

Extractants for the Removal of Mixed Contaminants from Soils

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The development of improved and effective remediation technologies for soils contaminated by heavy metals as well as polycyclic aromatic hydrocarbons (PAHs) has emerged as a significant environmental priority. One technology that appears to have considerable promise is the ex-situ soil washing that involves the use of extracting agents such as surfactants, cosolvents, cyclodextrins, chelants, and weak acids. This study investigates the use of various single and sequential flushing schemes using different extracting agents (two surfactants, two cosolvents, two cyclodextrins, two chelants, and phosphoric acid and six organic acids) for the simultaneous removal of PAHs and metals from three different soils. Specifically, this study examines the effectiveness of different extractants on the removal of phenanthrene (representative PAH) and nickel, lead, and zinc (representative heavy metals) from the soils and evaluates the optimum composition of extractants in sequential flushing schemes. Soils used in this study were artificially spiked kaolin soil (a representative clayey soil with negligible organic content), Soil A collected from a former manufactured gas plant (MGP) site dominated by sand and high organic content, and Soil D collected from a different MGP site having high clay and low organic contents. Batch experiments with a single extraction step using surfactants showed that the removal of phenanthrene varied from 4.9% to 52% for kaolin, 40% to 100% for Soil A, and 21% to 72.6% for Soil D. 1M phosphoric acid and 1M citric acid were found to be effective for the removal of the three heavy metals from all soils. Sequential extraction schemes were designed and investigated for the simultaneous removal of phenanthrene and metals from all the soils. Results showed that 5% Tween 80 followed by 1M citric acid or 1M citric acid followed by 5% Igepal CA-720 schemes have potential for the removal of both phenanthrene and nickel from kaolin soil. However, 5% Tween 80 followed by 1M citric acid scheme or 0.2M EDTA followed by 5% Tween 80 scheme showed maximum removal of phenanthrene, lead, and zinc from Soil A and Soil D. Overall this study demonstrates that the removal of both heavy metals and PAHs from soils can be accomplished by developing a sequential flushing scheme based on specific site soil composition.

Keywords remediation, soils, heavy metals, organics, mixed contaminants, soil washing, extractants

Introduction

It has been estimated that 3,000 to 5,000 former manufactured gas plant (MGP) sites exist across the United States (USEPA, 2000). A major factor complicating the cleanup of many of these hazardous waste sites is the co-occurrence of organic compounds (e.g.,

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polycyclic aromatic hydrocarbons (PAHs), benzene and phenols) and heavy metals (e.g., lead, zinc, and nickel), often designated as mixed waste sites (Williamson et al., 1998; Hatheway, 2002). Previous research on the advancement of remediation technologies such as chemical oxidation, bioremediation, thermal desorption, incineration, and pump and treat had targeted either organic contaminants or metals, with very little attention to the mixed wastes (Chen, 1992; Pina et al., 2002; Sharma and Reddy, 2004). As a result, a variety of available technologies have been found to be less effective and/or more expensive for these complex mixed waste sites.

Recently, soil washing technologies with suitable extractants have shown potential as an alternative to some of the conventional techniques for the remediation of contaminated soils (USEPA, 1990). Principally, adding suitable extractants/chemical agents to the contaminated soil can enhance the apparent solubilization/extraction/dissolution of the contaminants. Under controlled conditions, this may result in efficient and cost-effective contaminant removal. Several classes of extractants that are being used for soil washing include surfactants, cosolvents, cyclodextrins, chelating agents, and organic acids (USEPA, 1990; Wood et al., 1990; Abumaizar and Smith, 1999; Tanada et al., 1999; Boving and Brusseau, 2000; Chu and Chan, 2003; Gao et al., 2003). All these soil washing extractants have been developed on a case-by-case basis depending on the contaminant type at a particular site. For example, surfactant based remediation systems were investigated for the remediation of organics, and cosolvent based schemes were applied for the removal of dense non-aqueous phase liquids (DNAPLs) from soils. Cyclodextrins were used for the removal of certain metals and low polarity organics from soils, while chelants and organic acids were used for the removal of different heavy metals from soils.

A few studies have indicated that solubilization/exchange/extraction of contaminants due to washing solutions differs drastically for different soil types. It is found that it depends upon the soil composition, heterogeneity, and organic content of the soil to be treated. Joshi and Lee (1996) reported that the effectiveness of surfactant-based remediation can be limited by adsorption of surfactants to clays, silts, and organic matter. The efficacy of chelant-aided extraction of metals depends upon the soil pH and soil type (Ghestem and Bermond, 1998). Thus, soil composition as well as types of contaminants can limit the effectiveness of soil washing-based remediation.

The overall objective of this study was to investigate various extraction-based soil washing schemes for the removal of mixed contaminants from soils. This study evaluated soil washing of three soils (having varying clay and organic content) using different extractants (including two surfactants, two cosolvents, two cyclodextrins, two chelants, and phosphoric acid and six organic acids). A major factor complicating the remediation of many of the hazardous waste sites is the co-occurrence of organics and heavy metals; therefore, sequential use of these extractants was examined to enhance the solubilization and removal of these contaminants from different soils.

Materials and Methods

Soils

Three different soils were chosen for evaluation in this study based on their varying physicochemical properties such as specific gravity, grain size distribution, Atterberg limits, hydraulic conductivity, pH, and organic content. The properties of these soils and their classification according to the Unified Soil Classification System are presented in Table 1. The

Table 1
Properties of clean kaolin soil and contaminated manufactured gas plant site soils

Property	Test method	Kaolin soil	Soil A	Soil D
Specific Gravity	ASTM D854	2.6	2.63	2.54
Grain Size Distribution	ASTM D422	% Gravel = 0 % Sand = 4 % Fines = 96	% Gravel = 0 % Sand = 84 % Fines = 16 Non-Plastic	% Gravel = 1.4–15.4 % Sand = 50.1–87.7 % Fines = 10.9–34.5 Non-Plastic
Atterberg Limits	ASTM D4318	Liquid Limit = 50% Plastic Limit = 27%		
Hydraulic Conductivity	ASTM D2434	1×10^{-8} cm/s	1.6×10^{-4} cm/s	2.1×10^{-4} cm/s
pH	ASTM D4972	4.9	7.05	6.9
Organic Content	ASTM D2974	~ 0	11.1%	2.7–3.7%
USCS Classification	ASTM D2488	Silty clay, CL	Organic silty sand, SM	Organic silty sand, SM

first soil selected was clean kaolin soil (EM Science) because it has high fines content, low hydraulic conductivity, and negligible organic content. It mainly consists of the kaolinite mineral with traces of muscovite and illite. Kaolin soil was spiked with phenanthrene (a representative PAH, concentration 500 mg/kg of dry soil) and nickel (representative heavy metal contaminant, concentration 500 mg/kg of dry soil). Phenanthrene and nickel were selected because these contaminants are commonly encountered at the contaminated sites and they were also used in previous remedial investigations (e.g., Maturi and Reddy, 2006).

The other two soils, designated as Soil A and Soil D, were collected from actual contaminated MGP sites. These soils were contaminated for several decades; therefore, they are representative of typical field contaminated soils more than the artificially spiked kaolin soil. The field soils differ in their composition (fines content and organic content). As shown in Table 1, Soil A is dominated by sand, but possesses high organic content, whereas Soil D contains higher amount of fines than Soil A, but possesses low organic content. Both field soils (Soil A and Soil D) were analyzed for total metals and PAHs. Total metals were analyzed using USEPA Method SW6020/SW7471A, and the PAHs were analyzed using USEPA Method SW8270/SW8270C. The results summarized in Tables 2a and 2b show the presence of elevated levels of phenanthrene, lead, and zinc in both Soil A and Soil D; therefore, phenanthrene was selected as representative PAH, while lead and zinc were selected as representative heavy metals in these soils for the purpose of this study.

