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Research article

Diagnostic screening of organic contaminant level in solidified/stabilized pre-treated oil-based drill cuttings

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ABSTRACT

The reuse of solidified/stabilized low-temperature thermally desorbed (pre-treated) oil-based drill cuttings for construction purposes is becoming increasingly attractive in recent times; though, without screening a priori the levels of target residual organic contaminants against environmental guidelines to ensure compliance. In this study, pre-treated oil-based drill cuttings were collected from a waste treatment facility in the Niger Delta Province (5.317^{o}N; 6.467^{o}E), Nigeria and subjected to cement-based solidification/stabilization (S/S) followed by chemical leaching and screening of the data against local environmental guidelines. S/S was done with drill cuttings contents of 0 (control), 2, 4, 6, 8, and 10 % as part replacement for fine aggregate at 0.6:1, 0.65:1, 0.7:1, 0.75:1, and 0.8:1 water-to-cement ratios using 1:2:4 mix design for a grade-20 concrete. Afterwards, the surface microstructure, elemental composition, and unconfined compressive strength (UCS) of the solidified/stabilized matrix were determined. Amounts of heavy metals and total petroleum hydrocarbons (TPH) leached were also assessed. Results showed that the 2 % drill cuttings addition yielded the highest UCS (22.22–26.22 N/mm^2) at water-to-cement ratio of 0.6:1, which were well above the recommended minimum UCS of 20 N/mm^2 for a grade-20 concrete. The average amount of residual TPH in the solidified/stabilized matrix (62.41 mg/kg) was slightly higher than the local regulatory target value of 50 mg/kg; suggesting that the cement-based S/S failed to immobilize completely all the hydrocarbons in the pre-treated oil-based drill cuttings. This shows that the solidified/stabilized matrix is not in compliance with environmental guidelines on TPH for sustainable reuse as construction materials.

1. Introduction

The resulting waste stream during crude oil drilling operations is an admixture of rock fragments, soil, crude oil, produced water, and spent drilling mud and mud additives (among others); altogether referred to generally as whole mud. Entire mud can be broadly divided into the liquid and solid phases. The solid phase is referred to as drill cuttings, named according to the type of drilling mud used during drilling. The three types of drilling mud generally used in drilling are oil-based mud (OBM), water-based mud (WBM), and synthetic-based mud (SBM) (Lyons, 1996; Ratnayake and Sampei, 2019).

The amount of drill cuttings unavoidably generated during crude oil drilling operations has remained one of the main environmental concerns in the oil-producing countries. This is in addition to the hazardous nature of the drill cuttings occasioned by the presence of harmful organic and inorganic compounds including heavy metals, hydrocarbons, water-soluble salts such as sulphates and chlorides (Ayotamuno et al., 2007). Petroleum hydrocarbons such as polycyclic aromatic hydrocarbons (PAHs) in drill cuttings originate from petrogenic and pyrogenic sources (Okparanma et al., 2010), as well as geological processes involving recent and ancient mud/mudstones (Ratnayake and Sampei, 2015). Heavy metals and water-soluble salts are from the drilling mud and mud additives used during drilling (Ayotamuno et al., 2007). The adverse environmental effects of disposing untreated drill cuttings on land and sea are well documented (see Okparanma et al., 2018). To assuage these environmental impacts, a number of treatment technologies have been developed; one of which is thermal desorption.

Thermal desorption describes the heating of drill cuttings indirectly

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in a thermal desorption unit. As distinct from incineration, the indirect heating enables the vapourization of the volatile and semi-volatile components without necessarily converting the drill cuttings to ash. This allows the recovery of the solid components for subsequent reuse as construction materials (IOGP, 2016), application on land for forage production (Kogbara et al., 2017), or other forms of application. Depending on the target hydrocarbon fraction to be removed, two types of thermal desorption units are available. Low-temperature thermal desorption units (LTTDUs) operating between 250 and 350 °C) are often used to remove the light aromatic hydrocarbons (e.g., benzene, toluene, ethylbenzene, and xylenes) and aliphatics; and the resulting dry residues are referred to as low-temperature thermally desorbed drill cuttings. To remove heavier aromatic hydrocarbons such as the polycyclic aromatic hydrocarbons (PAHs), high-temperature thermal desorption units (HTTDUs) operating at temperarures of up to 520 °C are used (Owens et al., 1993). However, according to a recent report (IOGP, 2016), some levels of contamination still remain even after the thermal desorption of the drill cuttings.

Nevertheless, through cement-based solidification/stabilization (S/S), drill cuttings have been reused as construction materials, especially as partial replacement for sand or cement in concrete production (IOGP, 2016). This has been made possible because the drill cuttings react with the solidifying/stabilizing agents, preventing contaminants retained in the drill cuttings from leaching when the solidified/stabilized product is in normal use. S/S of drill cuttings have been widely reported in the open literature (e.g., Akinlade et al., 1996; Shaffer et al., 1998; Fleming, 2000; Al-Ansary and Al-Tabbaa, 2007; Leonard and Stegemann, 2010; Opete et al., 2010; Ghasemi et al., 2017).

However, most of these studies focused more on synthetic-based drill cuttings than oil-based drill cuttings. This may be partly attributed to the compliance with the ban on the use of OBMs during drilling. Oil-producing countries that have outlawed the use of OBMs during drilling include (among others) Nigeria, Norway, and Indonesia (DPR, 2002; Norwegian Oil Industry Association, 2003; Permata and McBride, 2010). Here in Nigeria, there are reports suggesting that OBMs are still being used in deep-well drilling despite the ban (e.g., Okparanma et al., 2010). It is, therefore, necessary for further studies to be conducted for a better understanding of residual concentrations of contaminants and elemental compositions of solidified/stabilized pre-treated oil-based drill cuttings to help identify specific compounds present. This is in line with the principles of sustainable reuse of hazardous wastes. According to IOGP (2016), one of the principles of sustainable reuse of hazardous wastes is to ensure that before the wastes are subjected to the intended use they satisfy stipulated environmental guidelines, which are designed to protect the immediate and future environment. To determine compliance before subjecting the resulting solidified/stabilized matrix to the intended use, the levels of target residual organic and inorganic contaminants in the matrix are screened against environmental guidelines to check if the observed concentrations of the contaminants are either below or above the guideline values. However, in recent studies (e.g., Opete et al., 2010), screening of the level of residual organic contaminants like petroleum hydrocarbons in the resulting solidified/stabilized matrix against environmental guidelines has often been ignored.

In order to ascertain whether or not some form of action may be required to avert immediate and future problems arising from the use of the solidified/stabilized matrix for construction purposes, there is need to screen the levels of target residual organic contaminants against local environmental guidelines. The objectives of the current study were to carry out cement-based S/S of pre-treated oil-based drill cuttings, assess the leaching characteristics of the solidified/stabilized matrix, and screen the levels of target residual contaminants against local environmental guidelines.

