Sorption and desorption of fluorene on five tropical soils from different climes

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ABSTRACT

The main processes controlling soil–polycyclic aromatic hydrocarbon interaction is sorption–desorption as influenced by the soil physicochemical conditions. Sorption–desorption phenomena can influence translocation, persistence and bioavailability. Hence, laboratory batch experiments were undertaken to investigate the sorption characteristics of fluorene on five tropical soils from varying tropical agro-ecological zones having different physicochemical properties. Fluorene concentrations used for the study ranged from 20 to 100 μg/L, and results showed that fluorene sorption equilibria were attained usually within 24 h. Increase in pH had a negative effect on fluorene sorption. Fluorene sorption was concentration dependent and exothermic. The sorbed fluorene molecules were distributed between surface adsorption sites and phases in soil. Sorption was controlled by weak hydrophobic forces, such as the π–π interactions and Van der Waal's forces. Desorption hysteresis were most pronounced in soils with high organic matter contents than lower ones. The sorption was characterized as multiple reaction phenomena composed of several linear and non-linear isotherms. The physicochemical conditions of the soil must be understood in order to predict the fate and bioavailability of fluorene in soil.

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1. Introduction

Persistent organic pollutants are introduced into the soil environment via numerous anthropogenic activities (Diagboya et al., 2014; Okoli et al., 2014; USEPA, 2007). Most organic pollutants, especially the polycyclic aromatic hydrocarbons (PAHs), are known to be toxic, some being mutagenic and/or carcinogenic to biota; and thus they have been classified as priority pollutants (USEPA, 2007; ATSDR, 1995). Their effect on biota can be amplified by bioaccumulation in the food chain because PAHs like most organic pollutants are very soluble in fat. Once in the environment, they are subjected to various physical and/or chemical processes that determine their environmental fate (Okoli et al., 2014; Teixeira et al., 2011; Ramirez et al., 2001). Information on the bioavailability of pollutants in the environment is important because bioavailable pollutants are linked to the negative health disorders experienced by biota.

Among the various processes that determine the environmental fate of PAHs, sorption is the relatively most studied (Teixeira et al., 2011; Ramirez et al., 2001) because data obtained can give valuable information on suitable remediation strategy for the polluted soil. Sorption experiments can be used to determine the quantity of PAHs retained by a soil and, hence, the leachable or bioavailable quantity (Sparks, 2003). Some studies have reported the sorption characteristics of some PAHs in some soils (An et al., 2010; Cottin and Merlin, 2007; Hwang and Cutright, 2002; Guo et al., 2010; Sun and Yan, 2007; Haftka et al., 2010; Teixeira et al., 2011; Ramirez et al., 2001), however there is a dearth of information on the sorption characteristics of these pollutants in several soils especially soils from tropical Africa. Moreover, this kind of information is vital because data obtained from other parts of the world may not be useful for prediction of PAHs' sorption characteristics/remediation strategies for African soils since these soils are unique; formed from different parent materials under different environmental conditions (temperature, moisture, and biota).

The objective of this work was to study the sorption and desorption of fluorene on representative soils obtained from five major sub-Saharan agro-ecological zones (AEZs) varying extensively in physical and chemical properties. The effects of time, pH, and temperature were evaluated and the data obtained were used to predict the mechanism(s) of the sorption process.

2. Materials and methods

2.1. Sampling and physicochemical characterization

Five representative surface soils (0–30 cm) were obtained from different sub-Saharan AEZs (Table 1a) by compositing randomly collected samples from locations which are relatively free from human activities

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Table 1a
Physico-chemical properties of the soil samples.

Soil	*AEZ	Sampling coordinate	pH water	pH 1 N KCl	EA	*OM (%)	Particle size analysis (%)			Oxides (wt.%)	
							*Sand	*Silt	*Clay	Fe_2O_3	Al_2O_3
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).

or impacts, such as locations far from road traffic sites, wastes dumps, places where little or no fertilizers have been applied, etc. The samples 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 were determined in Millipore ultra-pure water and 1.0 M of KCl (ratio 1:1) (Benton, 2001). Particle size determination was done by the laser particle analyzer (Mastersizer-2000) after removal of carbonates by washing with hydrochloric acid, treatment with 30% H_2O_2 to remove organic matter, and dispersing in 0.1 M of sodium hexametaphosphate (Breuning-Madsen and Awadzi, 2005). Organic matter was determined by the Walkley and Black (1934) wet digestion method. Metals (oxides, exchangeable and trace) were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300DV), except for Cd which was done by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500). The soil mineralogy was obtained by a Bruker phaser diffractometer system using the whole sample procedure (randomly oriented mounts) and the spectra were analyzed using PANalytical X'Pert HighScore software.

