

Diffusion and Adsorption Characteristics of Crude Oil-Contaminated Silty Clay Soil Stabilised with Freshwater Limpet Shell Ash and Cement Combination

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ABSTRACT

The diffusion of Total Petroleum Hydrocarbon (TPH) pollutants to groundwater at crude oil-contaminated sites in Nigeria's Niger Delta is a problem that severely affects drinking water. But the inclusion of cementitious materials will reduce the diffusion rate to groundwater. This study analyses the Effective Diffusion Coefficient (EDC)/Tortuosity Factor (TF) and Retardation Factor (Rd) of Crude Oil-Contaminated Soils (COCS) stabilised with Freshwater limpet shell ash and cement combination (FWLSA-C). Uncontaminated soils were sampled at a depth of 1.0 m and mixed with 0, 2, 5, 10, 15 and 20% of crude oil by weight to produce artificially contaminated soils. Freshwater limpet shells were sourced from the Esaman River, Delta State, calcined to ash at 887°C for four hours and ground to powder. The ash oxide content was determined with X-ray fluorescence. The soil samples were mixed with different amounts of cement and ash. The combinations were: 0% cement and 0% ash, 5% cement with 2% ash, 5% cement with 3% ash, 5% cement with 5% ash, 5% cement with 10% ash, 5% cement with 15% ash, and 5% cement with 20% ash. The EDC/TF and Rd were determined using standard methods. The EDC/TF and Rd for 0% COCS without FWLSA-C were 0.00 m²/s/0.00 and 0.00; 20% COCS without FWLSA-C were 2.06E-10 m²/s/7.09E-02 and 11.64; and the average of 9.31E-11 m²/s/6.92E-02 and 28.49 by adding the FWLSA-C. The FWLSA-C reduced the EDC/TF from 2.06E-10 to 3.50E-11 m²/s/7.09E-02 to 6.66E-02 and increased Rd from 11.64 to 40.16, respectively. Therefore, this study revealed that freshwater limpet shell ash and cement combination (FWLSA-C) will slow the diffusion rate of Total Petroleum Hydrocarbon (TPH) contaminants to groundwater in crude oil-contaminated sites within the Niger Delta in Nigeria.

Key Words: Crude Oil-Contaminated Soils (COCS), Effective Diffusion Coefficient (EDC), Retardation Factor (Rd), Tortuosity Factor (TF)

INTRODUCTION

The release and movement of pollutants, such as crude oil spills, chemicals, pesticides, and nutrients, from industrial and other sources are detrimental to the economy and significantly threaten the quality of surface water and, ultimately, groundwater (Ewim *et al.*, 2023; Ramakrishna *et al.*, 2011). There are many physical, chemical, and biological processes that control how contaminants move through porous media. The physical processes include diffusion, advection, and dispersion, whereas the chemical processes often entail sorption, dissolution, precipitation, complexation, hydrolysis/substitution, and oxidation (Talabi and Kayode, 2019; Oluremi *et al.*, 2016; Wojnarowicz *et al.*, 1998; Shackelford and Daniel, 1991a). Numerous populations in developing nations, like Nigeria, depend on surface and groundwater as their principal source of potable water, which faces various risks to its quality (Ewim *et al.*, 2023; Bello and Osinubi, 2010). Field studies have demonstrated that diffusion governs

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contaminant transport in numerous fine-grained soils. While assessing hydraulic conductivity in fine-grained soils is a standard practice among geotechnical engineers, measuring diffusion coefficients is not (Shackelford and Daniel, 1991a; Wojnarowicz *et al.*, 1998). Groundwater contaminants are influenced not only by physical transport processes and physico-chemical phenomena within the aqueous phase but also significantly by reactions at the interfaces between groundwater and other phases. The interactions that result in interphase partitioning or the binding and release of contaminants to these interfaces are referred to as sorption reactions (Weber *et al.*, 1991; Larson and Weber, 2018). Sorption is a method used to remove contaminants from contaminated solutions or groundwater (Oluremi *et al.*, 2016). Sorption isotherms are favoured in groundwater literature for modelling and predicting the interaction between groundwater pollutants and the porous matrix (Weber *et al.*, 1991). Clayey soil has a high retention capacity because it can adsorb substances, which makes it difficult for pollutants to move through the soil (Jaime *et al.*, 2012; Hong *et al.*, 2009; Shackelford and Daniel, 1991b). Cementitious materials adsorb pollutants in contaminated soils and mitigate the adverse impact of contaminant leachate on groundwater by adsorbing to the soil matrix and inhibiting its conductivity through diffusion (Oluwatuyi *et al.*, 2019; Ojuri and Epe, 2016). This study aims to analyse the Effective Diffusion Coefficient (EDC), Tortuosity Factor (TF), and Retardation Factor (Rd) of crude oil-contaminated silty clay soil stabilised with a combination of Freshwater Limpet Shell Ash and cement (FWLSA-C).

MATERIALS AND METHOD

Materials

Silty Clay Soil/Site Description

Uncontaminated soil was sampled at a depth of 1.0 m, close to a flow station owned by Nigeria Petroleum Development Company (NPDC)/Heritage Company/Shore Line OML 30, in the Afiesere community in Ughelli North LGA, Delta State, Nigeria. Afiesere is situated at the coordinates 5°32'36.02" N and 6°01'13.41" E, with an elevation ranging from 12 to 17 meters.

Contaminant

The crude oil was obtained from the flow station operated by the Nigeria Petroleum Development Company (NPDC)/Heritage Company/Shore Line OML 30 in the Afiesere community in Ughelli North LGA, Delta State, Nigeria.

Freshwater Limpet Shell Ash and Cement

Freshwater limpet shells were sourced from the Esaman River, Delta State. The shells were then burnt in the open air to remove the dark brown layer, before they were calcined in an electric furnace at a temperature of 887°C for four hours. The shells were ground to powder and sieved with a 75-micron sieve (Abdelmalik and Sadiq, 2021; Adekunle *et al.*, 2015). The ash oxide content was determined with X-ray fluorescence. Portland cement was also made available.