2. Materials and methods

2.1. *The study area*

The study area is the Niger Delta region (5.317^{o}N; 6.467^{o}E), which is in the southern part of Nigeria. The region is largely a natural wetland area on a 70,000-km^{2} of land (NDES, 1995). According to reports in the literature (Okparanma, 2013), the soil type in the Niger Delta is predominantly Oxisols. The population of the region is over 10 million (NDES, 1995). Most of the oil and gas infrastructure supporting the country's economy are locaed in the region (NDES, 1995). According to multiple sources, due to the concentration of oil and gas industries in the region, there have been several reports of exploration and production (E & P) wastes, including drill cuttings, discharges both on land and sea in the region with negative environmental impacts. In a recent study, the total E & P wastes generated in six offshore platforms alone in Nigeria from 2010 to 2013 have been conservatively estimated as 4,492,057.9 tons (Nwokedi et al., 2015). Thus, it has been suggested that the total E & P wastes generated both offshore and onshore in Nigeria since records began would be several millions of tons with a greater proportion of the wastes coming from the Niger Delta region where most of the E & P activities are concentrated (Okparanma, 2013).

2.2. *Sample collection*

Fig. 1 (a) and (b) show the two forms of drill cuttings collected from a commercial treatment, storage, and disposal facility in the Niger Delta region. Fig. 1 (a) shows the untreated oil-based drill cuttings while Fig. 1 (b) shows the pre-treated oil-based drill cuttings. Using plastic containers, composite samples of each form of the drill cuttings were collected and taken to the laboratory for treatment and analyses. A priori

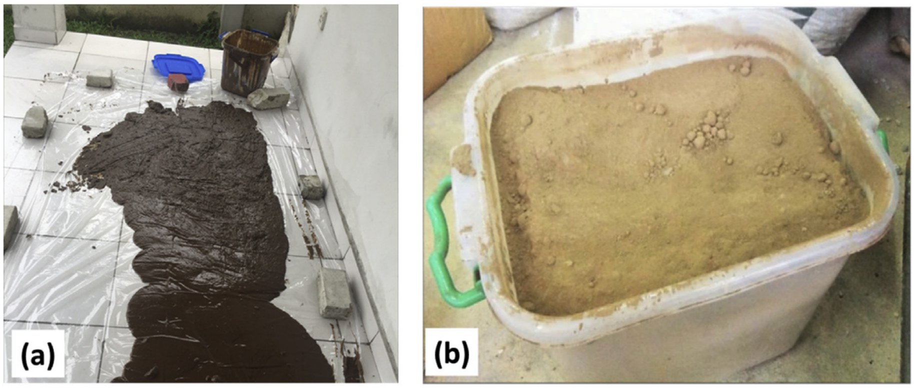

Fig. 1. The two forms of oil-based drill cuttings collected: (a) untreated oil-based drill cuttings being air-dried for 48 and 96 h, and (b) low-temperature thermally desorbed oil-based drill cuttings in plastic container.

air-drying of the untreated wet drill cuttings were done for 48 and 96 h.

2.3. Solidification/stabilization of pre-treated oil-based drill cuttings and determination of unconfined compressive strength (UCS)

Since there is no mix design procedure for low-temperature thermally desorbed oil-based drill cuttings at the moment, solidified/stabilized drill cuttings test cubes were prepared using the Marshal design-procedure for asphalt concrete mixes as described in Igwe et al. (2009). However, for the purpose of this study, asphalt was replaced with low-temperature thermally desorbed oil-based drill cuttings. In this approach, a series of test cubes were prepared with a range of low-temperature thermally desorbed oil-based drill cuttings contents of 0, 2, 4, 6, 8, and 10 % as part replacement for fine aggregate at 0.6:1, 0.65:1, 0.7:1, 0.75:1, and 0.8:1 water to cement ratio using 1:2:4 mix design. This mix design was chosen because it yields a grade-20 concrete, which is commonly used in most medium-weight concrete structures like lintels, pavements, and slabs. The test cubes were replicated two times for each drill cuttings content used and the average results were taken as representative. Fig. 2 shows the stages involved in the preparation of the test cubes. As can be seen in Fig. 2, prior to the preparation of the test cubes, the aggregates (Fig. 2a) were first subjected to specific gravity tests (Figure not shown) and then dried in a low-temperature oven overnight (Fig. 2c). Then, the mix was poured into a cubic mould of volume 2.667×10^{-4} m^3 and compacted with 35 blows using a 6.5 kg-rammer falling freely from rest at a height of 450 mm. The compacted test cubes were then left in the mould for 24 h to set (Fig. 2d), removed from the mould afterwards, and cured in water for 7, 14, 21, and 28 days (Fig. 2e). Before subjecting the test cubes to unconfined compressive strength (UCS) tests (Fig. 2f), they were reweighed to check their densities. Afterwards, some of the crushed cubes (Figure 2g and h) and the untreated and thermally desorbed drill cuttings were collected in Ziploc bags for shipment to Cranfield University in the United Kingdom (Fig. 2i) for further tests, including surface microstructure analysis by scanning electron microscopy (SEM).

2.4. Laboratory chemical analysis

2.4.1. Determination of total petroleum hydrocarbon (TPH) content of sample

TPH content of the drill cuttings samples was determined according to EPA (1994a) method 8270 for alkanes and EPA (1994b) method 8270B for PAHs. The leaching procedure used to extract TPH compounds was the 5-hour sonication water bath method. The extraction solvent used was a mixture of dichloromethane and *n*-hexane in the ratio of 1:1. For the solidified/stabilized matrix, 5.0 ± 0.1 g of the crushed, pulverized, and sieved (<2 mm with a 2-mm sieve) sample was used. For the pre-treated drill cuttings; no crushing was done, but the same 5.0 ± 0.1 g of the sieved sample was used. A 7890B gas chromatograph (GC) coupled to a 5977 mass spectrometer (MS) (Agilent Technologies Inc., USA) was used for TPH analysis. The GC-MS operating conditions and the type of autosampler installed, cleanup of the sample extract, TPH quantification method, instrument calibration, and quality control measures adopted are as described by Okparanma et al. (2017).

2.4.2. Determination of heavy metal content of sample

Levels of heavy metals in the samples were analyzed by flame atomic absorption spectrometry using a UNICAM-969 Atomic Absorption Spectrophotometer by measuring the light absorbance of the sample at the wavelength range of 357.9–228.8 nm according to APHA (1998) method 3111C. For the solidified/stabilized matrix, the leaching protocol used prior to analysis involved the crushing and grinding of the solidified/stabilized matrix to fine powder while only grinding was done for the pre-treated drill cuttings. The samples were then digested by microwave-assisted acid digestion method according