2.2. Fluorene sorption

Fluorene solution was prepared in 10% v/v methanol/Millipore ultra-pure water using 0.005 M of $CaCl_2$ and 0.01 M of NaN_3 as background electrolyte and biocide to eliminate microbial degradation, respectively. Sorption experiments were carried out by adding 10 mL of 100 μg/L (except for the effect of concentration experiments) fluorene solution into brown vials containing 0.50 g of the soil sample and then 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 at 100 rpm in a temperature (25 °C) controlled shaker. For the effect of time, the vials were incubated from 30 to 4320 min. Equilibrium studies and effect of temperature were investigated in the concentration range of 20–100 μg/L at 25 and 40 °C. After the equilibrium experiments fluorene desorption was carried out immediately by thoroughly decanting the incubated solution and replacing it with a fresh background solution of methanol/Millipore ultra-pure water solution containing the same concentration of $CaCl_2$ and NaN_3 but no fluorene. These were incubated in similar conditions as above, centrifuged after 4320 min, and fluorene concentration determined. All experiments were done at the ambient soil pH except the effect of pH which was done from pH 3 to 9 using 100 μg/L fluorene concentrations at 25 °C. Control experiments without soil samples were done to account for possible losses due to volatilization and sorption onto the vial walls (and these were found to be negligible). After incubation, the vials were centrifuged at 4000 rpm for 20 min, and the concentration of fluorene in solution determined by Perkin Elmer fluorescence spectroscopy (model LS 55) using the synchronized scan at a wavelength difference (Δλ) of 45 nm and scanning from 200 to 350 nm. The synchronous peak at 264 nm was used to monitor the sorption. All experiments were done in triplicate and the averages of the data have been used for computation.

2.3. Data treatment

The amounts of fluorene removed from solution were calculated from the initial (C_o) and final (C_e) concentrations in solutions after the incubation using the Eq. (1):

$$q_e = \frac{(C_O - C_e)V}{M} \tag{1}$$

where q_e, V and M are the amount of fluorene sorbed (μg/g), volume of the solution (mL) and mass (g) of sample, respectively.

The sorption data was explained using four kinetics models (Lagergren (1898) pseudo-first and -second order, Elovich (Olu-Owolabi et al., 2012) and Weber and Morris (1963) intra-particle diffusion kinetics models); three adsorption isotherm models (Langmuir (1916), Freundlich (1906), and the distributed reactivity model (Weber et al., 1992)); as well as the thermodynamic parameters — standard free energy (ΔG^o), enthalpy change (ΔH^o), and entropy change (ΔS^o) (see supporting materials SM1–3 for further data treatments).

3. Results and discussion

3.1. Soil properties

The physicochemical characteristics of the soils are shown in Tables 1a and 1b. The pH values were mainly neutral (6.0–7.5) except for MG which was alkaline (8.0–9.0). Soil organic matter (SOM) values were high except for MA and MG soils which have been described as medium and very low, respectively (Fagbami and Shogunle, 1995). AG and PH had the highest SOM contents. The mineralogical compositions (Table 1b) indicated that the major minerals in the soils are aragonite, calcite, dolomite, gibbsite, hematite, kaolinite, quartz, and siderite. Quartz was the most common mineral followed by the Al oxide mineral — gibbsite. Kaolinite and the carbonate minerals (aragonite, calcite, siderite, and dolomite) are common features of these soils. The 2:1 expansive clay minerals, montmorillonite and illite, were observed in MA and MG, respectively. The textural measurements (Table 1c) showed that the soils are majorly sandy loam (PH, IB, and MA) and loamy sand (AG and MG) (soil survey staff, 2006).

