DOI: https://doi.org/10.24425/amm.2022.141043

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NEW RAY ON REMEDIATION OF HIGH RINGS POLYCYCLIC AROMATIC HYDROCARBONS: REMEDIATION OF RAW PETROLEUM SLUDGE USING SOLIDIFICATION AND STABILIZATION METHOD

Solidification/Stabilization (S/S) method with cement as a binder to remediate metals in petroleum sludge has been successfully proven. However, this technique has not yet been explored to remediate organic contaminants since a high concentration of Total Petroleum Hydrocarbon (TPH) was also detected in the sludge. This study focuses on remediating 16 Polycyclic Aromatic Hydrocarbons (PAHs) compounds in raw petroleum sludge with Portland cement as a binder using the S/S method. The initial concentration of 16 PAHs in the raw sludge was first measured before the performance of the S/S method to remediate the PAHs were evaluated. The S/S matrices were tested for leaching behavior and strength after 7 and 28 days by air curing. The leaching test was measured using the Toxicity Characteristics Leaching Procedure (TCLP), and the remaining PAHs concentration in the matrices was analyzed using a Gas Chromatography-Mass Spectrometer (GC-MS). In the raw sludge, all 16 PAHs compounds were below the standard limit except for Benzo(a)anthracene, Benzo(a)pyrene, Dibenzo(ah)anthracene, and Indeno(1,2,3- cd_ pyrene), which are considered as high rings PAHs. The high rings PAHs show lower concentration in leachate than low rings PAHs, which indicates the potential of the S/S method in remediating high rings PAHs. The high sludge ratio in S/S matrices has shown that the percentage strength is increasing, similar to Portland cement. Therefore, this study contributed to the possibility of the S/S method in the remediation of PAHs in petroleum sludge by using only Portland cement as a binder.

Keywords: Remediation; Solidification/stabilization; organic contaminant; hazardous waste

1. Introduction

Nowadays, in Malaysia, the growth of petroleum industries leads to an enormous amount of hazardous waste that mostly comes from petroleum refineries [1]. The production of petroleum has generated a huge amount of waste, including petroleum sludge from the bottom tank, petroleum wastewater, and drilling fluid. The amount of the sludge produced reaches the capacity of 105,000 barrels per day with 50 tons of oily sludge per year [2]. Petroleum industries have contributed 32% of the world's energy sources, and it is expected to remain the main source for the next two decades [3]. Commonly, sludge is made up of hydrocarbon, asphaltenes, paraffin, water, and inorganic solids, which contain sand, iron sulphides, and iron oxides [4]. Besides, the conditioned sludge is changed when crude oil properties are changed. In addition, petroleum sludge is recorded as hazardous waste based on Resources Conservation and Recovery Act (RCRA) [5].

In environmental pollution, organic and inorganic contaminants become issues worldwide that need to be a concern. Inorganic contaminants such as heavy metals and organic contaminants such as pesticides, polycyclic aromatic hydrocarbons, herbicides, endocrine disrupting compounds, pharmaceuticals, and other compounds usually can be found in ground/surface water, wastewater, soil, sludge, and other media [6,7]. For petroleum sludge, it contains various toxic in a hydrocarbon such as aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). It was reported that about 40-52% alkanes, 28-31%

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aromatics, 8-10% asphaltenes and 7-22.4% resins compound contain in petroleum sludge [8,9]. Organic contaminants in petroleum sludge have mutagenic and carcinogenic properties [10]. Based on the United States Environmental Protection Agency (USEPA) list, 43 organic contaminants are considered potential environmental health [11]. Organic contaminants in petroleum sludge were measured as total petroleum hydrocarbon (TPH) are in the range of 510,000 to 640,000 mg/kg [12]. Therefore, in ecological agriculture, untreated petroleum sludge is prohibited from disposing of in landfills due to the high content of contaminants [13]. Thus, the remediation of petroleum sludge is needed to ensure heavy metal and organic contaminants within tolerated limits are disposed.

PAHs are compounds that consist of carbon and hydrogen atoms. It is a combination of two or more benzene rings bonded and a pair of carbon with a fused aromatic ring that shares in some molecules [14]. PAHs have become one of the environmental concerns as a primary pollutant because they can affect the aquatic food chains [14,15]. The higher spread PAHs are always from the production of all types of combustion of organic materials and anthropogenic sources [16]. In addition, the increasing industrial development contributes to the increase of PAHs in the natural environmental [17,18]. According to Jaturapitakkul et al., the high toxicity of PAHs might be affected by the metabolism and photo-oxidation, where toxic produced more in the presence of ultraviolet light. From a health effect perspective, it leads to chronic and acute sickness[19].

Recently, tremendous researchers have tried to innovate a treatment involving sludge to decrease harm to the environment. The several methods that have been used to treat and dispose of petroleum sludge are thermal, mechanical, biological, and chemical method [20,21]. The most common method in the remediation of organic contaminants is based on biological processes. The effectiveness of the biological process depends on the species of microorganisms known as degrading agents used to remediate the organic contaminants [22]. The main disadvantage associated with this process is the long remediation time required to achieve the target level. Organic contaminants from anthropogenic activities constitute a new additional compound to the natural environment, and a smaller number of microorganisms is able to use the contaminants as carbon or energy source. This problem contributes to the low survival of microorganisms in contaminated soil [22].

