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Equilibrium adsorption modelling of selected crude oil components following a spill on Niger Delta soil

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ABSTRACT

When crude oil spills on land, it may leach into the soil and reach the groundwater thus posing a threat to drinking water resources. The Niger Delta region provides such an opportunity to study the migration of environmentally important constituents of crude oil in the soil using adsorption models. Soil properties were determined and data obtained from batch equilibrium experiments were applied to nine adsorption isotherms and the characteristic parameters were obtained from the isotherm models. The results show that the clay and organic matter content controlled the rates of infiltration of contaminants into underground water. The correlation values (R^2) for the isotherms models studied showed that the data from the selected compounds fitted differently to individual isotherms. Adsorption was not monolayer for all adsorbates and the experimental optimum sorption capacity was phenanthrene (100.01 mg g^{-1}), pyridine (33.23 mg g^{-1}), phenol (13.20 mg g^{-1}) and crude oil (10.20 mg g^{-1}). These results indicate that differences in oil residue components and soil property following spillage will determine the type of sorption processes taking place. The model discussed in the study may contribute to the knowledge of the sorption process for technically informed remediation strategy in the Niger Delta region of Nigeria.

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Introduction

The discovery of crude oil in Nigeria and the subsequent large-scale extraction has led to the spillage of petroleum hydrocarbon on land. The Niger Delta region is one of the worst regions destroyed by these spillages has lost other sources of water such as rivers and lakes [1,2]. When an oil spill occurs, factors such as soil pH, temperature, the supply of oxygen, nutrients, micro-organisms and weathering processes (volatilisation, photolysis and biodegradation) bring about structural changes in the spilt oil composition by changing properties, such as toxicity, water solubility and its adsorption onto soil surface [3,4]. However, contamination of groundwater by these organic contaminants may pose a threat to what is almost the only viable drinking water source in the region.

Naturally, nanomaterials (NM) that have adsorptive properties are produced in bulk by nature from events such as chemical and physical weathering of rocks, combustion,

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volcanic eruptions, bio-mineralisation, mineralisation and precipitation reactions. In particular, nanoparticles (NPs) that are naturally found in soils and geologic system includes haematite (α-Fe_2O_3) and magnetite (Fe_3O_4) [5]. These oxides have been used to remediate trichloroethylene from groundwater in the same way that triblock copolymers incorporated into the NP have been found to drive adsorption of the NP into the non-aqueous phase liquid–water (NAPL–water) interface [6]. In recent studies, due to their unique properties, clay material has been modified as nanoceramics with several applications that have impacted our daily lives. However, environmental concerns have been raised due to the difficulty in the degradation of some NPs [7]. This example shows how surface modifications of NPs can greatly alter their transport potential in environmental media. Therefore, natural clay present in soil may still be relevant in reducing contamination of groundwater following an oil spill.

Clay is an important part of the soil that belongs to a group of minerals collectively called alumino-silicates. They contain aluminium oxide and silicon dioxide as universal minerals [8] and have special properties ranging from catalytic, sorption, ion exchange, discolouring, filter aid to catalyst support [9] and have been applied widely in environmental studies due to their unique adsorption properties [10]. Kaolinite is the abundant type of clay mineral found in the Niger Delta region [11], formed from igneous acid diorites which are structurally different from alkaline intrusive magmatic turfs from which smectites are formed [12]. The structure and porous nature of the clay materials may allow for the conservation of the composition of the oil spill that allows for percolation of high loading deep into the adsorbent where they are protected from further weathering processes. Therefore, the transfer of these organic compounds to groundwater may be limited due to this process. Mass transfer of petroleum hydrocarbon in the soil is controlled by sorption processes. Thus, contaminants that adhere strongly to the soil may not degrade and remain in the soil for a long time [13–16]. Recent studies at a laboratory scale have simulated and focused on the adsorption of specific fractions such as asphaltenes which consist of a fused aromatic ring connected by aliphatic chains and possess various functional groups such as carboxylic acid, hydroxyl ethers, ketones, aldehyde, amine and amide of crude oil on mineral surfaces [17], single-component systems [18,19], the evaluation sorption of crude oil on clay minerals [20–22] and removal of dyes from solution [23,24]. A good number of papers have also reported the treatment of soil materials and modified mineral adsorbents for the removal of hydrocarbons, VOCs and PAHs from the environment [25–30].