Methods

Basic Characterisation Test

The uncontaminated soil was analysed to ascertain its index properties and classification. The tests performed encompassed moisture content, sieve analysis, specific gravity and atterberg limits (BSI, 1990). Furthermore, the elemental composition of the soil was examined using the Epsilon 3X XRF Spectrometer. The chemical makeup of Portland cement (PC) and freshwater limpet shell ash (FWLSA) was examined using a Bruker S4 Pioneer XRF spectrometer. The physical and chemical characteristics of the crude oil were evaluated following the ASTM standards from 2012. Viscosity measurements followed the (ASTM,

2006). The acid and sulfur contents were determined using the (ASTM, 2013), and water content was measured by the (ASTM, 2012).

Sample Preparation

The uncontaminated samples were mixed with 0, 2, 5, 10, 15 and 20% of crude oil by weight to produce artificially contaminated soils (Khomehchiyan *et al.*, 2006). The artificially contaminated soils were mixed with FWLSA-C in the following weight percentages: 0% cement and 0% FWLSA, 5% cement with 2% FWLSA, 5% cement with 3% FWLSA, 5% cement with 5% FWLSA, 5% cement with 10% FWLSA, 5% cement with 15% FWLSA, and 5% cement with 20% FWLSA.

Batch Equilibrium Adsorption Tests (BEATS)

The method described by Shackelford and Daniel (1991b) was utilised for the experiment. A mixture of silty clay soil-FWLSA-C and crude oil was prepared in a 1:4 ratio, involving 50 grams of the clay soil-FWLSA-C and 200 grams (or 200 cm³) of a crude oil solution with a known initial concentration, all contained within a 500 ml sealed plastic container. These mixtures were then placed on a table shaker (HS 500 Janke and Kunker, Ika-Werk) operating at a speed of 30 oscillations per minute. The shaking process continued for 48 hours, after which the supernatant was collected by decanting and filtering it into a plastic container. The crude oil concentrations were measured using gas chromatography (GC). The results from the initial analysis were presented as adsorption isotherms, illustrating the relationship between the sorbed concentration (C_s) and the dissolved equilibrium concentration (C) of the solute for each tested concentration. The amount of solute adsorbed per unit mass of solid soil was calculated using equation 1 (Oluremi *et al.*, 2016; Bello and Osinubi, 2010; Shackelford and Daniel, 1991b).

$$C_s = \frac{(C_o - C)V}{M_s} \tag{1}$$

Where,

- C_s = Adsorbed concentration (µg/g);
- C_o = Initial concentration of solute (mg/g);
- C = Equilibrium concentration of the solute (mg/g);
- V = Volume of solution (cm³); and
- M_s = Mass of the dry soil (g).

The gradient of the adsorption isotherm, which illustrates the connection between the sorbed concentration and the equilibrium concentration, is known as the distribution coefficient, *K_d*, or the partition coefficient, *K_p*

$$K_d = K_p = \frac{dC_s}{dC} \tag{2}$$

The distribution or partitioning coefficient is employed to determine the retardation factor, *R_d*, through the following equation (Shackelford and Daniel, 1991b):

$$R_d = 1 + \frac{P_d}{nc} K_d \tag{3}$$

$$R_d = 1 + \frac{P_d}{\theta} K_d \tag{4}$$

where *P_d* and *nc* represents the dry, or bulk density and effective porosity, respectively, of the soil in its natural state, while *θ* denotes volumetric water content.

Effective Diffusion Coefficient (EDC)/Tortuosity Factor (TF)

The connection between the moisture content and the density of the specimens was evaluated using the British Standard Heavy compaction method. This involved applying 27 blows with a 4.5 kg rammer, dropped from a height of 450 mm to each layer of soil sample. The samples were arranged in five layers within a 1000 cm³ mold. The testing followed the procedures specified in BS 1924:1990.

The diffusion test employed the single reservoir decreasing source method as outlined by Shackelford and Daniel (1991b). The silty clay samples were stabilised with freshwater limpet shell ash and cement (FWLSA-C) at designated weight percentages. The materials were compacted at 2% moisture content above the optimal water content using the British Standard Heavy compaction method, reaching a height of 12 cm within a PVC pipe measuring 0.25 m in height and 0.1 m in diameter. This configuration guaranteed uniform maximum dry density and soil volume. Deionised water was applied to the compacted, stabilised soil for 30 days to attain complete saturation and reduce pollutant mass transfer. Subsequently, the water was evacuated, and the diffusion cells were secured. Crude oil was meticulously introduced into the cell to prevent the formation of air bubbles on the solution's surface. The diffusion cells were then left undisturbed for 90 days to facilitate the permeation of crude oil through the saturated, compacted, and stabilised soils under hydraulic conditions (Olumremi *et al.*, 2016).

After the diffusion process concluded, each cell's compacted soil sample was removed and cut into slices, each with a thickness of 1.1 cm. A subset of these slices was left to dry in atmospheric conditions before undergoing digestion and extraction. The Total Petroleum Hydrocarbons (TPH) concentration in the slices was analysed using gas chromatography (GC).

The Effective Diffusion Coefficient (EDC) for each sample was determined via equation 5. The retardation factors (Rd) were derived using the batch equilibrium results and reservoir concentration data, as specified in equations 1 and 4 (Olumremi *et al.*, 2016; Bello and Osinubi, 2010).

$$\frac{C(x \geq 0, t)}{C_0} = \frac{\alpha}{1 + \alpha} + \sum_{m=1}^{\infty} \frac{2\alpha}{1 + \alpha + \alpha^2 q^2 m} \exp\left(\frac{-D^* q^2 m}{Rd L^2}\right) \frac{\cos[qm(1 - \frac{x}{L})]}{\cos(qm)} \tag{5}$$

Where:

C_0 is the initial concentration of the solute in the source reservoir,

C_t is the concentration of a given solute in the reservoir at any time after the start of the diffusion,

D^* is the effective diffusion coefficient,

$L = a$ is the length of the soil specimen,

x is the direction of diffusive transport,

L_r is the effective length of the reservoir,

Rd is retardation factor from batch adsorption test,

$\alpha = \frac{L_r}{\theta R d a}$ is a dimensionless coefficient (Shackelford, 1988)

qm is the nonzero positive roots of the following function, $\tan qm = -\alpha qm$

But,

$$D^* = D_0 \theta^n \text{ best value of } n \text{ is } 2 \text{ (Shackelford, 1988)} \tag{6}$$

$$\tau = \theta^{-2} \text{ is conservative tortuosity}$$

where,

θ is Volumetric water content

$$\theta = n S_r \text{ (Shackelford and Daniel, 1991a)} \tag{7}$$

n is Total porosity

S_r is the degree of saturation.