PAHs can be divided into two large groups, i.e., low rings and high rings. For low rings, high numbers of studies were successfully done on removing or degrading by using the biological process. However, high rings PAHs with high hydrophobicity and low aqueous solubility required strenuous efforts to be completely degraded [23,24]. These characteristics also may lead to more interaction of PAHs with non-aqueous phases such as sludge. Thus stabilization/solidification (S/S) method which is aimed to immobilizing contaminants by converting them into a less soluble form (stabilization); and encapsulating them by the creation of a durable matrix (solidification), and it may be potential in PAHs remediation, especially for high rings PAHs [25]. The S/S method used Portland cement, lime and ash as a binder to treat waste treatment has mostly been studied because it is quicker and more inexpensive.

S/S method is mostly conducted to treat inorganic contaminants such as heavy metals. The compound measured in heavy metals usually is barium (Ba), lead (Pb), zinc (Zn), mercury, chromium (Cr), arsenic (As), and nickel (Ni) [26-29]. Commonly, heavy metal is volatile at high temperature and condense at a lower temperature, known as a semi-volatile compound, e.g., Pb, Cd, Cu, and Zn [30]. Portland cement is a common binder used in the S/S method to treat inorganic contaminants due to pozzolanic matter [31]. Besides, Du et al. studied the leaching behavior of Pb using Portland cement as a binder in S/S and projected Pb was leached after adding 12-18% of Portland cement in S/S matrices. Other studies showed that the soil contaminated by Pb, Zn, Copper (Cu), Ferum (Fe), and Manganese (Mn) could be treated by using Portland cement as a binder. This treatment proved the condition of Portland cement at pH $\geq$ 12 could reduce the concentration of heavy metals as well as in alkaline conditions [31,32]. The effect of lead on cement strength has shown that the increase of lead content in S/S matrices decreases the strength of cement strength [31,33]. Studies of the S/S method by using geopolymers as a binder were successful in the remediation of heavy metals in hazardous waste [34]. A study conducted by Ahmari and Zhang has successfully solidified Zn and Cu in mine tailing [34]. Galiano et al. have solidified the Municipal Solid Waste Incineration fly ash containing Pb, Cd, Cr, and Zn in geopolymer. The leachability of heavy metals was reduced due to low permeability, acid resistance, and geopolymer matrices durability [35]. Many studies have shown the success of immobilization of inorganic contaminants, especially heavy metals, by using the S/S method. However, fewer studies were conducted to measure the efficiency of S/S method for organic contaminants.

Immobilization of organic contaminants depends mainly on physical entrapment in the binder matrix and sorption onto the surface of binder hydration products. S/S method is better in reducing organic contaminants with the characteristics of high surface area and good pore size distribution of media [36]. Few studies were conducted using the S/S method on organic contaminants, such as Coffi et al., who used organophilic bentonite in cement paste as a binder to remediate chlorophenol loaded in bentonite [37]. The study has mentioned that the organic contaminants, including n-alkane, polycyclic aromatic hydrocarbons (PAHs), sence of 1-chloronaphthalene in cement paste, increased the porosity and lowered the mechanical strength. Other than that, the hydration and structure of cement using 2-monochloroaniline (2-MCA) are not significant without using any adsorbent, which result has recorded about 75% of 2-MCA being released in leachate solution [38]. In another study, immobilizing oily sludge using the S/S method is reliable due to the decrease in leaching behavior. This was proved by Karamalidis and Voudrias using I42.5 cement addition to reduce the leachability of most alkanes and PAHs compounds. The cement usage has formed excess cavities, which where can be broken and projected the higher hydrocarbon leaching together with cement addition [39].

S/S method is commonly applied in immobilizing inorganic contaminants, which are mostly heavy metals. However, very limited studies have shown the potential of this method on organic contaminants, especially hydrocarbons in raw petroleum sludge. This study is attempted to remediate raw petroleum sludge, which focuses on the remediation of PAHs. Presently in Malaysia, this sludge is burnt at a high temperature in the incinerator then the ash is remediated using the S/S method. Thus, findings from this study will contribute to the potential of PAHs remediation without going through the incineration process. In addition, the behavior of each PAHs compounds during S/S method is an engrossing part to be evaluated, and the contribution is very significant in the future study. Therefore, this study aimed to remediate 16 priority PAHs compounds by using S/S method in raw petroleum sludge with Portland cement as a binder. The specific objectives of this study are to measure the concentration of 16 PAHs in raw petroleum sludge and to evaluate the performance of the S/S method based on the leaching test and compressive strength test.

2. Materials and methods

2.1. Material

In this research, there are two materials used to accomplish the aim of this study. Petroleum sludge was taken from Petronas Lubricant Refinery in Melaka. The sample was stored at 4°C before use. Portland cement (TASEK) was obtained from the Advance Material Laboratory at Universiti Tun Hussein Onn Malaysia (UTHM).

2.2. Extraction of PAHs from raw samples

PAHs extraction was performed by using a Soxhlet extraction method [40]. The 10 g sample was mixed equally with Na2SO4, and tissue papers were wrapped and put into an extraction thimble. The 180 mL of mixture acetone: n-Hexane (1:1) were added to a 250 mL receiving flask for PAHs extraction. The extraction was carried out below solvent boiling temperature for 24 hours. Then, the extract was concentrated using rotary evaporation at 40°C and a pressure of 350 mbar. The cartridge used by filtration 0.45 µm PTFE (polyetrafluoroethylene) syringe filter prior to analysis.