Lee and Kim [25] partitioned naphthalene onto the surface of kaolinite and halloysite by the surfactant HDTMA. They obtained a linear adsorption process that could be described by a dependent on the arrangement of the surfactant cations distribution process. Bastani et al. [26] calcined diatomite to the improved surface area with increased sorption capacity. Functionalised modification using surfactants changes the character of mineral materials such as organoclays [27], activated carbon and bentonite [28] and Zeolites [29,30] surfaces from hydrophilic to hydrophobic, which usually increases the affinity of the sorbent for organic pollutants. This modification is expensive and presents toxicity-related problems because of the quaternary ammonium salts [31]. The goal was to understand the mechanism of interaction of contaminants or crude oil components with natural soil in the Niger Delta region. For instance, the organic carbon content in soil determines the degree of sorption of non-polar organic compounds in soil [32,33], while non-ionisable nitrogen, sulphur and oxygen compounds (NSOs) such as benzothiophene, non-specific interaction (namely van der Waals forces) appear to be dominant in the sorption to clay till [34]. Also, compounds such as pyridine, pyrrole carbazole, indole, benzene and thiophene show a certain polarity which indicates an additional interaction may be playing an important role. Since crude oil is a mixture of complex compounds, this study aims at determining the mechanism of the sorption of crude oil onto the soil in the Niger Delta region through the use of environmentally important constituent of crude oil (phenol, pyridine and phenanthrene) to elucidate the sorption mechanism.

Materials and methods

Sample collection

The soil samples selected for this study were collected from uncontaminated surface soil (0–30 cm) in Abudu, Edo State, Nigeria. Before sorption experiments, the soil samples were air-dried, crushed and sieved through a 230 mesh size sieve and the fine fractions retained for the study.

Physiochemical analysis

The physicochemical characteristics of the soil such as pH, cation exchange capacity, organic carbon and soil type were determined before adsorption studies. The pH of the soils (1:5 w/v) was determined using a digital pH meter in millipore ultra-pure water. The particle size distribution (PSD) of soil was determined using the wet sieving and sedimentation described by the British Standard [35]. Organic matter was determined by the Walkley and Black wet digestion method [36]. Bulk density was estimated by dividing the oven-dry mass of the soil by the volume of the soil as described by Grossman and Reinsch [37]. Metals (exchangeable and trace) in the soils were determined using Atomic Absorption Spectrophotometer (Buck Scientific, Model 210VCP) [38]. The crude oil was fractionated using silica gel column chromatography [39]. Fractions present in the oil residue were then eluted using 20 mL of hexane (Saturate), followed by 20 mL of 1:4 mixture of DCM:hexane (Aromatics) and then 30 mL of 50:50 mixture of chloroform: methanol (resin and polar fraction) using the principle of liquid/liquid extraction. The portion remaining in the column was labelled as the 'asphaltenes' fraction.

Compounds used for adsorption

Three organic molecules of different properties were selected for adsorption onto soil: pyridine, phenanthrene and phenol. The adsorbates were purchased from Sigma with purity ≥99.5% and hexane was used to prepare the solutions for the sorption studies to avoid the effect of water on the interaction with the clay surface since it is hydrophilic [40]. The principal properties of the studied adsorbates are described in Tables 1 and 2. These compounds were selected based on their environmental importance and presence in crude oil residue.

Table 1. Physiochemical properties of crude oil used in this study

Parameters	
Specific gravity at 25 °C	0.829
Viscosity (cps)	33
API °	39.18
Saturate (%)	62.97
Aromatic (%)	15.00
Polar (%)	19.20
Asphaltene (%)	2.83
Absorption maxima (nm)	226

Infrared spectroscopic analysis of soil

Infrared attenuated total reflectance (IR-ATR) measurements were done on the soil used for adsorption studies using a Bruker-Alpha FTIR Spectrophotometer (Bruker Optics GmbH Ettlinger, Germany) equipped with deuterated triglycine sulphate (DTGS) detector. The Alpha-p ATR accessory is equipped with a single-reflection diamond ATR hemisphere and a spring-loaded mechanical press for compacting solid samples at the ATR waveguide surface with uniform reproducible pressure. Data were recorded in the MIR spectral range from 400 to 4000 cm^{-1} at a spectral resolution of 2 cm^{-1}. Twenty-four scans were averaged for backgrounds and sample spectral, respectively. This was done at an ambient condition ($T = 24 \pm 1$ °C).