RESULTS

Soil Characterisation Results

Table 1a: Sieve Analysis Result of Uncontaminated Soil

Sieve (mm)	Percentage Retained	Percentage Passing
9.50	0.0	100.00
4.75	0.0	100.0
2.00	0.0	100.00
1.18	0.03	99.97
0.600	0.5	99.50
0.425	2.0	98.00
0.300	4.5	95.00
0.150	34.5	61.00
0.075	6.4	55.00
0.05	-	50.00
0.02	-	42.00
0.01	-	35.00
0.005	-	20.00
0.002	-	6.00

Table 1b: Physio-Chemical Properties of the Uncontaminated Soil

Physical Properties	Values	Oxides	Values (%)
PH	7	SiO ₂	52.31
Liquid Limit (%)	32	TiO ₂	3.54
Plastic Limit (%)	15.2	Al ₂ O ₃	20.62
Plasticity Index (%)	16.8	Fe ₂ O ₃	3.37
US Classification	CL	MnO	0.04
AASHTO	A-6	MgO	2.76
MDD (g/cm ³)	1.88	Na ₂ O	1.90
OMC (%)	11.2	CaO	2.14
Specific gravity	2.56	P ₂ O ₅	-
		SO ₃	1.80
		K ₂ O	1.80
		ZnO	0.15
		Chemical index of alt.	-
		Loss on ignition	9.68
		CEC (cmolc/kg)	3.62

Freshwater Limpet Shell Ash Characterisation Results

Table 2: Chemical Constituents of Portland Cement (PC) and Freshwater Limpet Shell Ash (FWLSA)

Oxides	PC (%)	FWLSA (%)
SiO ₂	21.60	48.21
CaO	65.46	26.68
Fe ₂ O ₃	3.07	9.51
Al ₂ O ₃	5.36	13.11
MgO	0.91	-

K₂O	0.15	0.13
Na₂O	0.11	-
TiO₂	0.24	-
MnO₂	0.04	0.98
P₂O₅	0.26	0.83
SO₃	1.99	0.40
ZnO	-	0.01
Cl	-	0.02
LOI	0.81	0.12

Crude Oil Characterisation Results

The physio-chemical properties of crude oil, shows that Specific gravity at 60/60 °F was 0.8808, API gravity at 60/60°F was 39.10, Kinematic viscosity (cst) centistokes at 100 °F was 7.00, Sulphur Content (w/w, %) was 0.11, Pour point (°F) was + 25.00 and Total acid content (mg KOH/g) was 0.33.

Retardation Factor (Rd) Results from Batch Equilibrium Adsorption Tests (BEATS)

Table 3: Results of Retardation Factors (RF) from BEATS of Soil Stabilised with Binder at Different Percentage Combinations and Contaminated with Crude Oil

Sample ID	B(0%C+0%A)	B(5%C+2%A)	B(5%C+3%A)	B(5%C+5%A)	B(5%C+10%A)	B(5%C+20%A)
2-COCS	15.297	20.621	25.319	29.916	34.577	40.162
5-COCS	14.460	19.987	24.979	29.508	33.823	39.438
10-COCS	13.730	19.442	24.859	29.286	33.306	38.525
15-COCS	12.886	18.256	24.694	28.590	32.390	37.506
20-COCS	11.642	17.424	23.281	27.949	31.189	36.159

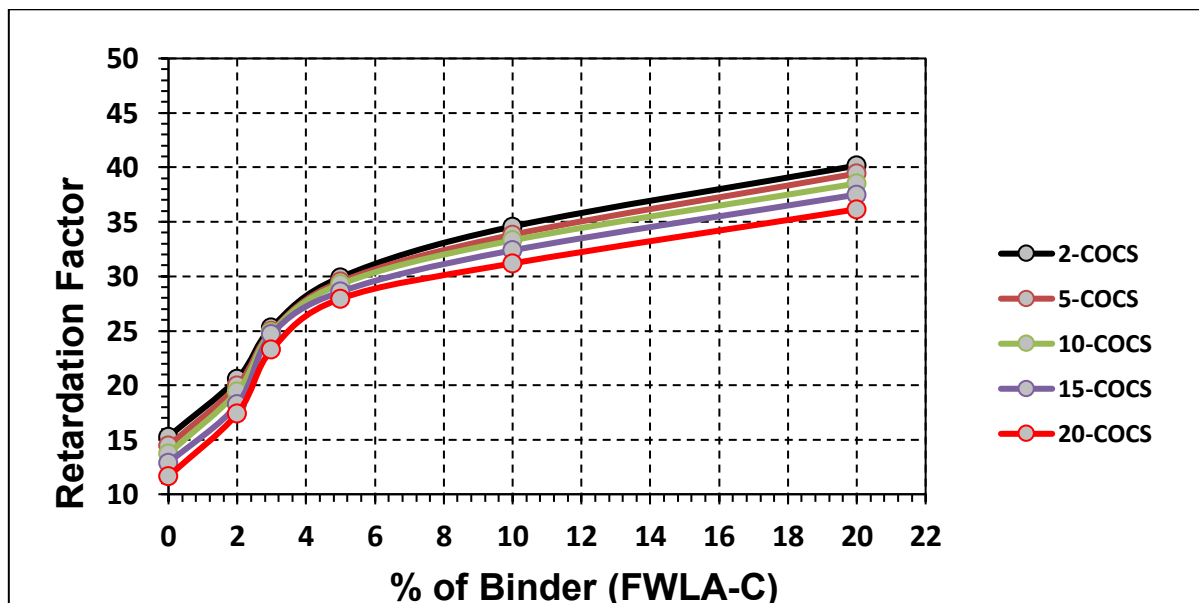


Figure 1. Graph of Retardation factor against Binder (%)