Analysis of PAHs was carried out using a Gas Chromatography-Mass Spectrometer (GC-MS), equipped with BPX-5 (5% phenyl polysilphenylene-siloxane) capillary column (30 m length, 0.25 mm dia., 0.25 µm film thickness) with the operating conditions: GC inlet pulsed 75 kpa, 1,2 mL/min, carrier gas helium (He) flow 93 mL/min; injection volume 5 µL, splitless injection at 300°C, a detector at 280°C and initial oven temperature 70°C held for 2 min then increase at 8°C/min to final temperature 290°C. Lastly, the retention time and mass spectra of selected PAH were recorded for GC-MS analysis.

2.3. Preparation S/S matrices

The preparation of S/S matrices involved three steps, i.e., mixing, casting, and curing. The control sample was 100% Portland cement, and other samples containing a different ratio of Portland cement and petroleum sludge, as shown in TABLE 1, were mixed for approximately about 5 minutes to ensure no lump was left. Then, the water ratio used for this sample was 0.485, which was added to the mixture [12]. For the casting procedure, a mold cube size of 100 mm^3 was used to place the samples. The samples were casted in three layers, which were compacted manually and shook about 50 hits to yield a good packing mixture. Lastly, samples were left for 7 and 28 days for air drying of the solidified samples at controlled conditions, i.e., temperature 25±2°C and humidity more than 90%.

TABLE 1

Different ratios of Portland cement and petroleum sludge

Portland cement %	Petroleum sludge %	Water cement ratio
100	0	0.485
90	10	0.485
80	20	0.485
70	30	0.485
60	40	0.485
50	50	0.485

2.4. Leaching Procedure

Toxicity Characteristics Leaching Procedure (TCLP) is commonly adopted in many studies and was referred for leachability test [12,19,41]. The leaching fluid, namely ultra-pure water, was selected for TCLP due to its applicability for semi volatiles contaminants, i.e., PAHs. For mixture samples, leaching fluids were prepared in screw-capped polyethylene bottles, which were filled with crushed brick samples (40 g) and leachant (400 mL) at the ratio of 1:10 was used to simulate the earlier leaching period, and this agrees with the European leaching protocol for hazardous waste and other researchers [5]. In the TCLP test, the sample was crushed with a size less than 9.5 mm due to TCLP test requires particle sizes to comply with the standard [5]. The bottles were agitated at 30 rpm for 18 hours. The leachate collected then was filtered and extracted by using the Soxhlet method and was measured by using a Gas Chromatography-Mass Spectrometer (GC-MS) for analyses concentration of PAHs.

2.5. Unconfined Compressive Strength Test (UCS)

The UCS test was conducted in order to evaluate the strength of the mixture at higher stress, as well as to imitate the disposal standardization of the solidified samples according to BS 1881 – 116: 1983 [42]. UCS of samples for 7 and 28 days hydrations were measured by using a compressive test machine 3000kN. All tests were followed ASTM C-109, which is below the compressive strength of hydraulic cement mortar. For this study, the cube was tested at age 7 days and 28 days of hydration period and dried in an air cabinet under controlled conditions (temperature 25±2°C, humidity more than 80%). The total maximum load was measured by using the formula in equation 3.1:

$$fm = \frac{P}{A} \quad (1)$$

Where, *fm* indicates compressive strength in MPa, *P* is total maximum load in (N) and, *A* is the area of loaded surface in mm^2.

3. Results and discussion

This section is divided into three subsections. In the first subsection, the concentration of 16 PAHs in raw materials was discussed. For the second and third subsections, the S/S method was elaborated in detail on the measurement of the performance of S/S matrices through the leaching test and compressive strength test.

3.1. PAHs Concentrations in Raw Materials

TABLE 2 shows the concentrations of 16 PAHs that were extracted from raw materials, which are Portland cement and petroleum sludge. The 16 PAHs were compared with the Contaminated Land Management and Control Guidelines standard [40] for comparison of safe disposal into landfill soil. For cement, all 16 PAHs were below the standard limit in the range from 0.10 mg/kg to 0.50 mg/kg. Whereas, for sludge, the 16 PAHs were below the standard limit except for four compounds, namely, Benzo (a) anthracene (32.02 mg/kg), Benzo (a) pyrene (31.02 mg/kg), Dibenzo (ah) anthracene (30.12 mg/kg) and Indeno(1,2,3-cd) pyrene) (30.11 mg/kg). These PAHs compounds were detected at 15 times higher than the concentration in the standard limit. Whereas Indeno(1,2,3-cd)pyrene) was detected 1.5 times higher than t concentration in the standard limit.

According to Lawal, there are seven PAHs compounds were listed as hazardous to humans and the environment, such as Benzo(a)anthracene, Chrysene, Benzo(a)pyrene, Benzo(b) fluoranthene, Benzo(k)fluoranthene, Dibenzo(a,h)anthracene and Indeno(1,2,3-cd)pyrene [43]. These high rings compounds are identified as carcinogenic, mutagenic, and toxic, which are needed to remediate before disposal to landfill soil [14]. From the result, four out of these seven PAHs compounds were detected above the standard limit. Thus, the sludge requires to be remediated before disposing into landfill soil.

