

Effect of different extraction agents on metal and organic contaminant removal from a field soil

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Received 26 July 2003; received in revised form 19 April 2004; accepted 17 May 2004

Available online 19 December 2004

Abstract

This paper presents an evaluation of different extracting solutions for the removal of phenanthrene, lead and zinc from a contaminated soil obtained from a former manufactured gas plant site. The field soil contained 50%–88% sand, 11%–35% fines, 2.7%–3.7% organic matter and high concentrations of phenanthrene (260 mg/kg), lead (50.6 mg/kg) and zinc (84.4 mg/kg). A series of batch extraction experiments were conducted using the field soil with different extracting solutions at various concentrations to investigate the removal efficiency and to optimize the concentration of each extractant. The results showed that removal efficiencies of different flushing systems were significantly influenced by their affinity and selectivity for the contaminants in the soil matrix. Non-ionic surfactants (Igepal CA720 and Tween 80) were found to be effective in removing phenanthrene, but they were ineffective in removing lead and zinc. Chelating agents (ethylenediamine tetra acetic acid, EDTA and diethylene triamine penta acetic acid, DTPA) and selected acids were effective in removing lead and zinc, but they were ineffective for the phenanthrene removal. Co-solvents and cyclodextrins were not effective for removal of any of the contaminants. A sequential use of the 0.2 M EDTA followed by 5% Tween 80 or 5% Tween 80 followed by 1 M citric acid was found to be effective for the removal of lead, zinc, and phenanthrene. Overall, it can be concluded that sequential use of different extracting solutions is required for the removal of both heavy metals and organics from field contaminated silty sand soils.

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Keywords: Extractions; Phenanthrene; Lead; Zinc; Co-solvents; Organic acids; Surfactants; Cyclodextrins; Chelating agents

1. Introduction

In the United States (US), numerous sites have been severely contaminated due to improper waste disposal practices, industrial activities, and spillage of chemicals such as pesticides, wood preserving agents, and petroleum products [1]. Most of the national priority list (NPL) sites contain three contaminant groups such as volatile organic carbons (VOCs), metals and semi-volatile organic carbons (SVOCs). Most sites require re-mediation for more than one of these contaminant groups. Approximately, 25% of the sites contain two contaminant groups and 41% of the sites contain all three types [1]. The conventional re-mediation methods for phenanthrene (PAH) contamination include bio-remediation, thermal treatments using hot water, steam or heaters, stabilization or solidification processes, and soil flushing [2,3].

Technologies available for re-mediating metal contaminated soils can be divided mainly into two groups, namely, immobilization methods and separation/concentration methods. In the first type of re-mediation, contaminants are immobilized thereby preventing the leaching of contaminants into the groundwater. Containment, in-situ and ex-situ solidification and stabilization, in-situ and ex-situ vitrification fall under this category. The second-type of re-mediation deals with separating the containment from the soils or reducing the volume of contaminated soil. The reduced volume of the soil may be deposited in the landfills and the separated contaminants may be treated on-site or off-site with suitable treatment methods. In low permeability soils, the conventional re-mediation methods are ineffective because it is difficult to introduce the appropriate reagents or nutrients into the sub-surface due to the low permeability of the soils. Furthermore, conventional re-mediation technologies are applicable to treat both heavy metals and PAHs, when they co-exist.

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Electrokinetic re-mediation has shown a great potential to re-mediate low permeability soils contaminated with both heavy metals and PAHs [4,5]. According to the USEPA [1], 41% of the NPL sites contain both heavy metals and PAHs. Therefore, a single capable technology, such as electrokinetic re-mediation can save both money and time. Because of the different nature of the heavy metals and the PAHs, extracting solutions that can remove both contaminants must be carefully selected.

In this study, the use of various extracting solutions, namely surfactants, co-solvents, chelating agents, cyclodextrins, and acids was examined for the solubilization/desorption of heavy metals (zinc and lead) and PAHs from the an actual field contaminated soil from a former manufactured gas plant (MGP) site. A series of batch extraction experiments was performed to determine the ability of each selected extractant to remove lead, zinc and phenanthrene from the field soil. Zinc and lead can be found in soils as divalent cations in the soil solution, as complex hydroxides, as metal-bound to soil minerals, chelated to soil organic matter, and as insoluble oxides.

2. Materials and methods

2.1. Soil

The soil used in this investigation was collected from an actual contaminated field site. Properties of the field soil are summarized in Table 1. The field soil was a silty soil with approximately 3% organic matter. The field soil was contaminated with both PAHs and heavy metals. The concentrations of contaminants are listed in Tables 2 and 3, for PAHs and heavy metals, respectively. The field soil was mainly contaminated with 260 mg/kg of phenanthrene, 84.4 mg/kg of zinc, and 50.6 mg/kg of lead.

2.2. Extractants

Surfactants are shown to be effective extractants for PAHs [6–8]. Two non-ionic surfactants, namely Tween 80 and Igepal CA-720, were selected based on the previous research [9]. The properties such as critical micelle concentration

Table 2
PAHs in field soil

PAH	Concentration (mg/kg)
Naphthalene	460
Acenaphthene	25
Fluorene	90
Acenaphthylene	84
Phenanthrene	260
Anthracene	69
Benzo(a)anthracene	66
Chrysene	39
Pyrene	130
Fluoranthene	92
Benzo(b)fluoranthene	33
Benzo(k)fluoranthene	23
Benzo(a)pyrene	59
Dibenzo(a,h)anthracene	9.1
Indeno(1,2,3-cd)pyrene	21
Benzo(g,h,i)perylene	33
Total PAHs	1493.1

(CMC) and the hydrophile–lipophile balance number (HLB) were taken into consideration during the selection and are shown in Table 4. Batch experiments were performed at four different surfactant concentrations (0.5%, 1%, 3%, and 5%), to optimize the best extracting concentration to be utilized for the removal of phenanthrene under ambient conditions.