Effective Diffusion Coefficient (EDC)/Tortuosity Factor (TF) Results

Table 4: Results of Effective Diffusion Coefficients (EDC) of Soil Stabilised with Binder at Different Percentage Combinations and Contaminated with Crude Oil

Sample ID	B(0%C+0%A) (m ² /s)	B (5%C +2%A) (m ² /s)	B (5%C + 3%A) (m ² /s)	B (5%C + 5%A) (m ² /s)	B(5%C+10 %A) (m ² /s)	B(5%C +20%A) (m ² /s)
2-COCS	1.1343E-10	1.06405E-10	1.01239E-10	9.99999E-11	9.15649E-11	3.50389E-11
5-COCS	1.24116E-10	1.08572E-10	1.04152E-10	1.00339E-10	9.4923E-11	3.6344E-11
10-COCS	1.33518E-10	1.11512E-10	1.09058E-10	1.02029E-10	9.58403E-11	3.74428E-11
15-COCS	1.70657E-10	1.16529E-10	1.09349E-10	1.06604E-10	9.69738E-11	3.84311E-11
20-COCS	2.05718E-10	1.52248E-10	1.25175E-10	1.10178E-10	9.8076E-11	4.00093E-11

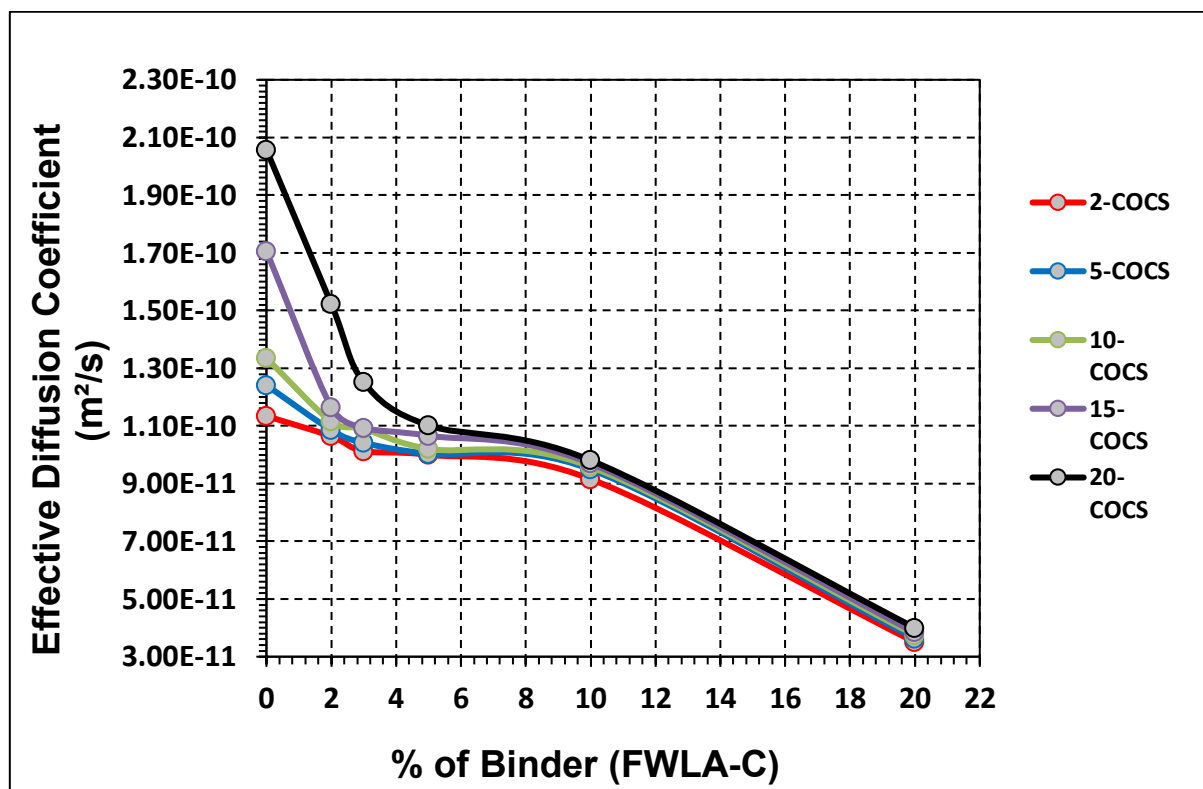


Figure 2. Graph of Effective Diffusion Coefficient (m²/s) against Binder (%)

Table 5: Results of Tortuosity factors (TF) of Soil Stabilised with Binder at Different Percentage Combinations and Contaminated with Crude Oil

Sample ID	B(0%C+0%A)	B (5%C +2%A)	B (5%C + 3%A)	B (5%C + 5%A)	B(5%C+10 %A)	B(5%C+20 %A)
2-COCS	0.0698	0.0692	0.0686	0.0681	0.0676	0.0666
5-COCS	0.0701	0.0698	0.0695	0.0692	0.0689	0.0672
10-COCS	0.0703	0.0701	0.0698	0.0695	0.0692	0.0678
15-COCS	0.0706	0.0703	0.0701	0.0698	0.0695	0.0683
20-COCS	0.0709	0.0706	0.0703	0.0701	0.0698	0.0689