Sorption experiment

To obtain information about the capability of the soil to retain pollutants and to investigate the mechanisms of retention on surfaces, experiments using the soil samples collected from Abudu in Edo state, fresh crude and organic phase solute of the adsorbate compounds using a 100 mL conical flask as individual reactors in the so-called shake-flask was performed. In this measurement, each point on the adsorption isotherm is determined in an individual tube by equilibrating a given solution of the solute with a given quantity of sorbent. 5.0 g of soil and 50 mL of a hexane solution of phenol, phenanthrene, pyridine and crude oil with initial concentrations ranging from 20 to 500 mg L^{-1} was placed in each flask. The flask was then placed in a dark chamber to avoid exposure to light and prevent photo-oxidation and allowed to sit at 25 °C for 7 days. Controls containing only soil and hexane were run alongside the isotherm tubes to determine where any significant loss of hexane (generally, the % loss of hexane should be $<2\%$). The sealed flask was periodically shaken for a time to allow solution/sorbate equilibration. After the required time had elapsed, the supernatant solution was centrifuged for 10 min at 4000 rpm to exclude any soil particle. The supernatant was immediately withdrawn from each tube after centrifugation and the solute concentration in the hexane solution

Table 2. Physiochemical properties of probe compounds used as adsorbates for this study

Compound	Pyridine	Phenanthrene	Phenol
Molecular formula	C_5H_5N	$C_{14}H_{10}$	C_6H_6O
Molecular weight (g mol^{-1})	79.10	178.23	94.11
Density (g cm^{-3})	0.9819	1.18	1.07
Solubility in water (mg L^{-1})	Miscible	1.29	830
Absorption maxima (nm)	250	330	274

was analysed using UV-Visible spectrophotometer [41]. The absorbance at different soil-solution contact times was measured for each tube at the corresponding wavelengths (190–500 nm) of the adsorbate compounds and crude oil.

To provide evidence for a possible correlation between the amount retained and the total stoichiometric concentration of the adsorbate, the amount of substance adsorbed (q_e) by 5.0 g of the soil in batch equilibrium was calculated according to the below equation

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where C_0 is the concentration (mg L^{-1}) of the analyte before sorption and C_e is the equilibrium concentration (mg L^{-1}), V is the total volume of solution (mL) and m is the mass (g) of the soil [42].

A well-established method for determining concentrations of compounds based on Beer's law calibration plots was applied following a UV-Visible spectrophotometric analysis (Shimadzu, 2600). The wavelength resolution and bandwidth were 2 and 1 nm, respectively. The maximum absorption wavelength was determined by scanning the solutions of each adsorbate of a concentration of 25 mg L^{-1}, then the calibration plot (20–500 mg L^{-1}) was constructed. The linearisation of this plot gave a determination coefficient $>$99.8%.

Adsorption isotherms

An isotherm describes the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbent's surface at a given condition. It gives the most appropriate equilibrium correlation [43]. Isotherms are also important for comparing sorption performance, optimisation, design and prediction purposes [44]. The sorption of the organic compound on soil was determined by analysing equilibrium curve of the following eight (8) isotherm models listed in Table 3.

Table 3. Adsorption isotherm and model equations

Isotherm	Linear form of isotherm	Characteristic parameters
Henry's	$q_e = K_{HE} C_e$ (2)	K_{HE} = Henrys adsorption constant
Freundlich	$\log q_e = \frac{1}{n} \log C_e + \log K_f$ (3)	K_f = adsorption capacity $(mg/g)(L/mg)^{1/n}$ $\frac{1}{n}$ = adsorption intensity
Langmuir	$\frac{C_e}{q_e} = \frac{b}{q_m} C_e + \frac{1}{q_m}$ (4)	q_m = maximum adsorbate uptake b = Langmuir equilibrium constant (L/mg)
Temkin	$q_e = B \ln C_e + A \ln A_T$ (5)	A_T = equilibrium binding constant(L/mg) $b_T = \frac{RT}{B}$ = adsorption energy (kJ/mol)
Dubinin–Radushkevich	$\ln q_e = \ln q_D - B_D \varepsilon^2$ (6)	B_D = constant related to the adsorption $(mol^2 kJ^{-2})$energy q_D = adsorption capacity (mg/g)
Jovanovich	$\ln q_e = \ln q_{max} - K_j C_e$ (7)	K_j = Jovanovich equilibrium constant (L/mg) q_{max} = maximum adsorbate uptake (mg/g)
Halsey	$\ln q_{e=}[(\frac{1}{n_H}) \ln (K_H)] - \left(\frac{1}{n_H}\right) \ln (\frac{1}{C_e})$	K_H and n_H are Halsey isotherm constant
Harkins-Jura	$\frac{1}{q_e^2} = [\frac{B_{HJ}}{A_{HJ}}] - [\frac{1}{A_{HJ}}] \log C_e$ (9)	A_{HJ} and B_{HJ} are Harkin-Jura constants

Results and discussion

Properties of crude oil and model compounds

The crude oil and soil samples used for this study were from the Niger Delta region of Nigeria. The nature of the crude oil was characterised based on the physicochemical properties [45]. The results of this characterisation of the fresh crude oil are presented in Table 1 while Table 2 shows the physicochemical properties of the model compounds. These model probe adsorbates are known as part of the components compounds from crude oil degradation [33].