Extractants

Based on the previous studies dealing with soil washing (e.g., USEPA, 1990), different extracting agents were selected and investigated in this study for the removal of both PAHs and heavy metals from the three soils. Two nonionic surfactants, Tween 80 and Igepal CA-720, were investigated at four different concentrations ranging from 0.5%–5% by weight.

Table 2a
PAHs in the manufactured gas plant site soils A and D

PAH	Concentration in Soil A (mg/kg)	Concentration in Soil D (mg/kg)
Naphthalene	6.03	460
Acenaphthylene	263	84
Acenaphthene	37.7	25
Fluorene	39	90
Phenanthrene	193	260
Anthracene	32.8	69
Fluoranthene	58	92
Pyrene	40.2	130
Benz(a)anthracene	4.81	66
Chrysene	8.65	39
Benzo(b)fluoranthene	1.71	33
Benzo(k)fluoranthene	2.28	23
Benzo(a)pyrene	0.419	59
Indeno(1,2,3-cd)pyrene	0.345	21
Dibenz(a,h)anthracene	0.124	9.1
Benzo(g,h,i)perylene	0.286	33

Table 2b
Heavy metals in manufactured gas plant site soils A and D

Heavy Metal	Concentration in Soil A (mg/kg)	Concentration in Soil D (mg/kg)
Arsenic	3.81	11
Cadmium	8.39	<0.5
Chromium	19.5	8.3
Copper	263	13
Lead	1477.72	50.6
Nickel	18.6	14
Silver	1.48	<1
Mercury	9.31	<0.05
Zinc	776.15	84.4

Performance of two cosolvents, n-butylamine and tetrahydrofuran, was investigated in the concentration range of 5%-20%. Efficacy of chelating agents, EDTA and DTPA, were tested in the concentration range of 0.01M-0.2M. Two cyclodextrins, HP- β -CD (1%–10% concentration range) and β -CD hydrate (0.05%–1%), were employed. The lower range of concentrations was selected for β -CD hydrate because of its low aqueous solubility. Phosphoric acid and six organic acids (lactic acid, n-butyric acid, propionic acid, oxalic acid, citric acid, and acetic acid) were investigated at the same concentration of 1 M.

Testing Program

Initially, single step batch experiments were performed to determine the removal of phenanthrene and nickel by using selected extractants at varying concentration range. Due to limitations of each single step extraction scheme for the simultaneous removal of PAHs and heavy metals, two-step sequential extraction schemes were designed and evaluated. The different sequential extraction schemes investigated in this study are shown in Table 3.

The batch soil washing experiments were conducted by placing a known ratio of each soil to extracting solution (5 g/25 mL) in 40-mL glass vials sealed with a Teflon screw-type top, at room temperature. Each vial was then shaken by hand for about a minute to ensure the soil was fully saturated with solution, and then the vials were placed on a rotary shaker

Table 3
Different sequential extraction schemes investigated

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

table at 250 rpm for 24 hours. After the shaking was completed, the solution was decanted into a clean polycarbonate centrifuge tube, and the soil-solution mixture was centrifuged at 4000 rpm for 28 minutes. Then, the supernatant was separated from the soil through a glass funnel holding a Whatman GF/C glass fiber filter (1.2 μm particle retention). The supernatant obtained from kaolin soil samples was again centrifuged at 4000 rpm for 28 minutes as the supernatant still contained fine particles that tended to stay suspended in solution. Once the supernatant was observed to be clear of any suspended particles, the supernatant and the soil samples were saved for phenanthrene and respective heavy metal analyses (nickel in kaolin, and lead and zinc in Soils A and D).

Contaminants Analysis

The initial phenanthrene concentration in all the three soils was determined using a Soxhlet extraction procedure that involves extracting contaminated soil with methylene chloride followed by quantification by gas chromatography (GC) in accordance with USEPA test method 3540C (USEPA, 1986). The GC used was an Agilent Model 6890 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 was a J&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 ramp was started at 100°C and increased to 250°C at 18°C/min for 1.5 minutes and then held at 250°C until the end of the run time. 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 concentration of nickel in kaolin soil sample was determined by standard acid digestion in accordance with USEPA 3050 procedure (USEPA, 1986) followed by analysis using atomic absorption spectrophotometry (AAS) in accordance with USEPA method 7520 (USEPA, 1986). Similarly, lead and zinc from field soils were extracted following the same acid digestion procedure. The resulting extractant was then analyzed using AAS to determine the concentration of lead and zinc in accordance with USEPA methods 7420 and 7950, respectively (USEPA, 1986).

Quality Assurance

To ensure accuracy of the test results, the following precautions were taken: (1) all the glassware, such as vials and sample bottles, used for each test were new from the manufacturer and certified to be clean; (2) all the instruments used, such as GC and AAS, were carefully calibrated and checked frequently after sample analysis; (3) chemical analyses were performed in duplicate; (4) chemicals used as extractants during test were new from the manufacturer and of high grade purity; and (5) a mass balance was calculated for each contaminant for all the tests performed.

Results and Discussion

Evaluation of Surfactants

The removal efficiencies of phenanthrene and heavy metals from the three different soils using two different nonionic surfactants, Tween 80 and Igepal CA-720, at varying concentrations (0.5% to 5%) are summarized in Table 4. In general, these results show that

Table 4
Evaluation of surfactants for contaminant removal

Surfactant solution	Removal Efficiencies for Kaolin			Removal Efficiencies for Soil A			Removal Efficiencies for Soil D		
	Phenanthrene	Nickel	Zinc	Phenanthrene	Lead	Zinc	Phenanthrene	Lead	Zinc
0.5% Igepal 720	12.5%	7.2%	0%	40%	0%	0%	21%	0%	1.0%
1% Igepal 720	28.4%	10.8%	0%	59.8%	0%	0%	37%	1.0%	1.0%
3% Igepal 720	40.2%	10.2%	0%	100%	0%	0%	59.5%	3.2%	0.7%
5% Igepal 720	33.6%	6.5%	0%	100%	0%	0%	72.6%	2.0%	1.4%
0.5% Tween 80	4.9%	16%	0%	65%	0%	0%	21.5%	1.0%	2.4%
1% Tween 80	29%	14.2%	0%	97%	0%	0%	55.2%	2.4%	2.2%
3% Tween 80	39.8%	11.6%	0%	100%	0%	0%	37%	3.0%	1.8%
5% Tween 80	52%	13.5%	0%	100%	0%	0%	48.3%	3.0%	2.1%

the removal of phenanthrene from all the three soils increases with an increase in surfactant concentration (for both Igepal and Tween). Phenanthrene removal varied from 4.9% to 52% for the spiked kaolin soil, 40% to 100% for Soil A, and 21% to 72.6% for Soil D. Phenanthrene removal was lower in kaolin as compared to that observed in field soils. Tween 80 performed better than Igepal in kaolin and Soil A, while Igepal performed better than Tween 80 in Soil D. These variations in the removal of phenanthrene from the three soils may be attributed mainly to their differences in their clay and organic contents.

