

Removal of Nickel and Phenanthrene from Kaolin Soil Using Different Extractants

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ABSTRACT

Numerous sites exist where low permeability clayey soils have been contaminated with both polycyclic aromatic hydrocarbons (PAHs) and heavy metals. To remediate these sites, innovative treatment methods are urgently required. Electrokinetically enhanced *in situ* flushing offers great potential to remediate low permeability soils, but this method is highly dependent on the type of extracting solution used. This study investigated the feasibility of using different extracting solutions at various concentrations to remove PAHs as well as heavy metals from low permeability clayey soils. The most efficient extracting solutions could be used as purging/extracting solutions in electrokinetic remediation and other technologies such as soil washing. For the present study, kaolin was selected as a model clayey soil, and it was spiked with phenanthrene as well as nickel at concentrations of 500 mg/kg each to simulate typical field contamination. Several batch tests were conducted using a known amount of the spiked kaolin mixed with different extracting solutions at various concentrations to enhance the removal efficiency and to optimize the concentration of each extractant. The extraction solutions selected were surfactants, cosolvents, chelating agents, organic acids, and cyclodextrins. Based on the test results, surfactants and cosolvents were effective for the removal of phenanthrene, but they were inefficient for the removal of nickel. On the other hand, chelating agents and organic acids were effective for the removal of nickel, but were ineffective for the removal of phenanthrene. Cyclodextrins were found to be ineffective for the removal of both nickel and phenanthrene. To remove both phenanthrene and nickel, sequential use of the extractants was investigated, and it was found that 5% Tween 80 followed by 1 M citric acid or 1 M citric acid followed by 5% Igepal CA-720 were effective for the removal of both nickel and phenanthrene from the kaolin soil. Overall, it can be concluded that sequential use of selected extracting solutions can be effective for the removal of both heavy metals and PAHs from clayey soils such as kaolin.

Key words: extractions; kaolin; phenanthrene; nickel; cosolvents; organic acids; surfactants; cyclodextrins; chelating agents

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INTRODUCTION

IN THE UNITED STATES, the total number of sites that need to be remediated are over 217,000 [U.S. Environmental Protection Agency (U.S. EPA), 1997]. Most of the National Priority List (NPL) or Superfund sites contain three contaminant groups: volatile organic compounds (VOCs), metals, and semivolatile organic compounds (SVOCs). Most sites require remediation for more than one of these contaminant groups. Twenty-five percent of the sites contain two contaminant groups and 41% of the sites contain all three contaminant groups. Although, there are several remediation techniques available to remediate PAH contaminated sites, very few technologies are available for the remediation of heavy-metal contaminated sites. The conventional *in situ* remediation methods for PAH contamination include bioremediation, thermal treatments using hot water, steam, or heaters, stabilization or solidification processes, and soil flushing (Roote, 1998; U.S. EPA, 2000). Technologies available for remediating metal contaminated soils can be divided mainly into two groups, namely, immobilization methods and separation/concentration methods. In the first type of remediation, contaminants are immobilized thereby nullifying the leaching of contaminants into the groundwater. Containment, *in situ* and *ex situ* solidification and stabilization, *in situ* and *ex situ* vitrification come under this category. The second type of remediation deals with separating the containment from the soils or reducing the volume of contaminated soil. The reduced volume of the soil may be deposited off in the landfills and separated contaminants may be treated on-site or off-site with suitable treatment methods. In low permeability soils, methods such as solidification/stabilization fail because it is hard to introduce the appropriate reagents or nutrients into the subsurface due to the low permeability of the soils. Therefore, the potential *in situ* treatment technologies available to treat metal-contaminated clays are limited to *in situ* vitrification, phytoremediation, and electrokinetic remediation.

Most of the remediation technologies are ineffective for the remediation of soils containing PAHs and heavy metals together. Previous research has shown that electrokinetic remediation has the potential to remove either heavy metals (Reddy *et al.*, 1997) or PAHs (Reddy and Saichek, 2003) from soils. However, according to the data provided by the U.S. EPA (1997), 41% of the NPL sites contain both heavy metals and PAHs. Therefore, a single capable technology, such as electrokinetic remediation, to remediate both heavy metals and PAHs can save both money and time. But because of the different nature of the heavy metals and the PAHs, extracting solutions

must be carefully selected to remove both the contaminant groups simultaneously.

In this study, several batch tests were performed using kaolin soil spiked with known concentration of phenanthrene and nickel. These tests helped to assess the capability of using different types of extracting solutions such as surfactants, cosolvents, chelating agents, cyclodextrins, and organic acids for the solubilization and removal of phenanthrene and nickel from the kaolin soil.

MATERIALS AND METHODS

Contaminants

In the present study, phenanthrene (C_4H_{10}), a neutral organic compound that contains three aromatic rings, was selected as a representative PAH. It has environmental properties such as aqueous solubility, octanol-water partition coefficient (K_{ow}), and vapor pressure that are similar to other PAHs, such as acenaphthene, fluoranthene, and fluorene (Schwarzenbach *et al.*, 1993). Although higher molecular weight and more carcinogenic PAHs, such as benzo(a)pyrene, may have higher K_{ow} values and lower aqueous solubilities, it was hypothesized that since the parent structures are similar, phenanthrene would be an adequate representative compound that would give a general indication of the PAH behavior. All PAHs are hydrophobic, and phenanthrene has an aqueous solubility of 1.1 mg/L at 25°C (Schwarzenbach *et al.*, 1993).

Nickel was selected as a representative heavy metal in the present study as it is one of the most prevalent heavy metals at many contaminated sites. The major sources of nickel contamination in the soil are metal plating industry, combustion of fossil fuels, and nickel mining and refining. Nickel (Ni) is a transition element with atomic number 28 and atomic weight 58.69. In low pH regions, nickel exists in the form of the nickelous ion (Ni^{+2}). In neutral to slightly alkaline solutions, it precipitates as nickelous hydroxide [$Ni(OH)_2$], which is a stable compound. This precipitate readily dissolves in acid solutions forming Ni^{+2} and in very alkaline conditions, nickel exists in the form of stable nickelo-nickelic oxide (Ni_3O_4) that is soluble in acid solutions. Other nickel oxides such as nickelic oxide (Ni_2O_3) and nickel peroxide (NiO_2) are unstable in alkaline solutions and decompose by giving off oxygen. However, in acidic regions, these solids dissolve producing Ni^{+2} (Pourbaix, 1974).

