of the World Academy of Sciences (TWAS), Trieste Italy and the Chinese Academy of Sciences (CAS), China for the award of CAS-TWAS Postgraduate Fellowship (FR number: 3240255024) to P.N. Diagboya; and late Mrs. Rebecca A. Okoh and Mr. V.P.O. Okoh, Department of Estate Management, Yaba College of Technology, Lagos Nigeria, for partial funding.

## Appendix A. Supporting data

SM 1: Soil characterization; SM 2: Data Treatment; SM Table 1. Soil types and other descriptions; SM Fig. 1. XRD spectra; SM Fig. 2. Effect of time, pH, concentration and temperature on sorption, SM Figs. 3–4. Desorption of pyrene and fluorene; SM Fig. 5. Simultaneous sorption and desorption trends; comparison of the sorption and desorption trends for single and simultaneous studies; SM Fig. 6. Effect of temperature on the simultaneous PAHs sorption; SM Fig. 7. Effect of temperature on simultaneous PAHs sorption and desorption. Supplementary data associated with this article can be found in the

online version, at doi: <https://doi.org/10.1016/j.clay.2017.11.037>.

## References

- Adesina, O.A., Sonibare, J.A., Diagboya, P.N., Adejwon, A., Famubode, T., Bello, J.O., 2017. Periodic characterization of alkyl-naphthalenes in stack gas and ambient air around a medical waste incinerator. *Environ. Sci. Pollut. Res.* 24, 21770–21777.
- An, C., Huang, G., Yu, H., Wei, J., Chen, W., Li, G., 2010. Effect of short-chain organic acids and pH on the behaviors of pyrene in soil–water system. *Chemosphere* 81, 1423–1429.
- ATSDR, 1995. *Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs)*. <http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf>.
- Biswas, B., Sarkar, B., Mandal, A., Naidu, R., 2015. Heavy metal-immobilizing organoclay facilitates polycyclic aromatic hydrocarbon biodegradation in mixed-contaminated soil. *J. Hazard. Mater.* 298, 129–137.
- Changchaivong, S., Khaodhiar, S., 2009. Adsorption of naphthalene and phenanthrene on dodecylpyridinium-modified bentonite. *Appl. Clay Sci.* 43, 317–321.
- Chilom, G., Kohl, S.D., Rice, J.A., 2005. The influence of lipids on the energetics of uptake of polycyclic aromatic hydrocarbons by natural organic matter. *J. Environ. Qual.* 34, 1055–1062.
- Cottin, C.N., Merlin, G., 2007. Study of pyrene biodegradation capacity in two types of solid media. *Sci. Total Environ.* 380, 116–123.
- Diagboya, P.N., Olu-Owolabi, B.I., Adebowale, K.O., 2015. Effects of time, soil organic matter, and iron oxides on the relative retention and redistribution of lead, cadmium, and copper on soils. *Environ. Sci. Pollut. Res.* 22, 10331–10339.
- Diagboya, P.N., Olu-Owolabi, B.I., Adebowale, K.O., 2016. Distribution and interactions of pentachlorophenol in soils: the roles of soil iron oxides and organic matter. *J. Contam. Hydrol.* 191, 99–106.
- Fagbami, A.A., Shogunle, E.A.A., 1995. Nigeria: reference soil of the moist lowlands near Ife (Oshun state). In: *Soil Brief Nigeria 3*. University of Ibadan, and International Soil Reference and Information Centre, Wageningen (Pp 3).
- Freundlich, H.M.F., 1906. Über die adsorption in lösungen. *Z. Phys. Chem.* 57A, 385–470.
- Guo, X., Luo, L., Ma, Y., Zhang, S., 2010. Sorption of polycyclic aromatic hydrocarbons on particulate organic matters. *J. Hazard. Mater.* 173, 130–136.
- Haftka, J.J.H., Govers, H.A.J., Parsons, J.R., 2010. Influence of temperature and origin of dissolved organic matter on the partitioning behaviour of polycyclic aromatic hydrocarbons. *Environ. Sci. Pollut. Res.* 17, 1070–1079.
- Huang, W., Peng, P., Yu, Z., Fu, J., 2003. Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments. *Appl. Geochem.* 18, 955–972.
- Hwang, S., Cutright, T.J., 2002. Biodegradability of aged pyrene and Phenanthrene in a natural soil. *Chemosphere* 47, 891–899.
- Javadi, S., Ghavami, M., Zhao, Q., Bate, B., 2017. Advection and retardation of non-polar contaminants in compacted clay barrier material with organoclay amendment. *Appl. Clay Sci.* 142, 30–39.
- Javier Rivas, F., García de la Calle, R., Alvarez, P., Acedo, B., 2008. Polycyclic aromatic hydrocarbons sorption on soils: some anomalous isotherms. *J. Hazard. Mater.* 158, 375–383.
- Joseph-Ezra, H., Nasser, A., Mingelgrin, U., 2014. Surface interactions of pyrene and phenanthrene on Cu-montmorillonite. *Appl. Clay Sci.* 95, 348–356.