Moreover, the result from this study was compared to a study conducted by Bojes, which measured 16 PAHs of aged crude oil in the bottom of a storage tank. The study showed that three compounds, i.e., Benzo(a)anthracene, Benzo(a)pyrene, and Dibenzo(ah)anthracene were above the standard limit, which is similar to this study. However, the difference between PAHs concentrations and the standard limit was in the range of 2 to 10 times higher than the standard limit, which is lower when compared to this study [44]. In contrast, the study detected a high concentration of two rings PAHs, naphthalene that was above the standard limit. This is supported by Castaldi, which found a higher concentration of low ring PAHs in petroleum sludge than high rings PAHs [45]. Therefore, this is suggested that the concentration of PAHs in sludge might be modified and degraded by the weathering process. The characteristics of the low ring PAHs are degradable, volatile, less hydrophobic, and more soluble compared to high rings PAHs, which easily been volatile and leached when exposed to the weather. When less exposed, the low ring PAHs can be detected even in aged petroleum sludge. Unlike in this study, below the standard limit of low ring PAHs is detected, which indicates the petroleum

TABLE 2

PAHs concentration in raw material

PAHs compounds	Concentration of PAHs (ppm)		Bojes and Pope [42]	*SSL (industrial)
	OPC	PS		
Napthalene	0.53±0.11	30.12±0.15	**254.5**	200
Acenaphthylene	0.51±0.09	29.02±0.26	24.2	2300
Acenaphthene	0.52±0.21	30.09±0.42	34.8	37164
Fluorene	0.51±0.23	28.22±0.21	80.6	22000
Phenanthrene	0.51±0.24	31.00±0.04	19.9	18582
Anthracene	0.52±0.13	32.07±0.06	24.8	170000
Fluoronthene	0.53±0.42	29.12±0.14	15.5	22000
Pyrene	0.53±0.08	31.02±0.17	19.9	17000
Benzo (a)anthracene	0.51±0.31	**32.02**±0.34	**9.4**	**2.1**
Chrysene	0.53±0.16	28.02±0.08	24.5	2100
Benzo (b) fluoranthene	0.11±0.12	61.12±0.13	8.2	210
Benzo (k) fluoranthene	0.10±0.31	59.09±0.23	7.3	210
Benzo (a)pyrene	0.50±0.14	**31.02**±0.34	**8.4**	**2.1**
Dibenzo(ah) anthracene	0.51±0.21	**30.12**±0.41	**4.1**	**2.1**
Benzo (ghi) perylene	0.50±0.25	29.23±0.07	5.9	18582
Indeno(1,2,3-cd) pyrene	0.52±0.46	**30.11**±0.06	5.8	**21**

*SSL – Contaminated Land Management and Control Guidelines No 1 sludge underwent a significant weathering process and most probably influenced by the native microorganism that degrades the PAHs [46].

Besides petroleum sludge, a concentration of 16 PAHs was also detected at 20.67±4.14 mg/kg in sewage sludge. The study has also detected a higher concentration of high molecular weight (81%) compared to low molecular weight (19%). Most of the carcinogenic PAHs come from high molecular weight [47]. The result from Khillare et al. was different compared to Chen et al., in which very low 16 PAHs were detected, i.e., 0.5342-1.0666 mg/kg [47,48]. The study has also found that 4-ring PAHs, fluoranthene, pyrene, and chrysene were predominants (47.6%) in sewage sludge. Clearly that these sludges contain a high concentration of high rings PAHs, which tend to adsorb in the hydrophobic surface (sludge) due to its hydrophobic behavior. However, these PAHs can be desorbed by biogeochemical process and leach into groundwater and surface water. Eventually accumulate in aquatic life and threaten human life who take fish in their diet. The existence of the high rings PAHs in petroleum and municipal sludge indicates the need for cost-efficient and environmentally friendly treatment to avoid the mobilization of these pollutants in the environment in a fast way.

3.2. Leaching Test

Based on the result in Section 3.1, there are four PAHs compounds concerned in this study regarding high concentrations of PAHs, which are above the permissible limit. The leaching of these compounds was measured as shown in Figs 1 and 2 for 7 days and 28 days, respectively.

Based on TCLP testing, samples with a ratio of 50% cement and 50% sludge show the highest leaching concentration. The highest concentrations were recorded at 14.336 ppm, 22.428 ppm, 25.436 ppm, and 14.836 ppm for Benzo(a)anthracene, Benzo(a) pyrene, and Dibenzo(ah)anthracene and Indeno(1,2,3-cd)pyrene, respectively, on 7 days of curing. Then, the concentrations for these compounds were gradually decreased with the reduction of the sludge ratio in the sample. A similar trend was observed for 28 days of curing, in which the concentrations of these compounds were much lower compared to 7 days of curing. The permissible limit for these compounds is 2.1 ppm except for Indeno(1,2,3-cd)pyrene, in which the limit is 21 ppm. Thus, only Indeno(1,2,3-cd)pyrene was below the permissible for all ratios of PS usage in S/S matrices. Whereas other compounds were above the permissible limit.

Based on the result in TABLE 2, the concentration of these four PAHs compounds was 0.5±0.01 ppm in OPC. Meanwhile, in petroleum sludge, the concentration of these four PAHs compounds was 30±0.2 ppm, which is approximately six-fold than OPC. Thus, this result has affected on different of ratios used in this study. Means the higher ratio of sludge used in S/S matrices, the higher concentration of PAHs in leachate.

By comparing these four compounds, Benzo(a)anthracene (four rings PAHs) shows the lowest concentration in leachate after the TCLP testing. Then, followed by Benzo(a)pyrene and Dibenzo(ah)anthracene which are five rings PAHs. Based on these trends, it was expected that Indeno(1,2,3-cd)pyrene (six rings PAHs) would show the highest leaching. However, the finding from this study has not supported these trends may be due to the chemical structure of Indeno(1,2,3-cd)pyrene being different from other compounds. This PAHs compound has a ring that bounds indirectly with carbon and hydrogen [24]. This chemical structure could be beneficial for minimizing the mobilization of this compound in leachate. This study has also found that five rings PAHs, namely Benzo(a)pyrene and Dibenzo(ah) anthracene, were less immobilized using the S/S method with cement as a binder. Benzo[a]pyrene is the most widely studied compound, and most information on the occurrence and toxicity of PAHs is related to it [46]. As far as the author's knowledge, there is a very limited study reported in detail on the behavior of PAHs leaching in the S/S method.