The stability of the surfactants solution is highly affected by the high sorption properties of clay minerals due to high surface area as well as protonated surface of clay minerals. In kaolin soil, phenanthrene may be strongly bound to the soil minerals due to the high surface area and availability of the protonated clay particles at the surface due to the characteristic low pH. When the artificially contaminated kaolin was treated with surfactant solutions, low desorption of phenanthrene was observed. Some of the surfactants may have adsorbed to the kaolin soil and hence few stable micelles may have formed, resulting in low solubilization and removal of phenanthrene. The pH of kaolin decreases with an increase in the concentration of Igepal and this may also be a reason for the comparatively low removal of phenanthrene using Igepal (Maturi, 2004).

Soil A possesses high sand content, thus relatively low surface area, and when this soil is treated with surfactant solutions more stable micelles are formed that may also desorb the humic substances present in the soil. Desorption of humic substances from the Soil A enhances the mobilization of phenanthrene under similar surfactants concentration range. Thus, maximum removal (40%–100%) of phenanthrene was obtained in Soil A. On the other hand, Soil D contains some clay minerals that moderately increase the surface area of this soil that may influence the stability of the surfactant solutions at low concentration. However, using high surfactant concentration results in higher removal of phenanthrene (21%–73%) from the Soil D due to the formation of more stable micelles.

In general, the selected nonionic surfactants were ineffective for the significant removal of heavy metals from the soils (Table 4). None of the heavy metals were removed from Soil A, 1 to 3% removal of lead and zinc was observed in Soil D, and 7 to 14% removal of nickel was achieved in kaolin soil. These results show that heavy metals (lead and zinc) are strongly bounded within Soil A, and very low removal of lead and zinc from Soil D indicates that these metals were released due to the dissolution/complexation of the soil minerals with surfactants. Relatively higher removal of nickel from kaolin indicates that surfactants may partially mobilize metals in similar soil systems.

Evaluation of Cosolvents

Table 5 presents the removal efficiencies using the cosolvents for phenanthrene and respective heavy metals for the three soils. Both n-butylamine and THF are cosolvents that are water miscible or partially water miscible organic compounds. This group of solvents, when dissolved in water, reduces the polarity of the aqueous phase and increases the solubility of hydrophobic organic compounds. The results in Table 5 show that removal of heavy metals is insignificant to very low with both cosolvents in all soils. However, the removal of phenanthrene depends on the cosolvent as well as soil composition.

It can be seen that THF was found to be ineffective for the removal of phenanthrene from all three soils. N-butylamine resulted in increased removal of phenanthrene with an increase of its concentration. The maximum removal of phenanthrene was 46%, 100%, and 18% for kaolin, Soil A and Soil D, respectively, using 20% n-butylamine. The higher

Table 5
Evaluation of cosolvents for contaminant removal

Cosolvent solution	Removal Efficiencies for Kaolin			Removal Efficiencies for Soil A			Removal Efficiencies for Soil D		
	Phenanthrene	Nickel	Zinc	Phenanthrene	Lead	Zinc	Phenanthrene	Lead	Zinc
5% n-butylamine	2%	0%	2.2%	2%	0.5%	2.2%	4%	0%	1.8%
10% n-butylamine	4.4%	0%	5.6%	5.1%	0.6%	5.6%	4%	0%	1.4%
15% n-butylamine	15.1%	0%	5.2%	39.9%	0.1%	5.2%	9.6%	0%	1.2%
20% n-butylamine	46.2%	0.2%	6.4%	100%	0%	6.4%	18.4%	0%	1.25%
5% THF	2%	4.3%	0%	1.8%	0.1%	0%	2%	1.1%	0.4%
10% THF	2.4%	2.0%	0%	3.2%	0%	0%	2.5%	1.7%	0.2%
15% THF	3.2%	1.6%	0%	6.7%	0%	0%	2.5%	0.8%	0%
20% THF	8.0%	0.1%	0%	10%	0%	0%	3%	0%	0%

removal efficiencies are attributed to the extent of reduced surface tension of the soil solution, increasing desorption of phenanthrene and humic substances from the soils. Soil A is a sandy soil with less clay content, which allowed better desorption of phenanthrene as compared to the kaolin and Soil D.

Evaluation of Cyclodextrins

Cyclodextrins, a class of complexing agents, are comprised of several glucose molecules and are produced at commercial scales from the enzymatic transformation of starch by bacteria. These toroidal-shaped molecules have a hydrophobic cavity within which organic compounds of appropriate shape and size can form inclusion complexes. This unique property provides cyclodextrins with a capacity to increase the apparent solubilities of many low-polarity organic contaminants. Cyclodextrins have the potential to form inclusion complexes with heavy metals as well. Table 6 presents the removal efficiencies of two selected cyclodextrins, namely hydroxypropyl- β -cyclodextrin (HPCD) and β -cyclodextrin hydrate (β -CD hydrate), for phenanthrene and respective heavy metals from the three soils. The concentrations selected for these cyclodextrins were different because their different aqueous solubility.

Results show that the removal of heavy metals varied from 0.5% to 7.4% with HPCD and CD hydrate while the phenanthrene removal increased with increase in concentration for both cyclodextrins. The removal of phenanthrene was significantly higher with HPCD as compared to CD hydrate, with a maximum removal of 44%, 96%, and 23% from kaolin, Soil A and Soil D, respectively, using HPCD at 10% concentration. The higher removal of phenanthrene with HPCD may be due to the high stability of the 1:1 inclusion complexes of HPCD and phenanthrene as compared to those formed with CD hydrate.

In kaolin soil, 52% phenanthrene was removed at 5% HPCD concentration and the removal decreased to 44% on further increasing the HPCD concentration to 10%. It is also observed that 6%–7% of heavy metals were removed from kaolin indicating the partial complexation of both phenanthrene and nickel with HPCD. The decrease in phenanthrene removal at high HPCD concentration may be due to the formation of complexes with other dissolved soil metals. It is seen that in Soil A, 96% of phenanthrene was removed at 10% HPCD concentration. No appreciable dissolution of soil minerals occurred as trace amounts of heavy metals were only detected in the soil solution after the treatment. In Soil D, phenanthrene removal increased from 5% with 1% HPCD to 23% with 10% HPCD. The removal efficiency increased significantly on increasing the HPCD concentration, indicating that at high concentration more stable complexes are formed with phenanthrene with HPCD. No significant increase in heavy metal removal was observed in all soils, indicating that HPCD does not incorporate the heavy metals into their cavities, probably because of their size differences.

Evaluation of Chelants

The contaminant removal efficiencies with two chelants, EDTA and DTPA, in three soils, kaolin soil, Soil A and Soil D, are shown in Table 7. The results show poor affinity of chelants for the removal of phenanthrene from the tested soils. In contrast, chelants showed significant heavy metal removal from the three soils. In the artificially spiked kaolin, nickel removal was 90% with EDTA and 83% with DTPA in the low concentration of 0.01M. The removal efficiency decreased when the concentration of the chelants is increased from 0.01M to 0.2M.