Extractants

Surfactants. Surfactants were considered as extractants for PAHs (Edwards *et al.*, 1994; Yeom *et al.*, 1996; Pat-

terson *et al.*, 1999). Surfactants increase PAH solubilization through the formation of micelles, which are essential aggregates of surfactant molecules that create a hydrophobic region in which PAH molecules may reside (Myers, 1988; Rosen, 1989). Cationic surfactants were not considered due to the possible complexation of cationic surfactants with soil minerals (Boubonais *et al.*, 1995). Anionic surfactants were not considered because they may counteract the electroosmotic flow in electrokinetic remediation (Pamucku, 1994; Taha, 1996; Saichek, 2002).

Two nonionic surfactants, namely Tween 80 and Igepal CA-720, were selected based on a previous research (Saichek, 2002). The properties such as critical micelle concentration (CMC) and the hydrophile-lipophile balance number (HLB) were taken into consideration during the selection and are shown in Table 1. 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.

Cosolvents. For a PAH such as phenanthrene, cosolvents, such as *n*-butylamine, tetrahydrofuran (THF), and acetone, could increase contaminant solubility by more than five orders of magnitude (Li *et al.*, 2000). Cosolvents were also considered for extraction of metals (Semer and Reddy, 1996; Pichtel and Pichtel, 1997). For this study, *n*-butylamine and tetrahydrofuran were selected among the cosolvents according to the results obtained in a previous study (Li *et al.*, 2000). These two cosolvents were very effective in increasing the solubility of organics such as PAHs (Peters and Luthy, 1993). The experiments were carried out at 5, 10, 15, and 20% concentrations of each cosolvent (i.e., *n*-butylamine and THF). Some properties of these cosolvents are shown in Table 2.

Chelating agents. Two chelating agents, ethylenediamine tetra acetic acid (EDTA) and diethylene triamine

penta acetic acid (DTPA), were investigated at concentrations of 0.01, 0.05, 0.1, and 0.2 M for the reclamation of the target contaminants. EDTA and DTPA were chosen as they were proven to be very effective for heavy metals (Tuin and Tels, 1990; Neale *et al.*, 1997; Reddy and Chinthamreddy, 2000).

Cyclodextrins. Cyclodextrins were used to investigate their potential to remove phenanthrene and nickel simultaneously (Brusseau *et al.*, 1997). Hydroxypropyl- β -cyclodextrin (HPCD) and β -cyclodextrin hydrate (β -CD hydrate) were selected among the different cyclodextrins based on the published literature (Wang and Brusseau, 1993; McCray and Brusseau, 1998; Ko *et al.*, 1999; McCray *et al.*, 2000). 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 spiked contaminants. Low concentrations of β -CD hydrate were selected because of its low solubility in water.

Organic acids. Organic acids have been shown to remove heavy metals from soils (Neale *et al.*, 1997; Reddy and Chinthamreddy, 2000). For this study, six different organic acids were selected and were investigated at the same concentration. 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 in further testing. These organic acids included lactic acid, *n*-butyric acid, propionic acid, oxalic acid, citric acid, and acetic acid. Although not an organic acid, phosphoric acid was also tested and compared with the performance of selected organic acids.

Soils

Kaolin, a clay mineral was selected as the model soil for the present study as it represents a low permeability soil. The composition and properties of this soil are sum-

Table 1. Nonionic surfactants used in 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

^aC represents the alkyl chain length (—CH₂—), P for phenol ring (—C₆H₆—), S₆ for sorbitan; ^bcritical micelle concentration; ^chydrophile-lipophile balance.

Table 2. Properties of cosolvents.

<i>Compound</i>	<i>Formula</i>	<i>Miscibility with water</i>	<i>Dielectric constant at 20°C</i>	<i>Vapor pressure (kPa) at 25°C</i>	<i>Viscosity (mPa.s) at 25°C</i>
Water	H ₂ O	—	78.5	3.17	0.890
<i>n</i> -Butylamine	C ₄ H ₁₁ N	Complete	4.7	12.2	0.574
Tetrahydrofuran	C ₄ H ₈ O	Partial	7.5	21.6	0.456

marized in Table 3. The colloidal laboratory grade kaolin was obtained from VWR scientific products and the manufacturer was EM science. Kaolin mainly consists of the kaolinite mineral.

Kaolin was spiked with phenanthrene at an initial target concentration of 500 mg/kg. This concentration was based on typical PAH concentrations that is found near source zones at contaminated sites (U.S. EPA, 2000). Initially, the phenanthrene required to yield the target concentration was measured and then completely dissolved in about 500 mL of hexane. Hexane was used because phenanthrene has an extremely low solubility in water. The hexane-phenanthrene mixture was subsequently mixed with the measured amount of soil, and additional hexane was added so that the soil-hexane-phenanthrene mixture could be easily stirred and blended homogeneously. The mixtures were stirred with stainless steel spoons in glass beakers. The motivation for this mixing technique was to ensure that the phenanthrene would be distributed evenly throughout the soil. The soil-hexane-phenanthrene mixture was then placed beneath a ventilation hood for nearly a week until hexane completely evaporated and the contaminated soil was dry. Occasional stirring was necessary during the drying period to increase the rate of drying and further ensure uniform phenanthrene distribution. A portion of the contaminant may volatilize along with the solvent. Therefore, a soil sample was taken to determine the actual initial concentration of phenanthrene in the soil using Soxhlet extraction procedure in accordance with the U.S. EPA test method 3540 (U.S. EPA, 1986).

After loading of kaolin with phenanthrene, the soil was spiked with nickel at a target concentration of 500 mg/kg. Nickel chloride was used to spike the soil by dissolution in deionized water and addition of dissolved nickel chloride to the soil followed by air drying of soil. The final moisture level was 35% by addition of deionized water. After its preparation, the spiked kaolin was placed in sealed glass bottles and equilibrated for at least 2 weeks. The initial nickel concentration in soil was measured based on the U.S. EPA acid digestion procedure followed by analysis with atomic absorption spectrophotometry (U.S. EPA, 1986).