By referring to the guideline in TABLE 2, these compounds are still above the allowable limit except for Indeno(1,2,3-cd) pyrene. The usage of the Portland cement as the only binder system in the S/S method is not effective for the immobilization of organic contaminants [49]. The result of this study was consistent with this statement. These PAHs compounds may inhibit binder hydration and are generally not chemically bound in binder hydration products [50]. However, by referring to all PAHs compounds, the concentrations were reduced after 7 and 28 days of curing, as shown in Fig. 2. The figure shows the

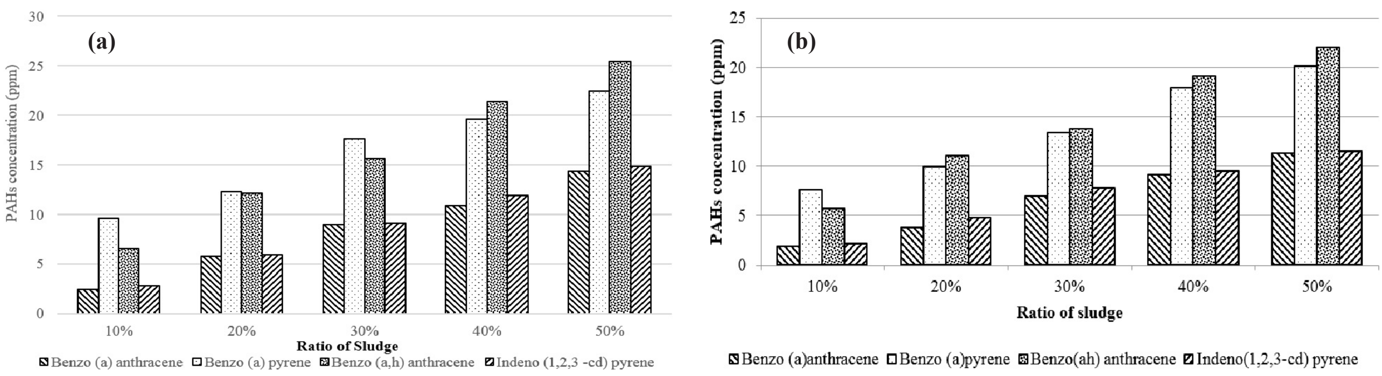

Fig. 1. Benzo (a)anthracene, Benzo (a)pyrene and Dibenzo (ah) anthracene and Indeno(1,2,3-cd)pyrene concentration from leaching test for 7 days (a) and 28 days (b)

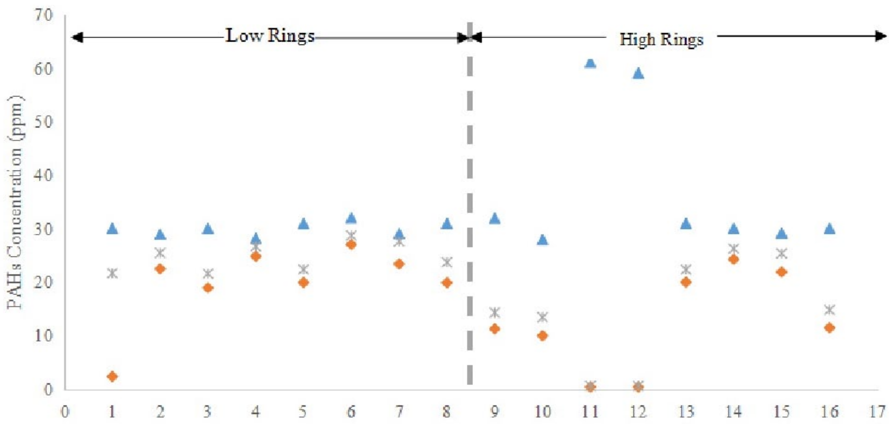

Fig. 2. Concentration of low rings and high ring of 16 PAHs in the raw sample (filled triangle), leachate after 7 days of curing (filled square) and leachate after 28 days of curing (filled diamond). Numbers 1 to 16 indicate the type of PAHs which the low rings are 1: Napthalene; 2: Acenaphthylene, 3: Acenaphthene; 4: Fluorene; 5: Phenanthrene; 6: Anthracene; 7: Fluoronthene; 8: Pyrene. Meanwhile high rings started at number 9: Benzo (a)anthracene; 10: Chrysene; 11: Benzo (b) fluoranthene; 12: Benzo(k)fluoranthene; 13: Benzo(a)pyrene; 14: Dibenzo(ah) anthracene; 15: Benzo(ghi)perylene; and 16: Indeno(1,2,3-cd)pyrene

16-PAHs concentration from the raw sample, leachate for 7 days and 28 days of curing.

Based on the low rings PAHs, only naphthalene shows the best performance, which is the concentration was reduced from the raw sample to 21.76 ppm and 2.43 ppm in leachate for 7 and 28 days of curing, respectively. Whereas other low rings compounds show, the concentration was reduced by more than 20 ppm, even though concentration in raw samples were almost the same, i.e., 30±0.2 ppm, as shown in Section 3.1. For high rings, the concentration of two compounds (no11 & no12) was doubled than other compounds. Despite these compounds being very high concentrations in the raw sample, the concentration in 28-days leachate was much reduced, which is less than 0.5 ppm. Other high rings have also shown better performance in which the concentration was 10±0.8 ppm in 28-days leachate. Only three compounds (no13, no14 & no15) of the concentration were detected at 20±2 ppm.

