



Electrokinetic remediation of arsenate spiked soil assisted by CNT-Co barrier—The effect of barrier position and processing fluid

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ABSTRACT

An enhanced electrokinetic (EK) remediation process coupled with permeable reaction barrier (PRB) of carbon nanotube coated with cobalt (CNT-Co) has been investigated for As(V) removal from soil under potential gradient of 2.0 V/cm for 5 days treatment. Results showed that removal efficiency of As(V) was greater than 70% in EK/CNT-Co system with EDTA as processing fluid, which was enhanced by a factor of 2.2 compared to EK system and EK/CNT systems. A better removal performance in EK/CNT-Co system was attributed to higher sorption of As(V) onto CNT-Co than onto CNT. Removal of As(V) in EK/CNT-Co system was mainly contributed by surface sorption on CNT-Co rather than by EK process. The surface characteristics of CNT-Co, which was qualified by SEM coupled with EDS, were clearly confirmed that arsenic was adsorbed on the passive layer surface. Among EK processes, As(V) removal was dominated by electroosmosis flow and electromigration in EK/CNT-Co system with groundwater and EDTA as processing fluid. An investigation with sequential extraction revealed that As(V) associated with soils was considerably shifted from strong binding forms, i.e., Fe-Mn oxide, organic, and residual, to weak binding forms, i.e., exchange and carbonate, after EK/CNT-Co treatment.

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1. Introduction

Arsenic contamination caused by anthropogenic activities in soil and groundwater has created a strong legacy throughout the environment. The toxicity of arsenic is dependent on the oxidation state and structure as in the order of arsenite > arsenate > monomethylarsenite > dimethylarsenite [1]. Arsenite was found under long-term anaerobic environment only [2]. Above 80% of arsenic exists as arsenate rather than as arsenite in the contaminated soil. Conventional off-site remediation technologies of soil replacement, solidification/stabilization, and acid washing have been used to remediate As-contaminated soils [3] which were unsuccessful due to high cost in labour and operation for ex-situ technologies. Consequently, a need exists for an in-situ effective technique to remediate arsenic contamination that heavily impacts the subsurface environment.

Many remedial techniques exist for contaminated land included immobilization, encapsulation, toxicity reduction, physical separation and extraction. Electrokinetic (EK) remediation is a promising

innovative technology for decontamination in low hydraulic permeability media. EK technique is based on the action of an electric field generated between inserted electrodes in the medium by applying a direct current or a constant voltage. The applied potential causes the migration of electrolyte solution contained soluble contaminants toward electrodes via electromigration, electroosmosis, and electrophoresis [4,5]. Various enhancement techniques, e.g. careful management of the pH within the reservoir [6–8], addition of hydroxyl ion membranes, chelating agent, and enhancing reagent in the cathode reservoir [9–13] were proposed to improve effectiveness in EK process. Other parameters included potential gradient and processing time also affect EK performance. It depends on the characteristics of soil texture and contaminants.

A typical configuration of permeable reaction barrier (PRB) system is placed in-situ across the flow path of a contaminated plume. As the plume flows through the PRB under hydraulic gradient, contaminants are retained or partially destroyed to non-toxic end products without soil excavation and groundwater pumping. Elemental iron was commonly applied in remediation of chlorinated organic compounds by de-chlorination reaction [14,15] and remediation of arsenic by promoting sorption on to the iron surface [16–18]. Recently, PRB combined with EK process was reported to enhance EK remediation performance. The common PRB materials applied included ion exchange membrane for metals removal [11], Fe(0)/FeOOH for As(V) removal [19] and atomizing slag (commercial name: PS Ball, worldwide patent) for trichloroethylene and

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Cd removal [20]. Removal performance of arsenic was reported to be related to the surface area and reactive materials of PRB. Carbon nanotubes (CNT) are promising for its high surface area and, therefore, there is high potential for As(V) removal by sorption onto surface of CNT or CNT composite.

This hybrid technology described herein involved the application of an electrical field across a porous medium to induce the movement of electrolyte solution and, then, the soluble contaminants, i.e., As(V), would be separated by sorption onto nano-composite barrier. In this study, the performance of processing fluid and barrier position in remediation of As(V) spiked clay with EK/CNT-Co were investigated.

2. Experimental materials and methods

2.1. Soil selection and characteristics

Soil samples were collected from a depth of approximately 0.7–1.5 m below the surface within a farmland located in southern Taiwan. The texture of soil sample was classified as clay by particle size analysis. A soil organic matter content of 3.73% was observed by the combustion method [21]. Soil pH of 8.5 was measured in water suspensions at 1:1 ratio of soil to solution by volume and soil pH_{ZPC} of 2.4 was determined by a zeta potential instrument (Pen Kem-Laser Zee 3.0, USA). A soil solid density of 2.64 g cm^{-3} was determined according to the method of ASTM D854-92. The soil specific surface areas of $16.4 \text{ m}^2/\text{g}$ was measured by a BET surface areas analyzer (ASAP 2010, Micromeritics, USA). The hydraulic conductivity of the soil sample was less than 10^{-8} cm/s measured by a falling-head permeameter.

After removing debris and air-drying, the soil sample was sieved to less than 2 mm in diameter and then treated by pressure sterilization of 118 kPa for 5 min. The arsenate contaminated soil was prepared by adding specific amount of sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$), 280 mL of de-ionized water, and 600 g of sieved soil into a 2 L polypropylene bottle. The mixture was then rotated at a speed of 50 rpm for 3 days to achieve uniform As(V) spiked soil. To measure the As concentration the soil sample was then digested with 15 mL of 30% H_2O_2 and 30 mL of 9.6 M HCl [22] and the arsenic in digested solution was determined by means of atomic emission spectrophotometer with inductively coupled plasma source (ICP, PerkinElmer Optima 2000DV, USA) at a wavelength of 193.7 nm. Triplicate soil samples were analyzed for quantification. This arsenate spiked soil was then ready for EK experiments.

Table 1
Characteristics of groundwater.

