Physico-chemical remediation of polycyclic aromatic hydrocarbons contaminated soil

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Abstract. This study exploited the solvent extraction and mechanical agitation techniques for the remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs). The removal of pollutants from diesel contaminated site through ethanol, hexane, and ethanol-hexane mixtures was evaluated. 50 g dried contaminated soil was placed in a Soxhlet extractor and 250 ml solvent (ethanol, or hexane, or ethanol-hexane mixture) was added with extraction occurring at different temperatures of 30, 35, 45, 50, and 60 °C for 16 h. Mechanically agitated method was carried out by weighing out an equal amount of 50 g of the contaminated soil, thoroughly washing with 250 ml of ethanol, hexane, and equal ratio of ethanol to hexane. Qualitative analysis recovered PAHs was done by Agilent series gas chromatography equipped with flame ionization detector. The chromatographic evaluations of the solvent extraction of the contaminated soil showed that more of the polluted compounds were removed when hexane was the solvent. The maximum yield of extracted diesel by the solvent hexane was 11.84% at 60 °C. Extracted diesel removal was also directly proportional to periods of extraction.

Keywords: Polycyclic aromatic hydrocarbons, remediation, solvent extraction, contaminants, mechanical agitation

1. Introduction

Polycyclic aromatic hydrocarbons or (PAHs) usually contains hydrogen (H), oxygen (O), sulphur (S), and carbon (C). Substitutions of nitrogen (N) atoms in the benzene ring occur to form heterocyclic aromatics. The aromatic rings are fused which may be linear or clustered [1]. Several hundred different combinations of PAHs exist, but up to 28 compounds have been identified as hazardous contaminants in January 2008 by the United State Environmental Protection Agency (USEPA) [2]. Soil pollution by petroleum hydrocarbons brings up critical issues looking at the world-wide environmental issues and health. As a result, an innovative and environmental-compatible technologies for its remediation are needed. Risks to human and the ecosystem occur due to soils contaminated with PAHs [1]. Soil cleanup guidelines for...
PAH contaminated soils include chemical, thermal, physico-chemical, bioremediation and phytoremediation technologies [3-7]. There are varied technologies for the remediation of diesel contaminated sites, solvent extraction and electrokinetics are emerging. The intimate contact between solvents for extraction and polluted soils indicates the effectiveness of the process. A particular contaminated site may require a combination of technologies to optimize remediation for the prevailing conditions. Biological, physical, and chemical technologies may be used in conjunction with one another to reduce the contamination to a safe and acceptable level [8]. Some of the techniques may also be used for the treatment of solid wastes [9, 10]. With solvent extraction techniques, individual or mixtures of solvents can be used for the removal of PAHs from soils. During extraction, a two-step process is involved. The first step involves the removal of compounds from the inner (matrix) material which were initially attached to a binding site. The next step involves migration of solutes into the extraction fluid [11].

In this study, physico-chemical treatment of polycyclic aromatic hydrocarbons contaminated soil was investigated. Solvent extraction method was used in redeeming the PAHs present in a diesel contaminated soil. Mechanically agitated method was also compared to the solvent extraction method in remediating the contaminated soil.

2. Materials and methods

2.1. Soil Preparation

The soil used was collected from a diesel spilled area around a power generator house from a university campus in the western part of Nigeria. It was discovered that the diesel leaked out from the generating set and from the diesel stored in the drum positioned around the power house. The sampling was carried out in an area of 0.2 by 0.2 m and a depth of 0.05 m. The contaminated soil was dried in a convection oven at 120 °C for 2 h to remove the water content resident in the mixture of sand and diesel. Particle sizes larger than 2 mm were screened out of the soil particle size distribution.