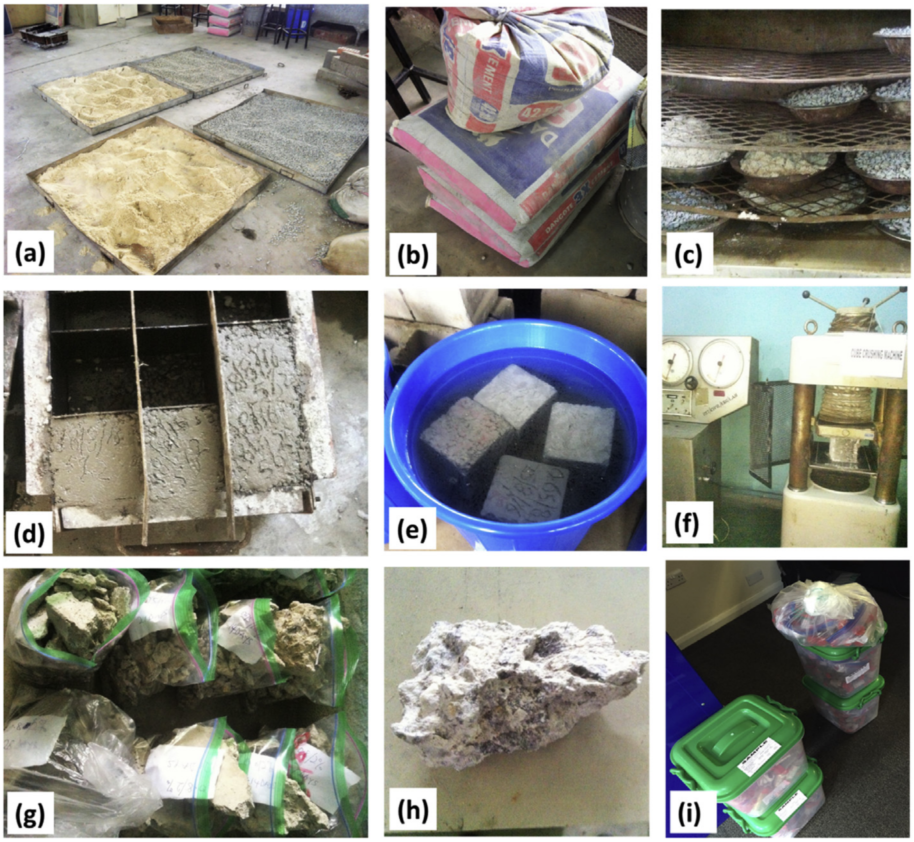

Fig. 2. Stages in the preparation and testing of test cubes showing: (a) coarse and fine aggregates used, (b) Portland limestone cement used, (c) a priori oven-drying of aggregates, (d) moulding of test cubes, (e) curing of test cubes in water, (f) determination of unconfined compressive strength (UCS) of test cubes, (g) crushed cubes in Ziploc bags for shipment to Cranfield University, UK for SEM analysis, (h) a lump of crushed cube, and (i) shipment of drill cuttings samples and crushed cubes at Cranfield University, UK.

to EPA (1996) method 3052. In this method, 0.25 ± 0.01g of the crushed and ground sample was carefully weighed out in a beaker and digested in 9 ml concentrated nitric acid (HNO_3) and 3 ml hydrofluoric acid for 15 min using a WX-6000 Microwave Digestion System (Persee, OH, USA). Instrument temperature was maintained at 95 ± 5 °C for 15 min. After cooling, the vessel content was allowed to settle and filtered in a 100 ml volumetric flask. The residue and filter paper were washed with 5 ml HCl and 5 ml hot deionized water. The wash was collected in the same volumetric flask while the residue was digested further with 5 ml HCl. Then the digestate and filtrate were combined in the same volumetric flask and the volume made up to the 100-ml mark on the flask and analyzed. Meanwhile, a priori instrument calibration was done using the respective standard solution of the analyte of interest.

2.4.3. Determination of sample surface microstructure and elemental composition

Sample surface microstructure and elemental composition were determined by scanning electron microscopy (SEM) using a Philips XL30 environmental scanning electron microscope coupled to a microanalysis system. Using a diamond blade circular saw, the crushed cubes were cut to size, mounted individually on carbon SEM stubs, and loaded into the chamber on carousel – 6 at once. For quantitative analysis, the crushed cubes were polished to a flat, unscratched surface while the thermally treated drill cuttings were vacuum impregnated before sample preparation. Then the chamber was pumped down. The following instrument operating conditions were used: voltage was 20kV; low-vacuum mode; spot size of 5; working distance set to 12 mm; and area selected for imaging and analysis was approximately 600^2μ. Samples were imaged in scattered electron and backscattered electron modes with energy-dispersive x-ray (EDX) analysis taken at 200x magnification for 60 s. This analysis was carried out at the Environmental Analytical Facility at Cranfield University, UK.

3. Results and discussion

3.1. Physicochemical characteristics of untreated and pre-treated oil-based drill cuttings

Table 1 shows selected physicochemical characteristics of the oil-based drill cuttings used in this study. It can be seen that oil-based drill cuttings contain TPH, PAHs, and heavy metals (Table 1) as corroborated in several literatures (e.g., Okparanma et al., 2010; IOGP, 2016). As shown in Table 1, the density of the drill cuttings obtained in this study falls within the range of 1.3–2.7 g/cm^3 reported in the literature (Al-Ansary and Al-Tabbaa, 2007). Furthermore, the TPH contents of the untreated, air-dried (for 48 and 96 h), and low-temperature thermally desorbed oil-based drill cuttings were way beyond the prescribed target value (DPR, 2002); suggesting that the drill cuttings even after thermal desorption is unsafe for discharge into the environment. However, it is important to note that there was a progressive drop in the level of TPH with the type of treatment applied. Between the air-drying and thermal desorption methods, the thermal desorption method resulted in the higher amount of TPH reduction than the air-drying method; although, the residual TPH content was way beyond the prescribed target value. This, therefore, justifies the need for further treatment of thermally desorbed drill cuttings before it can be finally disposed, applied on land for agricultural purpose, or reused for civil engineering works like concrete production and/or road construction.

Table 1 further shows that in the untreated drill cuttings, 60 % of the 16 USEPA priority PAHs were less than the limit of quantitation of 0.02 mg/kg for PAHs in Nigerian soils and sediments. Limit of quantitation is the lowest concentration at which an analyte can be reliably detected (Mitra, 2003). This, therefore, means that these PAHs are present in the drill cuttings, but not up to 0.02 mg/kg. Of the 16 USEPA priority PAHs in Table 1, benzo[a]anthracene, dibenzo[a,h]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, and chrysene are

Table 1
Selected physicochemical characteristics of untreated and low-temperature thermally desorbed oil-based drill cuttings from the Niger Delta region, Nigeria.

Property		Untreated oil-based drill cuttings	Air-dried oil-based drill cuttings		LTTD oil-based drill cuttings	DPR (2002) target value
			48 h	96 h		
Specific gravity		NDM	NDM	NDM	2.00	-
Density (g/cm^3)		NDM	NDM	NDM	1.46	-
TPH (mg/kg)		8,913.12	7,664.65	6,939.6	673.45	50
Heavy metals (mg/kg)	Copper	31.40	29.78	20.45	18.45	NR
	Iron	47.08	44.99	43.33	40.59	NR
	Barium	80.65	60.60	50.62	44.56	NR
	Chromium	21.00	20.10	19.01	10.19	380
	Manganese	5.35	4.95	5.11	4.61	NR
	Arsenic	<0.001	<0.001	<0.001	<0.001	55
	Nickel	14.27	13.63	13.19	12.30	NR
	Cadmium	0.31	0.30	0.31	0.29	12
Polycyclic aromatic hydrocarbons (mg/kg)	Naphthalene	3.01	2.00	1.10	<0.02	N/A
	Acenaphthylene	2.00	1.23	0.80	<0.02	N/A
	Acenaphthene	2.90	1.55	<0.02	<0.02	N/A
	Fluorene	0.29	0.11	<0.02	<0.02	N/A
	Phenanthrene	3.89	2.12	1.10	<0.02	N/A
	Anthracene	1.04	0.45	<0.02	<0.02	N/A
	Fluoranthene	<0.02	<0.02	<0.02	<0.02	N/A
	Pyrene	<0.02	<0.02	<0.02	<0.02	N/A
	Benzo[a]anthracene	<0.02	<0.02	<0.02	<0.02	N/A
	Chrysene	<0.02	<0.02	<0.02	<0.02	N/A
	Dibenzo[*a,h*] anthracene	<0.02	<0.02	<0.02	<0.02	N/A
	Benzo[*b*]fluoranthene	<0.02	<0.02	<0.02	<0.02	N/A
	Benzo[*k*]fluoranthene	<0.02	<0.02	<0.02	<0.02	N/A
	Benzo[*a*]pyrene	<0.02	<0.02	<0.02	<0.02	N/A
	Indeno[*1,2,3-cd*] pyrene	<0.02	<0.02	<0.02	<0.02	N/A
	Benzo[*g,h,i*]perylene	<0.02	<0.02	<0.02	<0.02	N/A