Batch extractions

The batch extraction experiments were conducted using a soil-to-water ratio of 1:5 w/v. Specifically, 5 g of the kaolin soil were agitated intermittently with 25 mL of solution. First, 5 g of dry, contaminated kaolin soil was measured and placed in a new, clean 40-mL glass vial. Then, 25 mL of the extracting solution were measured and added, and the vial was sealed with a Teflon screw-type top. Each vial was then shaken by hand for about 1 min to ensure the soil was fully saturated with solution. The vials were placed on a rotary shaker table at 250 rpm for 24 h. After the shaking was completed, the solution was decanted into a clean polycarbonate centrifuge tube, and the soil-solution mixture was centrifuged at 4,000 rpm for 28 min. Then, the supernatant was poured through a glass funnel holding a Whatman GF/C glass fiber filter (1.2 μm particle retention) to remove any floating particles or debris, and the effluent from the funnel flowed into a clean 40-mL glass vial. The supernatant from the samples containing kaolin soil was decanted into a clean polycarbonate centrifuge tube and

Table 3. Properties of kaolin soil (Reddy *et al.*, 1997).

<i>Mineralogy</i>	<i>Kaolinite 100% Muscovite: trace Illite: trace</i>
Particle size distribution (%) (ASTM D 422)*	
Gravel	0
Sand	4
Silt	18
Clay	78
Specific gravity (ASTM D 854)	2.6
Hydraulic conductivity [cm/s]	1.0 × 10 ⁻⁸
Organic content [%]	Near 0
pH (ASTM D 4972)	4.9
Cation exchange capacity (mEq/100 g) (ASTM D 9081)	1.0-1.6
USCS classification (ASTM D 2487)	CL

*ASTM (1996).

centrifuged again at 4,000 rpm for 28 min. This was necessary with the kaolin because, after only one run through the centrifuge, 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 nickel analyses. All extractions were carried out in duplicates except for the sequential extractions.

Phenanthrene analysis

As mentioned earlier, the initial phenanthrene concentration in the soil was determined using Soxhlet extraction procedure in accordance with the U.S. EPA test method 3540C (U.S. EPA, 1986). After the extraction was completed, the volume of the solvent remaining in

the Soxhlet extraction tube and flask was measured. Gas Chromatography (GC) analysis 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 performing a concentrating procedure.

The supernatant and liquid samples from the batch tests were analyzed for phenanthrene after performing liquid-liquid extraction. The extraction procedure consisted of placing 1 mL of the contaminated supernatant in a conical flask with the help of a syringe. Then, the sample was diluted in the ratio of 1:10 with water. The conical flask was shaken thoroughly before transferring the diluted sample in to 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

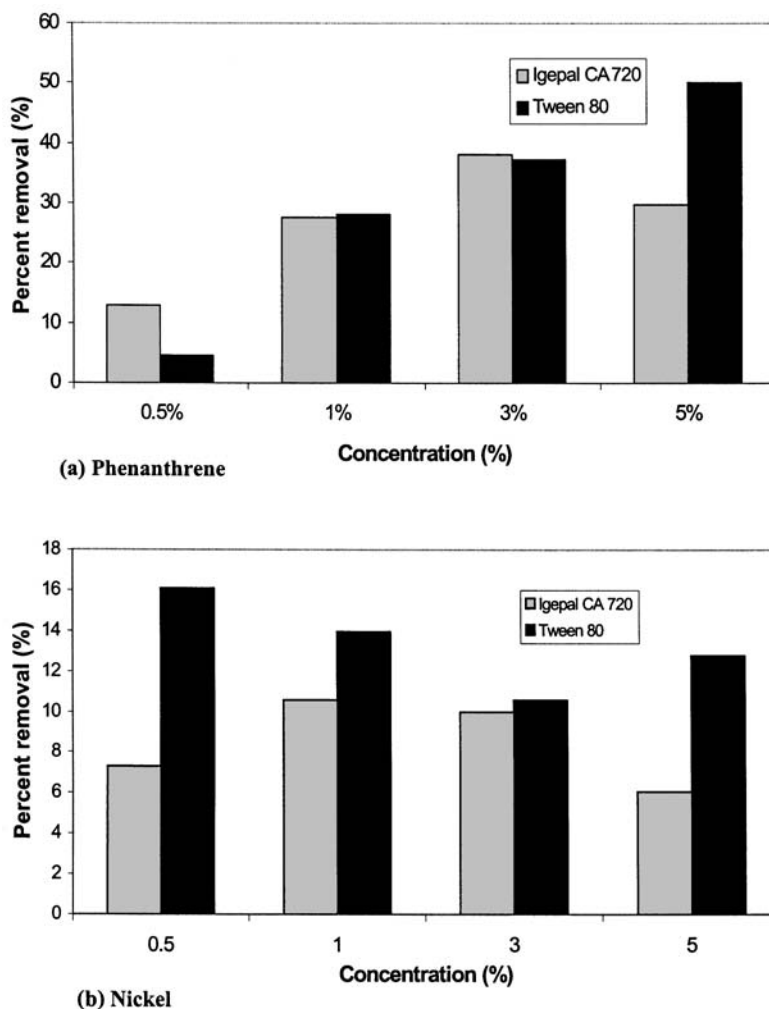


Figure 1. Removal of (a) phenanthrene and (b) nickel using surfactants.

for 5 min. Then, the two phases, methylene chloride phase and the aqueous phase, were allowed to separate. Approximately, 1 to 2 mL of the methylene chloride phase was taken with the help of a syringe into a 2-mL autosampler vial. The sample was then run on the GC. For quality control, all samples were run in duplicates.

The GC used was an Agilent Model 6890 GC equipped with a Flame Ionization Detector (FID). The injection volume was 1 μ L, and it was injected via an autoinjector at an inlet temperature of 250°C. The column used on the GC was a J&W Scientific (Folsom, CA) DB-5, 30 m \times 0.32 mm \times 25 μ m. 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 min 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 final phenanthrene concentration in the original soil extract was determined.

