

Application of Phosphate and EDTA on As(V) Removal in Gold Mine Tailings by Electrokinetic Remediation

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Abstract

The use of phosphate (PO_4^{3-}) and/or EDTA to enhance the removal of arsenate (As(V)) from gold mine tailings by electrokinetic remediation (EKR) was investigated. The effect of different concentrations of PO_4^{3-} or EDTA on As (50 mg/L) movement was first evaluated in a two-layered agar matrix with EKR at 2 V/cm for 72 h. Subsequently, the assay was repeated for As-contaminated mine tailings (60 mg/kg), by applying the EKR for 168 h and using the additive concentrations that gave maximal levels of As at the anode. The upper 10-cm layer of agar was uncontaminated, while the lower 10-cm layer was contaminated with As with or without the added PO_4^{3-} (P) and/or EDTA (E) at 25, 50, or 75 mg/L of agar. The As was translocated and accumulated at the anode at higher levels in the presence of 50 mg/L of PO_4^{3-} (P50) or EDTA (E50) than in the control. With the addition of P50, the As level increased in the upper layer, whereas with E50 the As mainly accumulated in the lower layer. The co-addition of both P50 and E50 (P50/E50) led to As accumulation in both the upper and lower layers at essentially the same level. The pH, Eh, and EC in the tailing under EKR changed less in P50 and E50 than in the control, but differed between each other. P50 supplementation caused As to accumulate at the anode by electromigration, whereas in the control As migrated to accumulate at the cathode and also in-between the cathode and anode by electro-osmosis. In contrast, E50 and the combined P50/E50 addition did not result in a significant As concentration in each zone, but showed a trend of a decreased concentration at the cathode.

Keywords: Arsenic; Gold mine tailing; Electrokinetic remediation; Phosphate; EDTA

1. Introduction

Mining processes produce a large amount of tailings, which are fine-grained particles that are often contaminated with a high concentration of heavy metal. For example, gold mining in Thailand produces more than 19 million tons of tailings (Changul *et al.*, 2010), with an arsenic (As) concentration at 50 mg/kg (Sampanpanish and Suwattiga, 2017). Gold

mine tailings are commonly contaminated with As in the form of arsenopyrite (FeAsS) and pyrite (FeS_2) (Paktunc, 2013), which are oxidized when exposed to the air. This causes As, in the form of soluble oxide compounds, to be adsorbed and co-precipitated with oxides and hydroxides of iron (Fe), aluminium (Al), and manganese (Mn), which are also abundant in tailings

(Bowell *et al.*, 2014; Khalid *et al.*, 2016). Most of the As in mine tailings is in the form of residual and Fe-Mn oxide bound (Ko *et al.*, 2008; Yang *et al.*, 2009; Wang *et al.*, 2016; Isosaari and Sillanpää, 2012; Gabarrón *et al.*, 2018), which causes the As to have low solubility and low mobility.

Electrokinetic remediation (EKR), which applies an electric current to remove contaminants by electro-osmosis and electromigration, is often used to enhance the efficiency of contaminant removal in fine-grained particles (Alshwabkeh *et al.*, 1999; Kim *et al.*, 2005; Baek *et al.*, 2009; Isosaari and Sillanpää, 2012; Yang *et al.*, 2014; Shin *et al.*, 2016). The efficiency of EKR depends on the properties of the soil and electrode configuration (Malekzadeh and Sivakugan, 2017). The application of sodium hydroxide (NaOH) and ethylenediaminetetraacetic acid (EDTA) to the tailings enhanced the As removal by EKR with a hexagonal electrode configuration to more than 50% in paddy soil at a depth of less than 1 m (Kim *et al.*, 2014). In addition, EDTA, a chelating agent that can be dissociated into an anion and has the ability to chelate certain metal cations (Maketon *et al.*, 2008), is also widely used to remove As from soil and mine tailings (Kim *et al.*, 2015, 2016). The EDTA-metal complex prevents the precipitation of metal cations in the oxide form which has a high affinity for As adsorption (Kim *et al.*, 2015; Wang *et al.*, 2018). Moreover, the use of phosphate (H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-}), which has a form with an ionic radius, bond length and chemical structure similar to those of arsenate (H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-}), the chemical forms of As in oxidizing conditions, has been reported to aid As removal (Brookins, 1988; Tawfik and Viola, 2011; Strawn, 2018). The ability of PO_4^{3-} to extract As from contaminated soil and tailings by anion exchange is well documented (Kim *et al.*, 2005; Im *et al.*, 2015; Jho *et al.*, 2015; Wang *et al.*, 2018). In this study, the removal of As from gold mine tailings by EKR with a hexagonal two-dimensional (2D) electrode configuration with the addition of PO_4^{3-} and/or EDTA was investigated.