Table 6
Evaluation of cyclodextrins for contaminant removal

Cyclodextrin Solution	Removal Efficiencies for Kaolin			Removal Efficiencies for Soil A			Removal Efficiencies for Soil D		
	Phenanthrene	Nickel	Zinc	Phenanthrene	Lead	Zinc	Phenanthrene	Lead	Zinc
1% HP- β -CD	9%	6.9%	0.25%	18%	0.15%	0.25%	5%	3.8%	1.2%
3% HP- β -CD	27.4%	6.5%	0.23%	45%	0.05%	0.23%	10%	2.4%	0.95%
5% HP- β -CD	52.5%	7.4%	0.4%	57%	0.1%	0.4%	12%	6.6%	0.9%
10% HP- β -CD	44%	6.6%	0.18%	96%	0.25%	0.18%	22.9%	5.7%	0.5%
0.05% β -CD hydrate	1%	3.5%	0.28%	1%	0.2%	0.28%	1%	4.5%	0.1%
0.1% β -CD hydrate	2%	3.5%	0.30%	2.5%	0.3%	0.30%	1.5%	2.0%	1.1%
0.5% β -CD hydrate	5%	3.5%	0.32%	6.2%	0.15%	0.32%	1.8%	2.5%	0.4%
1% β -CD hydrate	10%	2.9%	0.25%	10.8%	0.27%	0.25%	2%	2.0%	0.7%

Table 7
Evaluation of chelants for contaminant removal

Chelant Solution	Removal Efficiencies for Kaolin			Removal Efficiencies for Soil A			Removal Efficiencies for Soil D		
	Phenanthrene	Nickel	Zinc	Phenanthrene	Lead	Zinc	Phenanthrene	Lead	Zinc
0.01M EDTA	0.4%	90.5%	12%	2.5%	0.5%	12%	4.2%	14%	9.6%
0.05M EDTA	0.3%	87.4%	13%	0.4%	0.6%	13%	0.6%	19.5%	11.2%
0.1M EDTA	0.25%	76%	15%	0.4%	0.1%	15%	4.4%	21%	11.8%
0.2M EDTA	0.25%	78%	18%	0.4%	0%	18%	1.5%	22.5%	12%
0.01M DTPA	0.6%	83.2%	15.6%	1.0%	0.1%	15.6%	1.7%	19.5%	10.4%
0.05M DTPA	0.55%	83%	16%	0.7%	0%	16%	4.6%	23.5%	11.2%
0.1M DTPA	0.5%	80%	16%	0.7%	0%	16%	3.5%	22.4%	12%
0.2M DTPA	0.5%	75%	18.5%	0.5%	0%	18.5%	3%	22.9%	12%

In Soil A and Soil D, the removal of heavy metals was significantly lower than that observed in kaolin soil. In Soil A, only 12%–18% of zinc was removed while negligible amounts of lead were removed with chelants. The aged contamination and high organic content of the soil may have caused the heavy metals to adsorb strongly within soil leading to a lower removal. In Soil D, low removal efficiencies of chelants may also be attributed to strongly bound heavy metals to the soil matrix. Only 14%–23% lead and 9%–12% zinc was removed with both chelants. The stability of the heavy metal-chelates complexes may also be reduced in the presence of other competing ions present in the soil solutions, resulting in lower removal efficiencies.

Evaluation of Weak Acids

Phosphoric acid and six organic acids were investigated in the three soils to determine the feasibility of using these acids for the removal of phenanthrene and heavy metals, and the results are presented in Table 8. As expected, the phenanthrene removal was very low by all acids for all the investigated soils (Table 8). Phenanthrene removal efficiencies ranged from 1.5%–5% for kaolin, 0.8%–1% for Soil A, and 0.6%–4.6% for Soil D.

Results show that acids enhanced removal of metals in all three soils (Table 8). It is generally recognized that heavy metals incorporated into soils take different chemical forms including: (1) dissolved ionic form; (2) electrostatically adsorbed form; and (3) surface complexed form. Soil minerals having excess surface negative charge arising from isomorphous substitution adsorb heavy metal cations electrostatically. On the other hand, oxides and hydroxides of iron and aluminum as well as humic substances bind heavy metals strongly, forming surface complexes, in which bonding between heavy metal cations and surface functional groups of soil bears some covalency. The surface complexed heavy metal cations are, therefore, not exchanged by common ions in the pore water of soils. Thus the use of certain acids for the solubilization of such metals is highly feasible as they lower the pH of the soil system and hence enhance the protonation of the surface groups of soil, resulting in a change in soil polarity that enhances the release of these metals and organics from the soil surface.

The removal of nickel from kaolin ranged from 30% to 100%. The observed removal efficiencies of nickel from the kaolin were in the order of: phosphoric acid (100%) > acetic acid (80%) > n-butyric acid (68.4%) ≥ propanoic acid (68%) > citric acid (60.5%) > lactic acid (55%) > oxalic acid (30%). The pH of all acid solutions used was below 3.5. Maximum removal of nickel from kaolin was obtained using phosphoric acid as compared to acetic acid due to decreased soil pH. Phosphoric acid, a triprotic acid, decreases the soil pH more than the acetic acid, which is a monoprotic acid. Less nickel removal from kaolin observed in the other acid systems may be due to a change in organic ligand species at low soil pH and/or due to the change in soil polarity that decreases the stability of the other acids. Thus, if pH was the main factor responsible for the release of nickel from kaolin, at a given pH condition, relatively high amounts of ligands ions should exist in the presence of phosphoric acid, thus resulting in high amount of nickel desorption.

For Soil A, in the presence of phosphoric and organic acids, desorption of zinc and lead was found to be quite different (Table 8). The removal efficiencies are found to decrease in the order of: phosphoric acid ≥ citric acid > lactic acid > propanoic acid ≥ n-butyric acid > acetic acid > oxalic acid. This trend may be due to the high buffering capacity of the soil that reduces the amount of stable organic ligands ions available in presence of different acids. Further, it is observed that acetic acid removed more zinc as compared to lead.

Table 8
Evaluation of weak acids for contaminant removal

Acid	Removal Efficiencies for Kaolin			Removal Efficiencies for Soil A			Removal Efficiencies for Soil D		
	Phenanthrene	Nickel	Zinc	Phenanthrene	Lead	Zinc	Phenanthrene	Lead	Zinc
1M Phosphoric acid	1.5%	100%	64.6%	1%	64.2%	64.6%	4.6%	23.5%	11.2%
1M Lactic acid	1.8%	55%	54%	0.9%	25%	54%	4.2%	14%	9.6%
1M n-butyric acid	4.9%	68.4%	47%	0.9%	17.5%	47%	0.6%	19.5%	11.2%
1M Propanoic acid	3.0%	68%	47.2%	1%	25%	47.2%	4.4%	21%	11.8%
1M Oxalic acid	2.0%	30%	0%	0.8%	4%	0%	1.5%	22.5%	12%
1M Citric acid	3%	60.5%	64%	1%	64.2%	64%	1.7%	19.5%	10.4%
1M Acetic acid	2%	80%	45%	0.9%	20%	45%	3.5%	22.4%	12%

This indicates that lead is tightly bounded within the soil matrix as compared to zinc. On the other hand, complex stability of citric acid with lead and zinc is found to be significant, leading to higher removal efficiencies. These results indicate that stability of acids is the main controlling factor that influenced the heavy metal desorption from Soil A.

The removal efficiencies of all acids were significantly lower for Soil D (Table 8). The acids decrease the soil pH, and at lower pH, soil bears more positive charge at the soil surface. When the soil surfaces are positively charged, adsorption of strong organic ligands ions may leads to charge reversals. Such charge reversals could enhance adsorption of heavy metal ions. Thus, positively charged Soil D surfaces may have adsorb organic acid ligands or negatively charged heavy metal-organic acid complexes, this may have resulted in comparatively low removal of lead and zinc in Soil D as compared to Soil A.