Nickel analysis

The initial nickel concentration in the soil was determined by the acid digestion in accordance with U.S. EPA 3050 procedure (U.S. EPA, 1986). The liquid samples from the batch tests were directly tested using AAS for the nickel concentration in accordance with the U.S. EPA method 7520.

RESULTS AND DISCUSSION

For each extractant, the removal efficiency is calculated as the ratio of the mass of the contaminant extracted from the soil (determined from contaminant concentration in extracting solution) to the initial mass of the contaminant in the soil and multiplied by 100.

Removal with surfactants

Phenanthrene. Different surfactants have been examined based on the solution properties, such as CMC and the HLB. Thus, for this investigation, two nonionic surfactants namely Igepal CA-720 and Tween 80, were chosen to desorb and solubilize phenanthrene from the kaolin soil. Each surfactant at varying concentrations such as, 0.5, 1, 3, and 5% were used in these soil-washing studies. The pH of the soil-solution mixture was measured after the samples were shaken until the equilibrium time was reached.

As shown in Fig. 1(a), the removal efficiency of Igepal CA-720 system gradually increases when the concentra-

tion of Igepal is increases up to 3% but then decreases with further increase in concentration of 5%. As shown in Table 4, the pH values for Igepal CA-720 samples ranged from 6.98 to 7.19. It is known that the oxyethylene (polar) group, binds to the protonated soil particle surface at lower pH (Ko *et al.*, 1998a, 1998b). This might be a possible reason for the lower removal efficiency of Igepal CA-720 at 5% concentration compared to the removal efficiency at other concentrations.

In the case of Tween 80, the removal efficiency gradually increased as the concentration increased from 0.5% to 5% as shown in Fig. 1(a). Tween 80 at 5% concentration had the highest removal of 50%. As shown in Table 4, the pH values for Tween 80 extracting solutions ranged from 6.78 to 7.14. Ko *et al.* (1998a, 1998b) found that, with Tween 80, a lower amount of surfactant adsorbed to the soil at high pH. Therefore, at higher pH,

Table 4. pH of extracted sample solutions.

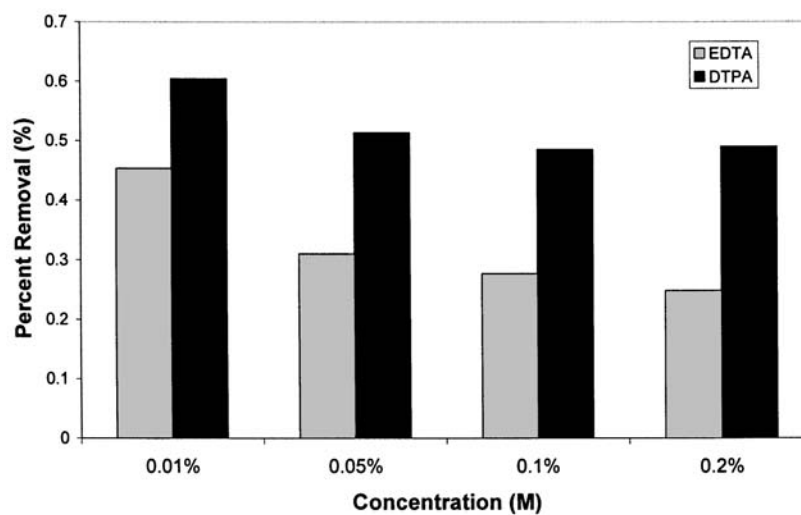
Soil	Extracting solution	pH range
Kaolin	Water	7.08–7.19
Kaolin	Igepal 0.5%	7.04–7.09
Kaolin	Igepal 1%	7.16–7.19
Kaolin	Igepal 3%	7.02–7.12
Kaolin	Igepal 5%	6.98–6.99
Kaolin	Tween 0.5%	6.78–6.79
Kaolin	Tween 1%	6.87–6.90
Kaolin	Tween 3%	7.06–7.07
Kaolin	Tween 5%	7.00–7.14
Kaolin	0.01 M EDTA	10.09–10.14
Kaolin	0.05 M EDTA	10.60–10.62
Kaolin	0.1 M EDTA	10.70–10.73
Kaolin	0.2 M EDTA	10.82–10.88
Kaolin	0.01 M EDTA	10.62–10.65
Kaolin	0.05 M EDTA	11.59–11.60
Kaolin	0.1 M EDTA	12.06–12.07
Kaolin	0.2 M EDTA	12.52–12.55
Kaolin	0.5% HP- β -CD	7.23–7.32
Kaolin	1% HP- β -CD	7.01
Kaolin	3% HP- β -CD	6.97–7.09
Kaolin	5% HP- β -CD	7.01–7.06
Kaolin	0.05% β -CD	7.11–7.12
Kaolin	0.1% β -CD	7.07–7.09
Kaolin	0.5% β -CD	7.08
Kaolin	1% β -CD	6.94–7.07
Kaolin	5% <i>n</i> -butylamine	12.13–12.15
Kaolin	10% <i>n</i> -butylamine	12.28–12.30
Kaolin	15% <i>n</i> -butylamine	12.36–12.38
Kaolin	20% <i>n</i> -butylamine	12.45–12.46
Kaolin	5% THF	7.06–7.11
Kaolin	10% THF	7.05–7.16
Kaolin	15% THF	7.12–7.14
Kaolin	20% THF	7.20–7.24

more surfactant will be available for the solubilization of phenanthrene. Moreover, at lower concentrations, fewer micelles will be present and the solubilization of phenanthrene will be lower. At surfactant concentrations less than the CMC, no micelles will be formed. At concentrations above the CMC, partial adsorption of surfactants onto the soil results in the formation of fewer micelles in the pore volume.