2. Materials and Methods

2.1 Distribution of As in an agar matrix under EKR in the presence of PO_4^{3-} or EDTA

2.1.1 Methodology

Evaluation of the removal of As from an agar matrix by EKR was set-up in a reactor using a stainless steel 316L electrode with a hexagonal 2D electrode configuration. The dimensions of experimental reactor is shown in Figure 1(a). The agar matrix was used to represent a clean media without the presence of ions that could inhibit the migration of As. Both of the two 10-cm deep layers of the agar matrix set was prepared by pouring 1.5% (w/v) food-grade agar in 2.5 mM KNO_3 solution (Putra *et al.*, 2013) for the total volume of 23.88 L, with the contaminated agar containing As at 50 mg/L ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) as the lower layer and the uncontaminated agar as the upper layer. Direct current (DC) at a constant electric field of 2 V/cm was applied continuously for 72 h. In total seven treatments were evaluated, comprised of the control (no other addition), and the addition of PO_4^{3-} (KH_2PO_4) at a concentration of 25 (P25), 50 (P50), and 75 (P75) mg/L or EDTA ($\text{Na}_2\text{-EDTA}$) at a concentration of 25 (E25), 50 (E50), and 75 (E75) mg/L in the contaminated agar layer. Finally, a mixture of PO_4^{3-} and EDTA at the concentration of each that caused the highest accumulation of As at the anode (P50/E50) was evaluated.

2.1.2 Agar sample collection and analysis

Agar samples were collected at the end of the EKR treatment from nine areas for both layers, as shown in Figure 1(b). Each agar sample was homogenized by re-dissolving into solution by adding a few drops of HNO_3 . The As concentration was then measured using inductively coupled plasma optical emission spectrometry (ICP-OES) on a Plasma PQ 9000 Elite (Germany) instrument according to USEPA 3015A (USEPA, 2007a).

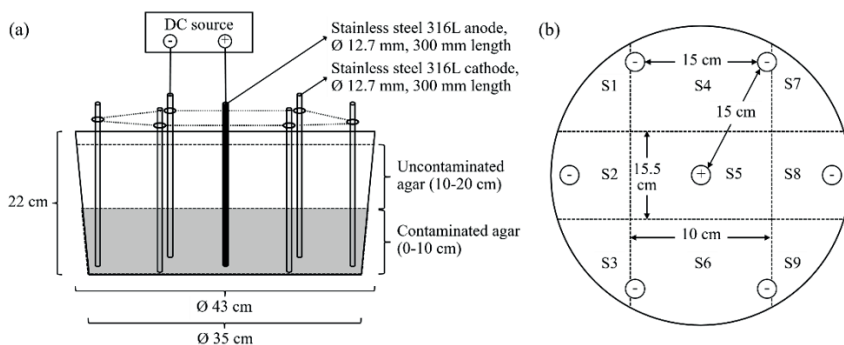


Figure 1. Schematic diagram of the experimental reactor showing the (a) Side view for the dimensional size and sectional agar matrix, and (b) Lateral image of the hexagonal 2D electrode configuration and sampling area (S1-S9).

2.2 Properties of the mine tailings

The mine tailing sample used in this study was excavated from the tailing storage facility of a gold mine at a depth of 0-30 cm. The mine tailing sample was air-dried and sieved to a size of < 2 mm. Particle size distribution was measured by pipette method (Gee and Bauder, 1986), and is classified as a sandy loam (Soil Science Division Staff, 2017), containing 56.6% of sand, 33.8% of silt, and 9.6% of clay, with a moisture content of 1.02 ± 0.04 . The suspension of 1:2 (w/v) of mine tailing and deionized water was prepared to measure pH (Hendershot *et al.*, 2007), redox potential (Eh), and electrical conductivity (EC) (Miller and Curtin, 2007). The properties results of mine tailing are shown in Table 1.