Anions	Values (meq/L)	Cations	Values (meq/L)
SO_4^{2-}	3.39	Mg^{2+}	2.21
Cl^-	1.65	Ca^{2+}	1.75
NO_3^-	0.27	K^+	1.33

2.2. Processing fluid and PRB

A local groundwater in field and 0.25 M of ethylenediaminetetraacetic acid (EDTA) were selected as processing fluid in this study. Major constituents of the groundwater were the anions of SO_4^{2-} , Cl^- , and K^+ and cations of Mg^{2+} and Ca^{2+} (see Table 1). EDTA has a low molecular weight and form water-soluble complex with most metal ions. Although EDTA is rather slowly biodegradable and persistent in the environment, it is still a good choice for chelating metals because their formation constants with metals are higher. Nitrilotriacetic acid (NTA) has been considered as an alternative to EDTA in various groundwater applications due to its biodegradability [23]. Two types of reactive materials were investigated in this study. One is CNT purified with 3 M HNO_3 solution at 120°C for 2 h, which was classified as multi-walled texture with pH_{ZPC} of 2.6, BET area of $122 \text{ m}^2/\text{g}$ and pore volume of $0.44 \text{ cm}^3/\text{g}$. The other was CNT coated with cobalt (CNT-Co) which was made according to the method of Wu et al. [24]. The 2 g NaBH_4 , 2 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and 0.25 g unpurified CNT was added in 400 mL de-ionized water. The reaction was complete after 10 min, filtered through a $0.45 \mu\text{m}$ filter and flushed with de-ionized water until pH of filtrate was near neutral. The CNT-Co residual on the filter was put into oven at 105°C for overnight and then it was ready for use. The CNT-Co composite was characterized with pH_{ZPC} of 8.5, BET area of $76 \text{ m}^2/\text{g}$ and pore volume of $0.27 \text{ cm}^3/\text{g}$.

2.3. Aqueous adsorption experiments

In order to further clarify removal behavior of As(V) in EK-PRB system, aqueous adsorption of As(V) on CNT-Co was investigated in this study. The adsorption experiment was conducted by adding 0.1 g CNT-Co in 100 mL polyethylene (PE) bottles to an As(V) solution (50–400 mg/L) and adjusting solution pH to a range of 2.0–12.5 with HCl and NaOH. The PE bottles were put on an oscillating shaker with 150 rpm at 25°C for 10 days to achieve equilibrium adsorption. The adsorption amount of As(V) on CNT was quantified by subtracting the amount of aqueous As(V) from the initial added amount of As(V).

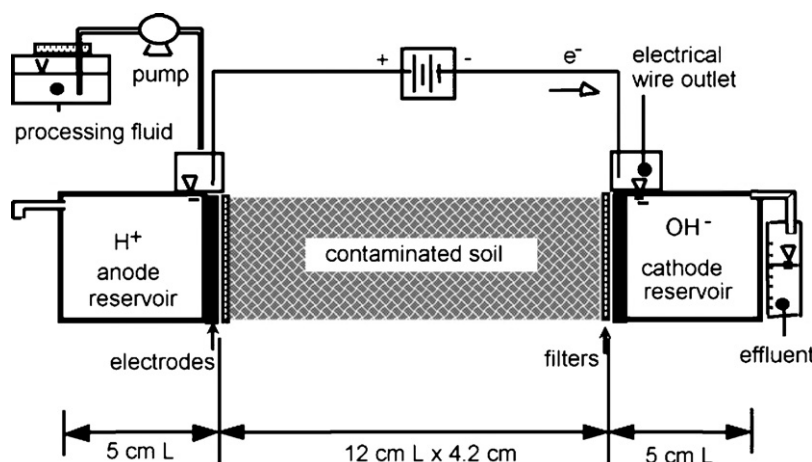


Fig. 1. Schematic setup of electrokinetic apparatus.

Table 2
Summary results in EK/CNT-Co system.

Test no.	Concentration of As(V) (mg/kg)	Processing fluid	Reaction zone			Q_e (cm ³ /day)	k_e (cm ² /Vs)	Power consumption (kWh/m ³)	Removal efficiency (%)
			Material	Quantity (g)	Position (cm from anode)				
1	855	Groundwater	–	–	–	15.6	6.4×10^{-6}	423.2	35
2	855	Groundwater	CNT	1.0	6	18.1	7.5×10^{-6}	515.2	34
3	914	Groundwater	CNT-Co	1.0	3	13.8	5.8×10^{-6}	342.9	62
4	914	Groundwater	CNT-Co	1.0	6	13.0	5.3×10^{-6}	272.2	66
5	914	Groundwater	CNT-Co	1.0	9	15.6	6.5×10^{-6}	331.7	64
6	972	0.25 M EDTA	CNT-Co	0.5	6	17.2	7.3×10^{-6}	487.1	71
7	953	0.25 M EDTA	CNT-Co	1.0	6	20.7	8.8×10^{-6}	722.3	74
8	972	0.25 M EDTA	CNT-Co	1.5	6	16.4	6.9×10^{-6}	563.8	75
9	972	0.25 M EDTA	CNT-Co	2.0	6	14.7	6.1×10^{-6}	496.4	77

(1) All experiments were conducted under potential gradient of 2 V/cm for 5 days; (2) the reaction zone was composed by CNT or CNT-Co with 10 g of Ottawa sand.