3.2. Sorption studies

3.2.1. Sorption time and kinetics mechanism

Result (Fig. 1a) of the effect of incubation time on sorption showed that equilibrium fluorene sorption on the whole soils were attained usually within 1440 min for these soils, except for PH soil which attained equilibrium in 2880 min. At equilibrium, fluorene sorption was constant and no significant desorption was recorded. Literature has shown that equilibrium attainment for fluorene sorption on soils does not occur at a specific time but is dependent on soil type (Kohl and Rice, 1999; Chilom et al., 2005). The variation in attainment of equilibria on these soils was attributed to the sorption characteristics of the soils' constituents. It was observed that soils with higher organic matter

Table 1b
The mineralogical composition of the soils determined from the XRD crystallography of soil samples.

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	–

content (AG and PH) attained equilibrium relatively fast. This was ascribed to the nearly instantaneous sorption of fluorene on organic matter. However, sorption on the IB soil with high organic matter took a longer time to attain equilibrium. This trend in the IB soil might be attributed to the kind of organic matter present in this soil; Weber et al. (1992) and Huang et al. (2003) have reported that there are two kinds of soil organic matter — the soft and hard organic matter. The soft organic matter is rich in hydrophobic materials and hence has high tendency for sorption of hydrophobic organic compounds, unlike the hard organic matter which is poor in hydrophobic materials. Thus the long equilibrium time observed in the organic matter-rich IB soil may not be unconnected to the presence of hard organic matter. Similar observation on the MA and MG soils with low organic matter contents was attributed to sorption on the clay mineral surfaces.

In order to identify the kinetic mechanism(s) involved in fluorene sorption on these soils, the generated data from the effect of time experiments were evaluated using four kinetics models: Lagergren pseudo-first and -second order, Elovich and intra-particle diffusion kinetics models (equations in supporting material). This was necessary because organic pollutant sorption and subsequent desorption from soils and sediments sometimes involve multi-step mass transfer of sorbate molecules across the solid–solution boundary and diffusion within the solid matrices (Huang et al., 2003). Though sorbate exchange between the bulk solution phase and external surfaces of soil aggregates can be relatively fast or even instantaneous under rapid mixing conditions, diffusion of sorbate molecules within SOM matrices and micro/meso-pores connecting the external solution phase and SOM trapped within soil aggregates can be extremely slow and often limits the overall sorption and desorption rates (Huang et al., 2003; Mittal et al., 2008). Results (Table 2) showed that the pseudo-second order kinetics fits the data better than the pseudo-first order kinetics; by comparing the pseudo-first and pseudo-second order kinetics, it was observed that the estimated model sorption capacity (q_e) values and coefficients (r^2) were better correlated (0.944–0.999) for the pseudo-second order kinetics. The q_e values of the pseudo-second order kinetics also better described and showed close proximity to the experimental values.

The estimated q_e values from the Elovich kinetics model indicated that fluorene sorption on these soils could be explained by the model.

The model which originated from chemical reaction kinetics suggests that if a plot of q_t against $\ln(t)$ (supporting material equation 3) does not yield a straight line which passes through the origin of the graph (Fig. SM1), then there was some degree of boundary layer control for the adsorption of fluorene. This boundary layer control was predicted to be associated with the rate controlling mechanism of the sorption process; and considering the uncharged nature of the fluorene molecule it might involve mainly π–π interactions and, to a lesser extent, Van der Waals forces between the fluorene molecules in solution and the soil sorption sites. Similar result has been reported by Olu-Owolabi et al. (2014) for pyrene sorption on soils.