Properties of soil and FTIR result

The mineralogical composition of the soil is sand (quartz) and clay (kaolinite and illite). Properties of the soil are: pH 5.7; organic matter 6.5%; bulk density 1.67; Na^+ 4.3 mg L^{-1}; $Ca^{2+} < 0.01$ mg L^{-1}; Fe^{3+}, 2.3 g kg^{-1}; Mg^{2+} 0.23 mg L^{-1}, sand 48%; Silt 10%; Clay 42% and CEC 19.3 meq/100 g. The soil is moderately acidic and organic matter content of 6.5% reveals its hydrophobic nature because of the rich deposit of biota remains from these forest regions. Organic matter can form bonds with the sorbed substances meaning that high organic matter will influence the rate or volume of substances adsorbed [46]. Hence, this sorption trend may be attributed to the polarity of soil organic matter [47–49]. Upon spillage on soil, crude oil increases the bulk density of the soil by blocking the pore spaces of the pollutant [50]. This blockage may not be the sample for single-component systems and thus adsorption will be controlled by the size of molecules. FTIR technique has been applied to the identification of various types of clay minerals [51,52]. It offers the advantage of differentiating between the crystallinity and non-crystallinity of both the organic and inorganic components of the soil. The soil sample is characterised by high clay content (42%). Clay minerals are arguably the most important property that influences the fate of organic pollutants in soil.

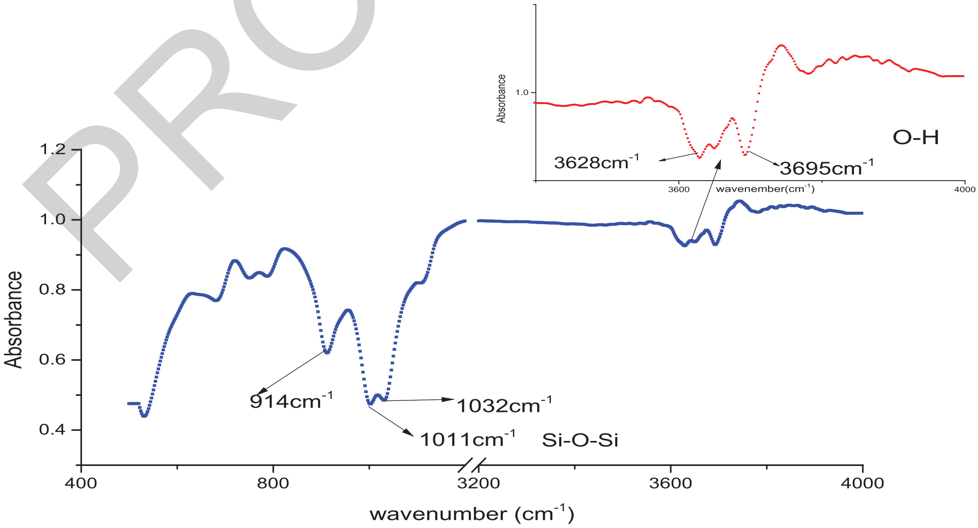

Figure 1 . FTIR identification of clay minerals in the soil.

Figure 1 shows that the clay is kaolinite with absorption bands at the –OH stretching region (inset Figure 1). Kaolinite has the chemical composition $Al_2Si_2O_5(OH)_4$ with an inner hydroxyl group (3620 cm^{-1}) lying between the tetrahedral and octahedral sheet [53]. The other two absorption bands at 3601 and 3653 cm^{-1} are assigned to the out-of-plane bending vibrations of the other –OH group in the octahedral surface of the layer [51]. The –OH groups form a weak hydrogen bond with the oxygen of the Si–O–Si bonds on the lower surface of the next layer. The appearance of bands at 1011, 914 and 535 cm^{-1} (Figure 1) suggests the presence of well-ordered kaolinite [51]. Thus, these surfaces which contain cation exchange capacity (CEC) or dissociated ion provide hydrophilic sites in addition to the hydrophobic sites provided by organic matter in the soil so that non-polar, polar and polarisable solutes present in the crude oil can interact with the soil.

It is necessary to understand the flow of crude oil in soil following a spill. This is essential as it helps to provide technically sound management decision concerning oil spill site characterisation and remediation. The adsorption of various concentrations of model compounds that represents acidic, basic and neutral components of the oil residue, with associated toxicity threat when leached to groundwater, were used.

Modelling of adsorption isotherm

Adsorption isotherms of the model compounds and crude oil by the soil are shown in Figure 2(a)–(g). All models were fitted linearly with fitting parameters listed in Table 4.