2.4. Setup of EK experiments

Nine EK experiments were conducted in an acrylic cell of 4.2 cm (φ) \times 22 cm (L), consisting of three compartments: cathode reservoir with 5 cm in length, anode reservoir with 5 cm in length, and soil specimen chamber with 12 cm in length, which was shown in Fig. 1. The processing fluid was initially added into both anode and cathode reservoirs and replenished in the anode reservoir every half day. All experiments were conducted under potential gradient of 2.0 V/cm for 5 days with the reactive zone located at three positions of 3, 6, and 9 cm away from the anode side, respectively. The PRB layer was composed of 0.5–2.0 g of reactive materials and 10 g of Ottawa sand, in which the addition of Ottawa sand was aimed to extend the retention time of As(V) in PRB. The electric current, reservoir pH, concentrations of As(V) and total arsenic, and electroosmotic flow were monitored during the test periods. The current density was calculated as dividing electric current by crossing area of EK cell. The pH of soil specimen was determined after treatment for each test. Among them, two were sampled at the end of anode and cathode side and the other six were sampled every 2 cm of soil specimen. The binding forms of arsenic associated with soil were characterized by sequential extraction after treatment. The As(V) and total As were analyzed by means of ionic chromatography (Dionex DX-120, USA) and atomic emission spectrophotometer with inductively coupled plasma source (PerkinElmer Optima 2000DV, USA), respectively.

2.5. Sequential extraction

Sequential extraction are widely used for exploration purpose and to study element speciation in soil and sediment [25–28]. It is also a powerful tool for detection of element mobilization and retention process [29]. Sequential extractions are operationally defined, i.e., the selectivity depends on such factors as chemicals employed, the time and procedures of contact, and the sample to volume ratio. The solubility of composition of interest may also differ significantly, due to the condition of formation.

To determine the binding form of arsenic associated with soils before/after EK treatment, a sequential extraction procedure according to Chao and Sanzalone [26] was conducted in this study. The solutions of 0.25 M KCl, 0.1 M KH₂PO₄, 4 M HCl, KClO₃/12 M HCl, and 9.6 M HCl were used to respectively extract four binding forms of arsenic associate with soils: exchangeable, carbonate, Fe-Mn oxide, and organic fraction. The residual fraction was quantified by the difference between total arsenate and the above four fractions.

3. Results and discussion

Experimental results are summarized in Table 2 and further discussed in the following sections.

3.1. Aqueous adsorption of As(V) on CNT-Co

Fig. 2 shows the aqueous adsorption of As(V) on CNT-Co at various pHs. It was found that As(V) uptake was 50–267 mg/g at pH of 2.6 and largely dropped to 33–127 mg/g at pH of 11.5. It is obvious that adsorption of As(V) on CNT-Co was limited at high pH environment. The reason of lower uptake of As(V) at extreme basic condition might be a result of resulted from higher potential release of Co from CNT at such environment [30]. As concentration of Co less than 100 mg/L, the effect of pH on As(V) uptake was insignificant at pH range of 4.0–7.5. Moreover, it was found that the uptake of As(V) was increased as increasing concentration of CNT-Co.

3.1.1. Surface characteristics of CNT-Co

The objective of surface characteristics studies was both to identify the existence of arsenic on CNT-Co surface and thus to speculate on the possible mechanisms of arsenic removal. The surface properties of CNT-Co were characterized by SEM coupled with energy dispersive spectroscopy (EDS) (INCAx-sight, 30761-5350-TV3-2907, Oxford, United Kingdom). Results showed that no arsenic was found on the surface of CNT-Co before EK treatment and cobalt crystal was successfully coated on CNT surface (Fig. 3a). Nevertheless, after EK treatment, two peaks of As were found in the spectrum of CNT-Co by EDS (Fig. 3b). This was evidently inferred that arsenic was sorbed on the surface of CNT-Co. This result was consistent with Farrell et al. [16] and Lackovic et al. [31], which reported that surface precipitation and adsorption appears to be the predominant mechanism for arsenic removal in aqueous environment, and Yuan and Chiang [19], which reported that As(V) was removed in

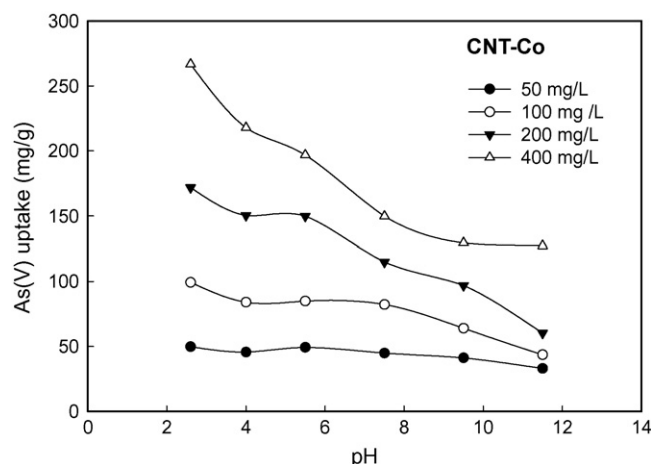


Fig. 2. Equilibrium adsorption of arsenate on CNT-Co in aqueous phase.