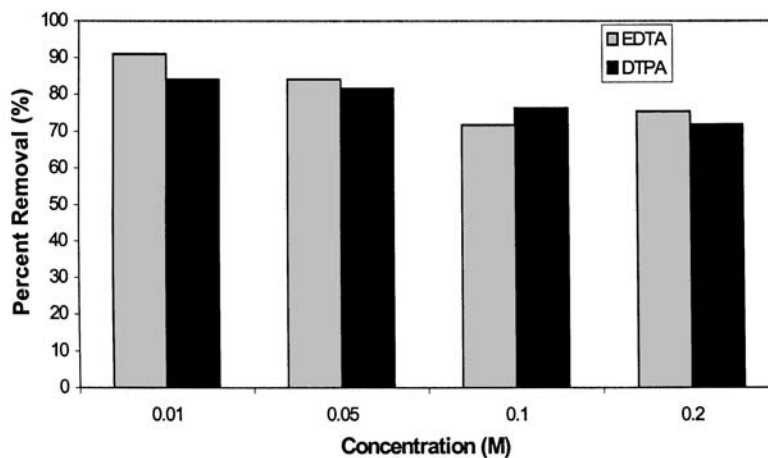
Tween 80 had a better removal efficiency over Igepal CA-720 at a concentration of 5% and almost the same at 1 and 3% concentrations. The removal efficiency for Tween 80 was less than half when compared to the removal efficiency for Igepal CA-720 at 0.5% concentration. Tween 80 has a lower CMC and a higher HLB value than Igepal CA-720, so in Tween 80, micelle formation should begin at a lower surfactant concentration.

Some of the surfactant solution may have adsorbed to the clay mineral in the kaolin soil by hydrogen bonding with the oxyethylene group and van der Waals forces (Rosen, 1989; Ko *et al.*, 1998b; Edwards *et al.*, 1994). This might have reduced the amount of surfactant solution, and hence, the number of micelles for the phenanthrene solubilization. The viscous nature of the surfactant molecules could have made it difficult to pass through the tiny void spaces of the clay mineral. More detailed studies are needed in the future on mechanisms and extent of the sorption of surfactants onto the soil minerals.

Nickel. The removal efficiency of 0.5% Igepal CA-720 was found to be quite low and was found to be only 7% that slowly increased to 10% at a concentration of 1%, and remained constant at a concentration of 3%.



(a) Phenanthrene



(b) Nickel

Figure 2. Removal of (a) phenanthrene and (b) nickel using chelating agents.

Thereafter, the removal efficiency decreased. The removal efficiency of 0.5% Tween 80 was found to be 16%, and it gradually decreased with surfactant concentration of 3% and then the removal efficiency slightly increased at a concentration of 5% as shown in Fig. 1(b). Among the two surfactant system tested, Tween 80 was found to be better than Igepal CA-720 at all concentrations in the removal of nickel. In general, in the case of heavy metals, surfactants do not solubilize the heavy metals because of the inorganic nature of the heavy metals.

Removal with chelating agents

Phenanthrene. As expected, both chelating agents were ineffective, in the removal of phenanthrene with removal efficiency less than 1% at all the tested concentrations as shown in Fig. 2(a). Neither chelating agent

was able to solubilize or desorb phenanthrene from kaolin as they are ligands. As expected, these chelating agents did not form any stable complexes with phenanthrene.

Nickel. The removal efficiency of EDTA was almost the same at all concentrations tested. Nearly 75 to 80% of the nickel was removed in the EDTA system, as shown in the Fig. 2(b). The pH values of EDTA were in the range of 10.0 to 10.90 (Table 4). The removal efficiency of DTPA was also almost the same at all concentrations and ranges from 75 to 85% for nickel. The pH values of DTPA were in the range of 11.5 to 12.60 (Table 4). The 0.01 M DTPA had a pH value of 10.63 and 0.2 M DTPA had a pH value of 12.53. The performance of EDTA was better when compared to DTPA at all the concentrations except at a concentration of 0.1 M. But the difference was not that significant. In the case of DTPA, its high

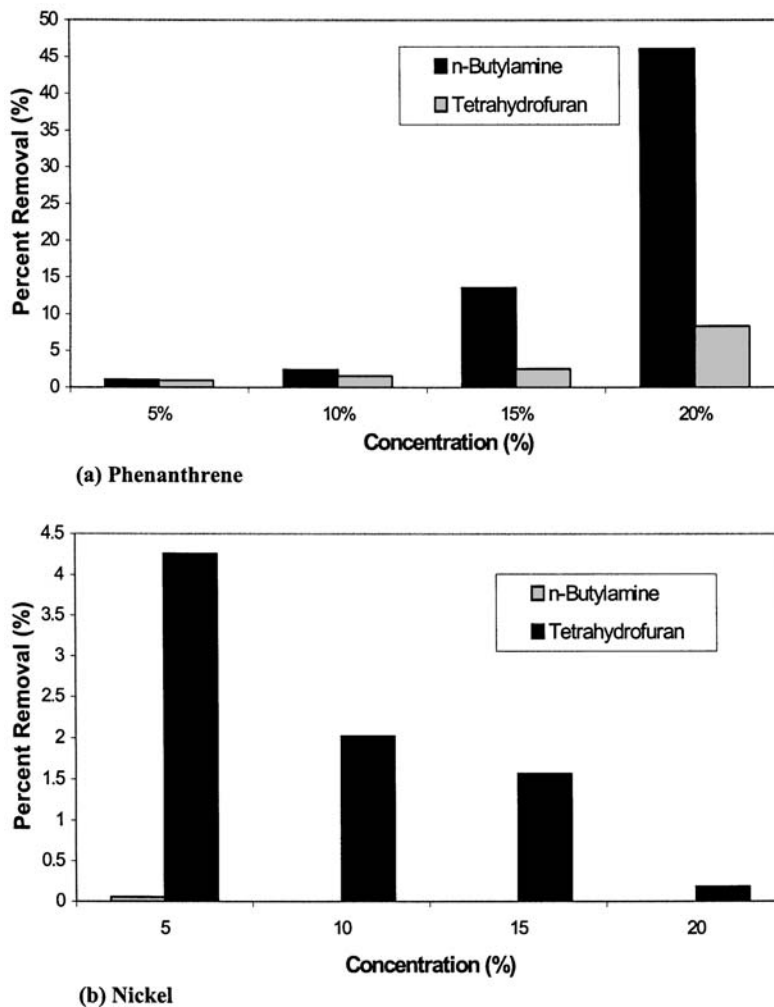


Figure 3. Removal of (a) phenanthrene and (b) nickel using cosolvents.

molecular weight might have limited its transport and hence the interaction with heavy metals.