The co-solvents, *n*-butylamine and tetrahydrofuran (THF), were selected among the co-solvents based on previous studies [10,11]. The experiments were carried out at 5%, 10%, 15%, and 20% concentrations of each co-solvent (i.e. *n*-butylamine and THF). These two co-solvents were very effective in increasing the solubility of organics such as PAHs [10]. For a PAH such as phenanthrene, the co-solvents could increase contaminant solubility by more than five orders of magnitude [11].

Two chelating agents, ethylenediamine tetra acetic acid (EDTA) and diethylene triamine penta acetic acid (DTPA), were investigated at concentrations of 0.01 M, 0.05 M, 0.1 M, and 0.2 M for the treatment of the MGP field soil. EDTA and DTPA were chosen as they possess proven efficiency for heavy metals [12–15]. EDTA forms stable complexes with zinc and lead, and the stability constants for EDTA and zinc complexes are 18.3, 21.7 and 19.9 for

Table 1
Properties of field soil

Characteristic	Method	Value
Gravel [%]	ASTM D422	1.4–15.4
Sand [%]	ASTM D422	50.1–87.7
Fines [%]	ASTM D422	10.9–34.5
Hydraulic conductivity [cm/s]	ASTM D2434	2.1×10^{-4}
Organic content [%]	ASTM D2974	2.69–3.75
pH	ASTM D 4972	6.9
USCS classification	ASTM D 2487	SM
Specific gravity	(ASTM D854)	2.54

Table 3
Metals in field soil

Metal	Concentration (mg/kg)
Arsenic	11
Cadmium	<0.5
Chromium	8.3
Copper	13
Lead	50.6
Nickel	14
Silver	<1
Mercury	<0.05
Zinc	84.4

Table 4
Non-ionic surfactants used in the study

Surfactant trade name	Structural chemical formula ^a	Approximate molecular weight	Type of surfactant	CMC ^b (mol/L)	HLB ^c
Igepal CA-720	C ₈ PE ₁₂	735	Octylphenol polyoxyethylene (POE)	2.3×10^{-4}	14.6
Tween 80	C ₁₈ S ₆ E ₂₀	1310	Polyoxyethylene (POE) (20) sorbitan monooleate	1.2×10^{-5}	15.0

^a C represents the alkyl chain length (–CH₂–), P represents a phenol ring (–C₆H₅–), S₆.

^b Critical micelle concentration.

^c Hydrophile–Lipophile balance.

ZnL, ZnHL, and ZnOHL, respectively, while the stability constants for EDTA and lead complexes are 19.8 and 23.0 for PbL and PbHL, respectively [16].

Research has shown that modified cyclodextrins could simultaneously complex with low-polarity organic compounds and heavy metals [17]. Hydroxypropyl- β -cyclodextrin (HPCD) and β -cyclodextrin hydrate (β -CD hydrate) were selected among the different cyclodextrins based on the published literature [18–20]. HPCD was investigated at concentrations of 1%, 3%, 5%, and 10% and β -CD hydrate was investigated at concentrations of 0.05%, 0.1%, 0.5%, and 1% for the solubilization of the contaminants from the MGP soil. Low concentrations of β -CD hydrate were selected because of its low solubility in water.

Acids have been previously used for the removal of heavy metals from soils [13–16,21]. Seven different organic acids were selected for this study and were investigated at the same concentration. These acids include lactic acid, *n*-butyric acid, propionic acid, oxalic acid, citric acid, phosphoric acid, and acetic acid. A high concentration of 1 M was selected for all the acids to compare the performance of different acids and to eliminate the number of acids required in further testing.

2.3. Batch extractions

The batch extraction experiments were conducted using a soil to water ratio of 1:5, or, specifically, five grams of the soil with 25 mL of extracting solution. First, five grams of contaminated soil was weighed and placed in a 40 mL glass vial. Then, 25 mL of the extracting solution were added, and the vial was sealed with a Teflon screw-type top. Each vial was then shaken by hand for about a minute to ensure the soil was fully saturated with solution, and the vials were then shaken in a rotary shaker table at 250 rpm for 24 h. After shaking was completed, the soil-solution mixture was centrifuged at 4000 rpm for 28 min. Then, the supernatant was poured through a glass funnel holding a Whatman GF/C glass fiber filter (1.2 μ m particle retention) to remove any floating particles or debris, and the concentration of phenanthrene in the solution was determined by liquid-liquid extraction followed by gas chromatography chemical analysis. Batch extractions were performed in duplicates to ensure reproducibility of the results.

2.4. Chemical analysis

2.4.1. Soxhlet extraction

To determine the initial phenanthrene concentration in the soil, a representative soil sample weighing 10 g was thoroughly mixed with about 10 g of Na₂SO₄ (Fisher Scientific, Pittsburgh, PA), and the mixture was placed into a Whatman cellulose extraction thimble. The phenanthrene was then extracted using a Soxhlet apparatus consisting of a 250 mL flask, a Soxhlet extraction tube, and a bulb-type Allihn condenser. The procedure is outlined in USEPA test method 3540C [22]. The solution used in the Soxhlet extraction process was 190 mL of a 1:1 mixture of methylene chloride and acetone (Fisher Scientific), and the process was operated at 4–6 cycles/h for at least 24 h. After the extraction was completed, the volume of the solvent remaining in the Soxhlet extraction tube and flask was measured, and analysis by gas chromatography (GC) was performed on a sample of the liquid. The soil was usually highly contaminated with phenanthrene, so the solvent-phenanthrene liquid samples obtained from the Soxhlet extraction could be directly analyzed using GC without further sample concentration.

2.4.2. Liquid–liquid extraction

The extraction procedure consists of placing 1 mL of the contaminated supernatant in a conical flask with the help of a syringe. The syringe was thoroughly rinsed with ethanol, before and after use. Then, the sample was diluted in the ratio of 1:10 with water. The conical flask was shook thoroughly, before transferring the diluted sample into a test tube. Then, 200 μ L of 2-fluorobiphenyl was added. After that, 2 mL of methylene chloride was added into the test tube. The test tube was hand shook at least for five minutes. Then, the two phases, methylene chloride-phase and the aqueous-phase, were allowed to separate. Approximately, 1–2 mL of the methylene chloride phase were taken with the help of a syringe into a 2 mL auto-sampler vial. GC analysis was then performed. For quality control, all the samples were run in duplicates.