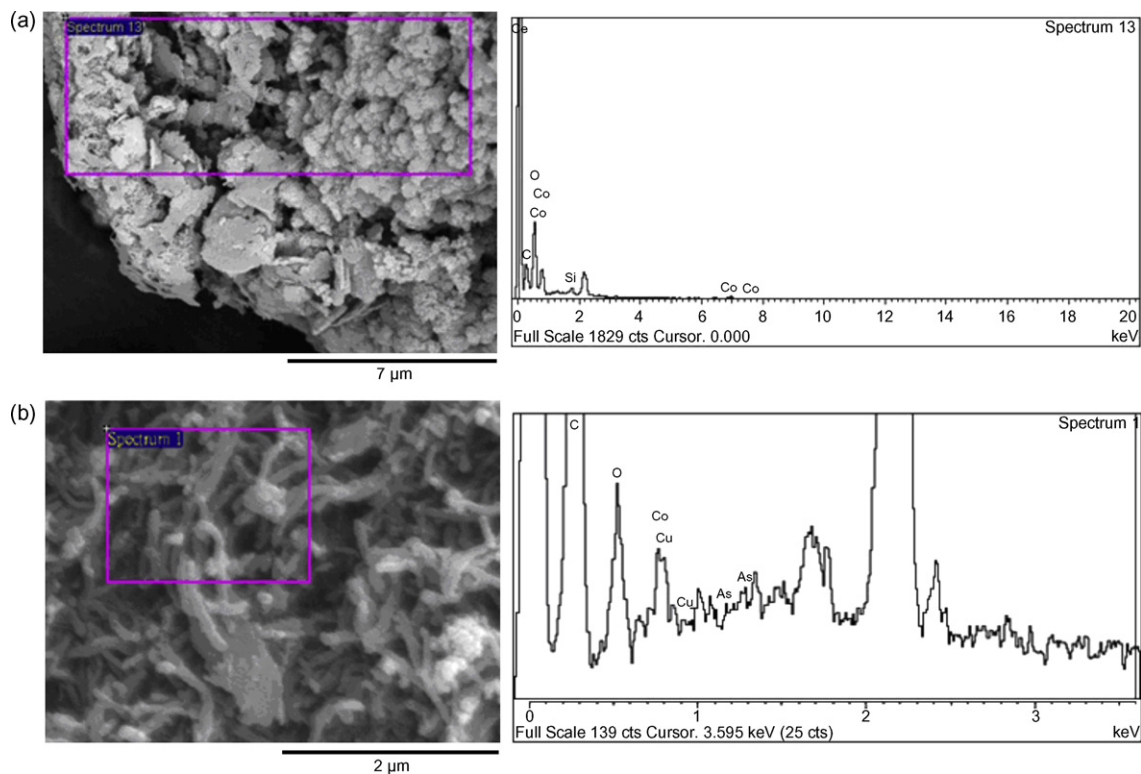


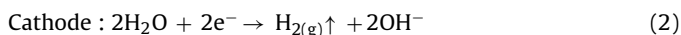
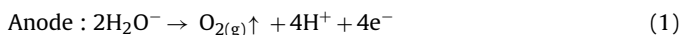
Fig. 3. SEM micrograph and EDS chromatography of CNT-Co: (a) before, and (b) after electrokinetic treatment.

EK/Fe(0) and EK/FeOOH systems by sorption on surface of Fe(0) and FeOOH.

3.2. Electrokinetic behavior in EK/CNT-Co systems

The variations of current density as function of time in EK/PRB systems are shown in Fig. 4. Current density was gradually increased to 5.3–7.2 mA cm⁻² within 48 h for Tests 1 and 2. Similar phenomenon was shown for all other EK/CNT-Co systems, however, lower current density was found. After processing time greater than 48 h, the current density of investigated systems was all decreased to less than 1.0 mA cm⁻². It was largely because the clogging of precipitates in the soil pore resulted in a low current density. This might be resulted from: (a) metal hydroxide precipitates formed at basic environment transported to cathode by electromigration; and (b) precipitates caused by processing fluid reacted with ions in soil matrix. It was shown that the variance of current density was more significantly related to quantity of the reactive material (Fig. 4b). Results of current density were quite similar to those observed by Zhou et al. [8] and Yuan and Chiang [19].

The generation of H⁺ and OH⁻ under an applied electric field (Eqs. (1) and (2)) will result in movement of acid and basic fronts in EK system and will change the soil pH drastically during EK process [7,32]. Moreover, consumption of hydroxyl ions in precipitation, surface complexation and adsorption on the soil, and formation of complexes in the bulk solution are additional factors affected the soil pH in EK system [33].



The soil pH profiles along EK cell in EK/CNT-Co systems are shown in Fig. 5. A general trend of low pH near the anode and high pH near the cathode was found in all EK/PRB systems (Fig. 5a and b). The acid front generated at anode reservoir flushed across the soil specimen, consequently lowered the soil pH from 8.5 to 2.1–3.4

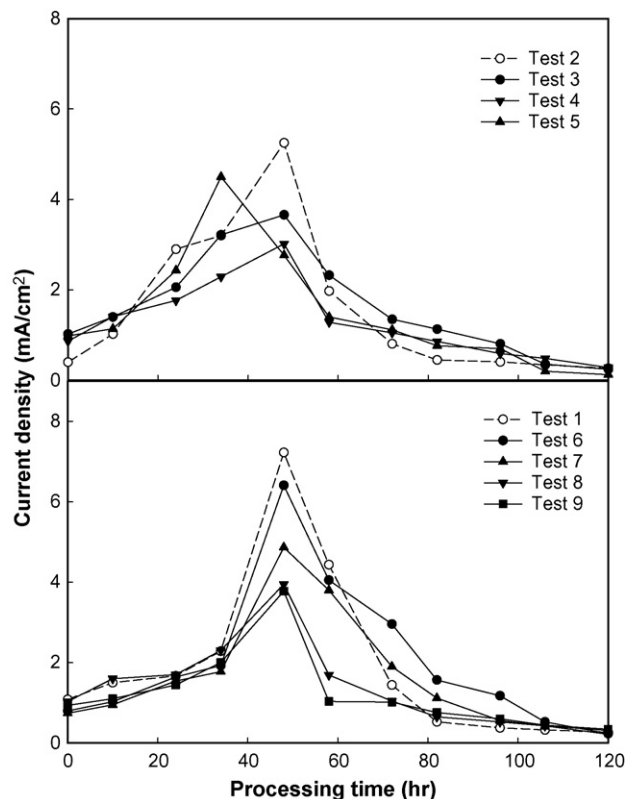


Fig. 4. The effect of (a) PRB materials and position; and (b) amount of PRB on current density in EK/CNT-Co system.

Table 3
Fractional distribution of As(V) in EK/CNT-Co system.