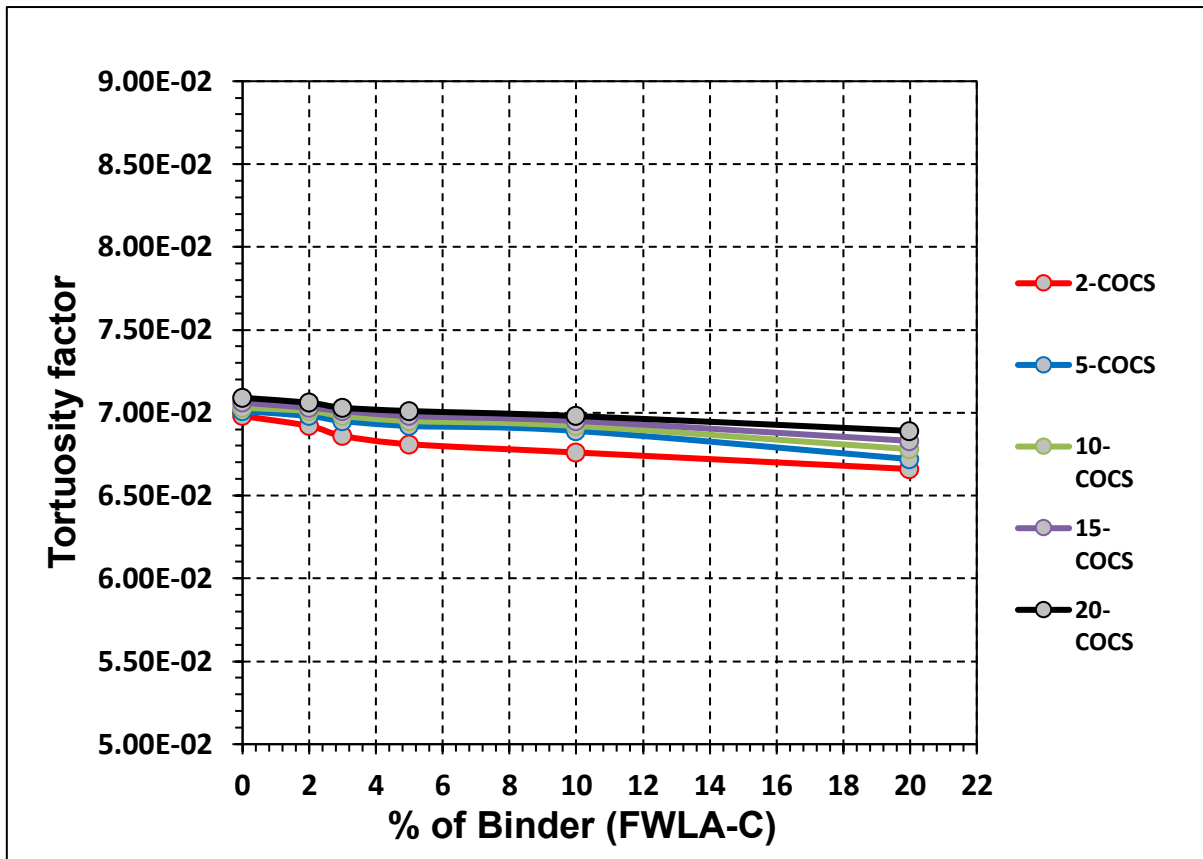


Figure 3. Graph of Tortuosity factor against Binder (%)

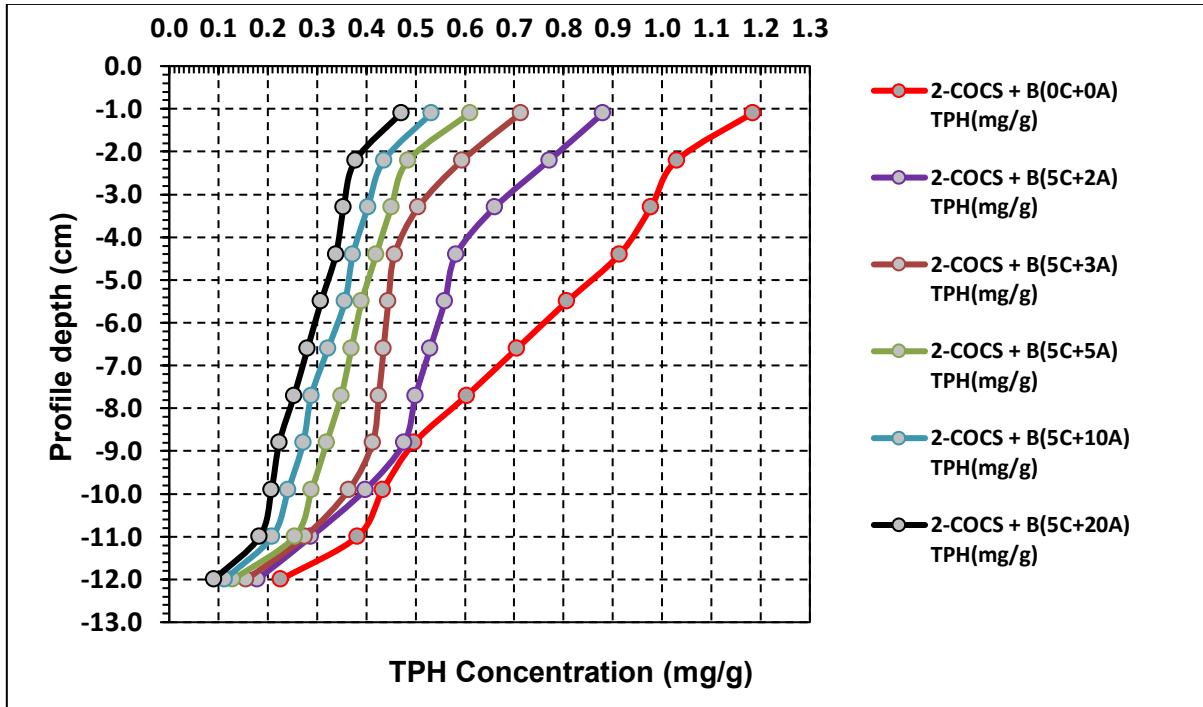


Figure 4. Profile graph of TPH concentration with depth for each layer of soil sample, both with and without binder, at various levels following the 90-day diffusion test - 2-COCS