TABLE 3 shows the analysis of variance for comparing rings number (low or high rings PAHs) and ratio, which is more significant. Both ring's number and ratio are less than the significance level (0.005); thus, these factors are statistically significant. By comparing F-value and F critical, F-value is higher than F critical, thus strengthening the previous statement. Both factors are significant, which means high rings tend to have a lower concentration in leachate across the ratio. Additionally, a high ratio of sludge tends to have a high concentration. The ratio shows a lower p-value compared to the number of the rings, which shows that the ratio is more significant. Interaction between these two factors' effects are not significant because their p-value is greater than the significance level.

TABLE 3

Analysis of variance between two factors, ring numbers and ration

Source of Variation	7 days			28 days		
	F	P-value	F crit	F	P-value	F crit
Rings Number	11.795	0.001	3.978	13.059	0.001	3.978
Ratio	8.490	1.209E-05	2.503	9.232	4.755E-06	2.503
Interaction	0.239	0.915	2.503	0.365	0.833	2.503

Based on performance for all PAHs compounds, the S/S method is more suitable for immobilization for high rings PAHs. The higher number of rings in the PAHs compound, the higher hydrophobicity and lower the aqueous solubility [51]. These physio-chemical characteristics of PAHs have an effect on PAHs immobilization in solid media such as sludge, soil, and other media [43]. In addition, the characteristics of high hydrophobicity may lead to more interaction of PAHs with non-aqueous phases. The mechanism of PAHs removal in the S/S method is based on the physical adsorption of contaminants on the surface of binding products. These PAHs are absorbed by organic particles and situated in small pores or blocks in solid components [36]. Thus, the S/S method brings an advantage to remediating high rings PAHs.

3.3. Compressive strength of S/S matrices

High organic contaminants in cement paste increased the porosity and lowered the mechanical strength [50]. According to USEPA [5], 0.35 MPa is the minimum compressive strength required for the safe disposal of stabilized waste. When the stabilized waste has a strength of less than 0.35 MPa, it can easily be degradable and disposed. In addition, compressive strength is an important factor to measure due to the potential of the matrices or stabilize waste for application in construction material. Thus, this method may reduce the quantity of waste that will be disposed into landfills. The strength of the mixture depends on the hydration day [52]. Thus, the compressive strength of all S/S matrices samples for 7 and 28 days of hydration was measured as shown in Fig. 3.

Based on the hydration day, a longer duration. i.e., 28 days shows higher strength compared to 7 days for all samples. The

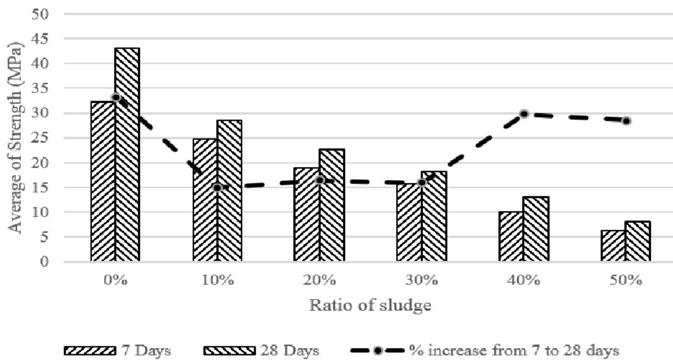

Fig. 3. Compressive strength of all S/S matrices samples

highest compressive strength was recorded for sample 0% sludge and the lowest strength for sample 50%, which was detected at 32.3 MPa and 6.3 MPa on 7 days, respectively. Based on the figure, with the increase of sludge, the strength of S/S matrices decreased gradually. Even though the strength of the mixture was decreased after being replaced with sludge, all samples were above the permissible limit of USEPA for safe disposal (0.35 MPa).

By referring to the percentage of strength increase from 7 days to 28 days (dotted line in Fig. 3), more than 40% of sludge shows this percentage was high, which was most similar to 0% of sludge. Even though the strength was low on day 7 for a high ratio of sludge, on day 28, the strength was increased, similar to Portland cement. This result shows that the matrices with a high ratio of sludge have the potential to achieve high strength in a longer duration. Thus, it is highly recommended to increase the duration of the curing day to measure the potential in the long term.

4. Conclusions

16 PAHs compounds were measured in Portland cement and sludge. All PAHs compounds were below the allowable limit for Portland cement. However, four PAHs compounds, namely, Benzo (a) anthracene (32.02 mg/kg), Benzo (a) pyrene (31.02 mg/kg), Dibenzo (ah) anthracene (30.12 mg/kg) and Indeno(1,2,3-cd)pyrene) (30.11 mg/kg) were above the allowable limit. These compounds were further analyzed in a leaching test to measure the potential of Portland cement in the encapsulation of these compounds.

In the leaching test, only Indeno(1,2,3-cd)pyrene) was successfully remediated, and the concentration is below the allowable limit. However, it is recommended to include other binders such as organic binders for the other three PAHs compounds to improve the remediation. Based on the leaching test for all compounds, most of the high rings PAHs showed a higher potential of the S/S method in PAHs remediation in sludge. Due to higher hydrophobicity for high rings PAHs compared to low rings PAHs, this method is suitable for remediation of high rings PAHs. Even though the compressive strength was reduced with increasing sludge, all samples have surpassed the allowable limit for safe disposal. The result of this study has also found that a high ratio of sludge with more than 40% has an increase of strength from 7 days to 28 days was similar with increasing in cement strength. Thus, in the long term, the strength may increase. It is highly recommended to measure the strength and leaching of PAHs in the long term. It is also recommended to replace or add an organic binder to increase the encapsulation of PAHs.