The Weber and Morris (1963) intra–particle diffusion kinetics model was used to determine whether the rate limiting step is film diffusion or intra-particle diffusion. This model suggests that if the sorption mechanism is intra-particle diffusion, then a plot of q_t versus $t^{1/2}$ will be linear, and if intra-particle diffusion is the sole rate-limiting step such a plot passes through the origin. However, for a sorption process comprised of two or more mechanisms then a plot of q_t versus $t^{1/2}$ will not be linear; and this was the case for fluorene sorption on these soils (Fig. 1b). The figure showed that the sorption were in two stages — an initial fast stage (circled part of Fig. 1b) and the later slow stage (parts of the curve beyond the fast stage). The fast stage is a gentle steep and represents migration of fluorene molecules towards the external surface of the soils (film diffusion) as well as the movement of the molecules within the soil pores (particle diffusion). The Weber–Morris model predicts that intra-particle diffusion was predominant (rate-limiting step) at this fast stage of the sorption process. This assumption was supported by the fact that an extrapolation of this portion of the curve towards the zero point of the graph will touch or be very close to the origin. The parts of the curve beyond the fast stage are characterized by its horizontal nature, and represent the points at which equilibrium has been achieved. The C ($\mu g\ g^{-1}$) values of the intra-particle diffusion model (supporting material equation 4) indicate the boundary layer thickness of fluorene on the soil surface; if the sorption is solely a surface phenomenon (adsorption), then C ($\mu g\ g^{-1}$) will be equal to q_e ($\mu g\ g^{-1}$), but if the sorption is comprised of both adsorption and partitioning within soil components then C will be much less than q_e. The C values were observed to be generally smaller than the experimental q_e values
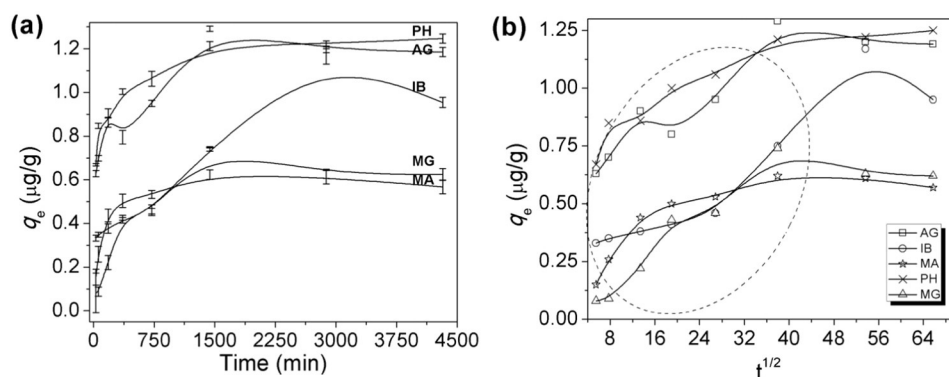

Fig. 1. (a) Fluorene sorption trend with time (error bars indicate mean and standard deviation values of three replicates); (b) intraparticle diffusion model plots.

Table 1c
Soil types and other descriptions.

Sampling location	ATR* (°C)	Soil temperature regime[a]	Soil type[b]	Clay activity[c]	Degree of weathering	Textural class
AG	19–32	Thermic	Ultisols	722.37	WW	Loamy sand
PH	17–30	Thermic	Inceptisols	172.41	WW	Sandy loam
IB	22–32	Thermic	Alfisols	21.64	MW	Sandy loam
MA	10–43	Hyperthermic	Vertisols	634.33	WW	Sandy loam
MG	9–45	Hyperthermic	Entisols	732.00	WW	Loamy sand

*ATR — Average temperature range; VSW — Very strongly weathered; SW — Strongly weathered; MW — Moderately weathered; WW — Weakly weathered;
[a] Soil survey staff, 2006.
[b] Fagbami (1993).
[c] Westin and Brito (1969).

(Table 2), and this implied that fluorene sorption on these soils comprised both surface adsorption and partitioning within soil components such as the organic matter and expansive clays.

3.2.2. Effect of pH on fluorene sorption

Fig. 2 showed the changes in fluorene sorption as the soil solution pH increased. The influence of pH on sorption of hydrophobic PAHs is very profound because it affects soil properties and constituents which are responsible for the sorption of these hydrophobic PAHs (An et al., 2010). Comparing the sorption at various pH ranges studied, it was observed that higher fluorene sorption occurred at lower pH. Sorption decreased continuously with an increase in pH. This trend was similar for all the soils studied irrespective of the soil properties, but the quantities of fluorene sorbed at any particular pH was directly proportional to such soil properties as the amount of soil organic matter. Zeledon-Toruno et al. (2007) have reported similar findings for adsorption of fluorene on immature coal; a sorbent which like the organic matter found in soils is composed of several aromatic compounds.