2.3 Effect of PO_4^{3-} and EDTA on the distribution of As in mine tailings subjected to EKR

2.3.1 Methodology

The evaluation of As migration in the mine tailing (60.0 mg-As/kg) by EKR was conducted in the same manner as in the agar matrix except using 32 kg of mine tailing in pots to obtain the two layers of 10 cm height each. The optimum concentration of PO_4^{3-} , EDTA, and a 1:1 (v/v) mixture of both these optimal PO_4^{3-} and EDTA levels, as obtained from the agar matrix, were used in the gold mine tailing. The mine tailing was adjusted

to an initial moisture content of 15% (w/w). Six h after the enhancing agent (PO_4^{3-} , EDTA or both) was added, the DC with a constant electric field of 2 V/cm was applied continuously for 168 h. The results were compared to the control, which had distilled water (DI) added in place of the enhancing agent solution. Moreover, 2 L of DI was added at 72 and 120 h of the experiment to maintain the moisture content of the mine tailings.

2.3.2 Collection and analysis of tailing sample

The mine tailing samples were collected along the depth of tailing in experimental reactor (0-20 cm) at 72, 120, and 168 h after initiation of the DC current from the cathode, in between the cathode and anode (in-between) and the anode (Figure 2.). Each sample was homogenized (air-dried) and the pH, Eh and EC and As levels were determined using ICP-OES analysis according to the USEPA method 3051A (USEPA, 2007b).

2.3.3 Statistical Analysis

The difference in As concentrations in the mine tailings at different time periods and areas of the reactor were analyzed by one-way analysis of variance (one-way ANOVA) and Duncan's multiple range test (DMRT), accepting significance at the 95% confidence level ($P < 0.05$). All analysis was performed using the SPSS vs 22.0 software.

Table 1. Mine tailing properties used in this study

Parameter	Result
Soil texture (%)	Sandy loam
Sand (0.05–2.00 mm)	56.6
Silt (0.02–2.00 mm)	33.8
Clay (0.05–2.00 mm)	9.6
Moisture content (%)	1.02 ± 0.04
pH	8.35 ± 0.05
Eh (mV)	242.2 ± 7.4
EC (dS/m)	2.46 ± 0.62
Heavy metal (mg/kg)	
As	60.0 ± 3.1
Fe	26,943 ± 478
Al	14,390 ± 634
Mn	1,194 ± 47
Zn	77.2 ± 2.2
Cu	73.9 ± 17.2
Cr	47.5 ± 12.7
Pb	14.1 ± 1.6

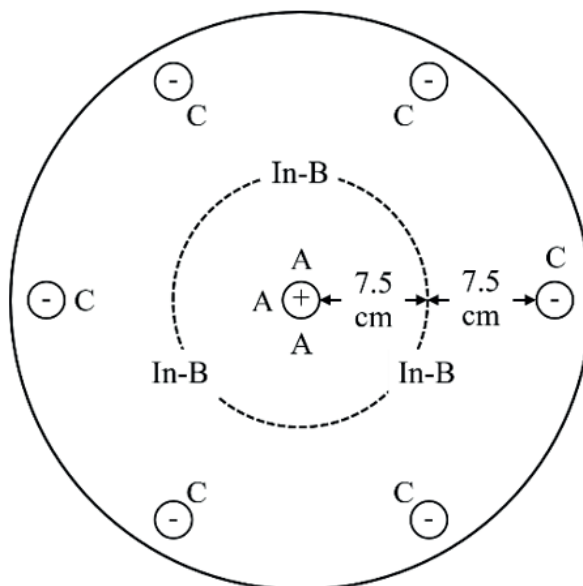


Figure 2. Sampling point of mine tailing experiment at the cathode (C), in-between (In-B) and anode (A).