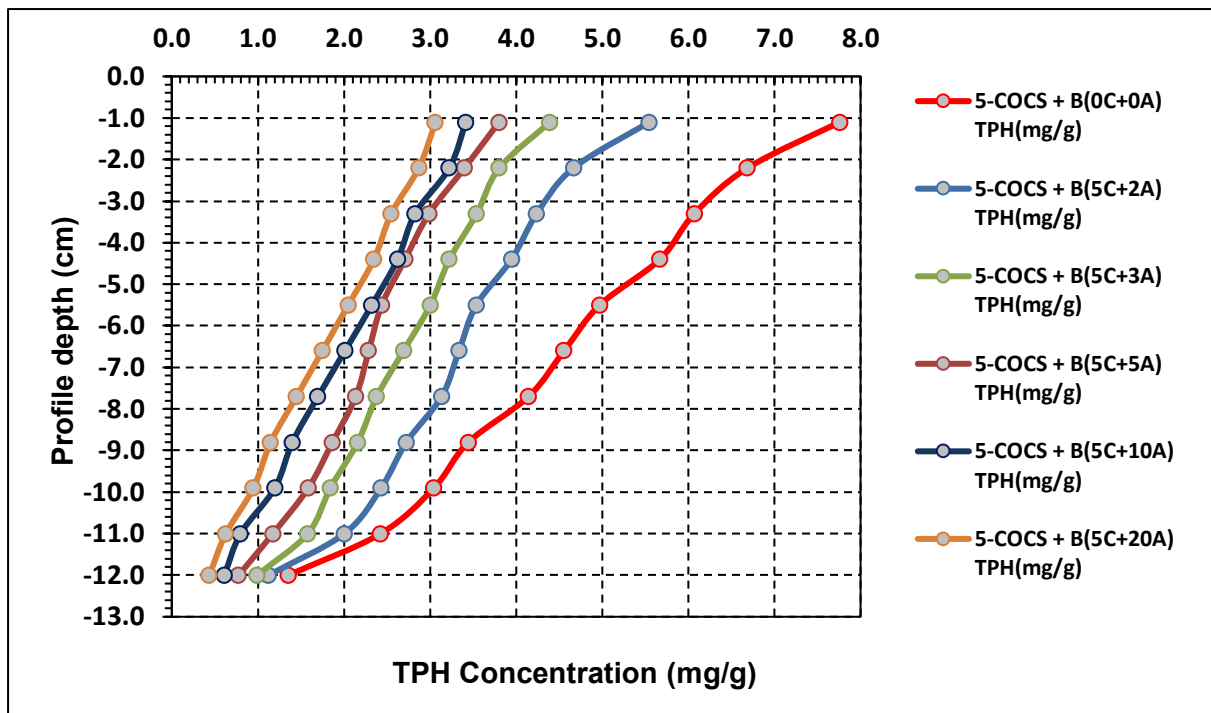


Figure 5. Profile graph of TPH concentration with depth for each layer of soil sample, both with and without binder, at various levels following the 90-day diffusion test - 5-COCS

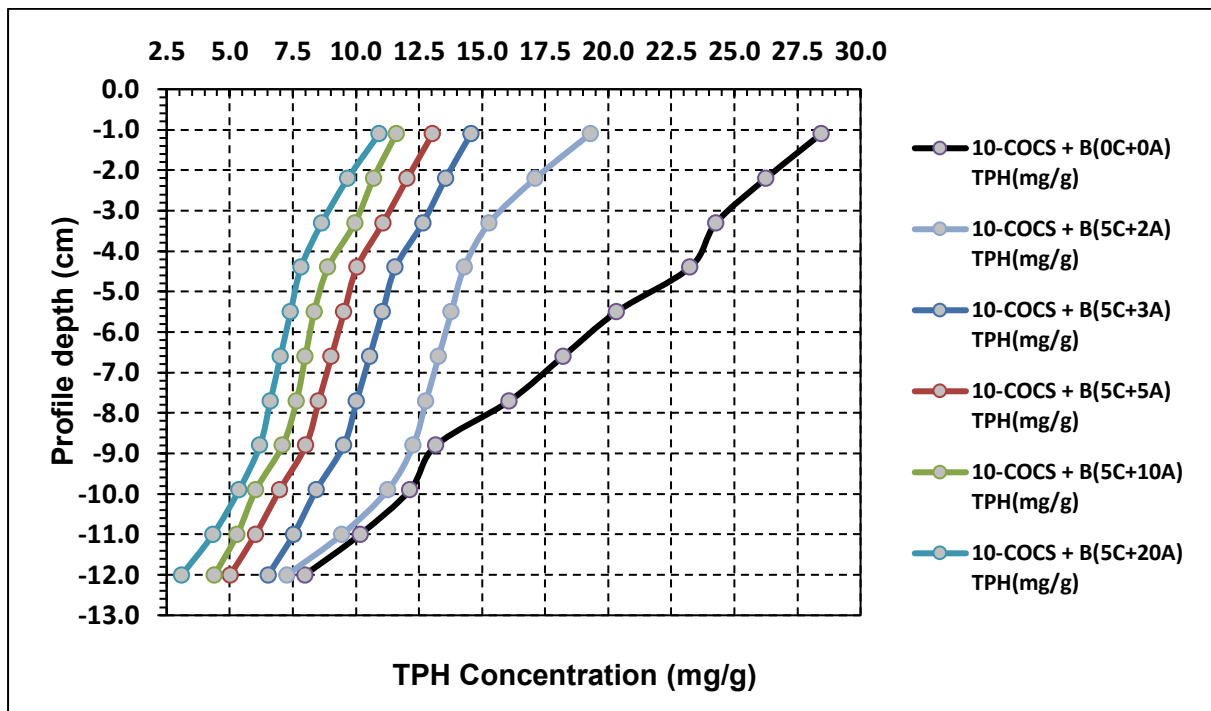


Figure 6. Profile graph of TPH concentration with depth for each layer of soil sample, both with and without binder, at various levels following the 90-day diffusion test - 10-COCS