This observed fluorene sorption trend has been related to the sorption behavior of the hydrophobic functional groups of aliphatic and aromatic compounds as well as phenols in the organic matter of these soils (An et al., 2010; Zeledon-Toruno et al., 2007). At very acidic pH values, the polarity of the sorption surfaces was low due to protonation of the positively charged functional groups of the adsorption sites especially those associated with the soil organic matter components. This resulted in shrinking of these hydrophobic molecules, a typical occurrence for polymers at such pH in order to shield off water and other polar compounds from the hydrophobic terminals. Hence, these functional groups are less dissociated at lower pH values, and these neutral sorbent species have higher sorption capacities for fluorene via π–π interactions. Increase in pH led to reduced protonation of the charged surfaces and increased ionization; and hence, increase in the soil polarity and reduced hydrophobicity resulting in loss of the acquired affinity for hydrophobic compounds and the reduced fluorene sorption. The possibility of increased solubility of organic matter at alkaline pH regions (Munch

et al., 2002) reducing fluorene sorption due to complex formations was assumed to be remote in this study because no significant change in sorption was observed at alkaline pH.

3.2.3. Equilibrium sorption of fluorene

Equilibrium sorption studies provide information on the sorbate–sorptive relationship at equilibrium. Results of fluorene equilibrium sorption and desorption studies conducted at different fluorene concentrations and temperature (25 and 40 °C) are shown in Fig. 3 (Fig. SM2). These figures showed that fluorene sorption was concentration dependent and increased with an increase in concentration. Sorption will be concentration dependent for a hydrophobic organic hydrocarbon such as fluorene when its transport on the soil external surface film and internal pores are equal and, the trans-boundary movement of fluorene is insignificant. Thus, the only significant force driving the increase in fluorene sorption is concentration via increased π–π interactions leading to multilayer adsorption of fluorene molecules on the already adsorbed molecules. This result was also supported by the better (in comparison to the Langmuir isotherm model) fit of the sorption data to the Freundlich isotherm model: a model which suggests the possible multi-layer adsorptions as concentration increases (Teixeira et al., 2011; An et al., 2010; Olu-Owolabi et al., 2014).

The figures showed that increasing the solution temperature from 25 to 40 °C led to a significant decrease in the sorption of fluorene on these soils; implying that fluorene sorption on these soils was not favored by high temperature. However, for MA and MG soils, increasing the temperature increased the sorption of fluorene at low fluorene concentrations. This observation was attributed to the presence of montmorillonite and illite on both soils, respectively. Both soil minerals expanded with the increase in temperature creating more sorption surfaces for fluorene on both soils; and hence the observed increased sorption at higher temperatures. However, as concentration was increased and the pores of the expansive clays become saturated in MA and MG soils, fluorene sorption on these soils other external surfaces is reduced considerable relative to sorption at 25 °C. For the other soils without

Table 2
Kinetics model parameters for fluorene sorption.

| Kinetics model	Model parameters	Soil samples				
		AG	IB	MA	JB	PH
Pseudo-first-order	q_e (µg g^{-1})	0.36	0.84	0.28	0.63	0.41
	K_1 (g µg^{-1} min^{-1})	0.00[a]	0.00[a]	0.00[a]	0.00[a]	0.00[a]
	r^2	0.242	0.539	0.438	0.781	0.840
Pseudo-second-order	q_e (µg g^{-1})	1.22	1.09	0.59	0.88	1.26
	K_2 (g µg^{-1} min^{-1})	0.01	0.00[a]	0.04	0.00[a]	0.01
	r^2	0.996	0.944	0.996	0.981	0.999
Elovich	q_e (µg g^{-1})	1.10	0.89	0.57	0.64	1.15
	β	7.94	6.54	11.24	6.45	8.70
	r^2	0.847	0.745	0.874	0.938	0.959
Intra-particle diffusion	C (µg g^{-1})	0.68	0.21	0.29	0.10	0.77
	K_{id}	0.01	0.01	0.01	0.01	0.01
	r^2	0.754	0.867	0.605	0.887	0.829
Experimental	q_e (µg g^{-1})	1.19	1.17	0.61	0.83	1.25

[a] Values are less than 0.01.
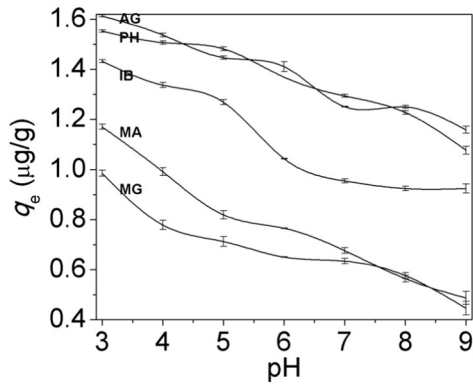
Fig. 2. Visual guide of the effect of pH on fluorene sorption (error bars indicate mean and standard deviation values of three replicates).