Evaluation of Sequential Extractions

The results with the selected extractants show that a single extractant is not sufficient to remove both heavy metals and PAHs. In order to remove heavy metals as well as PAHs simultaneously from soils, different sequential extraction schemes using combinations of the selected extractants were investigated. The specific combinations of extractants investigated are shown in Table 3.

Figure 1(a) shows the phenanthrene removal from kaolin soil using various sequential schemes: the first eight schemes used different surfactants at different concentrations during the first step, the next six schemes used different weak acids during the first step, and the final two schemes used EDTA during the first step. Weak acids, EDTA and surfactants were used during the second step of the various sequential extraction schemes tested in this study. It can be seen that phenanthrene was selectively removed when surfactants were used either in the first step or second step. It is observed that 18% to 21% phenanthrene was removed with 3% Igepal in the first step and is further increased to 29% on increasing the Igepal

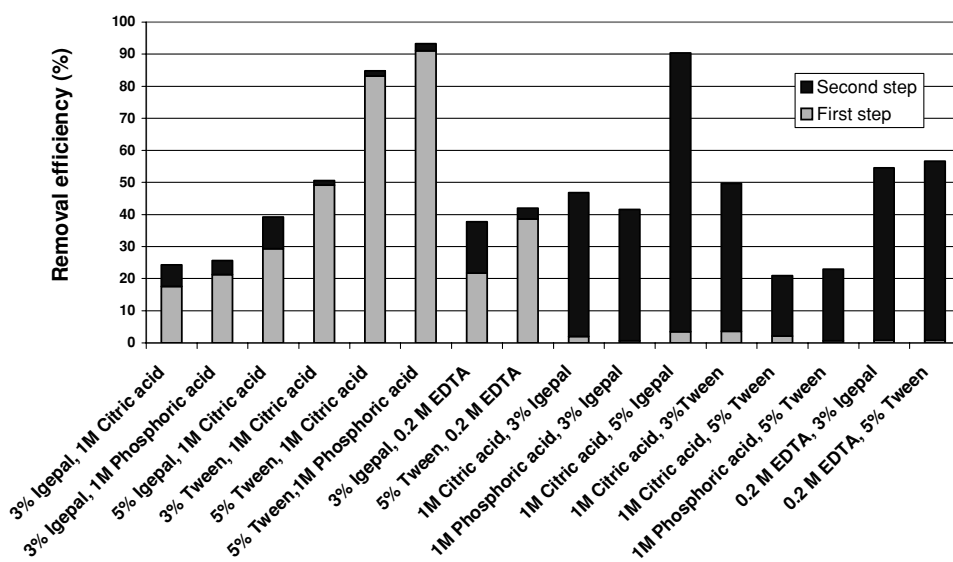


Figure 1a. Evaluation of sequential extraction schemes for the removal of phenanthrene from kaolin soil.

concentration to 5%. This indicates that more stable micelles are formed at higher Igepal concentration. When Igepal was employed in the second step, phenanthrene removal was dependent on the concentration of Igepal employed and also on the extractant type used in the first step. It can be seen that nearly 47% and 43% of phenanthrene was removed with 3% Igepal when, respectively, 1M citric acid or 1M phosphoric acid was used in the first step. A maximum of 90% of phenanthrene was removed using 1M citric acid followed by 5% Igepal. These findings indicate that the treatment of kaolin by a weak acid in the first step enhances the efficiency of Igepal as removal efficiency was improved and increased 2–3 fold at the same surfactant concentration range, possibly due to the lowering of soil pH. Further, it was also observed that 55% of phenanthrene was removed when 0.2M EDTA was used in the first step followed by 3% Igepal. This indicates that the solubilization of soil minerals due to the complexation of chelants also increases the mobilization of phenanthrene from the kaolin. Further, it was observed that nearly 21% of phenanthrene is removed using 3% Igepal in the first step and this was increased to 39% when 0.2 M EDTA was employed in the second step. This indicates that the solubilization of the soil minerals by chelants may also have increased the mobilization of phenanthrene in the soil.

The removal of phenanthrene with Tween was different than that observed with Igepal. About 49% of phenanthrene was removed using 3% Tween in the first step, while about 81%–91% of phenanthrene was removed using 5% Tween in the first step. This indicates that at low concentration, Tween may have adsorbed on the kaolin resulting in fewer stable micelles, but at high concentration comparatively more numbers of stable micelles were available to solubilize phenanthrene from the soil. Low phenanthrene removal (38%) using 5% Tween in the first step of the 5% Tween followed by 0.2M EDTA scheme may be attributed to the heterogeneously distributed phenanthrene in the kaolin. It can be clearly seen that first step treatment with acids or EDTA does not promote the solubilization of phenanthrene in the soil. These observations also demonstrate that Igepal can be employed at low concentration in the second step following the use either of acids or chelants in the first step for the effective removal of phenanthrene from kaolin. While a higher concentration of Tween can be used in the first step extraction of phenanthrene from kaolin, it is found that nearly 93% of phenanthrene can be removed using 5% Tween followed by 1M phosphoric acid. The use of 1M citric acid followed by 5% Igepal also resulted in nearly 90% of phenanthrene removal. Lowest removal efficiency for phenanthrene was observed in 1M citric acid followed by 5% Tween extraction scheme.

Figure 1(b) shows that 48%–86% of co-existing nickel was removed in all the investigated sequential schemes. Higher removal efficiencies for nickel was observed mainly in 3% Igepal followed by 1M phosphoric acid scheme, 5% Igepal followed by 1M citric acid scheme, 3% Tween followed by 1M citric acid scheme, and 0.2M EDTA followed by 3% Igepal or 5% Tween schemes. The first step treatment with 0.2M EDTA or acids resulted in partial removal of nickel and the use of surfactants in the second step appears to have caused additional nickel to be desorbed, leading to increased removal efficiency. Overall, these results show that 5% Tween 80 followed by 1M citric acid scheme or 1M citric acid followed by 5% Igepal scheme have potential for the simultaneous removal of PAHs and heavy metals from soils similar to kaolin soil.

Figures 2(a), 2(b) and 2(c) show the removal of phenanthrene, lead and zinc, respectively, from Soil A using various sequential schemes as described in Table 3. The data in Figure 2(a) shows the efficacy of the selected surfactant concentration range for the solubilization of phenanthrene from the Soil A. It is found that nearly 46 to 89% of phenanthrene can be removed using 3% Igepal during the first step extraction. The variation in the performance of Igepal may be attributed due to the heterogeneously distributed PAHs in the