2.4.3. Gas chromatography

The GC that was used was an Agilent Model 6890 GC equipped with a flame ionization detector (FID). The

injection volume was 1 μL , and it was injected via an auto-injector at an inlet temperature of 250 °C. The column used on the GC was a J and W Scientific (Folsom, CA) DB-5, 30 m \times 0.32 mm \times 25 μm . The carrier gas was nitrogen at 25-psi constant pressure. The oven temperature was ramped from 100 °C to 250 °C at 18 °C/min with a hold time of 3 min. The instrument was calibrated using 2-fluorobiphenyl as an external standard. The calibration range was from 1 to 40 mg/L. The extraction efficiency was calculated based on surrogate concentration obtained from the GC. The final phenanthrene concentration in the original soil extract was determined.

2.4.4. Analysis of lead and zinc

Lead and zinc contaminants in soil were extracted by performing acid digestion in accordance with USEPA Method 3050 [13,22]. Approximately, 1–2 g of a representative soil samples were weighed, in a conical beaker and then mixed with 10 mL of 1:1 (w/v) nitric acid (HNO_3). The mixture was stirred thoroughly, the beaker was covered with a watch glass and heated to 95 °C, and then it was refluxed for 15 min. The sample was cooled, 5 mL of concentrated HNO_3 were added, and it was refluxed again for 30 min. This last step was then repeated once. The conical beaker was then covered with a ribbed watch glass and the sample was allowed to evaporate to 5 mL. The sample was cooled, and 2 mL of deionized water and 3 mL of 30% hydrogen peroxide (H_2O_2) were added. The mixture was warmed to observe the peroxide reaction and heated until the effervescence subsided. The sample was then cooled and the addition of 1 mL H_2O_2 was continued until the effervescence was minimal. The maximum amount of H_2O_2 added was less than 10 mL. The sample was cooled and 5 mL of concentrated HNO_3 and 10 mL of deionized water were added and the mixture was refluxed for 15 min. The sample was centrifuged at 4000 rpm for 30 min to separate the supernatant and then diluted to 100 mL. The supernatant was then analyzed using an atomic absorption spectrophotometer (AAS), to determine the concentration of lead and zinc in accordance with USEPA Methods 7420 and 7950, respectively [22]. The supernatant from the batch tests was directly tested using AAS for the contaminant concentrations.

3. Results and discussion

In this field contaminated soil, heavy metals and organics co-existed. Chelating agents and acids were employed to examine their efficiency for removal of heavy metals. Non-ionic surfactants and co-solvents were employed to examine their efficiency for removal of organics. Cyclodextrins were employed to remove both metals and organics simultaneously. For informational purposes, the removal of organics while employing chelating agents and acids and the removal of metals while employing surfactants and co-solvents were examined.

3.1. Removal with surfactants

3.1.1. Phenanthrene

Different surfactant solutions were chosen based on the solution properties, such as CMC and HLB. Two non-ionic surfactants solutions were chosen to desorb and solubilize phenanthrene and these surfactant solutions include Igepal CA-720 and Tween 80. Their performance in the removal of phenanthrene was investigated at four different concentrations (0.5%, 1%, 3% and 5%). The pH of the soil-solution mixture was measured after the samples were shaken until the equilibrium time was reached.

It was observed that the removal efficiency of phenanthrene using Igepal CA-720 system gradually increased with concentration as shown in Fig. 1a. The pH values of all the Igepal samples at different concentrations ranged between 7.25 and 7.59. The pH value for 0.5% Igepal system was found to be 7.25 and it gradually increased to 7.59 for 5% Igepal system. Thus, it is evident that removal efficiency of Igepal increases as the concentration is increased. The removal efficiency was 21% for 0.5% Igepal and it gradually increased to 76% at 5% concentration as shown in the Fig. 1a. A concentration higher than 5% Igepal CA-720 may increase the phenanthrene removal efficiency, however, further studies are needed to confirm this. The increase in the removal efficiency with increasing concentration was because of the availability of more micelles for the solubilization of phenanthrene.

For Tween 80, the removal efficiency was 22% at 0.5% concentration which increased to 5% at 1% concentration. The removal efficiency then decreased to 33% at 3% concentration and later increased to 42% at 5% concentration as shown in the Fig. 1a. The pH value at 0.5% concentration was 7.58 and it gradually decreased to 7.44 at 5% concentration. The variation in the removal efficiencies can be attributed to the heterogeneous nature of the field soil.

Due to lower CMC and a higher HLB values for Tween 80 than for Igepal, the micelle formation should begin at a lower surfactant concentration for Tween 80. The Tween 80 had better removal efficiency over Igepal at concentrations of 0.5% and 1%. As described earlier, the heterogeneous nature of the field soil might be the reason for the variation in the removal efficiencies.

3.1.2. Zinc and lead

The data from Fig. 1b shows that the surfactants were not effective in the removal of zinc. Igepal was ineffective in the removal of zinc. The removal efficiency was less than 2.5% at all the concentrations for the reported pH values. The removal efficiency of 0.5% Tween 80 was 2.3% and it gradually decreased to 1.6% at a concentration of 3% and then it slightly increased to 1.8% as shown in Fig. 1b. Tween 80 performed better in the removal of zinc when compared to Igepal at all concentrations. The data from Fig. 1c shows