Acknowledgements

This research was funded under IGSP vot U680 and GPPS vot U789. Besides, this paper was also partly sponsored by the Centre for Graduate Studies, UTHM.

REFERENCES

[1] ML Hami, M.A. Al-Hashimi, M.M. Al-Doori, Desalination. **216** (1-3), 116-122 (2007). DOI: https://doi.org/10.1016/j.desal.2007.01.003

[2] C.C. Ling, M.H. Isa, J. Sci. Res. **65** (4), 364-9 (2006).

[3] S. Huang, M. Cao, L. Cheng, Experimental Study on Aquathermolysis of Different Viscosity Heavy Oil with Superheated Steam, Energy and Fuels **32**, 4850-4858 (2018).

[4] http://www.paratene.com/pdfs/brochures/tanksludgepaper, accessed: 06.11.2017.

[5] USEPA, Risk assessment guidance for superfund (RAGS) volume III - part a: process for conducting probabilistic risk assessment. Off. Emerg. Remedial Response US Environ. Prot. Agency III, 1-385 (2001).

[6] M. Huber, A. Welker, B. Helmreich, Sci. Total. Environ. **541**, 895-919 (2016). DOI: https://doi.org/10.1016/j.scitotenv.2015.09.033

[7] S. Chowdhury, R. Balasubramanian, Adv. Colloid. Interface. Sci. **204**, 35-56 (2014). DOI: https://doi.org/10.1016/j.cis.2013.12.005

[8] B. Lin, Q. Huang, Y. Chi, Fuel. Process. Technol. **177**, 275-282. (2018). DOI: https://doi.org/10.1016/j.fuproc.2018.05.002

[9] G. Hu, J. Li, G. Zeng, J. Hazard. Mater. **261**, 470-490. (2013). DOI: https://doi.org/10.1016/j.jhazmat.2013.07.069

[10] Y.L. Galiano, C.F. Pereira, J. Vale, J. Hazard. Mater. **185** (1), 373-381 (2011). DOI: https://doi.org/10.1016/j.jhazmat.2010.08.127

[11] R. Malviya, R. Chaudhary, J. Hazard. Mater. **137** (1), 267-276 (2006). DOI: https://doi.org/10.1016/j.jhazmat.2006.01.065

[12] G.E. Voglar, D. Leštan, J. Hazard. Mater. **192** (2), 753-762 (2011). DOI: https://doi.org/10.1016/j.jhazmat.2011.05.089

[13] B.C.A. Pinheiro, J.N.F. Holanda, J. Mat. Process. Technol. **209** (15-16), 5606-5610 (2009). DOI: https://doi.org/10.1016/j.jmatprotec.2009.05.018

[14] J. Arey, R. Atkinson, Photochemical reactions of PAH in the atmosphere, in: P.E.T. Douben (Ed.), PAHs: an ecotoxicological perspective, John Wiley and Sons Ltd, New York, pp. 47-63 (2003).

[15] EPA, Resource Conservation and Recovery Act: Hazardous Waste Regulations: Identification and Listing of Hazardous Waste, US Environmental Protection Agency (EPA), Washington DC, (1980).

[16] I.N. Sora, R. Pelosato, L. Zampori, D. Botta, G. Dotelli, M. Vitelli, Appl. Clay. Sci. **28** (1-4), 43-54 (2005). DOI: https://doi.org/10.1016/j.clay.2004.01.015

[17] S.A. Stout, SD. Emsbo-Mattingly, G.S. Douglas, A.D. Uhler, K.J. McCarthy, Polycycl. Aromat. Comp. **35** (24), 285-315 (2015) DOI: https://doi.org/10.1080/10406638.2014.891144

[18] MD. Fang, P.C. Hsieh, F.C. Ko, J.E. Baker, C.L. Lee, Mar. Pollut. Bull. **54** (8), 1179-1189 (2007). DOI: https://doi.org/10.1016/j.marpolbul.2007.04.012

[19] C. Jaturapitakkul, K. Kiattikomol, W. Tangchirapat, T. Saeting, Constr. Build. Mater. **21** (7), 1399-1405 (2007). DOI: https://doi.org/10.1016/j.conbuildmat.2006.07.005

[20] J. Shu, X. Sun, R. Liu, Z. Liu, H. Wu, M. Chen, B. Li, Ecotox. Environ. Safe. **171**, 523-529 (2019). DOI: https://doi.org/10.1016/j.ecoenv.2019.01.025

[21] R.N. Okparanma, J.M. Ayotamuno, P.P. Araka, World Applied Sciences J. **11** (4), 394-400 (2010).

[22] H.P. Zhao, L. Wang, J.R. Ren, Z. Li, M. Li, H.W. Gao, Isolation and characterization of phenanthrene-degrading strains *Sphingomonas sp* ZP1 and *Tistrella sp* ZP5, Journal of Hazardous Materials **152**, 1293-1300 (2008).

[23] L. Li et al., Degradation of naphthalene with magnetic bio-char activate hydrogen peroxide: Synergism of bio-char and Fe-Mn binary oxides, Water Research **160**, 238-248 (2019).

[24] NAF Mohd Kamil, N. Hamzah, S. Abdul Talib, N Hussain, Improving mathematical model in biodegradation of PAHs contaminated soil using gram-positive bacteria. Soil and Sediment Contamination: An International Journal **25** (4), 443-458 (2016).