LTTD, Low-temperature thermally desorbed; N/A, Not Available; NDM, Not Determined; NR, Not Reported; TPH, Total Petroleum Hydrocarbon; For PAHs 0.02 is the limit of quantitation, which is the lowest concentration at which an analyte can be reliably detected (Mitra, 2003). For heavy metals, the limit of quantitation is 0.001.

Table 2
Statistics of residual heavy metal and TPH contents of the solidified/stabilized product produced with 2–10% of low-temperature thermally desorbed oil-based drill cuttings from the Niger Delta region, Nigeria.

Chemical Property	Number of samples	LOQ (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)	Mean (mg/kg)	Range (mg/kg)
TPH	124	0.02	18.71	184.08	62.41	165.37
Cu	124	0.001	3.03	9.82	5.27	6.79
Fe (II)	124	0.001	3.34	10.81	5.80	7.47
Fe (III)	124	0.001	3.64	11.79	6.32	8.15
Ba	124	0.001	0.08	0.25	0.13	0.17
Cr	124	0.001	0.00	0.001	0.001	0.001
Mn	124	0.001	0.76	2.46	1.32	1.70
As	124	0.001	<0.001	<0.001	<0.001	<0.001
Ni	124	0.001	2.02	6.55	3.51	4.53
Cd	124	0.001	0.00	0.001	0.001	0.001

ND, Not Detected; TPH, Total Petroleum Hydrocarbon; LOQ, Limit of Quantitation — the lowest concentration at which an analyte can be reliably detected (Mitra, 2003).

known non-threshold genotoxic carcinogens (CL:AIRE, 2010). This implies that they can still cause cancer even if their concentrations are less than 0.02 mg/kg. In the absence of a corresponding PAH target value for compliance in Nigerian regulatory framework, the soil screening value of 0.24 mg/kg suggested in the literature for Nigerian soils (Okparanma et al., 2014) was used as a basis for comparison with the PAH values obtained in this study. It can be seen in Table 1 that in the untreated drill cuttings, 40 % of the PAHs exceeded the suggested 0.24 mg/kg screening value; suggesting that the drill cuttings are ecologically unsafe. After thermal desorption, the concentrations of the PAHs dropped below 0.02 mg/kg (Table 1). Even then, because of the presence of the non-threshold genotoxic carcinogens, the drill cuttings are still not safe for final disposed, application on land for agricultural purpose, or reuse as construction material.

For the heavy metals, the drill cuttings were found to not contain arsenic to any appreciable extent as the concentration of arsenic was below the detection limit of the instrument (Table 1). However, there was a preponderance of barium in the drill cuttings, constituting 40.31 % of the total heavy metal content of the drill cuttings (Table 1). This result agrees with reports in the literature that barium is by far the most abundant heavy metal in drill cuttings. Compared with local regulatory target values, Table 1 shows that some heavy metals were above their prescribed target values while others were below, making the drill cuttings environmentally unsafe to that extent.

3.2. Residual heavy metal and TPH contents of the solidified/stabilized pre-treated oil-based drill cuttings

Table 2 shows the statistics of the residual contents of heavy metals and TPH in the solidified/stabilized product containing 2–10 % of low-temperature thermally desorbed oil-based drill cuttings. As evident in Table 2, the average amount of TPH remaining after cement-based solidification/stabilization of the low-temperature thermally desorbed oil-based drill cuttings slightly exceeded the local regulatory target value of 50 mg/kg (see Table 1). On average, this suggests that cement-based solidified/stabilized low-temperature thermally desorbed oil-based drill cuttings are not suitable for use for construction purposes because of the potential environmental health risks. It must be stated that the assessment of the associated environmental health risks of solidified/stabilized low-temperature thermally desorbed oil-based drill cuttings is outside the scope of the current study. However, Table 2 shows that cement-based solidification/stabilization of low-temperature thermally desorbed oil-based drill cuttings was quite effective in reducing the level of heavy metals to less than their respective local regulatory target values (see Table 1). This suggests that, in terms of heavy metal contents, the cement-based solidified/stabilized low-temperature thermally desorbed

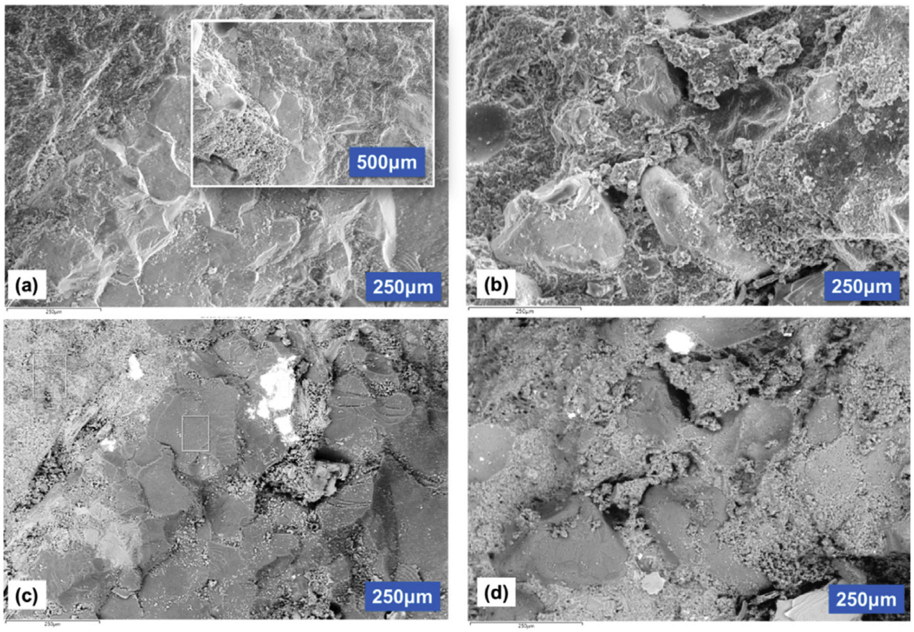

Fig. 3. SEM micrographs of solidified/stabilized test cubes produced with 4% low-temperature thermally desorbed Nigerian oil-based drill cuttings at (a) 7 days, (b) 14 days, (c) 21 days, and (d) 28 days of curing in water.