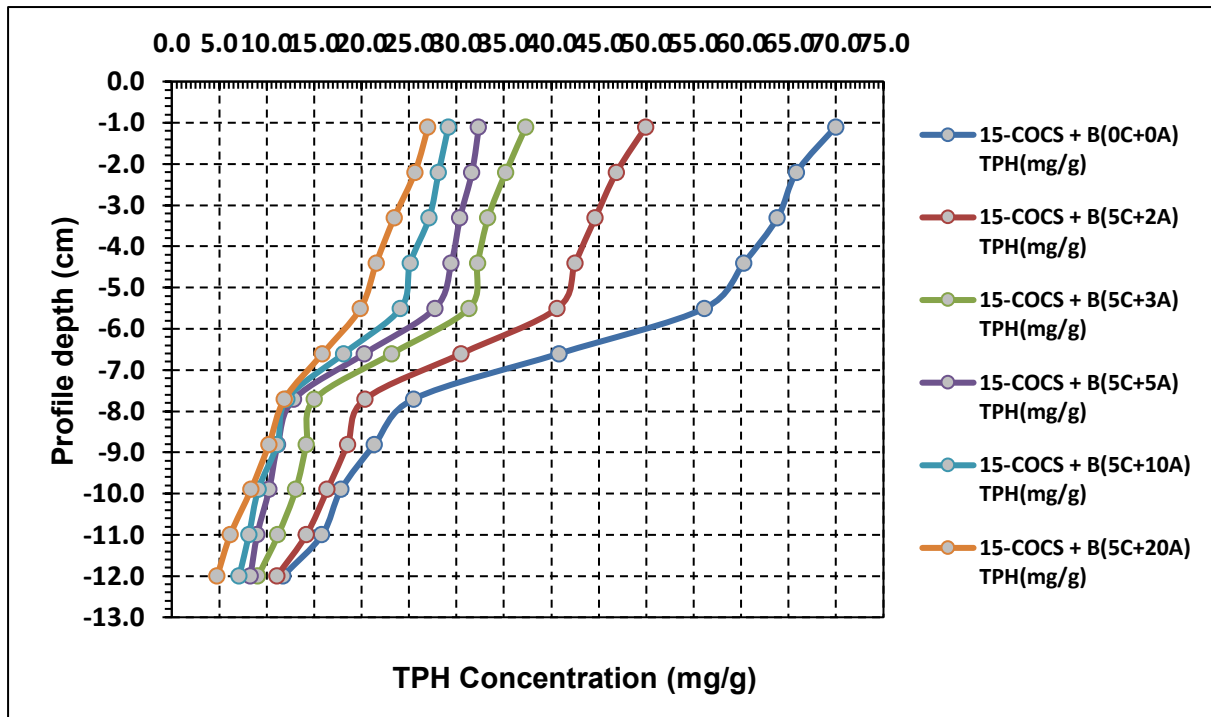


Figure 7. Profile graph of TPH concentration with depth for each layer of soil sample, both with and without binder, at various levels following the 90-day diffusion test - 15-COCS

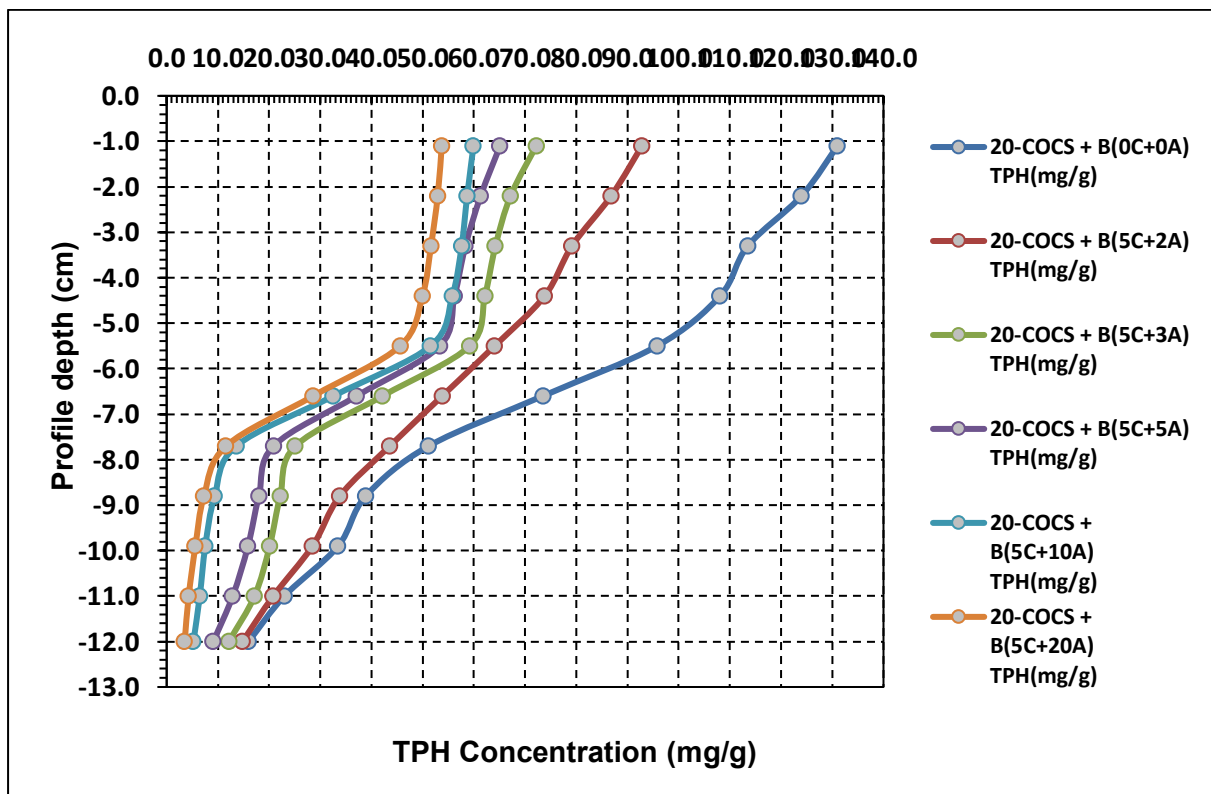


Figure 8. Profile graph of TPH concentration with depth for each layer of soil sample, both with and without binder, at various levels following the 90-day diffusion test - 20-COCS

DISCUSSION

Soil Characterisation Results

The sieve analysis of the uncontaminated soil results from Table 1a, shows that, the percentages passing sieve No. 200 (0.075 mm), No. 40 (0.425 mm) and No. 10 (2.00 mm) were 55.0%, 98.0% and 100.0%, respectively. The results indicates that it is a silty clay soil. Table 1b presents a summary of the physico-chemical properties of the silty clay soil.