Test no.	(1) Initial As(V) (mg)	(2) CNT/ CNT-Co (g)	Fraction of As(V)				Fractional removal mechanisms of As(V)	
			(3) Soil phase (mg)	Reservoir		(6) Sorbed onto CNT/CNT-Co (mg)	(7) EK process (%)	(8) Sorption onto CNT/CNT-Co (%)
				(4) Anode (mg)	(5) Cathode (mg)			
1	265	–	173.9	23.2 (25.3%) ^a	46.8 (74.7%) ^b	–	100	–
2	261	1.0	173.8	16.2 (45.6%) ^a	19.3 (54.4%) ^b	51.7	40.7	59.3
3	286	1.0	108.2	1.0 (18.7%) ^a	3.1 (81.3%) ^b	173.2	2.3	97.7
4	287	1.0	98.6	1.2 (44.4%) ^a	1.5 (55.6%) ^b	185.4	1.4	98.6
5	291	1.0	105.3	1.2 (28.6%) ^a	3.0 (71.4%) ^b	181.2	2.3	97.7
6	304	0.5	88.4	1.4 (56.0%) ^a	1.1 (44.0%) ^b	212.9	1.2	98.8
7	299	1.0	77.8	1.1 (57.1%) ^a	0.9 (42.9%) ^b	219.4	0.9	99.1
8	302	1.5	75.0	0.7 (53.8%) ^a	0.6 (46.2%) ^b	226.0	0.6	99.4
9	307	2.0	70.5	0.5 (62.5%) ^a	0.3 (37.5%) ^b	235.4	0.3	99.7

(6) = (1) – [(3) + (4) + (5)].

(7) = {[(4) + (5)] / [(4) + (5) + (6)]} × 100%.

(8) = {(6) / [(4) + (5) + (6)]} × 100%.

^a (4) / [(4) + (5)].

^b (5) / [(4) + (5)].

near the anode side for all cases. At the cathode side, the migration of OH⁻ advancing toward the anode and the concentration differences of OH⁻ between reservoirs and soils would increase soil pH to 9.6–12.1. Results showed that variance of soil pH were highly related to the position of the reactive zone (Fig. 5a) and, however, no evident correlations between soil pH and quantity of reactive material (Fig. 5b).

In EK process, the movement of electrolyte solution driven by an electrical field, which carries the soluble pollutants toward the electrodes, is considered to be one of the mechanisms leading to the pollutants removal from soils. The movement of electrolyte solution, i.e., electroosmotic flow, Q_e (mL/day), for a cylindrical soil core is direct proportional to the applied electric potential gradient, i_e

(V/cm):

$$Q_e = k_e \times i_e \times A \quad (3)$$

where A (cm²) is cross-section area of soil core and k_e (cm²/V s) is electroosmosis permeability. As shown in Table 2, the electroosmosis flow was in the range of 13.0–20.7 cm³/day and it was increased with k_e for all experiments. Among investigated systems with groundwater as processing fluid (Tests 1–5), lower k_e of 5.3×10^{-6} – 6.5×10^{-6} cm²/V s were found in EK/CNT-Co systems. It was because the Co coated on the CNT surface clogged the EO flow and resulted in lower k_e value. Whereas using EDTA as processing fluid (Tests 6–9), k_e values were increased up to 8.3×10^{-6} cm²/V s, which might be attributed to higher mobility of EDTA in EK/CNT-Co systems.

3.3. Removal of As(V)

As shown in Table 2, results indicated that the electrokinetic remediation efficiency of As(V) can be largely enhanced by CNT-Co barrier and EDTA. At the case of adding 1.0 g CNT reactive material in the middle of EK cell (Test 2), only 34% of As(V) was removed and this was similar to EK system alone (Test 1). It was largely increased to 66% removal with inserting CNT-Co reactive material in the middle of EK cell (Test 4). No As(V) removal was, however, enhanced by moving barrier to either anode end (Test 3) or cathode end (Test 5). This might be explained by results of As(V) uptake in aqueous phase shown in Fig. 2. Although high As(V) uptake was found under acid condition, less As(V) was removed by EO flow near anode side. When As(V) was pushed to cathode side, the removal efficiency was offset by lower adsorption uptake under basic condition. As shown in Table 3, removal efficiency of As(V) in EK/CNT-Co system with EDTA as processing fluid (Test 6–9) was enhanced to 71–77%, which was 2.1–2.2 times greater than that in EK/CNT systems (Test 2). It was found that the higher the quantity of CNT-Co applied in the system, the better the removal efficiency of As(V) was. Compared to results of As(V) removal by Yuan and Chiang [19] in EK/Fe(0) system (51%) and in EK/FeOOH system (60%), a better As(V) removal performance in EK/CNT-Co system was found in this study.

Energy expenditure in EK systems is calculated as follows:

$$E_u = \frac{P}{V_s} = \frac{1}{V_s} \int VI dt \quad (4)$$

where E_u = energy expenditure per unit volume of soil (kWh/m³); P = energy expenditure (kWh); V_s = volume of soil (m³); V = voltage (V); I = current (A); t = time (h). In the tests of con-

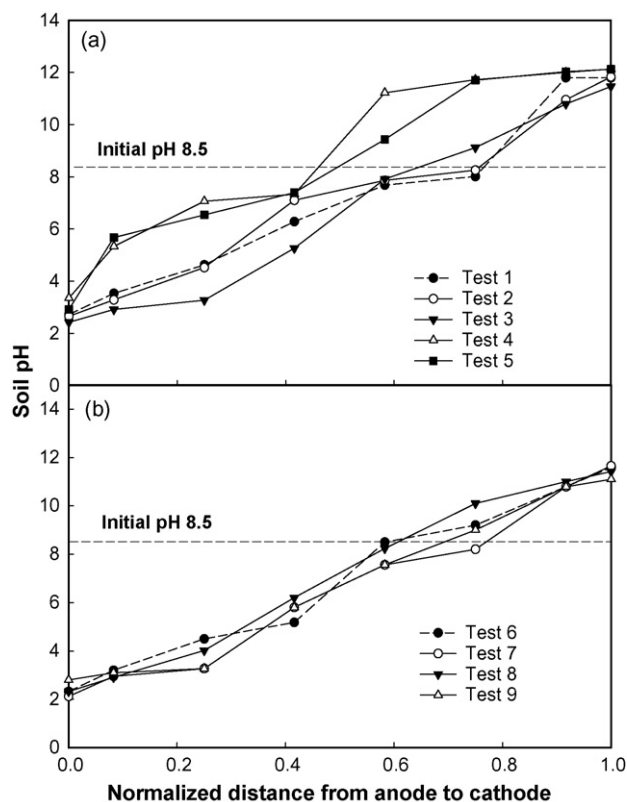


Fig. 5. Soil pH profiles: (a) PRB materials and position; (b) amount of PRB.