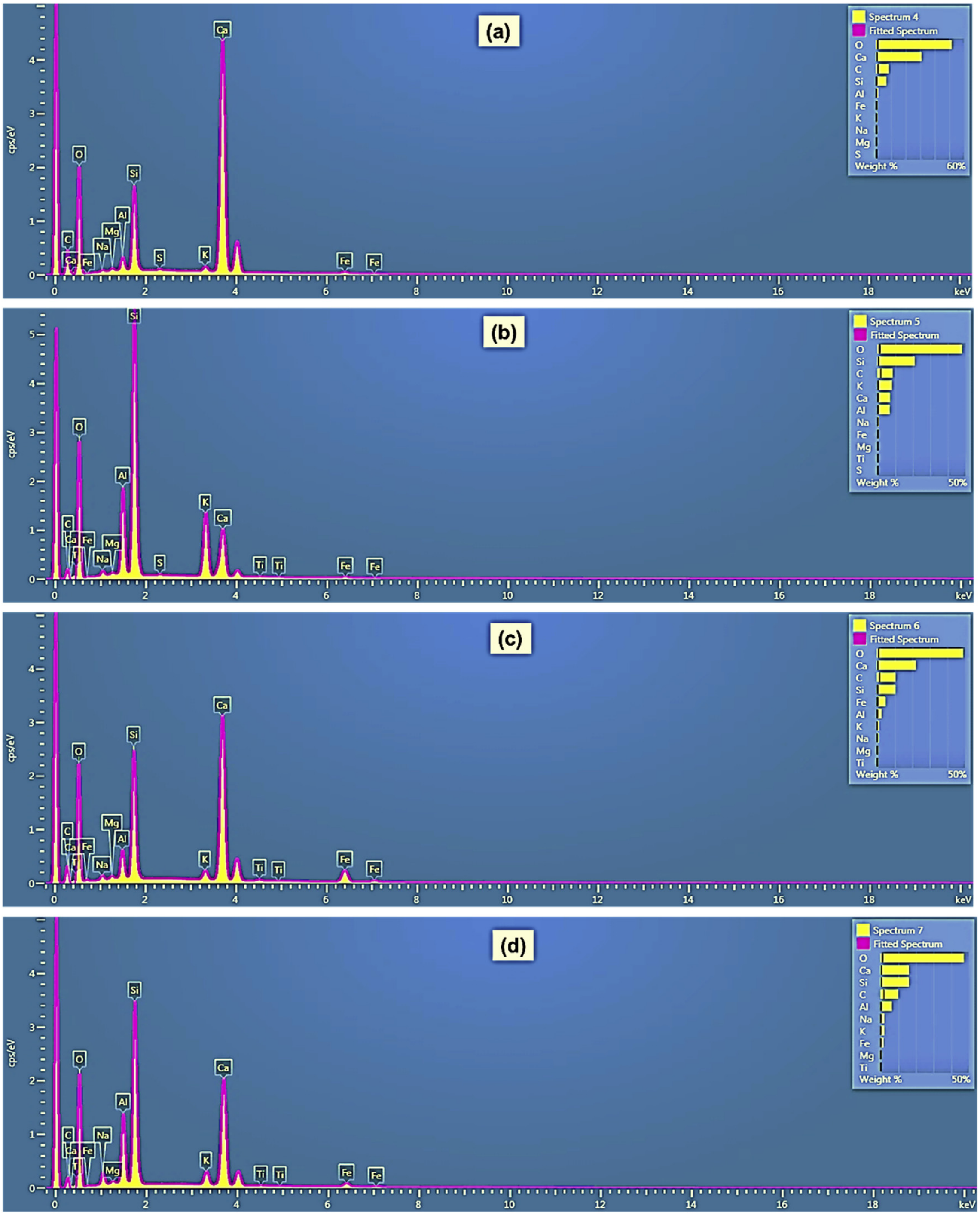

Fig. 4. Energy dispersive X-ray (EDX) spectra of scanning electron microscopy of solidified/stabilized cubes containing 4% low-temperature thermally desorbed oil-based drill cuttings at (a) 7 days, (b) 14 days, (c) 21 days, and (d) 28 days of curing in water. The shell levels associated with the energy level of the X-rays (keV) are not shown.

oil-based drill cuttings are ecologically sound for construction purposes.

According to a recent review (Vaddoriya, 2016), immobilization of contaminants in S/S processes involves chemical fixation of contaminants by interactions between the hydration products of binding material and the contaminants or physical adsorption of contaminants on the surface of binding products. It is likely that in the studied solidified/stabilized matrix, the mechanism for TPH removal was physical adsorption of TPH on the surface of binding products. On the other hand, chemical fixation may be the mechanism for heavy metal removal in the studied solidified/stabilized matrix. As it may be recalled from basic chemistry, chemical reactions result in entirely new products while physical reactions do not. The high amount of TPH leached (Table 2) suggests that TPH is merely sorbed to the surface of binding products in the solidified/stabilized matrix. The physical sorption of TPH on the surface of binding products in the solidified/stabilized matrix obviously will determine its fate and transport in the solidified/stabilized matrix. Chemical interactions between the hydration products of Portland cement and the heavy metals at early stages of hydration may likely convert the heavy metals into entirely new chemical complexes. This explains the poor heavy metal leaching characteristics (Table 2) of the cement-based solidified/stabilized pre-treated oil-based drill cuttings.

Table 3
The elemental composition (weight %) of solidified/stabilized cubes containing 4 % low-temperature thermally desorbed oil-based drill cuttings.

Spectrum Label	Elemental composition (weight %)[a]													Total (%)
	C	O	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Cu	
Spectrum a	8.38	51.5	0.28	0.24	1.11	6.51	ND	0.10	0.51	30.76	ND	0.61	ND	100
Spectrum b	8.52	47.75	0.61	0.15	6.70	21.05	ND	0.11	7.87	6.75	0.13	0.37	ND	100
Spectrum c	10.33	48.73	0.68	0.25	2.41	10.03	ND	ND	1.00	21.9	0.25	4.41	ND	100
Spectrum d	9.90	46.9	1.84	0.22	6.10	15.89	ND	ND	1.71	15.89	0.14	1.42	ND	100

ND, Not Detected.

[a] Data from the SEM EDX spectra shown in Figure 4 (a – d).

3.3. Surface microstructure and elemental composition of the solidified/stabilized pre-treated oil-based drill cuttings

The surface microstructure of the solidified/stabilized matrix was studied using the SEM. For obvious reasons, the SEM micrographs of all the 124 solidified/stabilized test cubes produced in this study cannot be shown here. However, typical SEM micrographs (250 μm) of the solidified/stabilized test cubes; all produced with 4 % low-temperature thermally desorbed oil-based drill cuttings at various days of curing are shown in Fig. 3. Variations in the micrographs are clear. It can be seen in the 250 μm micrographs as well as the 500 μm micrograph (inset in Fig. 3) that there is the absence of needle-like crystals of ettringite and the presence of gel-like hydration products characteristic of calcium silicate hydrate. A similar observation was reported by Al-Ansary and Al-Tabbaa (2007) for synthetic-based drill cuttings stabilized with ten different binder systems at 28 days of curing.