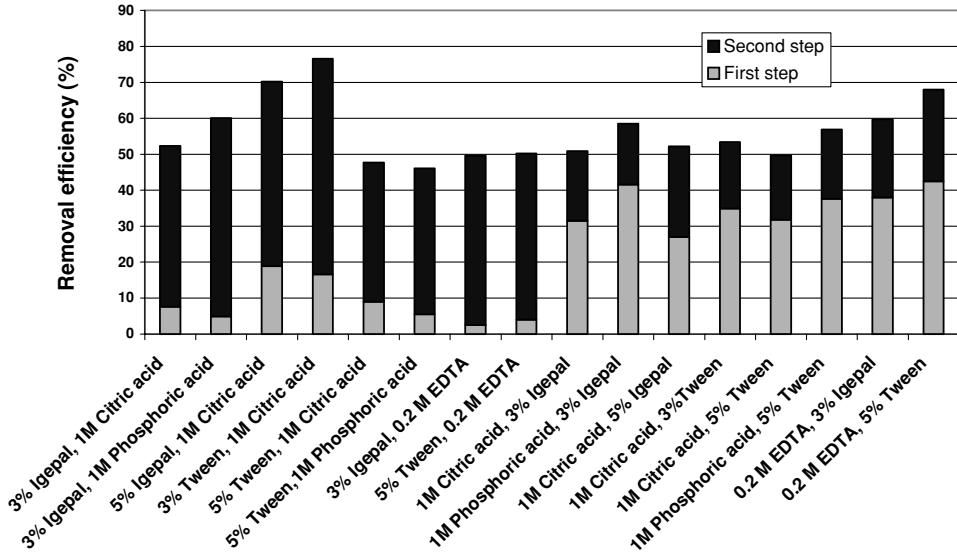


Figure 1b. Evaluation of sequential extraction schemes for the removal of nickel from kaolin soil.

soil and also due to the high buffering capacity of the Soil A that may hinder the formation of stable micelles. It is also observed that with 5% Igepal as a first step extractant, the removal of phenanthrene decreased to 65% but reached 100% removal with second step 1M citric acid treatment. This indicates that Igepal also solubilizes some humic acids present in Soil A that further increased the phenanthrene removal in second step treatment with

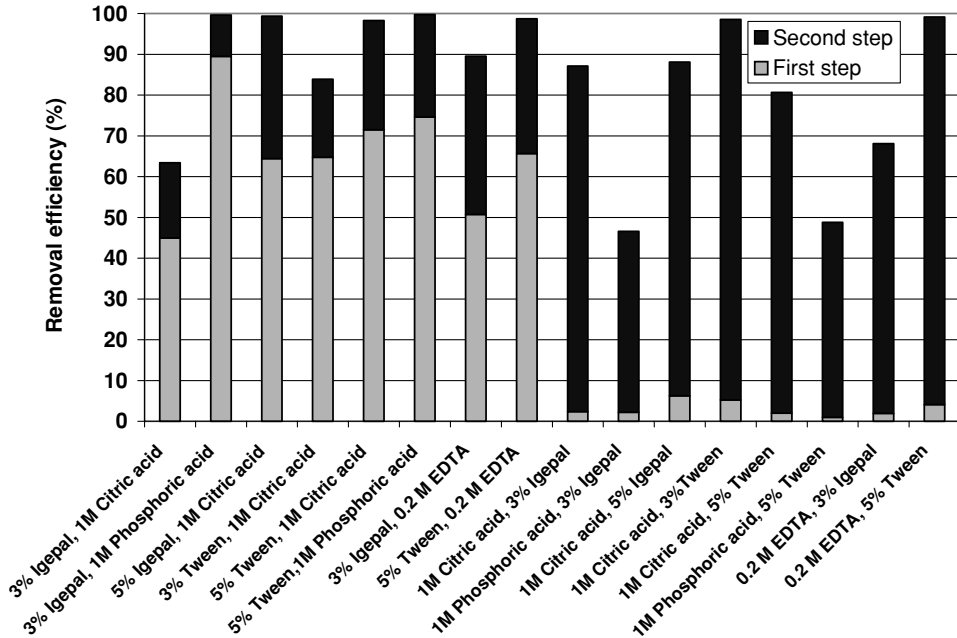


Figure 2a. Evaluation of sequential extraction schemes for the removal of phenanthrene from Soil A.

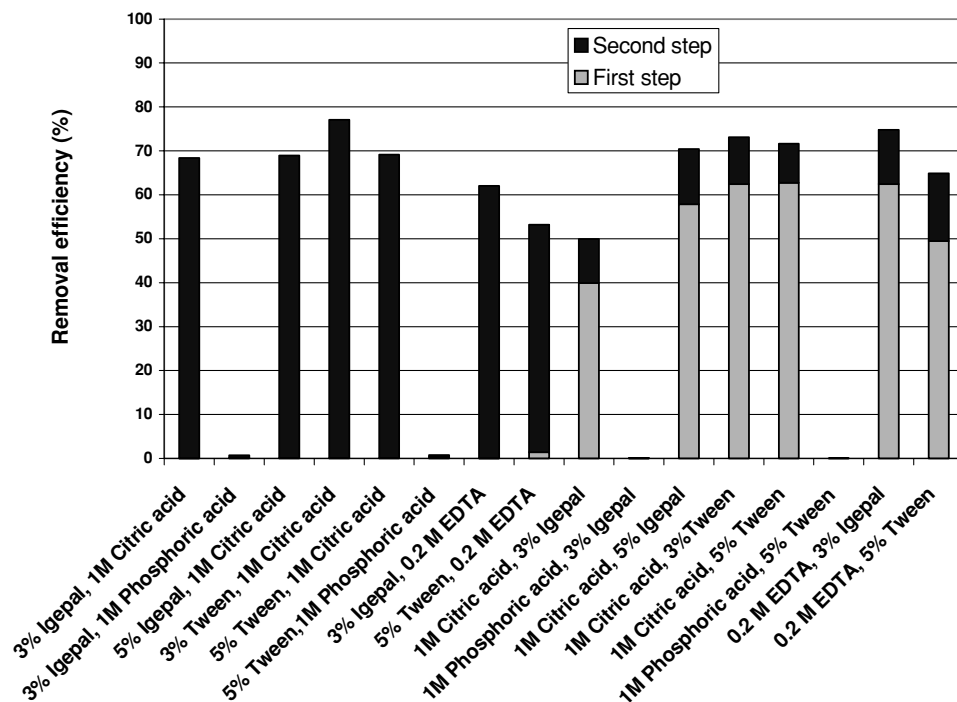


Figure 2b. Evaluation of sequential extraction schemes for the removal of zinc from Soil A.

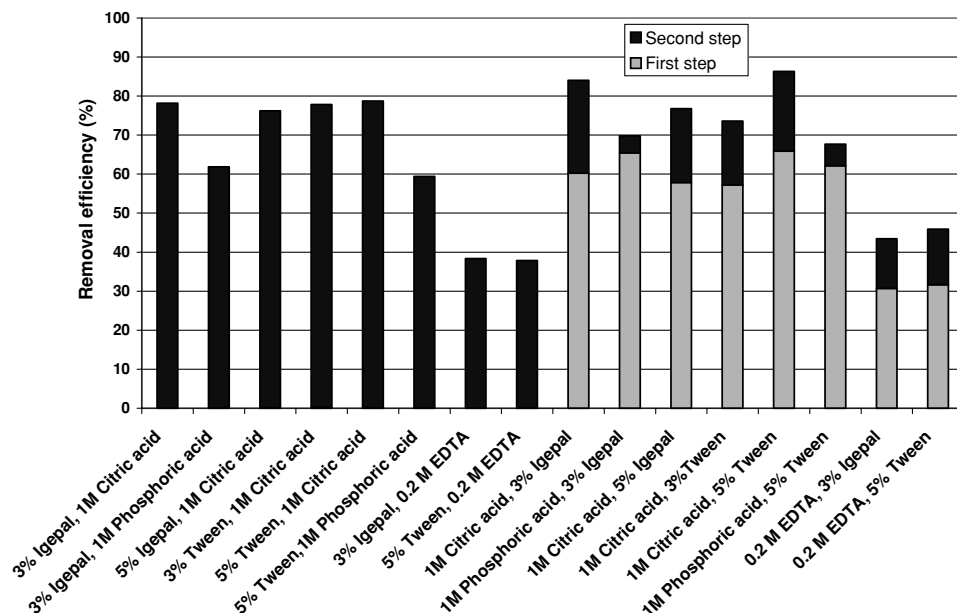


Figure 2c. Evaluation of sequential extraction schemes for the removal of lead from Soil A.