Freshwater Limpet Shell Ash and Cement Characterisation Results

Table 2 shows the chemical constituents of Portland cement and the Freshwater Limpet Shell Ash. The main oxides found in the ash were SiO₂ (48.2%), Al₂O₃ (13.1%), and Fe₂O₃ (9.5%); indicating it is a natural pozzolan.

Crude Oil Characterisation Results

The physio-chemical properties of crude oil indicates that the sulphur content in the crude oil is low.

Retardation Factor (Rd) Results from Batch Equilibrium Adsorption Tests (BEATS)

The results in Table 3 and Figure 1 illustrates the Retardation Factors (Rd) derived from batch equilibrium adsorption tests (BEATS) for soils contaminated with varying percentages of crude oil (COCS) at 0, 2, 5, 10, 15, and 20%-combined with different binder compositions: 0% cement and 0% ash, 5% cement with 2% ash, 5% cement with 3% ash, 5% cement with 5% ash, 5% cement with 10% ash, and 5% cement with 20% ash. While adsorption isotherms typically deviate from linearity (Shackelford and Daniel, 1991b), Rowe *et al.* (1996) proposed that linear isotherms effectively characterise the absorption of pollutants from runoff at contaminated sites with relatively low concentrations. Consequently, researchers presumed a linear distribution (Kd) of the isotherm to calculate the retardation factor (Rd). The data revealed a decrease in retardation factors (Rd) as the crude oil content in the soil increased: 15.297 for 2-COCS, 14.460 for 5-COCS, 13.730 for 10-COCS, 12.886 for 15-COCS, and 11.642 for 20-COCS. These findings align with existing research on adsorption mechanisms (Palmer and Johnson, 1991; Olumremi *et al.*, 2016; Bello and Osinubi, 2010). The incorporation of the binder (FWLSA-C) yielded results ranging from 17.424 to 40.162. This pattern emerges because a substantial portion of the contaminant mass adheres to the adsorbent/binder (FWLSA-C) and soil particles, thereby increasing the distribution coefficient and resulting in elevated retardation factors with higher binder (FWLSA-C) content (Palmer and Johnson, 1991; Weber *et al.*, 1991;). Thus, the data suggests that an adsorbent with a higher adsorption capacity for the solute (contaminant) produces a higher retardation factor, indicating greater adsorption of the contaminant onto the adsorbent surface and consequently slowing its movement in the liquid phase of the batch system. Therefore, retardation factor values exceeding 1.0 suggest that contaminant attenuation processes have occurred within the contaminated soil (Bello and Osinubi, 2010).

Effective Diffusion Coefficient (EDC)/Tortuosity Factor (TF) Results

The results in Table 4,5 and Figures 2,3 show the values of the Effective Diffusion Coefficient (EDC) and Tortuosity Factors (TF) for soil contaminated with crude oil (COCS) at concentrations of 0, 2, 5, 10, 15, and 20%. The soil was stabilised with FWLSA-C binder in different combinations: 0% cement and 0% ash, 5% cement with 2% ash, 5% cement with 3% ash, 5% cement with 5% ash, 5% cement with 10% ash, and 5% cement with 20% ash. The results in Table 4,5 and Figures 2,3 indicated that the value of EDC/TF increased with the rising content of crude oil in the soil. The results showed that for 2-COCS, the value of EDC/TF was 1.13E-10 m²/s/6.98E-02; 5-COCS was 1.24E-10 m²/s/7.01E-02; 10-COCS was 1.34E-10 m²/s/7.03E-02; 15-COCS was 1.71E-10 m²/s/7.06E-02; and 20-COCS was 2.06E-10 m²/s/7.09E-02. The results may be attributed to a higher concentration gradient of crude oil and pores in the soils, which will result in a faster rate of contaminant transportation in the soil

(Jekayinfa *et al.*, 2023; Adeniran *et al.*, 2023; Shackelford, 2014). Hong *et al.* (2009) explained that porosity influences the estimation of effective diffusion coefficient (EDC)/tortuosity factors (TF) in compacted clay soils. However, the addition of the binder (FWLSA-C) reduced the effective diffusion coefficient (EDC) and tortuosity factors (TF) from $2.06\text{E-}10$ m²/s to $3.50\text{E-}11$ m²/s and $7.09\text{E-}02$ to $6.66\text{E-}02$. Figure 4-8 illustrates the profile graph of total petroleum hydrocarbon (TPH) contaminant concentration at various depths for each soil sample slice, both with and without binder, after 90 days of diffusion testing for 2-COCS, 5-COCS, 10-COCS, 15-COCS, and 20-COCS. The graphs indicated that as the binder content in the soil increases, the concentration of the contaminant diffusion rate decreases. According to Jekayinfa *et al.* (2023), the variation in the contaminant concentration (TPH) within the soil profile creates a concentration gradient between the reservoir and the compacted soil. Over time, the concentration of crude oil in the reservoir diminishes (Weber *et al.*, 1991; Shackelford, 1990). Bello and Osinubi 2010 showed similar results in their study. Oluremi *et al.* (2016) also stated that the presence of a binder might reduce the EDC/TF in contaminated soils; this effect is due to the binding properties of the binder (FWLSA-C).

CONCLUSION

The diffusion and adsorption properties of crude oil-contaminated silty clay soil stabilised with a freshwater limpet shell ash and cement combination (FWLSA-C) indicated that a higher percentage of the binder (FWLSA-C) increases the Retardation Factor (Rd) in the Batch Equilibrium Adsorption Tests (BEATS) and reduces the Effective Diffusion Coefficient (EDC)/Tortuosity Factor (TF) results in the diffusion test. An increased estimate of Rd will yield a reduced estimate of EDC/TF, and conversely. This study revealed that locally sourced freshwater limpet shell ash and cement (FWLSA-C) will slow the diffusion rate of TPH contaminants to groundwater in crude oil-contaminated sites within the Niger Delta in Nigeria.

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