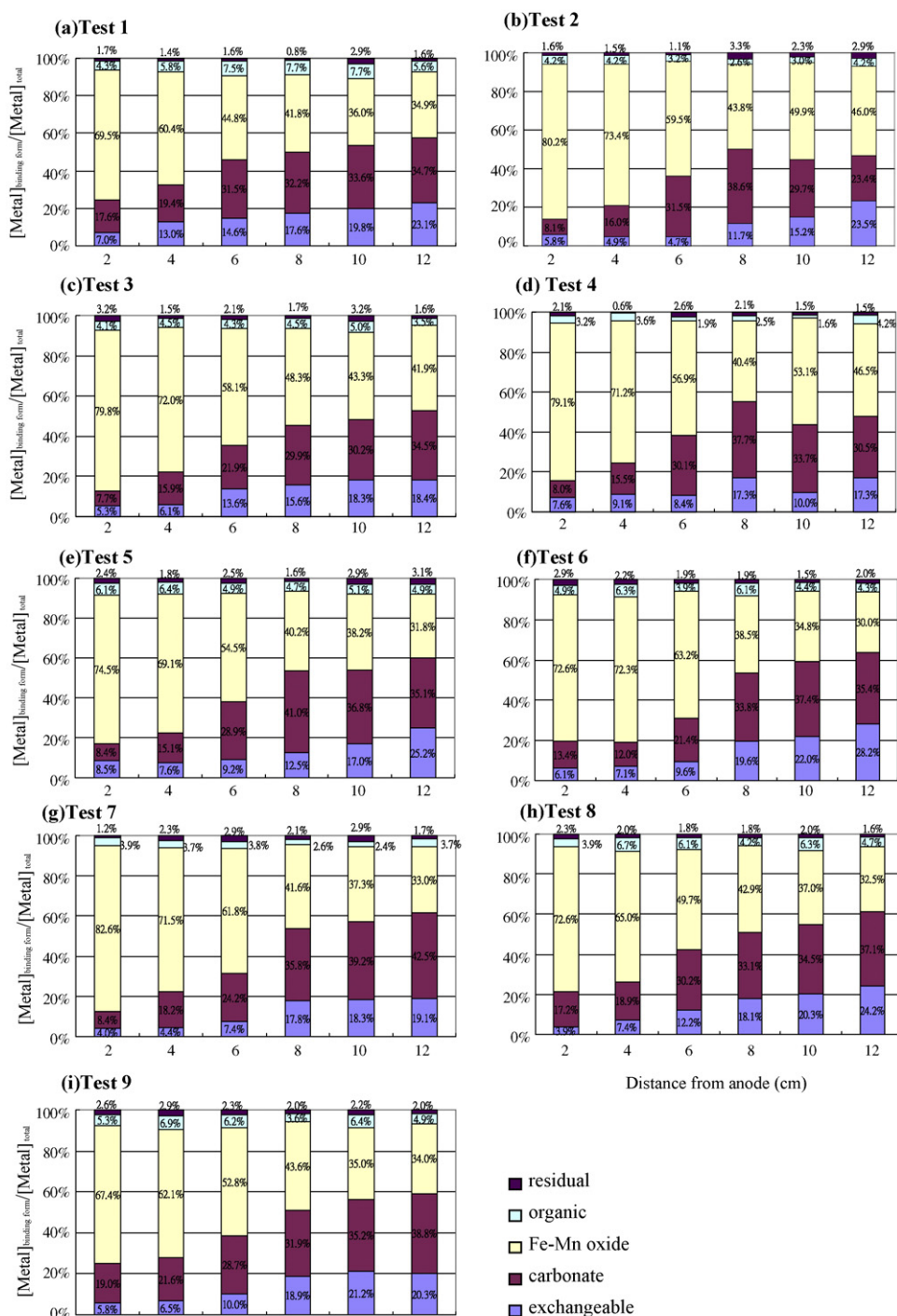


Fig. 6. Partition of As(V) binding in soil phase after EK/CNT-Co treatment.

stant voltage condition, the energy expenditure is directly related to the time integral of the current across the cell. The calculated energy consumption was 423, 515, 272–722 kWh/m³ for EK, EK/CNT, and EK/CNT-Co systems, respectively. It was apparent that processing fluid and PRB reactive material was the controlling factors with respect to energy consumption in EK process. Considering As(V) removal performance in this study, it was clear that energy applied was not enough for completion of remediation. However, this can be improved by either increasing potential gradient or prolonging the treatment periods [34].

3.3.1. Removal mechanisms of As(V)

Two mechanisms including migration to reservoirs by EO process [4,35] and sorption onto CNT-Co barrier [14,19,31] are dominant for As(V) removal in EK/CNT-Co system. Because As(V) mainly existed in the form of HAsO_4^{2-} and AsO_3^- in the soil, among the EK process, As(V) would either migrate toward anode reservoir by electromigration or toward cathode reservoir by electroosmosis flow.

During test periods, no reduction product of arsenite was found in investigated systems hence toxicity risks needed not to be considered. Arsenate would exist either (a) in the soil phase, which represented as the un-removed fraction; (b) in the reservoir solu-

tion, which represented as removal fraction by EK process; or (c) on the surface of CNT-Co, which represented as removal fraction by PRB. The fractional distribution of arsenate in this study is shown on Table 3. It showed that As(V) removal in EK system (Test 1) was dominated by EO flow removal only (74.7%) as expected. The removal fraction of As(V) by sorption on barrier was increased from 59.3% in EK/CNT system (Test 2) to above 97.0% in EK/CNT-Co systems (Tests 3–9). It indicated that sorption of As(V) on CNT and CNT-Co was the major removal mechanism in EK/PRB system. Results of Tests 3–5 showed that As(V) collected in anode and cathode reservoirs was in the range of 18.7–44.6% and 55.6–81.3% (Columns 4 and 5 in Table 3), respectively. It was inferred that As(V) was mainly removed by electroosmosis flow rather than by electromigration in EK process. With EDTA as processing fluid (Tests 6–9), more As(V) (53.8–62.5%) was collected in anode reservoir. It might be largely because less As(V), which mainly existed as the anionic form in systems, was associated with EDTA.