Henry's isotherm

The Henry's isotherm (equation (2)) applies to conditions where the contamination of the adsorption site is low, the concentration of the contaminants does not change rapidly with time and that all adsorbate molecules are secluded from their nearest neighbours [54]. This model was selected to show how K_{HE} would vary with different adsorbates on the same soil. The values obtained for K_{HE} (Table 4) for the four adsorbates decreased in the following order: phenol > pyridine > crude oil > phenanthrene and reflect the ability of the soil to sorb compounds differently. This observation is consistent with the work done by Zhang et al. [55]. Pyridine and crude oil showed a better linear adsorption plot (Figure 2(a)) than other adsorbed compounds up to a concentration of 200 mg L^{-1} for all adsorbate except at concentrations above 300 mg L^{-1}. The K_{HE} values obtained are consistent with the results of Lee and Kim [25] and indicates that the reactivity of the compounds with the active sites of the soil makes the process reversible. The plot fitting correlation coefficient was observed in the following order: for crude oil (0.9913), phenol (0.9619), pyridine (0.8850) and phenanthrene (0.9373). It is interesting to note that the non-linear curve fitting (not shown) for the crude oil adsorption shows a possible sigmoidal plot with points of inflexion. This curve shows that there are at least two opposite mechanisms where the non-polar components of the crude oil have a low affinity for the clay content of soil but as soon as the surface is covered by these compounds, other organic molecules are easily adsorbed [56].

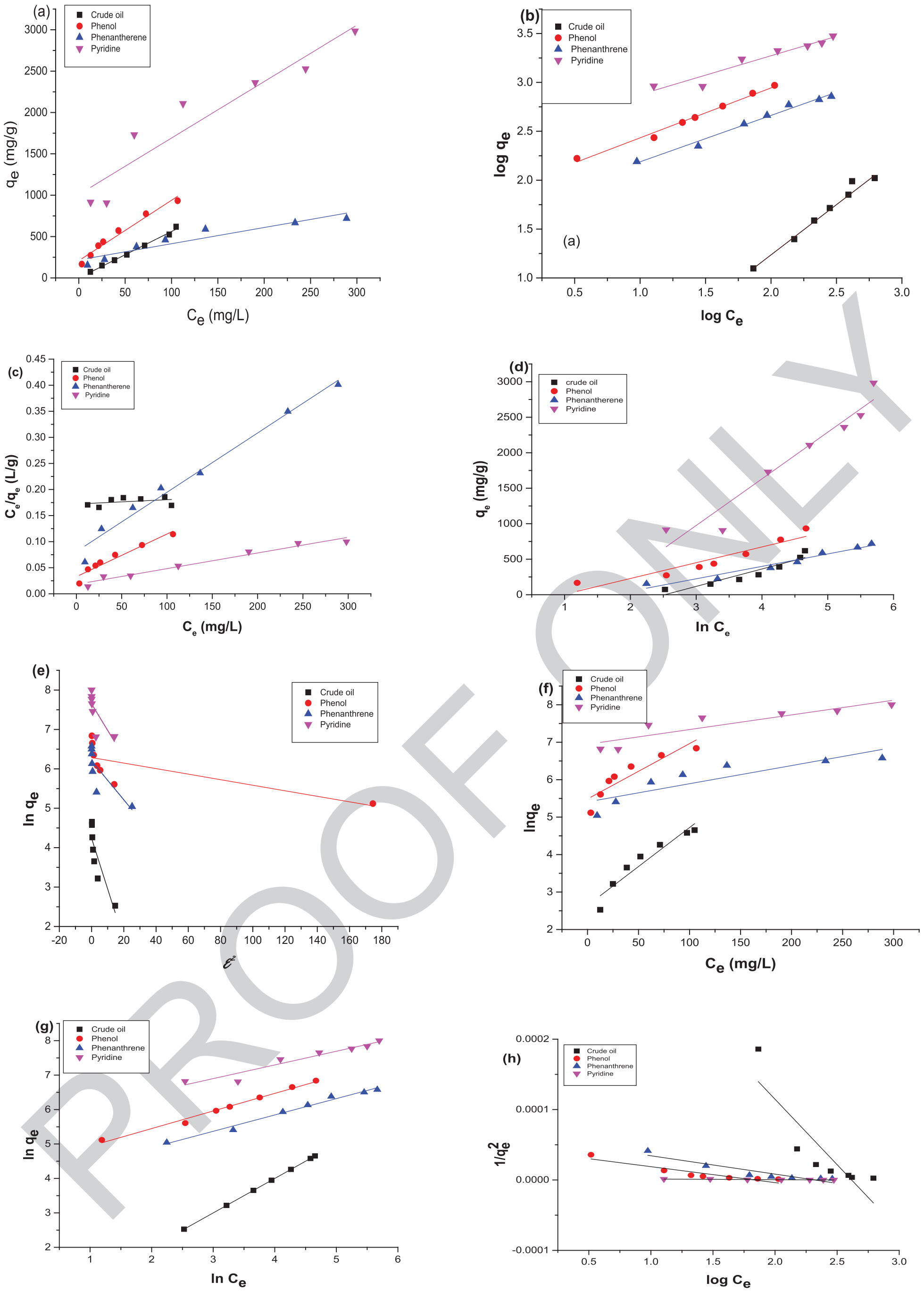

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Figure 2. Linear fitting of (a) Henry, (b) Freundlich, (c) Langmuir, (d) Dubinin–Radushkevich, (e) Temkin, (f) Jovanovich, (g) Halsey and (h) Harkin–Jura isotherm models for the four adsorbates (Crude oil, phenol, phenanthrene and pyridine).