Ettringite, also known as calcium sulphuraluminate, is normally found in Portland cement concretes (Portland Cement Association, 2001). Reports in literature show that the presence of ettringite in concretes is dependent on the ratio of calcium sulphate to tri-calcium aluminate; the higher this ratio is, the less likely it is for ettringite to convert to the calcium aluminate mono-sulphate phase at early stages of hydration (Portland Cement Association, 2001). The SEM energy dispersive X-ray (EDX) spectra showing the elemental compositions of some of the solidified/stabilized cubes produced in this study are shown in Fig. 4 while the percentage compositions by element on weight basis (insets in Figure 4 (a–d)) are interpreted in Table 3. Giving the little or no presence of sulphur in the studied solidified/stabilized cubes (Fig. 4 and Table 3), resulting in a low calcium sulphate to tri-calcium aluminate ratio, it is likely that primary ettringite formed at the early hours of hydration would have converted to the calcium aluminate mono-sulphate phase. This may explain the reason for the absence of ettringite in the micrographs in Fig. 3. It has also been reported in the literature that crystals of primary ettringite are often observed in air voids or cracks in concretes that have been exposed to water for long periods of time (Portland Cement Association, 2001). Therefore, the absence of ettringite in the micrographs of Fig. 3 may suggest the absence of air voids in the studied solidified/stabilized cubes, which may be attributed to the fluidity of the low-temperature, thermally desorbed oil-based drill cuttings as compared to the gritty nature of fine aggregates.

Furthermore, there is the abundance of calcium, silicon, and oxygen in the concrete as can be seen in the number of counts per second (cps) of their characteristic X-rays (Fig. 4) and their percentage weight composition (Table 3). This is indicative of the presence of reactive silicate and aluminate reported to be necessary for the formation of gel-like hydration products of calcium silicate hydrate (Payá et al., 2017).

3.4. Combined effects of drill cuttings content, age (days of curing), and water-to-cement ratio on the compressive strength of solidified/stabilized pre-treated oil-based drill cuttings

It should be stated that from this point onward, solidified/stabilized products containing low-temperature thermally desorbed oil-based drill cuttings would be referred to simply as treatment cubes while solidified/stabilized products not containing low-temperature thermally desorbed oil-based drill cuttings would be referred to simply as control cubes. Depending on the intended use of the treatment cubes, different minimum values of compressive strength apply. In the current study, the

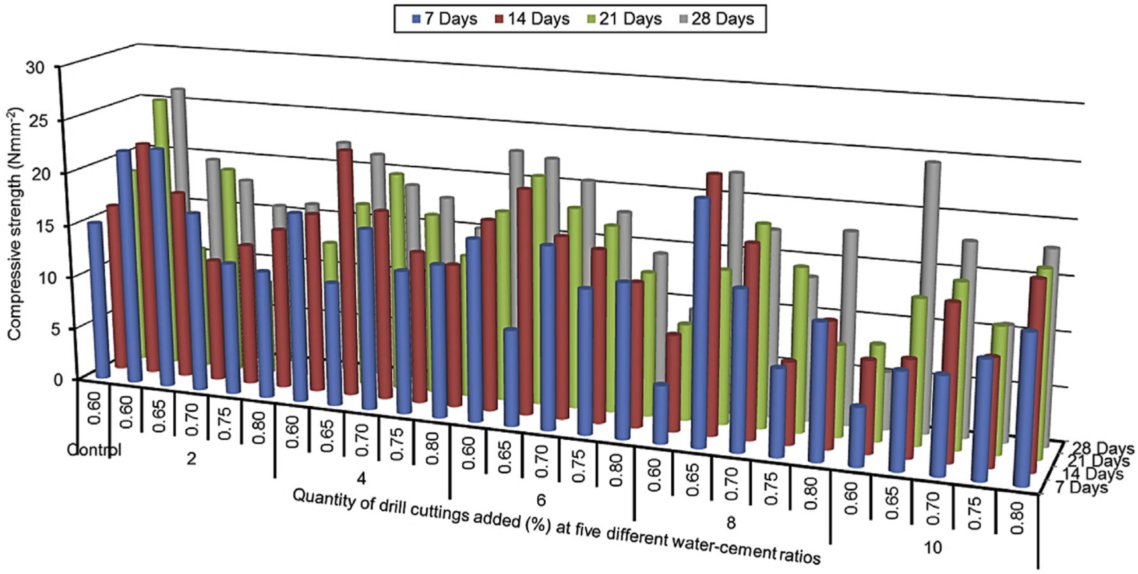

Fig. 5. Unconfined compressive strength of solidified/stabilized cubes produced with stated quantities of low-temperature thermally desorbed oil-based drill cuttings as part replacement for fine aggregate at 7, 14, 21, and 28 days of curing. The cubes not containing drill cuttings (control) were produced at 0.6:1 water-to-cement ratio.

treatment cubes were intended for use in the design of reinforced concrete columns, beams, and slabs. For these purposes, literature recommend a concrete grade/strength class of C20, for which the minimum value of compressive strength should be 20N/mm^2 (BSI, 2004). Fig. 5 shows the compressive strength values of solidified/stabilized products produced with various quantities of low-temperature thermally desorbed oil-based drill cuttings at different water-to-cement ratios and ages of curing. As shown in Fig. 5, the compressive strength of the control cubes varied between 15 and 20 N/mm^2 approximately; attaining the recommended minimum compressive strength of 20 N/mm^2 at 0.6:1 water-to-cement ratio at 21 days of curing. The choice of the control cubes was arrived at after a series of trial water-to-cement ratios using the design mix ratio of 1:2:4 (results not shown). It is important to state that due to cost other design mixes were not considered in this study. Further studies should, therefore, focus on other mix ratios.

Overall, Fig. 5 revealed that the compressive strength of the treatment cubes varied between 5 and 26 N/mm^2 approximately. In a similar study, concretes produced with synthetic-based drill cuttings using a water-to-cement ratio of 0.4:1 yielded compressive strength values ranging between 0.092 and 4.708 N/mm^2 (Al-Ansary and Al-Tabbaa., 2007). Fig. 5 further revealed that for the 2 % drill cuttings addition, the compressive strength ranged between 22.22 and 26.22 N/mm^2, for the 4 % between 11.56 and 23.11 N/mm^2, for the 6 % between 8.89 and 22.67 N/mm^2, for 8 % between 5.33 and 23.56 N/mm^2, and for 10 % addition between 5.33 and 24.44 N/mm^2. From the wide range of compressive strength values given above, it is clear that not all of the grade C20 concretes produced in the current study yielded the recommended minimum compressive strength of 20 N/mm^2. As expected, this is because of the effects of different proportions of drill cuttings and water-to-cement ratios used, as well as differences in the curing ages on the compressive strength. Although most of the treatment cubes yielded compressive strength values less than the required minimum value of 20 N/mm^2, the lower compressive strength values could be used in areas where low-grade concretes are needed such as production of blocks and bricks.