Removal with cosolvents

Phenanthrene. The removal efficiency increased as the concentration of *n*-butylamine increased as shown in Fig. 3(a). A removal efficiency of 2% was achieved with 5% *n*-butylamine, and it increased to 46% with 20% *n*-butyl-amine. The change in removal efficiency was gradual up to 15% *n*-butylamine but was drastic between 15 and 20% *n*-butylamine. The pH of 5% *n*-butylamine was 12.14 and it increased to 12.45 for 20% *n*-butylamine (Table 4).

Hydrophobic organic compounds (HOCs), such as phenanthrene, exhibit low concentrations in the aqueous phase (C_w). The Freundlich adsorption isotherm equation, $C_s = K(C_w)^n$, is often linear, which means that $n = 1$ (Li

et al., 2000). 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 (Schwarzenbach *et al.*, 1993). 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.* (1993) present a detailed summary of these factors. The effect on K_d that is caused by using cosolvents can be estimated by dividing the apparent distribution ratio in a water–cosolvent 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–cosolvent, water–cosolvent, and contaminant–cosolvent (cosolvency factor), re-

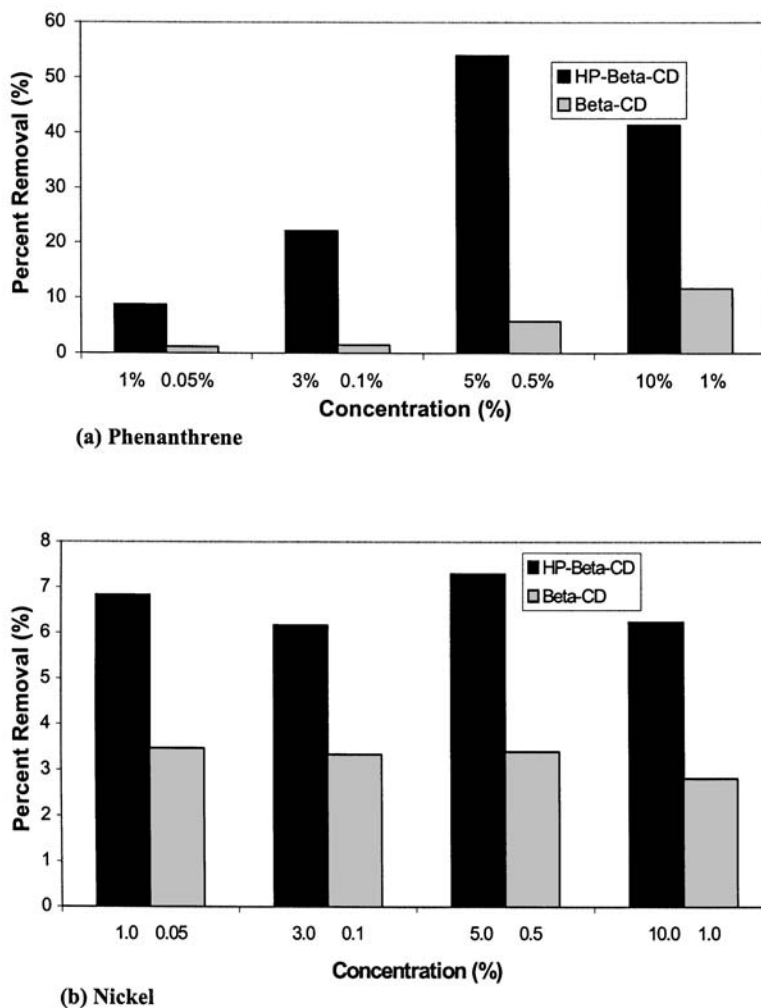


Figure 4. Removal of (a) phenanthrene and (b) nickel using cyclodextrins.

spectively, and f_c is the volume fraction of the cosolvent in the solution (Li *et al.*, 2000). Generally, if the product $\alpha\beta\sigma$ is higher, then the effect of the cosolvent on solubilization would be good. For a PAH such as phenanthrene, σ values range from 0.47 to 0.65 for 20% solutions of cosolvents such as *n*-butylamine and THF in water (Li *et al.*, 2000). 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 tetrahydrofuran, respectively (Li *et al.*, 2000).

THF was not very effective in the removal of phenanthrene. The removal efficiency at all concentrations was less than 8%. The removal efficiency was 2% for 5% THF, and it gradually increased to 8% as the concentra-

tion increased to 20% as shown in Fig. 3(a). The pH ranged between 7.08 and 7.22. The pH value increased as the concentration of THF increased. The pH value at 5% concentration was 7.08 and it gradually increased to 7.22 at 20% concentration. The performance of *n*-butylamine was better when compared to THF. The *n*-butylamine was effective because of the β -value that showed a positive indication of water–cosolvent interactions. These interactions favor the phenanthrene solubility. 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 solubil-