Table 4. Isotherm parameters for the adsorption of model compounds and crude oil on soil

	Crude oil	Phenol	Phenanthrene	Pyridine
Henry's isotherm				
K_{HE}	5.62	7.29	1.95	6.82
R^2	0.9913	0.9619	0.8770	0.8850
Freundlich				
k_f(mg/g)(L/mg)$^{1/n}$	6.57	98.17	51.64	300.60
n	0.97	1.96	2.10	2.51
R^2	0.9960	0.9860	0.9810	0.9640
Langmuir				
q_m (mg/g)	10.20	13.20	100.12	33.23
b (L/mg)	1.422	0.280	0.001	0.054
R_L	0.001–0.01	0.01–0.15	0.96–0.99	0.03–0.48
R^2	0.6430	0.9180	0.9778	0.9610
Temkin				
A_T (L/mg)	0.080	0.378	0.179	0.219
b_T (kJ/mol)	10.105	11.149	14.145	3.769
R^2	0.8725	0.8746	0.9475	0.9234
Dubinin–Radushkevich				
q_D (mg/g)	19.26	73.53	45.11	209.20
B_D (mol^{2}kJ^{-2})	0.128	0.007	0.0495	0.0674
E(kJ/mol)	1.97	8.45	3.17	2.72
R^2	0.7201	0.4932	0.5555	0.4418
Jovanovich				
q_{max} (mg/g)	14.02	41.04	22.96	104.02
K_J	0.02	0.014	0.004	0.003
R^2	0.8999	0.7970	0.7271	0.7710
Halsey				
n_H	1.000	1.960	2.109	2.518
K_H	1.000	5886.355	4116.608	1750330.000
R^2	1.0000	0.9860	0.9810	0.9160
Harkins–Jura				
A_H	−0.537	−0.442	−0.383	−0.112
B_H	2.616	1.835	2.318	0.248
R^2	0.7194	0.8345	0.8508	0.8099

Freundlich isotherm

The Freundlich isotherm is generally applied to estimate the sorption intensity of the sorbent towards the sorbate [21] and the model assumes that adsorption occurs on a heterogeneous adsorbent surface (i.e. multilayer adsorption) [57]. The experimental data were treated using the linearised equation (3). The values of n and K_f are presented in Table 4, while Figure 2(b) shows the plot of the linearised Freundlich isotherm. Previous studies have shown that values of n between 1 and 10 indicate favourable sorption. The values of n were 2.51, 2.10, 1.96 and 0.97 for pyridine, phenanthrene, phenol and crude oil, respectively. This shows that the adsorption is favourable and compound-specific. Also, high organic matter content (6.5%) and higher values of n show that the adsorption is on a heterogeneous surface [55]. The K_f value (Table 4) was high for pyridine (300.60 mg g^{-1}) and moderately for phenol (98.17 mg g^{-1}), phenanthrene (51.64 mg g^{-1}) and crude oil (6.57 mg g^{-1}). This trend may be based on the sorption capacity for which light and low molecular weight organic materials tend to adsorb more on the available micropores structure of the soil [58]. Calvet [59] have also suggested that due to the different adsorption energies of sites in soil, for non-ionic compounds such as the type used in this study, the monolayer coverage will not be a constraint since it is not likely to occur due to low solute water solubilities. This is also supported by the FTIR result

(Figure 1) that shows the presence of heterogeneous groups on the soil surface. These groups are all good binding sites for compounds that contain heteroatoms. This shows that leaching of polar compounds in aged oil residue into underground water can be attenuated. The Freundlich model was considered as the most appropriate for describing the observed sorption trends. Similar results were also obtained by Clark-Ehlers *et al*. [19] on the influence of the nature of soil organic matter on the sorption behaviour of pentadecane.