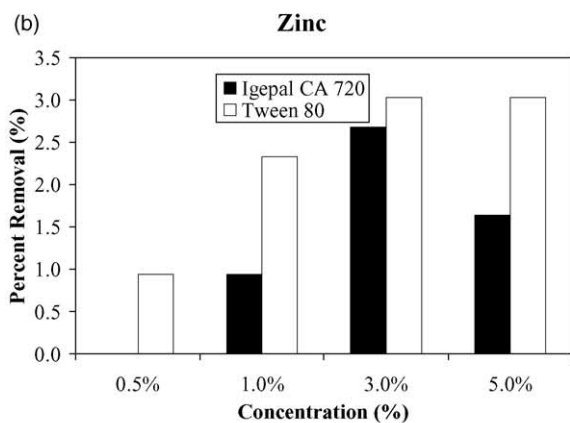
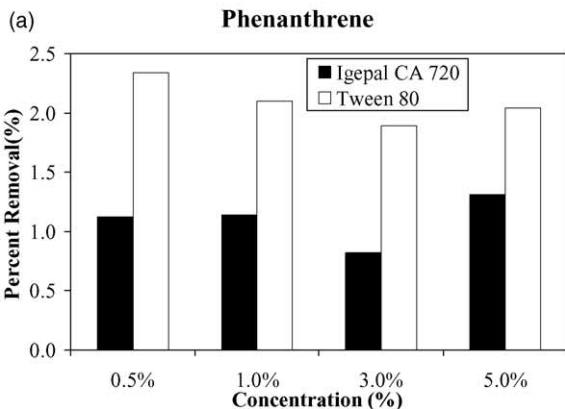
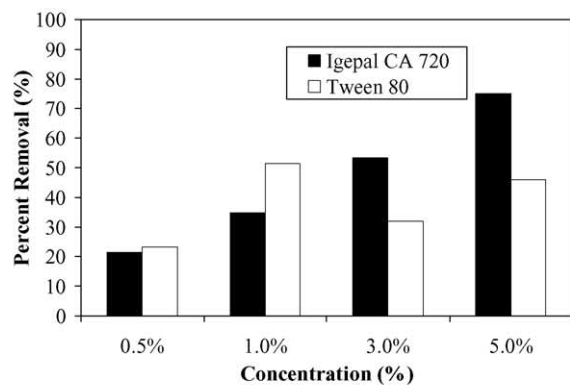


Fig. 1. Removal (% mass) of (a) phenanthrene, (b) zinc and (c) lead using surfactants.

that the surfactants were not that effective in the removal of lead.

3.2. Removal with chelating agents

3.2.1. Phenanthrene

Both chelating agents were ineffective, as predicted, in the removal of phenanthrene with removal efficiency less than 4% at all the concentrations as shown in Fig. 2a. DTPA was better than EDTA at all the concentrations except at 0.01 M. Neither chelating agent was able to solubilize or desorb phenanthrene from the soil, as they are ligands. These

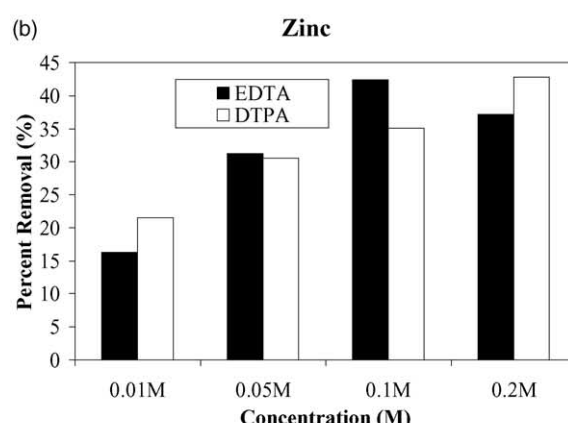
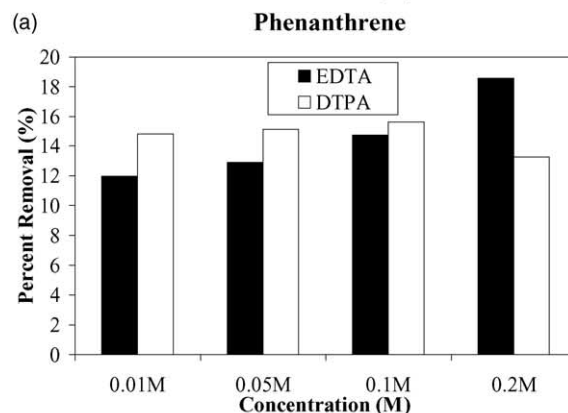
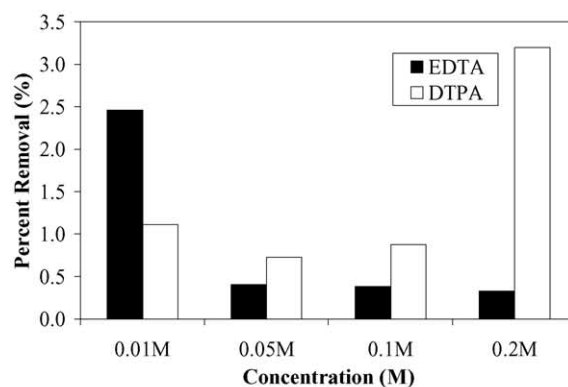


Fig. 2. Removal (% mass) of (a) phenanthrene, (b) zinc and (c) lead using chelating agents.

chelating agents could not form any stable complexes with phenanthrene because of their very chemical structure and affinity towards charged metals.

3.2.2. Zinc and lead

The removal efficiency of EDTA increased with increasing concentration. It was in the range of 12% and 18% as shown in the Fig. 2b. The pH values of EDTA ranged between 9.69 and 11.03. The pH values increased with increasing concentration of EDTA. The 0.01 M EDTA had a pH value of 9.69 and 0.2 M EDTA had a pH value of 11.03. The removal efficiency of DTPA increased with increasing

concentration upto a concentration of 0.1 M and then it decreased slightly at a concentration of 0.2 M. The removal efficiency ranged from 12% to 15%. The pH values of DTPA were between 9.80 and 12.18. The pH values increased with the increasing concentration. The 0.01 M DTPA had a pH value of 9.80 and 0.2 M DTPA had a pH value of 12.18. The performance of DTPA was better when compared to EDTA at all the concentrations except at a concentration of 0.2 M, as shown in the Fig. 2b. The difference in the removal efficiencies of the two chelating agents was not significant. Moreover, the difference in the removal efficiencies might be because of the heterogeneities that existed in the samples collected. The overall lower removal of zinc might be because of the presence of other heavy metals in the soil. The chelating agents might have formed complexes and removed the metals that were not analyzed.