2.2. Analytical methods

The gas chromatography (GC) used for the analysis of PAHs in contaminated soil was Agilent series 7890A (G3440A) equipped with a flame ionization detector and electron capture detector. The oven temperature for the GC was 50 °C and operated for 3 min using an increment of 25 °C/min until 310 °C. The gases used were hydrogen (34 ml/min), air (300 ml/min), and nitrogen (20 ml/min), nitrogen was the carrier gas. The injector temperature was 285 °C while the detector temperature was kept at 325°C. The gases used in chromatographic analysis were hydrogen, air. Nitrogen was use the carrier gas. Pure samples were used for calibration to know the elution time. Percentages of the PAHs (i's) present in the extracted diesel from contaminated soil as estimated from the gas chromatograph peaks were estimated as:

\[
\% \text{ Component } i = \left[ \frac{\text{area of } i}{\text{total area of peaks}} \right] \times 100
\]  

(1)

The chemicals used in this study viz. PAHs for standards on the gas chromatography, ethanol, and hexane were analytical grades. Distilled water was used in all experiments.
2.3. Soil–liquid extractions

The following procedure was chosen to evaluate the capacity of the ethanol, hexane, and ethanol-hexane mixtures for the soil’s contaminants removal: 50 g dried contaminated soil was placed in a Soxhlet extractor with 250 ml of solvent (ethanol, or hexane, or ethanol-hexane) added into the heating flask. The Soxhlet set up was position on electric heating plates for 16 h. Temperatures considered were 30, 35, 45, 50, and 60 °C. After each cycle, the solid portion was air dried and extracted soil was estimated based on the difference in weight before and after extraction. After each experimental run, extracted diesel samples were stored for the GC analysis of the PAH constituents. In addition, an equal solvents ratio of 1:1 ethanol to hexane was repeated for the procedure. Mechanically agitated method was carried out by weighing out an equal amount of 50 g of the contaminated soil, thoroughly washing with 250 ml of ethanol, hexane, and equal ratio of ethanol to hexane. The mixtures were then heated up at specified temperature intervals (30, 35, 45, 50, and 60 °C) for 3 h. Mixtures were cooled at room temperature. In each step, the diesel was separated from the solvents by simple distillation method. The yield of diesel from the contaminated soil was given as follows:

\[
\% \text{ Diesel yield (g diesel/g solid)} = \left(\frac{X}{Y}\right) \times 100
\]

where:

- \( X \) = diesel extracted from polluted soil (g)
- \( Y \) = extracted soil sample (g)

3. Results and discussion

3.1 Effect of Soxhlet extraction on remediation

The percent yields (g diesel extracted/g raw sample) using hexane, ethanol, and 1:1 hexane-ethanol mixtures for the Soxhlet extraction method are shown in Figure 1. Generally for the three cases, yields increased with increasing temperature. However, in all cases of increasing temperature, solvent extraction with hexane produced the highest yield of diesel. This is due to the fact that the temperature increase resulted in faster removal of the embedded diesel from the soil matrix as the transportation of analytes removed from the soil matrix into the bulk of the organic solvent and its solubility is improved. During the solvent extraction process, the viscosity of the solvent is reduced which increases the ability of the solvent to wet the sample and thereby dissolving the target contaminants. The added thermal energy (at increasing temperature) helps to break the analytes bond of complex hydrocarbon chain thus enabling the analytes diffuse into the extraction solvent. The yields of the mixture of hexane-ethanol (at ratio 1:1) as extraction solvent were next in values to hexane. Mixtures of some solvents such as N-butyl acetate, N-propyl acetate, ethanol mixture, dichloromethane, cyclohexane, ethanol, methanol and toluene in different formulations and soil are capable of increasing the efficiency of extracted PAHs from contaminated soils [12]. Ethanol gave the least %yield of diesel extracted from the sample. Results obtained showed that hexane was a better PAH removal from contaminated soil compared to ethanol. The maximum yield of extracted diesel by the solvent hexane was 11.84% at 60 °C. Extracted diesel removal was also directly proportional to periods of extraction.
Figure 1 Efficiency of solvents on diesel removal from contaminated soil using the Soxhlet extraction method

Figure 2 Efficiency of solvents on diesel removal from contaminated soil using the mechanical agitation method
3.2 Effect of mechanical agitation on remediation

The mechanical agitation method diesel yield followed the same trend with the Soxhlet extraction method. However, the yields were much lower in all temperature ranges compared to the Soxhlet extraction method. The yield of diesel at 60°C for ethanol-hexane extracted mixture (Soxhlet extraction) approximately increased twice that of mechanical agitation method (Figures 1 and 2). On the other hand, when compared to the extraction period (in this case 3 h to 16 h for Soxhlet extraction) and diesel yield, mechanical agitation method becomes more economical. Optimization in these areas needed to be investigated in future studies.