Langmuir isotherm

Although initially developed for gases, this isotherm has been extensively applied for the sorption process in the liquid phase [60,61]. The model assumes that all adsorption sites are similar and do not affect each other. However, adsorbent such as soil has non-uniform surface, thus yielding heterogeneous adsorption site. Sokker et al. [62] suggested that sorption mechanisms involve three routes; the diffusion of sorbate into the surface of sorbent; the diffusion into the pores of the sorbent and the sorption of the sorbate into the internal surface of the sorbent. The kinetics of this process has shown that the initial stages of the sorption process are affected by the concentration of sorbent and contact time with the first step as the rate-determining step [63]. The values of q_m and b were obtained from the slopes and intercepts of equation (4), as plotted in Figure 2 (c), while Table 4 shows the Langmuir isotherm parameters. The values of q_m were highest for phenanthrene (100.01 mg g^{-1}), pyridine (33.23 mg g^{-1}) and crude oil (10.20 mg g^{-1}) in that order. The R^2 values of the Langmuir Isotherm are in the order: phenanthrene > pyridine > phenol > > crude oil and are lower than the Freundlich R^2 values for all adsorbates indicating that the manner of sorption is not monolayer. The constant b expresses the affinity between the sorbent and the sorbate [64]. The low values of b obtained suggest that the soil used for this study has a high affinity for low molecular weight organic molecules such as pyridine and phenol than large molecules such as PAHs and asphaltenes found in the crude oil. However, other studies have shown that a modification of the clay content in soil can enhance the adsorption of large molecules [21]. The separation factor, R_L, which is considered as a more reliable indicator of the adsorption is defined by the below equation

$$R_L = \frac{1}{1 + bC_0} \tag{10}$$

where b (L mg^{-1}) is the Langmuir constant and C_0 (mg L^{-1}) is the initial concentration of the solute. For favourable adsorption, $0 < R_L < 1$, while $R_L > 1$, $R_L = 1$ and $R_L > 0$, respectively, describing unfavourable, linear and irreversible adsorption [65]. The R_L obtained was between 0 and 1 which indicated favourable adsorption of the compounds onto the soil.

The Temkin isotherm

The Temkin isotherm is based on the following assumptions: (1) The heat of adsorption of the adsorbates on the layer decreases linearly rather than logarithmically with coverage due to adsorbent–adsorbate interactions. (2) Adsorption is characterised by a uniform distribution of the binding energies up to some maximum binding energy [66,67]. A correlation R^2 value (Table 4) is $<$90% for crude oil and phenol and $>$90% for pyridine and phenanthrene was obtained. However, the b_T (adsorption energy (kJ mol^{-1})) values were $<$14 kJ mol^{-1} and indicate a physisorption mechanism.

The Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich model was initially formulated for adsorption onto pore spaces of sorbate. Generally, it is now applied for adsorption processes that have occurred onto both homogeneous and heterogeneous surfaces [68]. The linear expression of the Dubinin–Radushkevich isotherm model is given in equation (6) [69]. The higher the values of q_D, the higher the sorption capacity of sorbents [21,70]. The q_D values were in the order: pyridine (209.12) $>$ phenol (57.53) $>$ phenanthrene (45.11) $>$ crude oil (19.26) (Table 4). As the mean free energy expresses the energy for taking out a molecule from its location in the sorption space to the infinity, the model was usually useful to distinguish the physical and chemical adsorption of sorbates with its mean free energy, E, per molecule of adsorbate computed by the below equation [71]:

$$E = \frac{1}{\sqrt{2B_D}} \tag{11}$$

It can be seen from Table 4 that the values obtained for E are within the range of 1.97–8.45 kJ/mol. These results indicate that physisorption is the major sorption processes between the soil and the sorbate under study [72]. Figure 2(e) shows the DR linear plot. Based on the R^2 values, the DR isotherm fitted best for the sorbate in the order: pyridine $>$ phenol $>$ phenanthrene $>$ crude oil and were found in the range of 0.441–0.720, which were lower than all other isotherms.

The Jovanovic isotherm

Jovanovic [73] assumptions for adsorption on surfaces are the same as that made by Langmuir (i.e. monolayer adsorption of mobile hard discs) except that allowance is made in the former for the surface binding vibrations of an adsorbed species. The results show the Jovanovic model gave R^2 values (Table 4) less than that obtained from the Langmuir plot for all compounds under study. This means that the Jovanovic equation could not satisfactorily explain the sorption of the compound onto the soil.

The Halsey isotherm

This model is suitable for multilayer adsorption on a heterogeneous surface [74]. With R^2 values $>$ 98%, the Halsey isotherm results confirm the heterogeneous nature of the soil and the possibility of multilayer adsorption of model compounds and crude oil on its surface. The heterogeneous distribution of activated sites for soil is indicated by the presence of different groups such as O–H, Si–O, Si–O–Al revealed by FTIR analysis (Figure 1) as well as the quantity of organic matter in the soil.