Table 3
Thermodynamic parameters for the sorption of fluorene at 25 and 40 °C.

Soil	ΔH^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1} K^{-1})	ΔG^o (kJ mol^{-1})	
			298 K	313 K
AG	28.22	0.13	−10.93	−12.90
IB	12.46	0.08	−10.26	−11.40
MA	−25.79	−0.04	−14.25	−13.67
PH	40.42	0.17	−9.01	−11.50
MG	−43.89	−0.10	−14.46	−12.98

expansive clays, fluorene sorption was always lower at the higher temperature − 40 °C. This result is in line with Site (2001) who stated that for most organics sorption usually decreases with increasing temperature. This trend was attributed to the increased solubility and mobility of fluorene induced by the increase in temperature (Haftka et al., 2010), and this can be explained as follows: increased solubility of fluorene at a higher temperature implied that the thin surface fluorene film on the soil surfaces (low C ($\mu g\,g^{-1}$) values) will re-dissolve in solution and acquire kinetic energy which will facilitate the migration of these molecules away from the sorption sites on soil surfaces; hence the reduction of sorption on these soils. Abdel Salam and Burk (2009) and Shu et al. (2010) have reported similar reductions in sorption of PAHs with an increase in temperature.

The sorption processes for most hydrophobic organic compounds are reversible, but often a "hysteresis" effect (delayed reversibility of the process) is observed (Site, 2001). Hysteretic desorption phenomenon is practically important because the low desorption corresponds

to a lowered chemical activity of the sorbed chemical, suggesting a reduced biological reactivity and decreased toxicity of the chemical (Huang et al., 2003). Hence, desorption studies on the sorbed fluorene on the soils were carried out immediately after the equilibrium experiments at both temperatures. Fig. 3 (unfilled symbols and broken lines) showed that the quantities of fluorene desorbed from these soils were dependent on the amount of fluorene sorbed-desorption was directly proportional to sorption. Hysteresis was observed for all soils; however, the degree was higher in soils with higher organic matter and lower in soils with low organic matter, i.e. the amount of fluorene desorbed from the soils with low organic matter contents was higher than for those with higher organic matter. This result implied a risk of fluorene being present in the soil water solution of these low organic matter soils, and subsequent contamination of the aquifer.

One major mechanism ascribed for the observed desorption hysteresis in the soils with higher organic matter content is the entrapment of fluorene within the pores of inorganic and organic matrices (Huang et al., 2003; Site, 2001). Fluorene entrapment within the pores of the inorganic aggregates was majorly implicated in the MA and MG soils with lower organic matter contents. The irreversible chemical binding of fluorene to humic acids of organic matter may also be implicated in the high hysteresis (Huang et al., 2003).
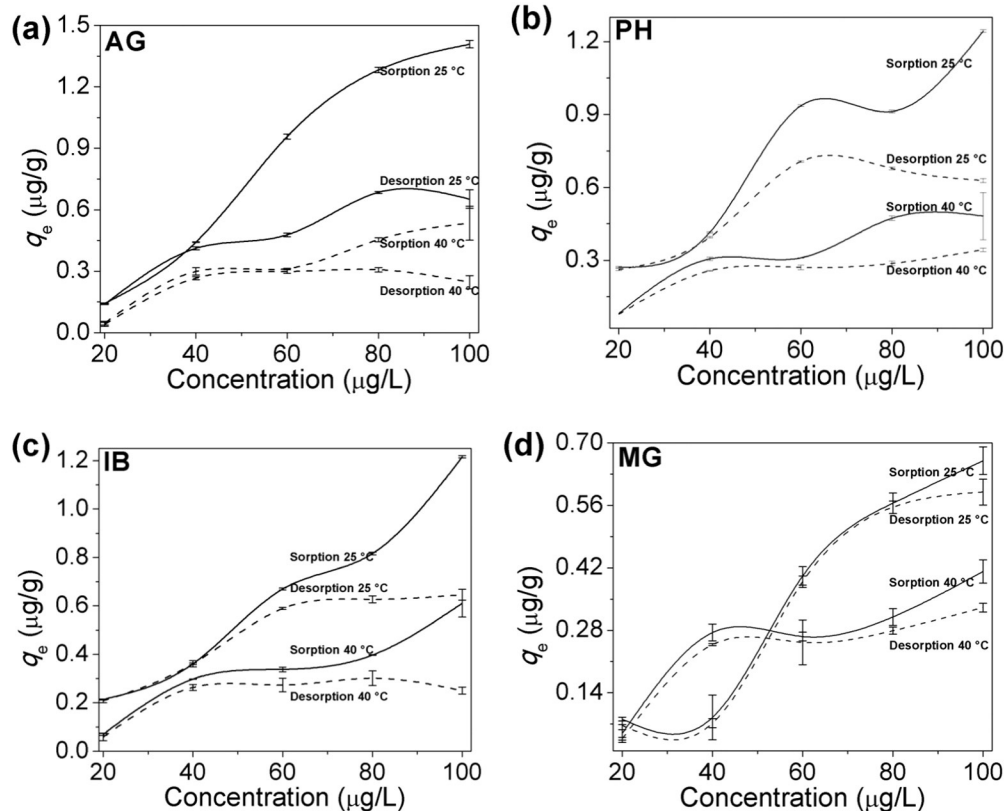