3.3 Eluted PAHs of treated samples

The compounds extracted using hexane, ethanol and 1:1 hexane and ethanol mixture as solvents are varied based on the elution time as revealed by the gas chromatographic analysis (Table 1). It was also observed that ethanol extracted Benzo(b) Fluoranthene unlike hexane or the mixture of both hexane and ethanol. Ethanol could not extract naphthalene which is a chief constituent of the extracted diesel while hexane and the mixture of hexane and ethanol was able to extract naphthalene from the soil sample but at different proportions as the 1:1 ratio mixture of hexane and ethanol extracted 1055.501 ng/ul of naphthalene from the sample while hexane extracted 3529.243 ng/ul of naphthalene from the sample.

| Time (min) | Amount (ng/µL) | Eluted compounds in treated samples after extraction |
|------------|----------------|------------------------------------------------------|
|            | M (Ethanol as solvent) | N (Hexane:Ethanol as solvent) | O (Hexane as solvent) |
| 4.277      | 1055.501         | Naphthalene                                         | - |
| 4.759      | 3529.243         | -                                                    | Naphthalene |
| 6.727      | 1.965 x 10^4     | -                                                    | Acenaphthylene |
| 6.829      | 244.344          | Acenaphthylene                                       | - |
| 6.969      | 5680.547         | -                                                    | Acenaphthylene |
| 7.010      | -                | -                                                    | Acenaphthylene |
| 7.166      | 9580.548         | -                                                    | Acenaphthene |
| 7.205      | 2.393x 10^5      | Acenaphthene                                         | - |
| 8.263      | -                | -                                                    | Fluorene |
| 8.326      | 62.692           | -                                                    | Fluorene |
| 11.638     | -                | -                                                    | Phenathrene |
| 11.673     | 2.261x10^10      | Phenathrene                                          | - |
| 11.751     | 1.961x10^10      | -                                                    | Anthracene |
| 11.819     | 3.438x10^10      | Phenathrene                                          | - |
| 11.843     | -                | -                                                    | Anthracene |
| 12.368     | 8.510x10^10      | Anthracene                                           | - |
| 18.062     | -                | -                                                    | Flouranthene |
18.124 1367.220 - Flouranthene
18.438 248.229 Flouranthene - -
19.222 1.890x10^4 - Pyrene -
19.783 247.371 Pyrene - -
19.808 7604.408 - - Pyrene
27.826 1262.809 - - Benzo(a) anthracene
28.325 1.047x10^4 - Benzo(a) anthracene -
28.558 - Benzo(a)anthracene - -
28.579 3763.994 - Chrysene -
28.836 577.007 - - Chrysene
28.943 - Chrysene - -
36.359 - - -
37.160 1.689x10^7 Benzo(k)Fluoranthene - -
37.358 2.135x10^4 Benzo(b) Fluoranthene - -
37.478 4.038x10^4 - Benzo(k) Fluoranthene -
37.478 2.495x10^4 - - Benzo(k) Fluoranthene
38.573 - Benzo(e)Pyrene - -
45.595 - - Benzo(e)Pyrene Benzo(e) Pyrene
45.627 - - Indeno(1,2,3,)Pyr ene -
45.853 - - Indeno(1,2,3,)Pyr ene Indeno(1,2,3,)Pyrene
46.101 - Dibenzoanthracene - -
46.952 - - Dibenzoanthracen e Dibenzoanthracene

4. Conclusions

These investigations showed that the Soxhlet extraction method with hexane, ethanol, and the mixture hexane-ethanol produced higher diesel yield than the extraction yield with mechanical agitation for all temperature ranges evaluated. The study also showed that hexane was effective in removing hydrocarbon compounds from the soils than ethanol or the mixture of hexane-ethanol, though hexane-ethanol mixture was promising. On the other hand, the effect of ethanol for the extraction of contaminants was minimal. The chromatographic evaluations of the solvent extraction of the contaminated soil also showed that more of the polluted compounds were removed when hexane was the solvent. Further studies on investigating different ratios of hexane-ethanol mixture on the remediation of the contaminated site are to be carried out.
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