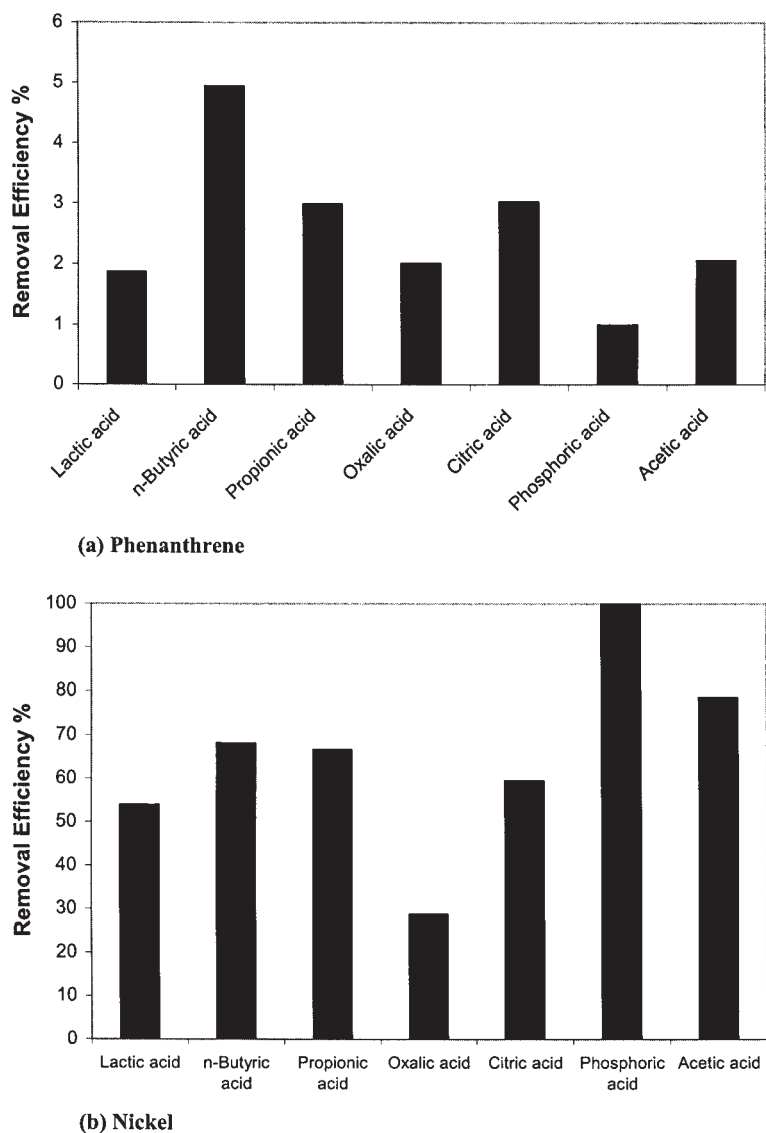


Figure 5. Removal of (a) phenanthrene and (b) nickel using organic acids.

ity. The higher pH might have also contributed to the greater removal of phenanthrene.

Nickel. The nickel removal efficiency of *n*-butylamine and THF was found to be negligible. They were found to be almost 0 and 4.5%, respectively, for nickel at all the tested concentrations, as depicted in Fig. 3(b). The removal efficiency of both the cosolvent systems decreased as their concentration increased. Cosolvents were not able to solubilize heavy metals, which are inorganic species. This was the primary reason for the poor removal efficiency of cosolvents. The pH of different soil-cosolvent mixtures are shown in Table 4. In low pH conditions, nickel exists in the form of nickelous ion (Ni^{+2}). In neutral to slightly alkaline solutions, it precipitates as nickelous hydroxide [$\text{Ni}(\text{OH})_2$] which is a stable compound. This precipitate readily dissolves in acid solutions forming Ni^{+2} and in very alkaline solutions, it forms nickelite ion (HNiO_2) that is soluble in water. In very oxidizing and alkaline conditions, nickel exists in the form of stable nickelo-nickelic oxide (Ni_3O_4) that is soluble in acid solutions. Other nickel oxides, nickelic oxide (Ni_2O_3) and nickel peroxide (NiO_2) are unstable in alkaline conditions and decompose by giving off oxygen. However, in acidic regions, these solids dissolve producing Ni^{+2} (Pourbaix, 1974).

Removal with cyclodextrins

Phenanthrene. The removal efficiency of HPCD was 9% when treated with 1% HPCD solution, and it gradually increased to 52% on further increasing the HPCD concentration to 5%. Further, the removal efficiency of HPCD system decreases with further increase concentration, as shown in Fig. 4(a). The pH of the soil-contaminant-extracting solution mixture was around 7.0 at all concentrations (Table 4). The removal efficiency gradually increased with increasing concentration. The removal efficiencies of β -cyclodextrin hydrate treated system were found to be 1, 2, 5, and 10% at the studied concentration of 0.05, 0.1, 0.5, and 1% β -cyclodextrin hydrate, respectively. The pH of β -CD hydrate system decreased from 7.11 (0.05% concentration) to 7.01 (at 1% concentration) with increasing concentration. Among the two cyclodextrin systems tested, HPCD system was found to be more efficient than β -CD hydrate treated system at all concentrations. This may be due to the better solubilization of phenanthrene by forming a more stable complex within the cavity of the HPCD due to the presence of the additional hydroxypropyl group in HPCD (Wang and Brusseau, 1993; Ko *et al.*, 1999; McCray *et al.*, 2000).

Nickel. Cyclodextrins were found to be ineffective for the removal of nickel as shown in the Fig. 4(b). A removal efficiency of less than 8% was observed. Com-

paratively, HPCD was better than β -CD hydrate. 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 (Wang and Brusseau, 1993). Other analytical techniques which may provide more insights into this hypothesis will be explored in future research.

Removal with organic acids

Phenanthrene. Organic acids at concentration of 1 M were not effective in removing phenanthrene. The removal efficiency was less than 5% for all the acids as shown in Fig. 5(a). *n*-Butyric acid, propionic acid, and citric acid performed better when compared to the other acids. The low pH conditions that prevails in these organic acid treated system (Table 4) might have caused the ineffective solubilization/desorption of phenanthrene from the soil.

Nickel. Organic acids were found to be effective in the removal of nickel from the kaolin. The removal efficiencies of phosphoric acid, acetic acid, *n*-butyric acid, and citric acid solutions were 100, 80, 68, and 60%, respectively, as shown in Fig. 5(b). The pH values of all acid solutions were well below 3.5 (Table 4). Phosphoric acid, a triprotic acid, decreases the soil pH, while acetic acid, which is a monoprotic acid, was not as effective.