It was concluded that both electrokinetic removal and sorption on PRB reactive material were contributed to the As(V) removal in EK/PRB systems. As installation of CNT-Co barrier, sorption of As(V) on CNT-Co became the major mechanism in investigated systems. Besides, further analysis of electrical removal mechanisms, electroosmosis flow and electromigration were dominant for As(V) removal in EK/CNT-Co system with groundwater and EDTA as processing fluid, respectively.

3.4. Sequential extraction of As(V)

Five binding types of As(V) associated with soil were existed as the forms of exchangeable, carbonate, Fe-Mn oxide, organic, and residual. Two binding form of exchangeable and carbonate were classified as weak binding and the other three forms were classified as strong binding. The fractional distribution of the above-mentioned binding forms was 2.1%, 4.2%, 77.5%, 7.6% and 8.6%, respectively, for arsenic spiked soil without EK treatment. Sequential extraction results of arsenic spiked soil after EK treatment are shown in Fig. 6. Results showed that the fractions of exchangeable and carbonate binding in EK system (Test 1) was 3.3–11.0 and 4.2–8.3 times, respectively, greater than that of spiked soil without EK treatment and, however, the fraction of Fe-Mn oxide in Test 1 was decreased to 0.5–0.9 times less than that for soil without EK treatment (Fig. 6a). Similar trend was found in EK/CNT system (Fig. 6b). As CNT-Co barrier inserted in EK system with groundwater as processing fluid (Fig. 6c–e), in general, fraction of binding form was affected by the position of CNT-Co barrier. Lower fraction of organic and residual forms (0.2–0.6% and 0.1–0.3%) was found in EK system with CNT-Co barrier located at the middle (Test 4) than that near anode end (Test 3) and near cathode end (Test 5).

With EDTA as processing fluid in EK/CNT-Co system (Fig. 6f–i), the variances of binding fraction near two electrodes become more significant. Binding form of Fe-Mn oxide was decreased from 72.6% at anode end to 30.0% at cathode end in Test 6 (Fig. 6f). Furthermore, the exchangeable and carbonate binding were all respectively increased from 6.1% to 28.2% and 13.4% to 35.4%. By increasing CNT-Co quantities (Fig. 6g–i), more exchangeable and carbonate binding and less Fe-Mn oxide were found at anode end and cathode end, respectively. This might a result from more As(V) adsorbed on barrier near the anode under acid environment (see Fig. 2).

In general, a good processing fluid could enhance removal efficiency of pollutants. Besides, it would change the binding distribution of metal associated with soil – shifting the strong binding forms to weak binding forms. It would be beneficial to contaminated soils for further treatment by other technologies.

4. Conclusions

This study shows that the electrokinetic remediation of arsenic spiked soil was largely enhanced by CNT-Co barrier. The important conclusions in this study have been summarized as follows:

- (1) Installation of CNT-Co barrier in EK system was clearly confirmed to enhance As(V) removal from soil matrix in this study. It showed that 70% of As(V) was removed in EK/CNT-Co system with EDTA as processing fluid, which was a factor of 2.2 greater than that in both EK system and EN/CNT system. A better removal performance in EK/CNT-Co system was attributed to higher adsorption of As(V) on CNT-Co than on CNT.
- (2) Both EK process and sorption on PRB reactive material were contributed to As(V) removal in EK/PRB systems. Results indicated that sorption of As(V) on CNT-Co barrier was the major removal mechanism in EK/CNT-Co system. Among As(V) removal by EK process, electroosmosis flow and electromigration was the dominant removal mechanisms in EK/CNT-Co system with groundwater and EDTA as processing fluid, respectively.
- (3) Based on concept of remediation train, if another remediation technology was used to further remove As, it will more easy to achieve higher removal efficiency. Owing to with sequential extraction analysis, it was concluded that the binding forms of As(V) associated with soils was considerably shifted from strong binding, i.e., Fe-Mn oxide, organic, and residual, to weak binding, i.e., exchange and carbonate, after EK/CNT-Co treatment.
- (4) To study performance more thoroughly, scale up and prolonging the EK/CNT experiments are recommended in the future investigations. For full-scale EK/CNT system, accurate dosage of processing fluid was important to achieve better remediation efficiency.

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References

- [1] R.W. Leinz, D.B. Hoover, A.L. Meier, EOCHIM: an electrochemical method for environmental application, *J. Geochem. Explor.* 64 (2000) 421–434.
- [2] P.L. Smedley, D.G. Kinniburgh, A review of source, behavior and distribution of arsenic in natural waters, *Appl. Geochem.* 17 (2002) 517–568.
- [3] S. Tokunaga, T. Hakuta, Acid washing and stabilization of an artificial arsenic-contaminated soil, *Chemosphere* 46 (2002) 31–38.
- [4] Y.B. Acar, A.N. Alshawabkeh, Principles of electrokinetic remediation, *Environ. Sci. Technol.* 27 (1993) 2638–2647.
- [5] S.K. Puppala, A.N. Alshawabkeh, Y.B. Acar, R.J. Gale, M. Bricka, Enhanced electrokinetic remediation of high sorption capacity soils, *J. Hazard. Mater.* 55 (1997) 203–220.
- [6] R.E. Saichek, K.R. Reddy, Effect of pH control at the anode from the electrokinetic removal of phenanthrene for kaolin soil, *Chemosphere* 51 (2003) 273–287.
- [7] K.R. Reddy, S. Chinthamreddy, Effect of initial form of chromium on electrokinetic remediation in clays, *Adv. Environ. Res.* 7 (2003) 353–365.
- [8] D.M. Zhou, C.F. Deng, L. Cang, Electrokinetic remediation of a Cu contaminated red soil by conditioning catholyte pH with different enhancing chemical reagents, *Chemosphere* 56 (2004) 265–273.
- [9] B.E. Redd, M.T. Berg, J.C. Thompson, J.H. Hatfield, Chemical conditioning of electrode reservoir during electrokinetic soil flushing of Pb-contaminated silt loam, *J. Environ. Eng.* 121 (1995) 805–815.
- [10] K.R. Reddy, S. Danda, R.E. Saichek, Complicating factors of using ethylenediamine tetraacetic acid to enhance electrokinetic remediation of multiple heavy metals in clayey soils, *J. Environ. Eng. ASCE* 130 (2004) 1357–1366.
- [11] W.S. Kim, S.O. Kim, K.W. Kim, Enhanced electrokinetic extraction of heavy metals from soils associated by ion exchange membranes, *J. Hazard. Mater.* 118 (2005) 93–102.
- [12] S. Amrate, D.E. Akretche, C. Innocent, P. Seta, Removal of Pb for a calcareous soil during EDTA-enhanced electrokinetic extraction, *Sci. Total Environ.* 349 (2005) 56–66.
- [13] C. Yuan, T.S. Chiang, Enhancement of electrokinetic remediation of arsenic spiked soil by chemical reagents, *J. Hazard. Mater.* 152 (2008) 309–315.