[25] O.A. Johnson, A.C. Affam, Petroleum sludge treatment and disposal: A review. Environmental Engineering Research **24** (2), 191-201 (2019). DOI: https://doi.org/10.4491/EER.2018.134

[26] B. Guo, B. Liu, J. Yang, S. Zhang, J. Environ. Management. **193**, 410-422 (2017). DOI: https://doi.org/10.1016/j.jenvman.2017.02.026

[27] M. Liu, Constr. Build. Mater. **24** (7), 1245-1252 (2010). DOI: https://doi.org/10.1016/j.conbuildmat.2009.12.012

[28] J.M. Neff, Composition, environmental fates, and biological effect of water based drilling muds and cuttings discharged to the marine environment: A synthesis and annotated bibliography, In: Report prepared for the Petroleum Environmental Research Forum (PERF). Washington DC: American Petroleum Institute (2005).

[29] UKOOA, Drill cuttings initiative final report-compilation of reports, research & development phases 1 and 2, Science Review Group, in: Stakeholder Dialogue Meetings (2001).

[30] BD. Bone, L.H. Barnard, D.I. Boardman, P. J. Carey, C.D. Hills, H.M. Jones, M. Tyrer, Review of scientific literature on the use of stabilisation/solidification for the treatment of contaminated soil, solid waste and sludges (SC980003/SR2). The Environment Agency, Bristol, 1-375 (2004).

[31] Y.J. Du, M.L. Wei, K.R. Reddy, Z.P. Liu, F. Jin, J. Hazard. Mater. **271**, 131-140 (2014). DOI: https://doi.org/10.1016/j.jhazmat.2014.02.002

[32] M. Nehdi, Concrete International **23** (4), 36-44 (2001).

[33] D. Lee, T.D. Waite, G. Swarbrick, S. Lee, Cement Concrete Res. **35** (11), 2143-2157 (2005).

[34] S. Ahmari, L Zhang, L, Constr. Build. Mater. **44**, 743-750 (2013).

[35] Y.L. Galiano, C.F. Pereira, J. Vale, J. Hazard. Mater. **185** (1), 373-381 (2011). DOI: https://doi.org/10.1016/j.jhazmat.2010.08.127

[36] S. Kwon, J.J. Pignatello, Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): pseudo pore blockage by model lipid components and its implications for N2-probed surface properties of natural sorbents, Environmental Science and Technology **39**, 7932-7939 (2005).

[37] R. Coffi, L. Maffucci, L., Santoro, F.P. Glasser, Waste. Manage. **21** (7), 651-660 (2001). DOI: https://doi.org/10.1016/S0956-053X(00)00116-1

[38] E.R. Bates, F. Akindele, D. Sprinkle, Environ. Prog. **21** (2), 79-84 (2002). DOI: https://doi.org/10.1002/ep.670210209

[39] A.K. Karamalidis, E.A. Voudrias, J. Hazard. Mater. **148**, 122-135 (2007). DOI: https://doi.org/10.1016/j.jhazmat.2007.02.032

[40] J. Arey, R. Atkinson, Photochemical reactions of PAH in the atmosphere, in: P.E.T. Douben (Ed.), PAHs: an ecotoxicological perspective, John Wiley and Sons Ltd, New York, pp. 47-63 (2003).

[41] A. Seco, F. Ramirez, L. Miqueleiz, P. Urmeneta, B. García, E. Prieto, V. Oroz, Types of waste for the production of pozzolanic materials – a review (pp. 141-150). INTECH (2012).

[42] British Standards Institution (2003). Testing concrete: Method for determination of compressive strength of concrete cubes. London: BS 1881-116:1983.

[43] AT Lawal, Cogent Environmental Science **3** (1), 1339841 (2017)

[44] H.K. Bojes, P.G. Pope, Regul. Toxicol. Pharm. **47** (3), 288-295 (2007). DOI: https://doi.org/10.1016/j.yrtph.2006.11.007

[45] F.J. Castaldi, Environ. Prog. **22** (1), 25-36 (2003). DOI: https://doi.org/10.1002/ep.670220114

[46] J. Harmsen, RPJJ Rietra25 years monitoring of PAHs and petroleum hydrocarbons biodegradation in soil. Chemosphere **207**, 229-238 (2018).

[47] P.S. Khillare, V.K. Sattawan, D.S. Jyethi, Environ. Technol. **41** (7), 842-851 (2020). DOI: https://doi.org/10.1080/09593330.2018.1512654

[48] C.F. Chen, Y.R. Ju, Y.C. Lim, S.L. Hsieh, M.L. Tsai, P.P. Sun, C.D. Dong, Int. J. Environ. Res. Public. Health. **16** (14), 2604 (2019). DOI: https://doi.org/10.3390/ijerph16142604

[49] K. Anastasiadou, K. Christopoulos, E. Mousios, E. Gidarakos, J. Hazard. Mater. **207**, 165-170 (2012). DOI: https://doi.org/10.1016/j.jhazmat.2011.05.027

[50] A.S. Leonard, J.A. Stegemann, J. Hazard. Mater. **174** (1-3), 463-472 (2010). DOI: https://doi.org/10.1016/j.jhazmat.2009.09.075

[51] NR. Couling, M.G. Towell, K.T. Semple, Environ. Pollut. **158** (11), 3411-3420 (2010). DOI: https://doi.org/10.1016/j.envpol.2010.07.034

[52] H.I. Abdel-Shafy, M.S.M. Mansour, Egyption Journal of Petroleum **25** (1), 107-123 (2016). DOI: https://doi.org/10.1016/j.ejpe.2015.03.011