Additionally, Fig. 5 revealed that the three factors considered here (i.e., drill cuttings content, water-to-cement ratio, and curing age) did have some discernible effects on the compressive strength of the treatment concretes. At the least drill cuttings content of 2 % and water-to-cement ratio of 0.6:1, the treatment cubes yielded the highest compressive strength values (22–26 N/mm^2, approximately) across the various curing ages, which were well above the recommended minimum compressive strength of 20 N/mm^2. At the higher water-to-cement ratios, especially from 0.7:1 to 0.8:1, the compressive strength of the treatment cubes dropped to below the recommended minimum value. This implies that for best compressive strength for studied grade C20 concrete, low quantities of drill cuttings of up to 2 % may be most appropriate at a water-to-cement ratio of 0.6:1. On the other hand, from 4 to 10 % drill cuttings addition, the treatment cubes had compressive strength values ranging from 20–24 N/mm^2 approximately, a majority of which occurring at the water-to-cement ratio of 0.65:1. It thus appears like higher water-to-cement ratios are not suitable for production of grade C20 concrete with low-temperature thermally desorbed oil-based drill

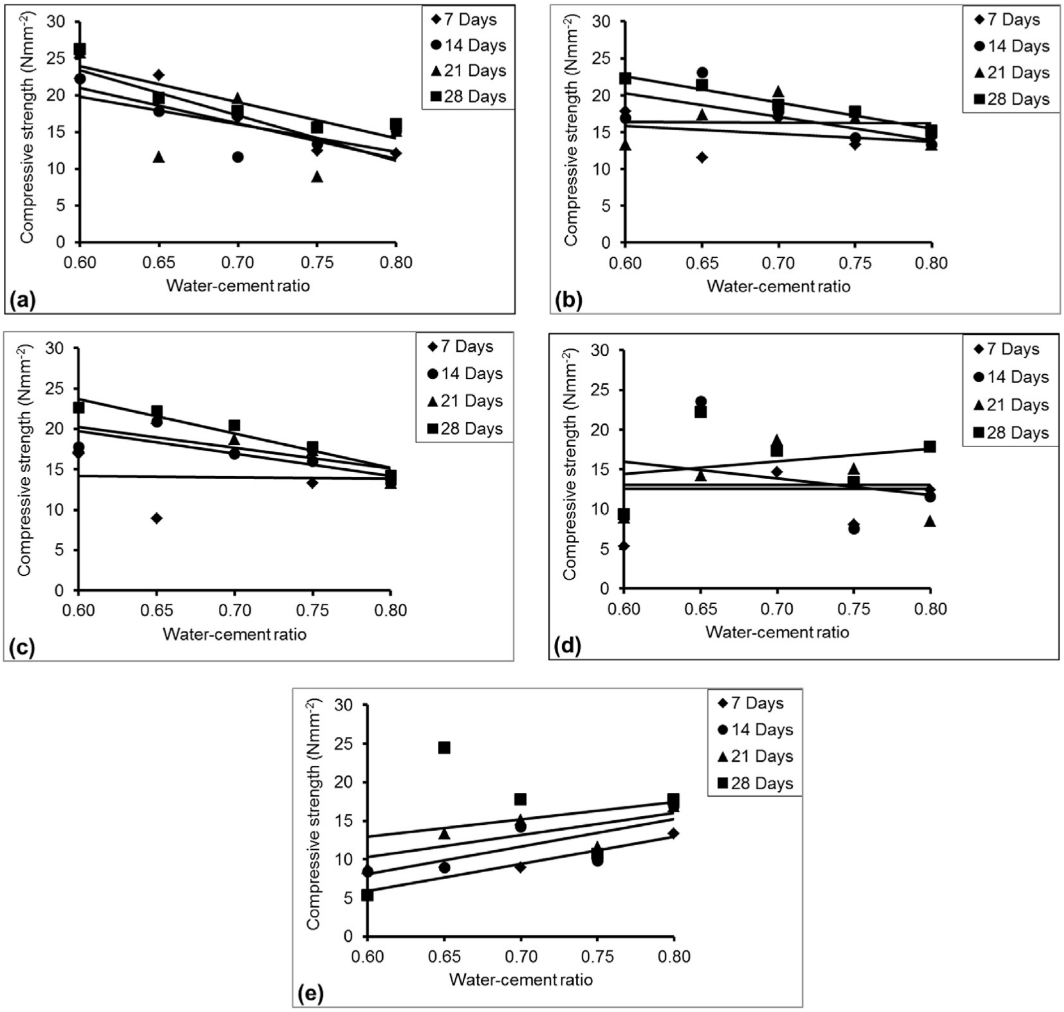

Fig. 6. Variation of compressive strength with water-to-cement ratio of grade C20 concrete produced with: (a) 2 %, (b) 4 %, (c) 6 %, (d) 8 %, and (e) 10 % of low-temperature thermally desorbed oil-based drill cuttings as part replacement for fine aggregate at stated days of curing.

cuttings, especially at higher drill cuttings content. This was evident in Fig. 6, which revealed that for the treatment cubes, the compressive strength decreased as the water-to-cement ratio increased for drill cuttings content of 2–6 % at the various curing ages. However, for 8 and 10 % drill cuttings content, this trend was less defined with the compressive strength becoming almost independent of the water-to-cement ratio at 8 % drill cuttings content (Fig. 6d) and increasing with water-to-cement ratio at 10 % drill cuttings content (Fig. 6e). The reason for this odd behaviour for the 8 and 10 % drill cuttings content is still unclear.

4. Conclusions

In this study, the diagnostic screening against local environmental guidelines of levels of target contaminants in cement-based solidified/stabilized low-temperature thermally desorbed oil-based drill cuttings was carried out. This was done to ascertain whether or not some form of action may be required to avert future problems that may arise from the use of solidified/stabilized pre-treated oil-based drill cuttings for construction purposes. Results obtained showed that the 2 % drill cuttings addition yielded the highest UCS (22.22–26.22 N/mm^2) at water-to-cement ratio of 0.6:1, which were well above the recommended minimum UCS of 20 N/mm^2 for a grade-20 concrete. The average amount of TPH remaining after cement-based S/S of the pre-treated oil-based drill cuttings was 62.41 mg/kg, which slightly exceeded the local regulatory target value of 50 mg/kg. This suggests that cement-based S/S failed to immobilize completely all the hydrocarbons in the pre-treated oil-based drill cuttings. Similarly, there were relics of heavy metals (albeit less than regulatory target values) in the solidified/stabilized matrix. This implies that the solidified/stabilized matrix is not in compliance with environmental guidelines on TPH for sustainable reuse of the pre-treated oil-based drill cuttings as construction materials. As a result, before putting the solidified/stabilized pre-treated oil-based drill cuttings to the intended use, some form of corrective action is required due to the potential environmental health risks of exposure to petroleum hydrocarbons.

Declarations

Author contribution statement

Reuben N. Okparanma: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Perez P. Araka: Performed the experiments.

Josiah M. Ayotamuno: Contributed reagents, materials, analysis tools or data.

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The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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References

Akinlade, M.O., Adenipekun, A., Wind, J.A., 1996. Drilling residue disposal: SPDC-E approach. In: Proceedings of the Annual International Conference and Exhibition of the Society of Petroleum Engineers - Nigeria Council, Warri, pp. 65–74.

Al-Ansary, M.S., Al-Tabbaa, A., 2007. Stabilisation/solidification of synthetic petroleum drill cuttings. J. Hazard Mater. 141, 410–421.

APHA, 1998. Method 3111C: Standard Methods for the Examination of Water and Wastewater, twentieth ed. American Public Health Association, Washington, DC.

Ayotamuno, M.J., Okparanma, R.N., Ogaji, S.O.T., Probert, S.D., 2007. Chromium removal from flocculation effluent of liquid-phase oil-based drill-cuttings using powdered activated carbon. Appl. Energy 84 (10), 1002–1011.

BSI, 2004. Eurocode 2: Design of Concrete Structures - Part 1-1: General Rules and Rules for Buildings (No. BS EN 1992-1-1). British Standard Institute, London.