citric acid. It is further found that 1M citric acid, 1M phosphoric acid or 0.2 M EDTA, when used as first step extractant, show insignificant phenanthrene removal. The results obtained with Tween surfactant show the same trend as with Igepal, but more stable micelles were formed at higher surfactant concentration of 5%. However, comparatively low phenanthrene removal with Tween indicates the adsorption of micelles to the soil in the later stage of treatment. In general, these results show that more than 90% of phenanthrene can be removed using the following sequential extraction schemes: 3% Igepal–1M phosphoric acid; 5% Igepal–1M citric acid; 5% Tween–1M citric acid; 5% Tween–1M phosphoric acid; 5% Tween–0.2M EDTA; 1M citric acid–3% Tween; and 0.2M EDTA–5% Tween. The other sequential extraction schemes removed 47 to 90% of phenanthrene from this field soil.

Figures 2(b) and 2(c) show some interesting results for the removal of zinc and lead under various sequential extraction schemes. It can be seen from Figure 2(b) that zinc is not removed by either of the two surfactants during the first stage of extraction. However, noticeable removal of zinc was observed when surfactants were used during the second stage of extraction following the use of 1M citric acid or 0.2M EDTA during the first stage of extraction. This indicates that treatment of citric acid and EDTA solubilizes the soil minerals and, therefore, releases organically bounded zinc that is mobilized by the surfactant in the second stage of extraction. Among acids employed, 1M phosphoric acid did not show any noticeable removal of zinc in either stage. However, maximum removal of zinc was achieved in sequential extractions involving 3% Tween followed by 1M citric acid, 1M citric acid followed by 3% Tween, or 0.2M EDTA followed by 3% Igepal. Figure 2(c) reveals similar removal trends for lead as observed for the removal of zinc except that phosphoric acid resulted in some lead removal for the selected concentration. It is found that surfactants, when used in the first stage, were completely ineffective for the removal of lead. Maximum removal of lead (more than 80%) was observed with 1M citric acid followed by 3% Igepal or 1M citric acid followed by 5% Tween. Phosphoric acid was effective for the removal of lead from Soil A in both stages of extraction. It can be seen that nearly 62%–64% of lead is removed when 1M phosphoric acid was employed in the first stage as compared to 58%–66% lead removal with 1M citric acid. 0.2M EDTA showed slightly higher removal when employed in second stage as compared to first stage extraction. This indicates that in first stage extraction, EDTA forms more stable heavy metal-ligand complexes with other heavy metals such as zinc, while in the second stage of operation it forms more stable complexes with lead. It can be concluded that maximum removal of zinc and lead can be achieved using 5% Tween–1M citric acid, 1M citric acid–3% Igepal or 1M citric acid–5% Tween 80 sequential schemes. It can also be concluded that 5% Tween–1M citric acid combination has potential to remove both heavy metals and PAHs from the soil. This may be primarily due to the mobilization /solubilization of humic substances by Tween in the first step that enhances the simultaneous removal of PAHs and heavy metals from Soil A.

Figures 3(a), 3(b), and 3(c) show the removal of phenanthrene, lead and zinc, respectively, from Soil D using different sequential schemes as shown in Table 3. As seen in Figure 3(a), both 3% and 5% Igepal was found to be inefficient in the removal of phenanthrene in the first stage of extraction because of high soil pH. However, using 5% Igepal in the second stage of extraction following the use of 1M citric acid extraction, 95% of phenanthrene was removed from the soil. This may be due to the formation of more stable micelles under slightly acidic conditions. On the other hand, 45% phenanthrene was removed with 3% Tween, while 78% to 91% phenanthrene was removed with 5% Tween in the first stage of extraction. When Tween was used in the second stage after the first stage extraction using acid, low phenanthrene removal was observed. However, 93% of phenanthrene was removed in sequential extraction scheme involving 0.2M EDTA followed by

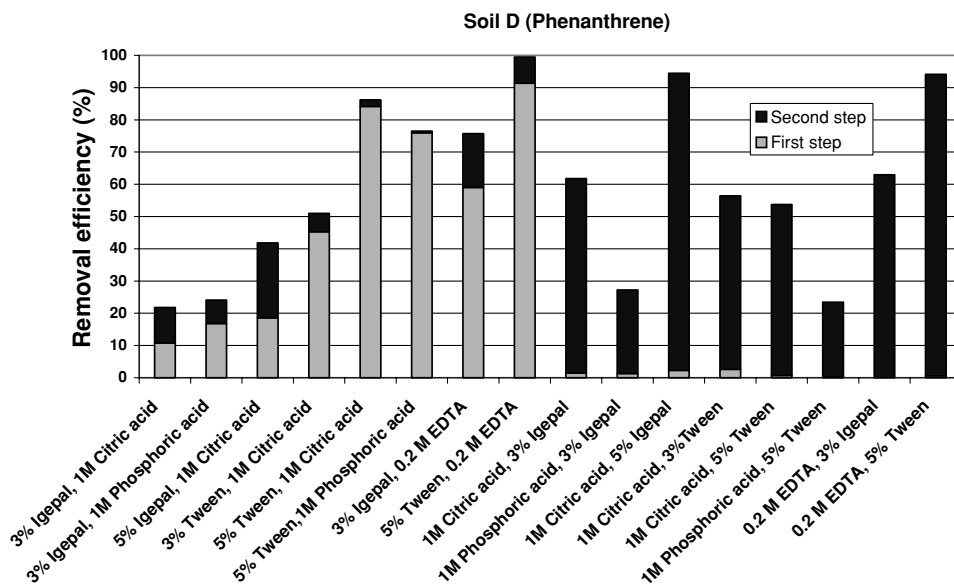


Figure 3a. Evaluation of sequential extraction schemes for the removal of phenanthrene from Soil D.

5% Tween. It was found that 1M citric acid and 1M phosphoric acid also remove small but noticeable amounts of phenanthrene in the second step of operation. This indicates that after the treatment of surfactant, acids may desorb some phenanthrene from the soil matrix. No significant removal of phenanthrene was achieved when phosphoric and organic acids were used in first stage of extraction. Nearly 100% of phenanthrene was removed using 5% Tween followed by 0.2M EDTA.