The removal of lead with EDTA increased with increasing EDTA concentration. The removal efficiency of EDTA was 17% at a concentration of 0.01 M and it increased to 42% at a concentration of 0.1 M as shown in Fig. 2c. Then, the removal efficiency decreased to 35% at 0.2 M concentration. The pH values of EDTA were between 9.69 and 11.03. The pH values increased with increasing concentration of EDTA. The 0.01 M EDTA had a pH value of 9.69 and 0.2 M EDTA had a pH value of 11.03.

The removal of lead with DTPA also increased with increasing concentration and it ranged from 23% to 44%. The pH values of DTPA were between 9.80 and 12.18. The pH values increased with the increasing concentration of DTPA. The 0.01 M DTPA had a pH value of 9.80 and 0.2 M DTPA had a pH value of 12.18. The performance of EDTA was better when compared to DTPA at all the concentrations except at a concentration of 0.2 M. But, the difference between the removal efficiencies of the two chelating agents was not significant.

3.3. Removal with co-solvents

3.3.1. Phenanthrene

For *n*-butylamine, the removal efficiency increased with increasing concentration of co-solvent as shown in Fig. 3a. A removal efficiency of 4% was achieved with 5% *n*-butylamine, increasing to 30% with 20% *n*-butylamine. The pH of *n*-butylamine at all concentrations was between 11.38 and 12.39. The pH of 5% *n*-butylamine was 11.38 and it gradually increased to 12.39 for 20% *n*-butylamine. HOCs exhibit low concentrations in the aqueous phase (C_w), the Freundlich isotherm equation, $C_s = K(C_w)^n$, is often linear, which means that $n = 1$. Under these conditions, the Freundlich constant is K_d , and it describes the distribution ratio of the HOC, or the concentration of contaminant in the sorbed phase divided by its concentration of contaminant in the aqueous phase [23]. K_d is a complex parameter, that depends on a number of factors that are related to the soil properties and the chemical species in the soil and solution; Schwarzenbach et al. [23] presented

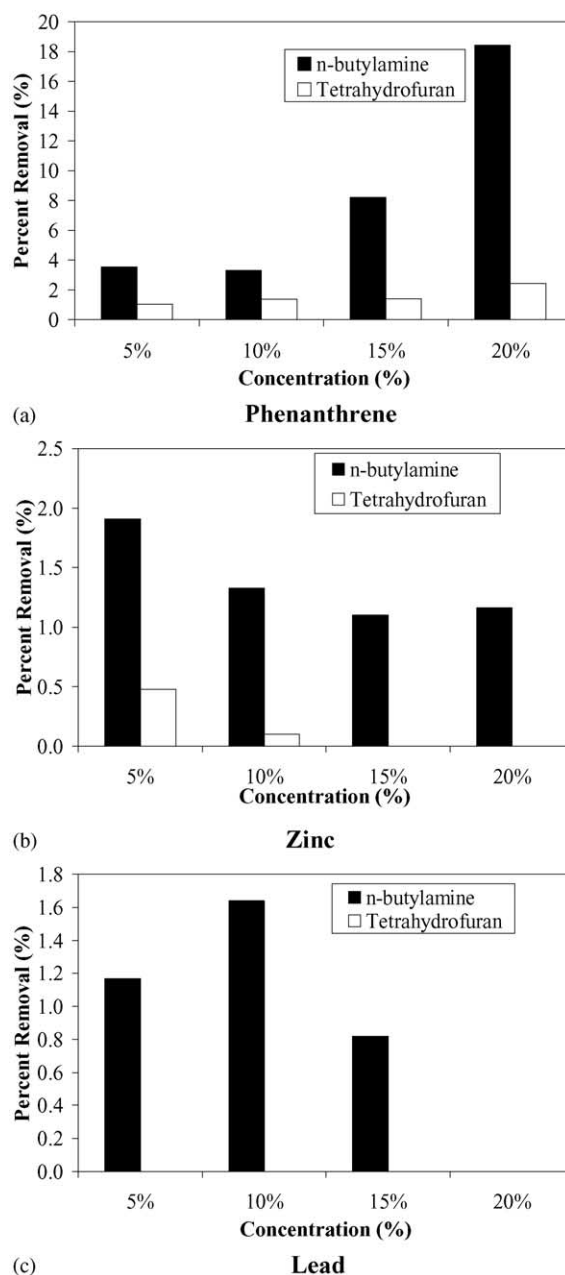


Fig. 3. Removal (% mass) of (a) phenanthrene, (b) zinc and (c) lead using co-solvents.

a detailed summary of these factors. The effect on K_d that is caused by using co-solvents can be estimated by dividing the apparent distribution ratio in a water–co-solvent mixture (K'_d) by the distribution ratio in pure water (K_d) by using the relationship:

$$\log \left(\frac{K'_d}{K_d} \right) = -\alpha\beta\sigma f_c$$

where α , β , σ are parameters that represent the molecular interactions between the soil–co-solvent, water–co-solvent, and contaminant–co-solvent, respectively, and f_c is the volume fraction of the co-solvent in the solution [11]. Gen-

erally, if the product of α , β , σ is higher, then the effect of the co-solvent is beneficial. For a PAH, such as phenanthrene and for the co-solvents *n*-butylamine and THF, σ values are high. For a PAH such as phenanthrene, σ values range from 0.47 to 0.65 for 20% solution of co-solvents such as *n*-butylamine and THF in water [11]. The values of α and β are reported to be 5.2 and 2.8 and 5.5 and 1.6 for *n*-butylamine and THF, respectively [11].