Fig. 3. Fluorene sorption and desorption trends (error bars indicate mean and standard deviation values of three replicates) for (a) AG, (b) PH, (c) IB, and (d) MG soils at 25 °C and at 40 °C.

3.2.4. Thermodynamics of fluorene sorption

The thermodynamic parameters; standard free energy ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) were calculated using equilibrium sorption data at the various temperatures (supporting material SM2). Parameters values (Table 3) were used in evaluating the feasibility and energetics of the fluorene sorption process. The $\Delta H°$ values showed that the sorption is endothermic (positive) except for MA and MG soils which showed exothermic (negative) values. The negative $\Delta H°$ values conform to the observed exothermic nature of fluorene sorption process on the MA and MG soils. For other soils, however, $\Delta H°$ was endothermic, requiring heat energy, though experimental results obtained from this study indicated otherwise. This might be explained as follows: theoretically, the input of energy will increase the sorption of fluorene by breaking the energy barrier (activation energy) required to be surpassed for sorption to occur, but in reality, input of heat energy increased the solubility and mobility of fluorene in solution. This increase in mobility (entropy) was reflected in the $\Delta S°$ values and it led ultimately to a decreased sorption of fluorene. These are typical examples of enthalpy-related sorption (Hamaker and Thompson, 1972; Site, 2001; Haftka et al., 2010). However, for the MA and MG soils, there were decreases in $\Delta S°$ as temperature increased because increase in temperature resulted in the swelling of expansive clay minerals in these soils leading to higher sorption of fluorene from solution especially at the lower fluorene concentration. This led to fewer fluorene molecules in solution and reduced randomness at the soil–solution interface as the sorption process proceeded towards equilibrium. Negative $\Delta G°$ values were observed for all studied soils at both temperatures indicating the feasibility and spontaneity of the sorption. The magnitudes of these thermodynamic parameters indicated that the energy of sorptive forces involved in fluorene removal from solution are of the type associated with the weak hydrophobic interactions such as the Van der Waal's forces and π–π interactions. Similar results have been reported (Olu-Owolabi et al., 2014; Haftka et al., 2010).

3.2.5. Sorption isotherm models

Data generated from equilibrium sorption studies of fluorene at 25 °C was fitted to the linear forms of the Langmuir (1916) and Freundlich (1906) adsorption isotherm models to ascertain which of these models described the sorption. The respective equations are shown in Eqs. (2) and (3).

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{2}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

where Q_o ($\mu g/g$) is the soil maximum adsorption capacity; q_e is the amount adsorbed at a particular time; b is the binding energy constant; C_e is the amount of sorptive left in the solution at equilibrium; K_f and n are Freundlich isotherm constants; and other parameters are as stated above.