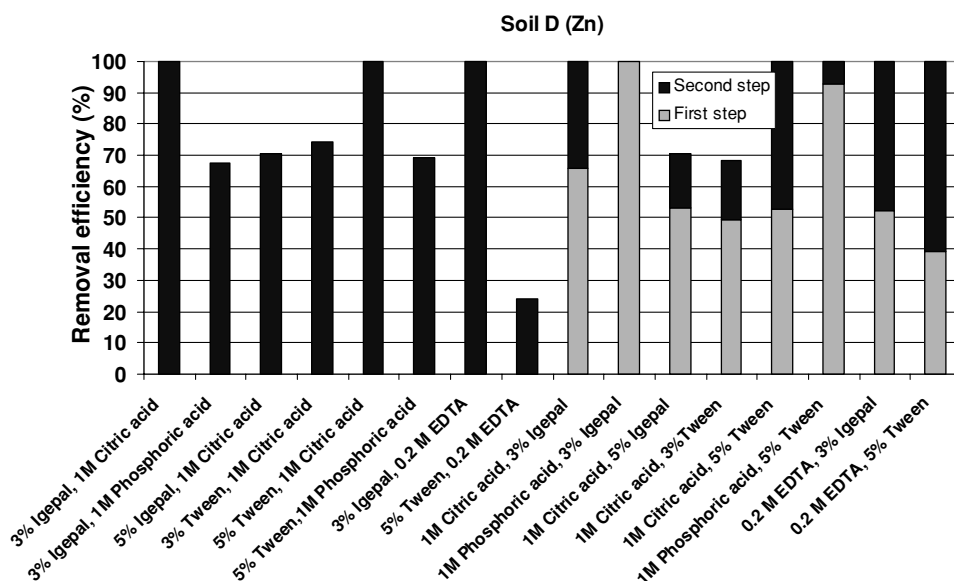


Figure 3b. Evaluation of sequential extraction schemes for the removal of zinc from Soil D.

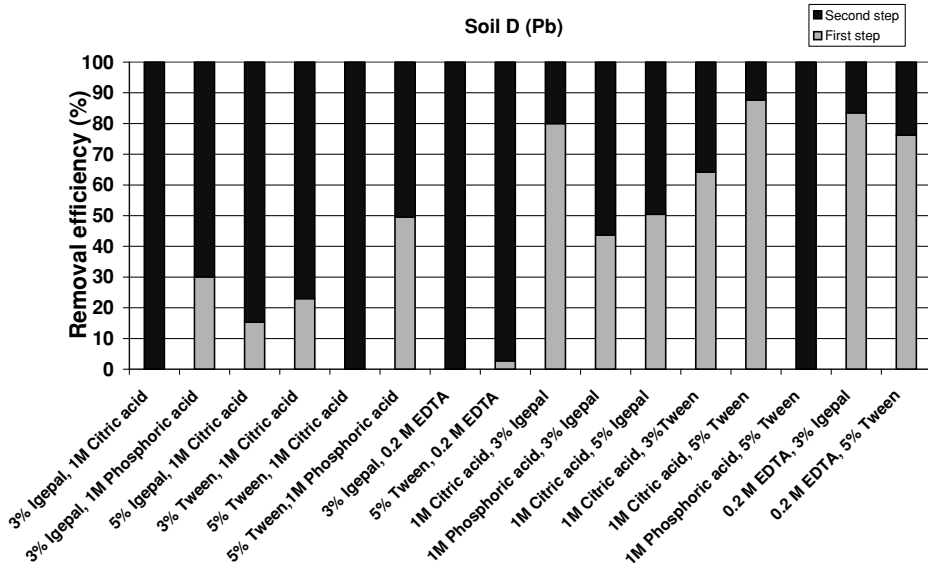


Figure 3c. Evaluation of sequential extraction schemes for the removal of lead from Soil D.

Figure 3(b) shows the removal of zinc using various sequential extraction schemes. It is observed that both surfactants (Igepal and Tween) did not remove zinc from Soil D when employed in the first stage of extraction. However, when these surfactants were employed in second stage, they removed all the remaining zinc metal. This may be due to the mobilization of zinc due to a decrease in interfacial tension of soil pore water. Use of 1M citric acid in the second stage following the use of surfactants in the first stage resulted in 70% to 100% removal of zinc, and when employed in the first stage it removed 51%–65% of zinc from Soil D. In contrast, phosphoric acid when employed in second stage removed only 68%–70% of zinc, while in first stage use of phosphoric acid showed nearly 92%–100% of zinc removal. It was also observed that when 0.2M EDTA was employed in the first stage, 39%–51% zinc was removed. In the second stage of extraction, the removal was dependent on the extractant used in the first stage of extraction.

Figure 3(c) shows the removal of lead from Soil D for the various sequentially extraction schemes. 100% removal of lead was achieved in all the extraction combinations used. Small but noticeable removal of lead was observed when Igepal and Tween were employed in the first stage of extraction. This indicates that some lead may be bound with organic content or may be present in the soil pore water that was readily mobilized on the treatment with surfactants. All the residual lead was removed by Igepal and Tween when employed in the second stage of extraction. 100% removal of lead was achieved with 1M citric acid when employed in second stage. Nearly 50%–88% of lead is desorbed from Soil D using 1M citric acid in the first stage. Nearly 100% removal of lead was achieved when phosphoric acid was used in second stage, while in the first stage use of phosphoric acid showed less ability to form complexes with lead as only 40% removal was achieved. Maximum and consistent removal of lead was observed when 0.2M EDTA was used in both stages of extraction. 75%–82% lead was removed when EDTA was used in the first step, while 100% removal of lead was observed when EDTA was used in second step. Overall, these results showed that 0.2M EDTA followed by 5% Tween has potential to remove phenanthrene, lead, and zinc from the Soil D.

Conclusions

The purpose of this study was to investigate different extractants for the removal of PAHs and heavy metals from soils. Several series of batch experiments were conducted using kaolin soil spiked with phenanthrene and nickel and two different field soils from former MGP sites contaminated with multiple metals and PAHs. For the purpose of this study, phenanthrene was selected as a representative PAH, and zinc and lead were selected as representative heavy metals for the field soils. Both single as well as sequential extraction schemes were evaluated for the simultaneous removal of PAHs and heavy metals. The following conclusions are drawn from this study:

- Surfactants are found to be effective for the removal of phenanthrene from all three soils in a single step extraction. Phenanthrene removal increased with an increase in surfactant concentration. Phenanthrene removal was low in spiked kaolin soil as compared to the field soils with low clay content, indicating that the formation and stability of micelles in surfactant extractions depends on the clay content that ultimately govern the solubilization of PAHs.
- Phosphoric and organic acids are found to be effective for the removal of metals from all three soils in single step extraction. 1M phosphoric acid and 1M citric acid are found to be effective for the removal of nickel from kaolin soil and lead and zinc from Soil A and Soil D. Further, it is found that removal of metals using acid extraction depends on the availability of the electrostatically bounded metals to the soil surface.
- In sequential extraction schemes, different combinations of the extractants were investigated for the removal of both phenanthrene and selected metals from the three soils. It is found that the use of 5% Tween 80 followed by 1M citric acid or 1M citric acid followed by 5% Igepal CA-720 can remove both phenanthrene and nickel from the kaolin soil, indicating the solubilization of phenanthrene is the most significant step. For Soil A, the 5% Tween 80-1M citric acid scheme was found to be effective for the removal of phenanthrene, zinc, and lead from the soil. Soil A contained the maximum organic content, thus application of 5% Tween enhances the solubilization of humic substance, enhancing the overall removal of phenanthrene and metals. For Soil D, 0.2M EDTA-5% Tween 80 sequential scheme was found to be more effective for the removal of phenanthrene, zinc, and lead from the soil.
- Overall, this study showed that the simultaneous removal of both PAHs and heavy metals is difficult to achieve by a single extraction method. However, sequential extraction schemes involving the use of surfactants followed by the use of weak acids or chelants have potential to remove both PAHs and heavy metals from soil. The optimal sequential extraction scheme must be selected based on the site-specific soil and contaminant conditions.

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