Tetrahydrofuran was found to be ineffective in the removal of phenanthrene. The removal efficiency at all the concentrations was less than 5% as shown in Fig. 3a. The pH ranged between 8.06 and 8.25. The pH value decreased as the concentration of THF increased. The pH value at 5% concentration was 8.25 and it gradually decreased to 8.06 at 20% concentration. The performance of *n*-butylamine was better than THF. This may be because of the greater hydrophobicity of *n*-butylamine over THF. The 20% *n*-butylamine had the highest removal efficiency and this may be because of the availability of more concentrated solution for greater solubility. The higher pH might have also contributed to the greater removal of phenanthrene. The *n*-butylamine was effective because of the β value that showed a positive indication of water–co-solvent interactions. These interactions favor the phenanthrene solubility.

3.3.2. Zinc and lead

The efficiency of *n*-butylamine in the removal of both metals was less than 2% at all concentrations while the removal efficiency of THF was less than 0.5% as shown in Fig. 3b and c.

Co-solvents, which are organic in nature, were not able to solubilize heavy metals which are inorganic in nature. This was the primary reason for the poor removal efficiency of co-solvents.

3.4. Removal with cyclodextrins

3.4.1. Phenanthrene

As shown in Fig. 4a, the removal efficiency of HPCD was 42% at a concentration of 1% and it decreased to 10% at a concentration of 3%. This decrease might be due to heterogeneities in the phenanthrene concentrations in the field soil. The removal efficiency thereby increased to 21% at a concentration of 10%. The pH of the soil-contaminant-extracting solution mixture was 7.56 at 1% concentration and then it gradually decreased to 7.37 at 5% concentration. For β -CD hydrate, the removal efficiency was constant at all the concentrations and it was almost zero at all the concentrations. The pH of β -CD hydrate decreased with the increasing concentration. The pH of 0.05% β -CD hydrate was 7.80 and it decreased to 7.58 for 1% β -CD hydrate. The β -CD hydrate was not effective in the removal of phenanthrene. The HPCD performed better when compared to β -CD hydrate at all the concentrations. This may be because of the better solubilization of phenan-

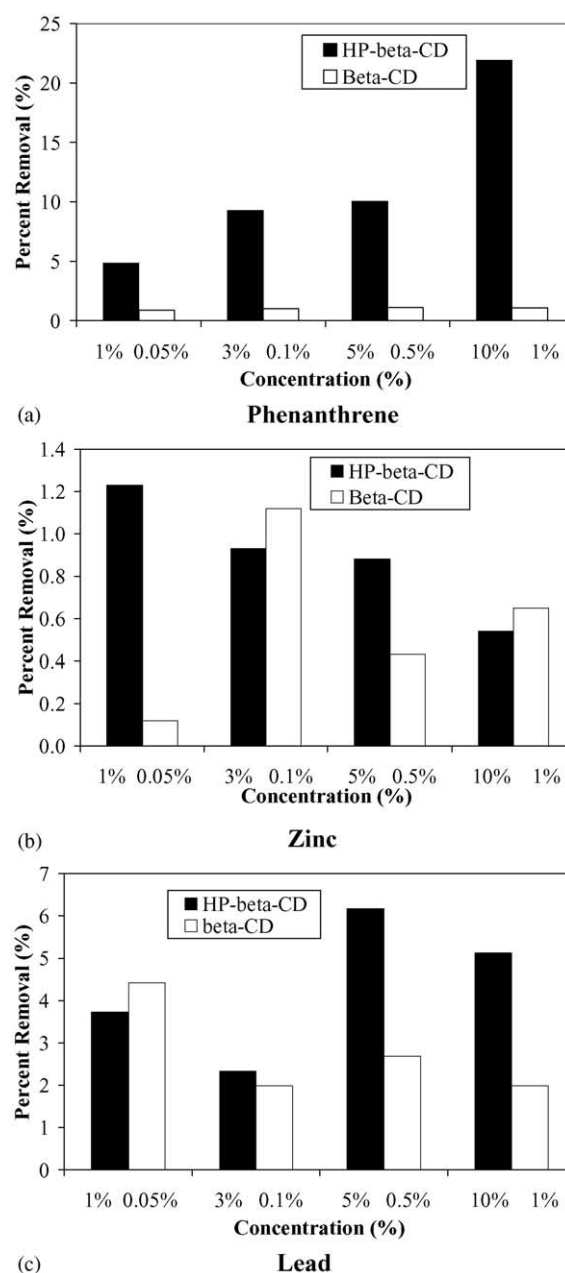


Fig. 4. Removal (% mass) of (a) phenanthrene, (b) zinc and (c) lead using cyclodextrins.

threne by forming a more stable complex with the cavity in HPCD due to the presence of the additional hydropropyl group in HPCD.

3.4.2. Zinc and lead

Based on the results, cyclodextrins were found to be ineffective in the removal of zinc and lead as shown in Fig. 4b and c, respectively. The poor removal of heavy metals with cyclodextrins may be due to the failure in incorporating the heavy metals into their cavities because of their size and also because of the organic nature of the cyclodextrins [19].