The calculated values of the isotherm parameters for both models are shown in Table 4. The correlation coefficients (r^2) indicated that the Langmuir isotherm could not describe fluorene sorption on these

soils. This is reasonable because soils are very heterogeneous and fluorene sorption could not form a monolayer on the sorption sites as suggested by this model. The r^2 values also showed that the Freundlich isotherm, relatively, better fit the fluorene sorption data on these soils. The small n values of the Freundlich isotherm indicated the non-linearity of the isotherms and represented fluorene sorption on predominantly heterogeneous sorption sites (Olu-Owolabi et al., 2014; Weber et al., 1992). This is in line with the intra-particle diffusion model results (discussed above) which suggested that sorption was both surface adsorption and partitioning within soil pores.

Since none of these adsorption isotherm models could appropriately fit the data, it was assumed that the sorption was not a simple one obeying the simple isotherm models above. Thus, the Weber et al. (1992) distributed reactivity model (DRM) (Eq. (4)) which describes a more complex scenario was further used to evaluate the equilibrium sorption data. The individual effects of organic matter and the other minerals in each soil were considered in the final sorption isotherm (supporting material SM3), and the DRM was treated as a composite of the general linear isotherms and the non-linear isotherms in the soil (Olu-Owolabi et al., 2014; Weber et al., 1992).

$$q_e = x_i K_D C_e + \sum_{i=1}^{m} (x_{nl})_i K_{Fi} C_e^{ni} \tag{4}$$

where x_i is the summed mass fraction of solid phases exhibiting linear sorption, K_D, is the mass-averaged partition coefficients for the summed linear components, $(x_{nl})_i$ is the mass fraction of the i nonlinearly sorption component, K_{F_i} and C_e are the same as in the Freundlich adsorption isotherm. The results of the fittings of the equilibrium sorption data of fluorene to the DRM (Table 4) showed that the data best fit the DRM model with r^2 values in the range of 0.962–0.999. Hence, fluorene sorption on these soils is composed of several linear and non-linear isotherms. A similar result has been reported for pyrene sorption on soils (Olu-Owolabi et al., 2014).

4. Conclusion

The present study shows data for understanding the sorption and desorption fluorene on tropical soils from varying climes. Sorption and desorption of fluorene on soils depends on the soil's physicochemical characteristics. Fluorene sorption equilibria were attained usually within 24 h. Sorption mechanisms were controlled by both film and intra-particle diffusion. pH had reciprocal effect on fluorene sorption: the lower the value the higher the sorption, and vice versa. Fluorene sorption was concentration dependent and exothermic. The sorbed fluorene molecules were distributed between surface adsorption sites and phases in soil. Fluorene sorption was controlled by weak hydrophobic forces, such as the π–π interactions and Van der Waal's forces, which require low sorption energy. The desorption hysteresis was higher in soils with high organic matter contents than in those with lower ones. The sorption was characterized as multiple reaction phenomena composed of several linear and non-linear isotherms. The results of this study demonstrate that in predicting the fate and bioavailability of fluorene

Table 4
Fluorene sorption isotherm parameters for the Langmuir, Freundlich, and Distributed Reactivity Model (DRM).

soil	Langmuir sorption model			Freundlich sorption model				DRM	
	Q_o (mg/g)	b	r^2	q_e (mg/g)	n	K_f	r^2	$q_{T(l + nl)}$ (mg/g)	r^2
AG	12.20	0.002	0.000	1.00	0.69	0.10	0.063	1.41	0.998
IB	1.49	0.011	0.472	1.02	1.37	0.01	0.935	1.21	0.992
MA	0.19	0.014	0.631	0.42	2.25	0.00	0.911	0.66	0.999
PH	10.53	0.003	0.016	1.09	0.68	0.04	0.676	1.24	0.997
MG	0.32	0.010	0.347	0.72	1.73	0.00	0.789	0.52	0.962

$q_{T(l + nl)}$ (mg/g) — Total linear (l) and non-linear (nl) sorption.

in soil, the physicochemical conditions of the soils must be understood, and environmental contamination is more likely in warmer climes and in soils having low organic matter content.

Appendix A. Supplementary data

Supporting information available. Further information on SM1: Adsorption kinetics data treatment; SM2: Thermodynamics data treatment; SM3: Distributed Reactivity Models (DRM); Figure SM1: Elovich model plots; Figure SM2. Fluorene sorption (half-filled symbols) and desorption (empty symbols) for MA at 25 °C and at 40 °C; are available. Supplementary data associated with this article can be found, in the on-line version, at http://dx.doi.org/10.1016/j.geoderma.2014.10.012.

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