Sequential removal of nickel and phenanthrene

On the basis of the results as described in the above sections, it was found that extractants have different affin-

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

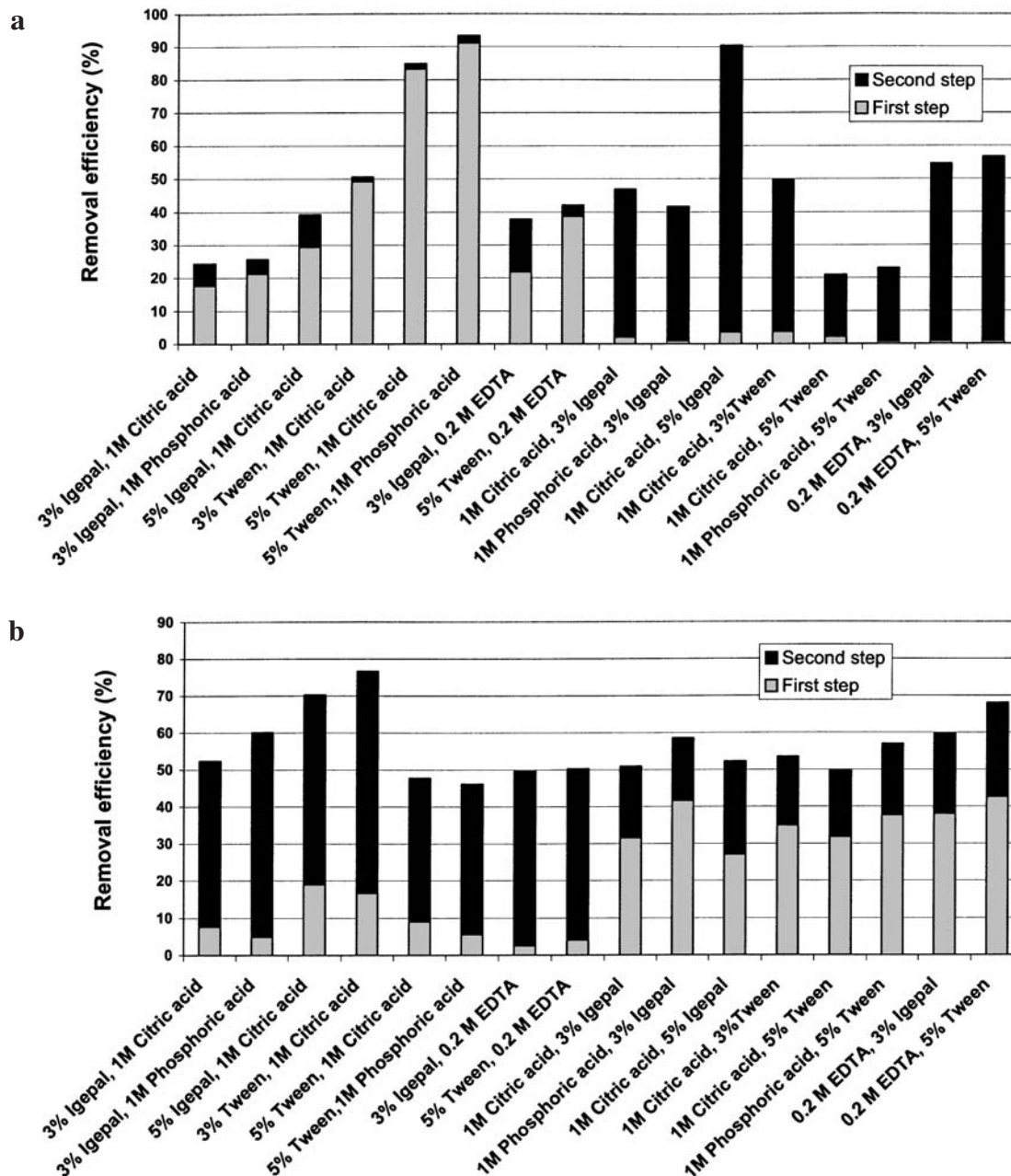


Figure 6. (a) Removal of phenanthrene using sequential extractions (b). Removal of nickel using sequential extractions.

ity and selectivity towards the removal of nickel and phenanthrene from kaolin soil. Unfortunately, none of the selected extractants were capable of removing both nickel and phenanthrene simultaneously. The most effective extractants for nickel were organic acids (phosphoric acid and citric acid) and chelating agent (EDTA), while the most effective extractants for phenanthrene were surfactants (Tween 80 and Igepal CA 720). To effectively remove both nickel and phenanthrene from

kaolin, several combinations of individual extractants, which had shown to be effective in extraction of either nickel or phenanthrene, were selected to sequentially extract both contaminants. The combinations of extractants selected for the sequential extractions are listed in Table 5.

Sequential removal of phenanthrene. The data from Fig. 6(a) shows various combinations of extractants

that have been employed for higher removal of phenanthrene from the kaolin soil. The sequential extraction data from Fig. 6(a) shows that the removal of phenanthrene (greater than 80%) can be achieved with sequential combination of extractants. The best sequential extraction of phenanthrene achieved in this study can be listed in the following order on the basis of their removal efficiency: 5% Tween 80–1 M phosphoric acid (92%) > 1 M citric acid–5% Igepal CA720 (90%) > 5% Tween 80–1 M citric acid (85%). Sequential extractions with 0.2 M EDTA–5% Tween 80 and 0.2 M EDTA–3% Igepal CA720 each obtained greater than 55% removal of phenanthrene. The other sequential extractions removed less than 50% of phenanthrene from kaolin.

Sequential removal of nickel. The data from Fig. 6(b) shows the removal of nickel using various combinations of extractants. The sequential extraction data show that the highest removal of nickel (greater than 70%) was obtained with the following combination of extractants: 3% Tween 80–1 M citric acid and 5% Igepal CA720–1 M citric acid. In both cases, the effective combination consisted of application of surfactant solution in the first extraction step followed by citric acid solution in the second extraction step. Sequential extraction with 0.2 M EDTA–5% Tween 80 and 3% Igepal CA720–1 M phosphoric acid each obtained greater than 60% removal of nickel. The other sequential extractions removed less than 60% of the nickel from kaolin.

CONCLUSIONS

The present study was carried out as a preliminary assessment of various extracting solutions to evaluate suitable extracting solutions for potential use in enhanced electrokinetic remediation of low permeability soils contaminated with both heavy metals and hydrophobic organic compounds. In single extractions, the removal efficiency of various extracting solutions depends upon their affinity and selectivity towards the target contaminants, that is, nickel or phenanthrene. Surfactant solutions were found to be effective in extracting phenanthrene from kaolin, while organic acids were found to be effective in extracting nickel from kaolin. For the removal of both nickel and phenanthrene from kaolin, a sequential use of surfactant and organic acids was tried, and it was found to be an effective strategy. Specifically, the sequential use of Tween 80 and citric acid was the most effective method for the extraction of both nickel (heavy metal) and phenanthrene (hydrophobic organic compound) from kaolin soil.

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