The Harkin–Jura isotherm

This model assumes the possibility of multilayer adsorption on the surface of adsorbents having heterogeneous pore distribution [75]. Results of this model are shown in Table 4 with R^2 values $> 90\%$ confirming the heteroporosity nature of the soil surface and the possibility of multilayer adsorption of sorbates on its surface.

Per cent initial adsorption

Figure 3 shows the plot of the percentage change in the number of sorbates adsorbed with initial concentration. It was observed from the plot that pyridine and phenol had initial high adsorption rates. These model compounds are polar and as such will interact well with the soil [76]. For crude oil, there was an initial decrease in sorption percentage until a minimum and then an increase in the amount of crude oil adsorbed increases with increasing concentration of sorbate.

The sorption percentage for crude oil was found to decrease as the oil concentration in hexane increases. The more sorption at lower concentrations may be described by the presence of more available sites on the heterogeneous soil [77]. At higher concentrations, the adsorbate molecules tend to form the aggregates due to the presence of asphaltenes making the sorption process more difficult by size exclusion [78]. As this concentration increases, the viscosity of the resultant solution makes the crude oil penetration hard within the interlayer spaces of the clay material and pores of the soil. Thus, less oil is released after saturation of the sorbent [79,80]. Consequently, crude oil is adsorbed more on the same amount of soil. The accessibility of the surface by pyridine was limited following an initial saturation of the soil particle surface at 300 mg L^{-1} that led to the formation of a multilayer coverage. This agrees with the Freundlich plot for pyridine obtained in our results. The low sorption percentage of phenanthrene maybe because of the differences in the mechanism of sorption on the soil type; hence, the multilayer model is not a good model to describe sorption of phenanthrene (and all other fused aromatics), but it is more useful for oil components containing heteroatoms such as pyridine and phenol.

By comparing the values of R^2 of the examined isotherm models, it can be concluded that the Freundlich, Halsey, Langmuir and Temkin isotherm models gave better fitting than the DR, Jovanovic and Harkins–Jura isotherm models. The adsorption could have firstly occurred in a monolayer followed by a multilayer [78]. Weber et al. [81] pointed

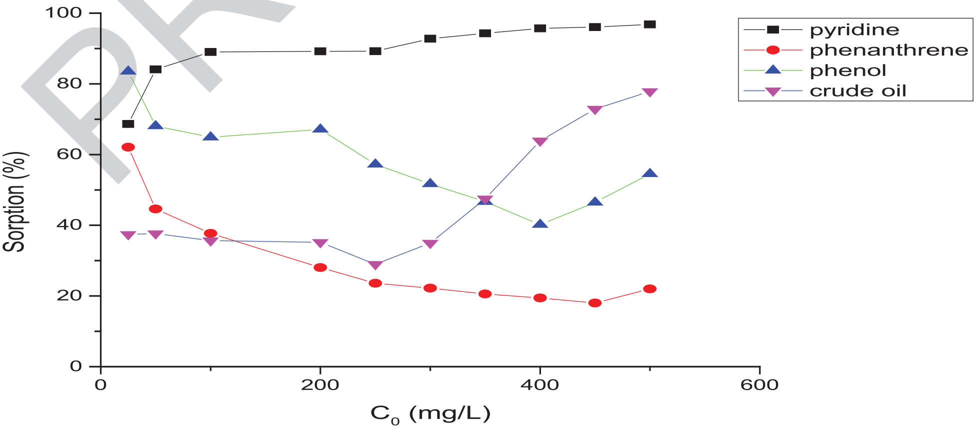

Figure 3. Per cent sorption versus C_o (mg L^{-1}) for, pyridine, phenol, phenanthrene and crude oil.

out that sorption capacities varied widely among soil, so we believe that differences in the chemical nature of compound will account for the observed differences in sorption of compounds onto the soil. Lastly, the changes in the composition of the oil spill following subsequent degradation as well as the properties of soil such as organic matter will determine the sorption migration of crude oil into the soil.

Conclusion

The sorption results for the model compounds and crude oil on the soil provided evidence for understanding how the different fractions of oil residue and compounds formed due to ageing will interact individually with the soil. Different isotherms were used to explain the nature of processes responsible for the compounds. The high % clay and organic matter content of the soil influenced the adsorption process and ultimately the rate of infiltration into underground water. The data fitted best with the Freundlich isotherm having the highest regression value with experimental optimum sorption capacity in the order for phenanthrene (100.01 mg g^{-1}), pyridine (33.23 mg g^{-1}), phenol (13.20 mg g^{-1}) and crude oil (10.20 mg g^{-1}) obtained from the Langmuir isotherm. Structural changes in oil residue in the overtime and soil characteristics influence adsorption to surfaces after a spill. The model discussed in this work may contribute to the knowledge of the sorption and eventual remediation of oil residue in the Niger Delta region of Nigeria.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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