CL:AIRE, 2010. Bioremediation of heavy hydrocarbons – reducing uncertainty in meeting risk-based targets: laboratory to field scale (PROMISE Project). Contam. Land: Appl. Real Environ. Res. Bull. RB10, 1–8.

Department of Petroleum Resources (DPR), 2002. Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN). Ministry of Petroleum and Natural Resources, Abuja, Nigeria, p. 314.

EPA, 1994a. Method 8270. Semi-volatile Organic Compounds (SVOCs) by Gas Chromatography/Mass Spectrometry (GC/MS): SW-846 Manual. United States Environmental Protection Agency, Government Printing Office, Washington, DC.

EPA, 1994b. Method 8270B. Semi-volatile Organic Compounds (SVOCs) by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique. United States Environmental Protection Agency, Government Printing Office, Washington, DC.

EPA, 1996. Method 3052. Microwave-Assisted Acid Digestion of Siliceous and Organically Based Matrices. United States Environmental Protection Agency, Government Printing Office, Washington, DC.

Fleming, C., 2000. A Discussion of Chemical Fixation and Stabilization (CFS), Solidification/stabilization, Micro-encapsulations and Macro-Encapsulation. Prepared for the API/NOIA Synthetic Based Fluids Research Group, June 15.

Ghasemi, S., Gitipour, S., Ghazban, F., Hedayati, H., 2017. Treatment of petroleum drill cuttings using stabilization/solidification method by cement and modified clay mixes. Iran. J. Health, Saf. Environ. 4 (3), 781–787.

Igwe, E.A., Ayotamuno, M.J., Okparanma, R.N., Ogaji, S.O.T., Probert, S.D., 2009. Road-surface properties affecting rates of energy dissipation from vehicles. Appl. Energy 86 (9), 1692–1696.

IOGP, 2016. Drilling Waste Management Technology Review. Report 557. International Association of Oil and Gas Producers, London.

Kogbara, R.B., Dumkhana, B.B., Ayotamuno, J.M., Okparanma, R.N., 2017. Recycling stabilised/solidified drill cuttings for forage production in acidic soils. Chemosphere 184, 652–663.

Leonard, S.A., Stegemann, J.A., 2010. Stabilization/solidification of petroleum drill cuttings. J. Hazard Mater. 174 (1–3), 463–472.

Lyons, W.C., 1996. Drilling muds and completion fluids. In: Lyons, W.C. (Ed.), Standard Handbook of Petroleum and Natural Gas Engineering, first ed. Gulf Publishing Company, Houston, Texas, pp. 650–715.

Mitra, S., 2003. Sample Preparation Techniques in Analytical Chemistry. Wiley and Sons Inc. Publication, Hoboken, NJ, USA.

NDES, 1995. Background and Mission: Briefing Note 1. Publication of the Steering Committee, Niger Delta Environmental Survey, Falomo, Lagos, Nigeria, pp. 1–7.

Norwegian Oil Industry Association, 2003. Guidelines for Characterization of Offshore Drill Cuttings Piles. Available from: http://www.olf.no. (Accessed October 2014).

Nwokedi, T.C., Okoroji, L.I., Nze, I.C., Ndukwu, I.P., 2015. Oil exploration and production waste management practices: a comparative analysis for reduction in hazardous E & P waste generation in offshore oil platforms in Nigeria. J. Environ. Earth Sci. 5 (4), 101–107.

Okparanma, R.N., Ayotamuno, J.M., Araka, P.P., 2010. Polycyclic aromatic hydrocarbons in Nigerian oil-based drill-cuttings; evidence of petrogenic and pyrogenic effects. World Appl. Sci. J. 11 (4), 394–400.

Okparanma, R.N., 2013. Rapid Measurement of Polycyclic Aromatic Hydrocarbon Contamination in Soils by Visible and Near-Infrared Spectroscopy. PhD Thesis. Department of Environmental Science and Technology, Cranfield University, United Kingdom. Available from: https://dspace.lib.cranfield.ac.uk. (Accessed October 2019).

Okparanma, R.N., Coulon, F., Mayr, T., Mouazen, A.M., 2014. Mapping polycyclic aromatic hydrocarbon and total toxicity equivalent soil concentrations by visible and near-infrared spectroscopy. Environ. Pollut. 192, 162–170.

Okparanma, R.N., Azuazu, I., Ayotamuno, J.M., 2017. Assessment of the effectiveness of onsite exsitu remediation by enhanced natural attenuation in the Niger Delta region, Nigeria. J. Environ. Manag. 204, 291–299.

Okparanma, R.N., Araka, P.P., Ayotamuno, J.M., Mouazen, A.M., 2018. Towards enhancing sustainable reuse of pre-treated drill cuttings for construction purposes by near-infrared analysis. J. Civ. Eng. Construct. Technol. 9 (3), 19–39.

Opete, S.E.O., Mangibo, I.A., Iyagba, E.T., 2010. Stabilization/solidification of synthetic Nigerian drill cuttings. Afr. J. Environ. Sci. Technol. 4 (3), 149–153.

Owens, C.K., Rycroft, D.R., Stephenson, M.T., Norris, G., Johnson, J.A., Crame, L.W., Grieg, A., 1993. Exploration and Production (E&P) Waste Management Guidelines (No. 2.58/196). London.

Payá, J., Monzó, J., Borrachero, M.V., Soriano, L., Akasaki, J.L., Tashima, M., 2017. New inorganic binders containing ashes from agricultural wastes. In: Savastano Jr., H., Fiorelli, J., Santos, S.F. (Eds.), Sustainable and Nonconventional Construction

Materials Using Inorganic Bonded Fibre Composites. Elsevier Ltd., pp. 127–164. Available from: (Accessed June 2018)

Permata, E., McBride, S., 2010. Regulatory challenges of drill cuttings waste management in Indonesia. In: Proceedings of Society of Petroleum Engineers (SPE) International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Indonesia, pp. 1232–1236.

Portland Cement Association, 2001. Concrete Information: Ettringite Formation and the Performance of concrete. PCA R&D Serial No. 2166. Skokie, Illinois, USA.

Ratnayake, A.S., Sampei, Y., 2015. Characterization of organic matter and depositional environment of the Jurassic small sedimentary basins exposed in the northwest onshore area of Sri Lanka. Res. Org. Geochem. 31, 15–28.

Ratnayake, A.S., Sampei, Y., 2019. Organic geochemical evaluation of contamination tracers in deepwater well rock cuttings from the Mannar Basin, Sri Lanka. J. Petrol. Explor. Prod. Technol. 9, 989–996.

Shaffer, G.P., Hester, M.W., Miller, S., Des Rochers, D.J., Southern, R.F., Childers, G.W., Campo, F.M., 1998. Restored Drill Cuttings for Wetland Creation: Results of a Two-Year Mesocosm Approach to Emulate Field Conditions under Varying Hydrologic Regimes (No. DOE/BC/14849-3). Houston, Texas. Available from: https://digital.library.unt.edu/ark:/67531/metadc687884/m1/2/. (Accessed April 2010).

Vaddoriya, K., 2016. Immobilization of heavy metals using solidification/stabilization treatment: a Review. Int. J. Adv. Res. Innov. Ideas Educ. 2 (3), 49–53.