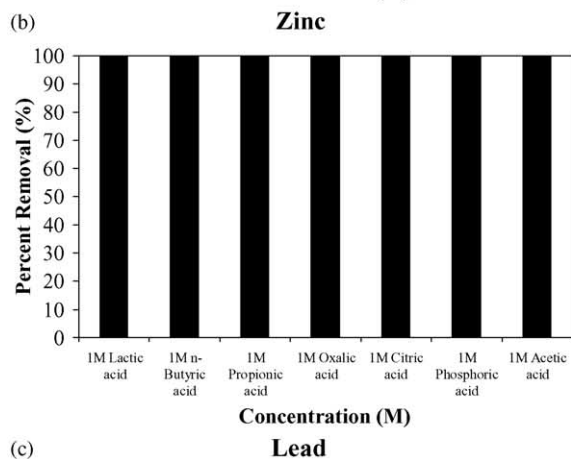
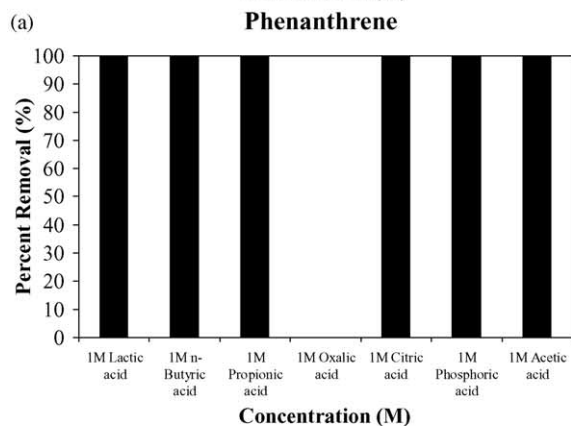
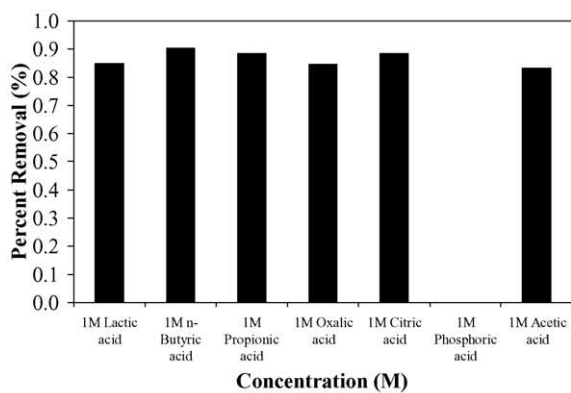


Fig. 5. Removal (% mass) of (a) phenanthrene, (b) zinc and (c) lead using organic acids.

3.5. Removal with acids

3.5.1. Phenanthrene

Selected acids were not effective in the removal of phenanthrene. The removal efficiency was less than 1% for all the acids as shown in Fig. 5a. The low pH conditions might have caused the ineffective behavior of the acids in the removal of phenanthrene.

3.5.2. Zinc and lead

Complete removal of zinc was observed using all the acids except oxalic acid as shown in Fig. 5b. All acids were effective

Table 5
Sequential extraction experiments

Extraction step 1	Extraction step 2
3% Igepal CA-720	1 M citric acid, 1 M phosphoric acid, 0.2 M EDTA
5% Igepal CA-720	1 M citric acid, 1 M phosphoric acid
3% Tween 80	1 M citric acid, 1 M phosphoric acid
5% Tween 80	1 M citric acid, 1 M phosphoric acid, 0.2 M EDTA
1 M citric acid	3% Igepal CA-720, 5% Igepal CA-720, 3% Tween 80, 5% Tween 80
1 M phosphoric acid	3% Igepal CA-720, 5% Tween 80
0.2 M EDTA	3% Igepal CA-720, 5% Tween 80

in the removal of lead. Organic acids were effective in removing heavy metals from the soil, mainly owing to the better solubilization of the metals at low pH conditions in the soil solution provided by the acids.

3.6. Sequential removal of phenanthrene, lead, and zinc

In the previous sections, the most effective extractants were identified for single extraction of either metals (zinc and lead) or phenanthrene. The most effective extractants for lead and zinc were chelating agents and acids. All acids with the exception of oxalic acid were equally effective in single batch extraction of both heavy metals. The removals for lead and zinc with chelating agents were significantly lower than the removals with organic acids. The most effective extractants for phenanthrene were surfactants (Tween 80 and Igepal CA-720). In order to effectively remove both metals and phenanthrene from the field soil, several combinations of individual extractants, which had shown to be effective in extraction of either metals or phenanthrene, were selected to sequentially extract all contaminants. The combination of extractants selected for sequential extractions are listed in Table 5.

3.6.1. Removal of phenanthrene

Fig. 6a shows the removal of phenanthrene using various combinations of extractants. The highest removal of phenanthrene (>90%) was obtained with the following combinations of extractants: 5% Tween 80–0.2 M EDTA, 1 M citric acid–5% Igepal CA-720, and 0.2 M EDTA–5% Tween 80. The following sequential extractions achieved between 75% and 90% removal of phenanthrene: 5% Tween 80–1 M citric acid, 5% Tween 80–1 M phosphoric acid, and 3% Igepal CA-720–0.2 M EDTA. The other sequential extractions removed less than 65% of the phenanthrene from the field soil. In all sequential extractions, phenanthrene was removed only due to the presence of surfactants. When the surfactants were used in the first step, most of the phenanthrene was removed. When acid or chelating agent was used during the second step, a small amount of additional phenanthrene was removed, and this removal is attributed to the presence of residual surfactant in the soil from the first-step. The differences in removal efficiencies

between the single extraction and the first- or second-step in sequential extraction for the same extractant may be attributed to heterogeneous distribution of phenanthrene in the soil.

3.6.2. Removal of zinc and lead

Fig. 6b shows the removal of zinc using various combinations of extractants. Complete removal of zinc was obtained with the following combination of extractants: 3% Igepal CA-720–1 M citric acid, 5% Tween 80–1 M citric acid, 3% Igepal CA-720–0.2 M EDTA, 1 M citric acid–3% Igepal CA-720, 1 M phosphoric acid–3% Igepal CA-720, 1 M citric acid–5% Tween 80, 1 M phosphoric acid–5% Tween

80, 0.2 M EDTA–3% Igepal CA-720, and 0.2 M EDTA–5% Tween 80. The other sequential extractions removed less than 75% of the zinc from the field soil. The data from Fig. 6c shows that the lead was completely removed from the field soil with all combinations of extractants. In general, zinc and lead were removed during the use of acids or chelating agent in either first-step or the second-step of sequential extraction schemes. When surfactants were used following the use of acids or chelating agents, some additional zinc and lead removal was observed, and this additional zinc and lead removal is attributed to the presence of residual acids or chelating agent in the soil from the first-step extraction process.