- [14] C. Su, R.W. Puls, Arsenate and arsenite removal by zerovalent iron: effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride, *Environ. Sci. Technol.* 35 (2001) 4562–4568.
- [15] S. Morrison, Performance evaluation of a permeable reactive barrier using reaction products as tracers, *Environ. Sci. Technol.* 37 (2003) 2302–2309.
- [16] J. Farrell, J. Wang, P. O'Day, M. Conklin, Electrochemical and spectroscopic study of arsenic removal from water using zero-valent iron media, *Environ. Sci. Technol.* 35 (2001) 2026–2032.
- [17] W. Zhang, P. Singh, E. Paling, S. Delides, Arsenic removal from contaminated water by natural iron ores, *Miner. Eng.* 17 (2004) 517–524.
- [18] A. Bednar, J.R. Garbarino, J.F. Ranville, T.R. Wildeman, Effects of iron on arsenic speciation and redox chemistry in acid mine water, *J. Geochem. Explor.* 85 (2005) 55–62.
- [19] C. Yuan, T.S. Chiang, The mechanisms of arsenic removal from soil by electrokinetic process coupled with iron permeable reaction barrier, *Chemosphere* 67 (2007) 1533–1542.
- [20] H.I. Chung, M.H. Lee, A new method for remedial treatment of contaminated clayey soils by electrokinetics coupled with permeable reactive barriers, *Electrochim. Acta* 52 (2007) 3427–3431.
- [21] D.W. Nelson, L.E. Sommers, Total carbon, organic carbon, and organic matter, in: L.A. Page, R.H. Miller, D.R. Keeney (Eds.), *Methods of Soil Analysis Part 2*, American Society of Agronomy, Madison, WI, USA, 1982, pp. 539–579.
- [22] TEPA (Taiwan Environment Protection Agency), Method No. NIEA S310.62C, Metals in soil—H₂O₂/HCl digestion method, 2002.
- [23] C.V. Chrysikopoulos, P. Kruger, Investigation of soluble indium chelates for groundwater and hydrothermal fluid tracing, *Appl. Geochem.* 2 (1987) 329–335.
- [24] C. Wu, F. Wu, Y. Bai, B. Yi, H. Zhang, Cobalt boride catalysts for hydrogen generation from alkaline NaBH₄ solution, *Mater. Lett.* 59 (2005) 1748–1751.
- [25] T.T. Chao, R.F. Sanzolone, Chemical dissociation of sulfide minerals, *J. Res. US Geol. Surv.* 5 (1983) 409–412.
- [26] T.T. Chao, R.F. Sanzolone, Fractionation of soil selenium by sequential partial dissolution, *Soil Sci. Soc. Am. J.* 53 (1989) 385–392.
- [27] E. Cardoso Fonseca, E. Ferreira da Silva, Application of selective extraction techniques in metal-bearing phases identification: a South European case study, *J. Geochem. Explor.* 61 (1998) 203–212.
- [28] B. Dold, Speciation of the most soluble phases in a sequential extraction procedure adapted for geochemical studies of copper sulfide mine waste, *J. Geochem. Explor.* 80 (2003) 55–68.
- [29] B. Dold, L. Fontboté, A mineralogical and geochemical study of element mobility in sulfide mine tailings of the Fe-oxide Cu-Au deposits from Punta and Cobre district, northern Chile, *Chem. Geol.* 189 (2002) 135–163.
- [30] J.C. Bailar, *Comprehensive Inorganic Chemistry*, vol. 3, Pergamon, Oxford, U.K., 1973.
- [31] J.A. Lackovic, N.P. Nikolaidis, G.M. Dobbs, Inorganic arsenic removal by zero-valent iron, *Environ. Eng. Sci.* 17 (2000) 29–39.
- [32] S.O. Kim, S.H. Moon, K.W. Kim, S.T. Yun, Pilot scale study on the ex situ electrokinetic removal of heavy metals from municipal wastewater sludges, *Water Res.* 36 (2002) 4765–4774.
- [33] R.A. Jacobs, M.Z. Senguin, R.E. Hicks, R.F. Probst, Model and experiments on soil remediation by electric fields, *J. Environ. Sci. Heal. A* 29 (1994) 1933–1955.
- [34] D.B. Gent, R.M. Bricka, A.N. Alshawabkeh, S.L. Larson, G. Fabrian, S. Granade, Bench- and field-scale evaluation of chromium and cadmium extraction by electrokinetics, *J. Hazard. Mater.* 110 (2004) 53–62.
- [35] J. Virkutyte, M. Sillanpaa, P. Latostenmaa, Electrokinetic soil remediation—critical review, *Sci. Total Environ.* 289 (2002) 97–121.