- Kohl, S.D., Rice, J.A., 1999. Contribution of lipids to the nonlinear sorption of polycyclic aromatic hydrocarbons to soil organic matter. *Org. Geochem.* 30, 929–936.
- Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.* 38, 2221–2295.
- Lee, S.Y., Kim, S.J., 2002. Adsorption of naphthalene by HDTMA modified kaolinite and halloysite. *Appl. Clay Sci.* 22, 55–63.
- Mokwenye, I.I., Diagboya, P.N., Olu-Owolabi, B.I., Anigbogu, I.O., Owamah, H.I., 2016. Immobilization of toxic metal cations on goethite-amended soils: a remediation strategy. *J. Appl. Sci. Environ. Manag.* 20, 436–443.
- Nasser, A., Mingelgrin, U., 2012. Mechanochemistry: a review of surface reactions and environmental applications. *Appl. Clay Sci.* 67–68, 141–150.
- Okoli, C.P., Diagboya, P.N., Anigbogu, I.O., Olu-Owolabi, B.I., Adebowale, K.O., 2017. Competitive biosorption of Pb(II) and Cd(II) ions from aqueous solutions using chemically modified moss biomass (*Barbula lambarensis*). *Environ. Earth Sci.* 76 (1), 33.
- Olu-Owolabi, B.I., Diagboya, P.N., Adebowale, K.O., 2014. Evaluation of pyrene sorption–desorption on tropical soils. *J. Environ. Manag.* 137 (1–9).
- Olu-Owolabi, B.I., Diagboya, P.N., Adebowale, K.O., 2015. Sorption and desorption of fluorene on five tropical soils from different climates. *Geoderma* 239–240, 179–185.
- Olu-Owolabi, B.I., Diagboya, P.N., Okoli, C.P., Adebowale, K.O., 2016. Sorption behaviour of pentachlorophenol in sub-Saharan tropical soils: soil types sorption dynamics. *Environ. Earth Sci.* 75, 1494.
- Olu-Owolabi, B.I., Alabi, A.H., Diagboya, P.N., Unuabonah, E.I., Düring, R.-A., 2017. Adsorptive removal of 2,4,6-trichlorophenol in aqueous solution using calcined kaolinite-biomass composites. *J. Environ. Manag.* 192, 94–99.
- Pan, B., Xing, B., 2010. Competitive and complementary adsorption of bisphenol A and 17 $\alpha$ -ethinyl estradiol on carbon nanomaterials. *J. Agric. Food Chem.* 58, 8338–8343.
- Shu, Y., Li, L., Zhang, Q., Wu, H., 2010. Equilibrium, kinetics and thermodynamic studies for sorption of chlorobenzenes on CTMAB modified bentonite and kaolinite. *J. Hazard. Mater.* 173, 47–53.
- Site, A.D., 2001. Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *J. Phys. Chem. Ref. Data* 30, 187–439.
- Soil Survey Staff, 2006. *Keys to Soil Taxonomy*, 10th Edition. United States Department of Agriculture, Natural Resources Conservation Service (p 331).
- Sparks, D.L., 2003. *Environmental Soil Chemistry*. Academic Press, San Diego (pp 16).
- Sun, H.W., Yan, Q.W., 2007. Influence of Fenton oxidation on soil organic matter and its sorption and desorption of pyrene. *J. Hazard. Mater.* 144, 164–170.
- Teixeira, S.C.G., Ziolli, R.L., Marques, M.R.C., Pérez, D.V., 2011. Study of pyrene adsorption on two Brazilian soils. *Water Air Soil Pollut.* 219, 297–301.
- USEPA, 2007. *Treatment Technologies for Site Cleanup: Annual Status Report (ASR)*, 12th edition. (EPA 542-R-07-012).
- Weber Jr., W.J., McGinley, P.M., Katz, L.E., 1992. A distributed reactivity model for sorption by soils and sediments: 1. Conceptual basis and equilibrium assessments. *Environ. Sci. Technol.* 26, 1955–1962.
- Weissenfels, W.D., Klewer, H.-J., Langhoff, J., 1992. Adsorption of polycyclic aromatic hydrocarbons (PAHs) by soil particles: influence on biodegradability and biotoxicity. *Appl. Microbiol. Biotechnol.* 36, 689–696.
- White, J.C., Pignatello, J.J., 1999. Influence of bisolute competition on the desorption kinetics of polycyclic aromatic hydrocarbons in soil. *Environ. Sci. Technol.* 33, 4292–4298.
- Xu, L., Zhang, M., Zhu, L., 2014. Adsorption–desorption behavior of naphthalene onto CDMBA modified bentonite: contribution of the  $\pi$ – $\pi$  interaction. *Appl. Clay Sci.* 100, 29–34.
- Zeledon-Toruno, Z.C., Lao-Luque, C., de Las Heras, F.X., Sole-Sardans, M., 2007. Removal of PAHs from water using an immature coal (leonardite). *Chemosphere* 67, 505–512.
- Zhao, D., Pignatello, J.J., White, J.C., Braida, W., 2001. Dual-mode modeling of competitive and concentration-dependent sorption and desorption kinetics of polycyclic aromatic hydrocarbons in soils. *Water Resour. Res.* 37, 2205–2212.