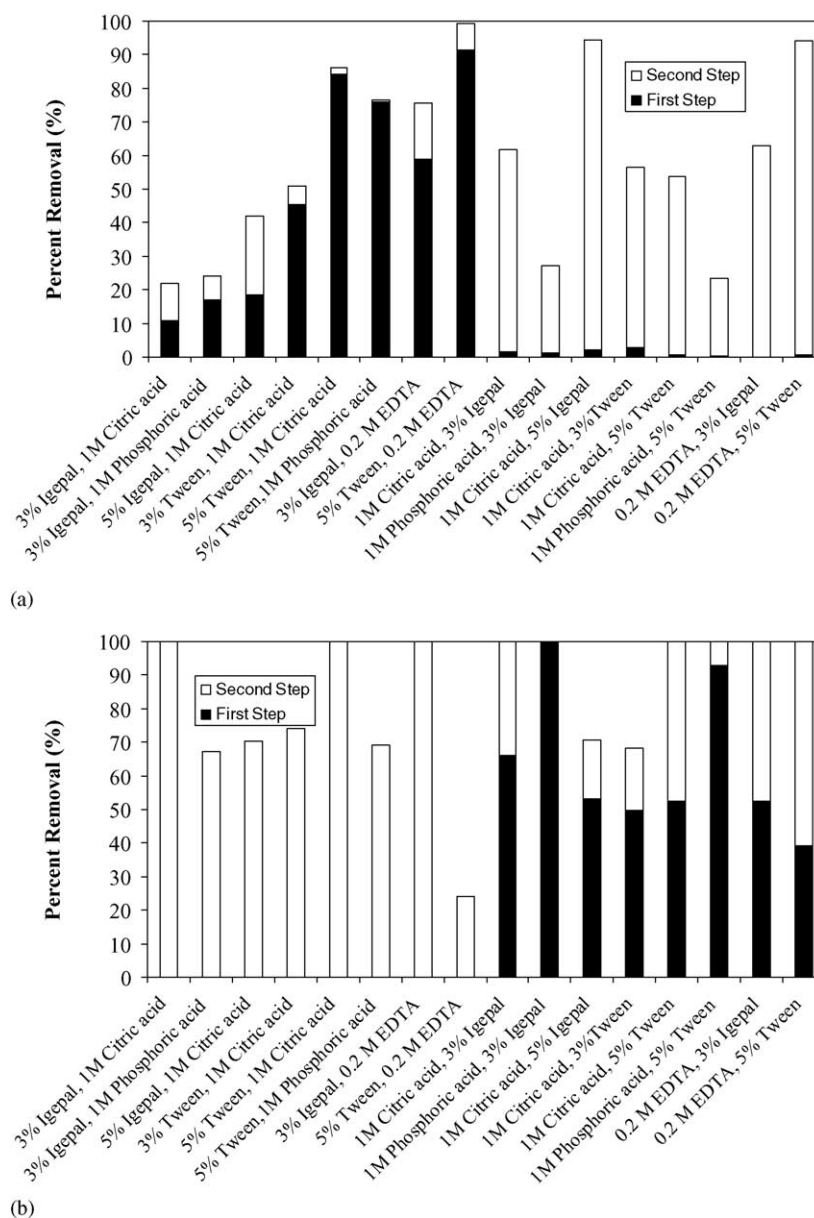


Fig. 6. (a) Removal (% mass) of phenanthrene using sequential extractions; (b) Removal (% mass) of zinc using sequential extractions; (c) Removal (% mass) of lead using sequential extractions.

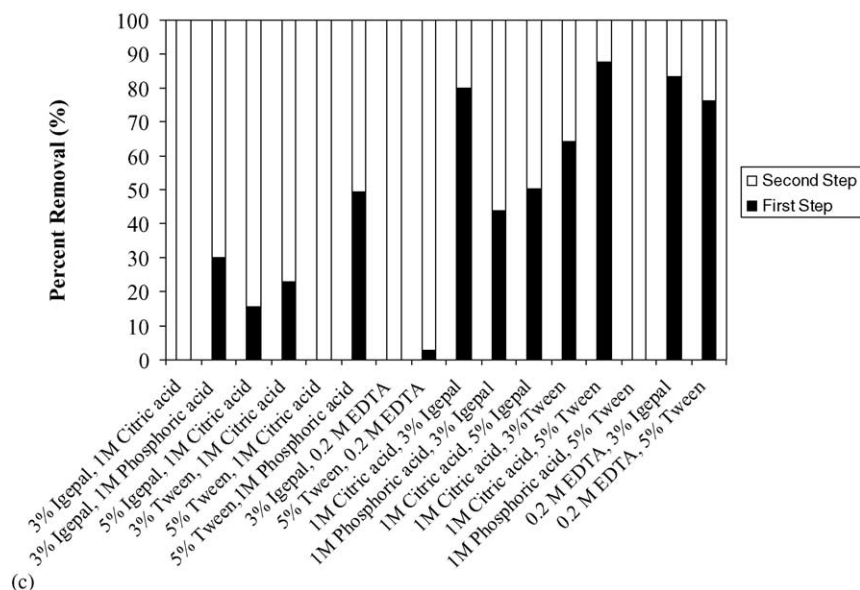


Fig. 6. (Continued).

4. Conclusions

It is feasible to extract metals and PAHs from the clayey soils using different extracting solutions. These investigations also indicate the selectivity and affinity of the extracting solutions towards the target contaminant from the field soil. Surfactant solutions were found to be most effective in extracting phenanthrene from the field soil, while organic acids have affinity in extracting both lead and zinc from the field soil. For removal of both metals and phenanthrene from the field soil, combinations of surfactant with either organic acid or chelating agent were found to be effective extracting solutions. A sequential extraction with 0.2 M EDTA followed by 5% Tween 80 or 5% Tween 80 followed by 1 M citric acid was effective in extraction of lead and zinc (heavy metals) as well as phenanthrene (hydrophobic organic compound), from the field soils. It should be noted that site-specific treatability studies, similar to this study, should be performed to optimize re-remediation plans, since soil composition and heterogeneity, contaminant types and concentrations, and other site-specific parameters can affect the remedial efficiency.

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