3. Results and discussion

3.1 Effect of EKR and the addition of PO_4^{3-} or EDTA on the distribution of As in the agar matrix

The migration of As in the agar matrix in each sample area of the control (no added PO_4^{3-} or EDTA) revealed that after EKR treatment As was mostly located at the anode (S5), as shown in Figure 3(a). In the lower (contaminated) layer of agar, As migrated horizontally to accumulate at the anode (S5), since the As(V) dissociated to $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} when the pH was in the range of 2–12, and migrated from the cathode to the anode by electromigration (Yang *et al.*, 2014; Shin *et al.*, 2016). Additionally, As also migrated vertically from the lower layer to the upper uncontaminated agar by water evaporation (Kim *et al.*, 2012a). The highest concentration of As was found at the anode (S5) in both the contaminated and uncontaminated agar at 69.1 ± 0.6 and 96.1 ± 1.2 mg/L, respectively.

The effect of adding PO_4^{3-} or EDTA on the migration of As in the agar matrix is summarized in Figure 3(b) and 3(c), respectively. The As migrated and accumulated at the anode by electromigration. Similar to in the control, the As concentration in the upper (uncontaminated) agar at the anode in the presence of PO_4^{3-} was higher than that at the anode in the lower layer. For example, in the P50 treatment, the As concentration at the anode of the contaminated and uncontaminated agar layers was 68.6 ± 0.7 and 158.0 ± 1.0 mg/L, respectively. This was explained based on the chemical analogy between arsenate ($H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}) and phosphate ($H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-}) (Tawfik and Viola, 2011; Strawn, 2018), which hence have the same migration behavior under the electric field.

For EDTA supplementation, As was also mainly accumulated at the anode, but in the contaminated agar. The highest As concentration was found at the anode in the presence of E50, being 96.2 ± 1.5 and 73.0 ± 0.7 mg/L in the contaminated and uncontaminated agar, respectively. The most likely cause is the dissociation into anions of EDTA (H_3EDTA^- , H_2EDTA^{2-} , $HEDTA^{3-}$, and

$EDTA^{4-}$) when the pH >2 (Maketon *et al.*, 2008). These anions have a larger molecular structure and high molecular mass, which inhibits the upward migration of As as the water evaporates.

The dissociation of PO_4^{3-} and EDTA into their respective anions decreased the electrical resistivity (R) of the agar matrix, which enhanced the As migration by electromigration (Isoaari and Sillanpää, 2012). However, when the concentration of PO_4^{3-} or EDTA was increased to 75 mg/L, the R value of the agar matrix decreased rapidly, while the rate of water electrolysis increased resulting in a high amount of H^+ at the anode. Thus, the anions of As, PO_4^{3-} , and EDTA which accumulated at the anode were reduced into lower charged or uncharged species. At a pH <2 , As and PO_4^{3-} were in the form of arsenic (H_3AsO_4) and phosphoric (H_3PO_4) acids, respectively, (Strawn, 2018; Tawfik and Viola, 2011), while EDTA was uncharged (H_4EDTA) or a cation (H_5EDTA^+) (Maketon *et al.*, 2008). The uncharged species migrated from the anode to the cathode according to water movement by electro-osmosis, which was in the opposite direction to the electromigration of the anionic forms. Therefore, As migrated from the anode to other areas when the concentration of PO_4^{3-} or EDTA was excessive (in this case, at 75 mg/L).

3.2 Effect of EKR on the distribution of As in the presence of 50 mg/L each of PO_4^{3-} and EDTA (P50/E50) in the agar matrix

For the addition of PO_4^{3-} or EDTA, the highest As concentration was found at the anode when added at 50 mg/L in both cases (P50 and E50), although it was highest in the uncontaminated agar for P50 and in the contaminated agar for E50. Thus, the effect of the co-addition of both PO_4^{3-} and EDTA at 50 mg/L each (P50/E50) was evaluated. However, the co-addition of P50/E50 showed a similar As distribution as in the control, as seen in Figure 3(d). Moreover, there was an accumulation of As in other areas, both in the contaminated and uncontaminated agar at 0.76–35.69 mg/L, which was related to the migration of As in lower charged or uncharged forms from the anode to cathode by electro-osmosis.

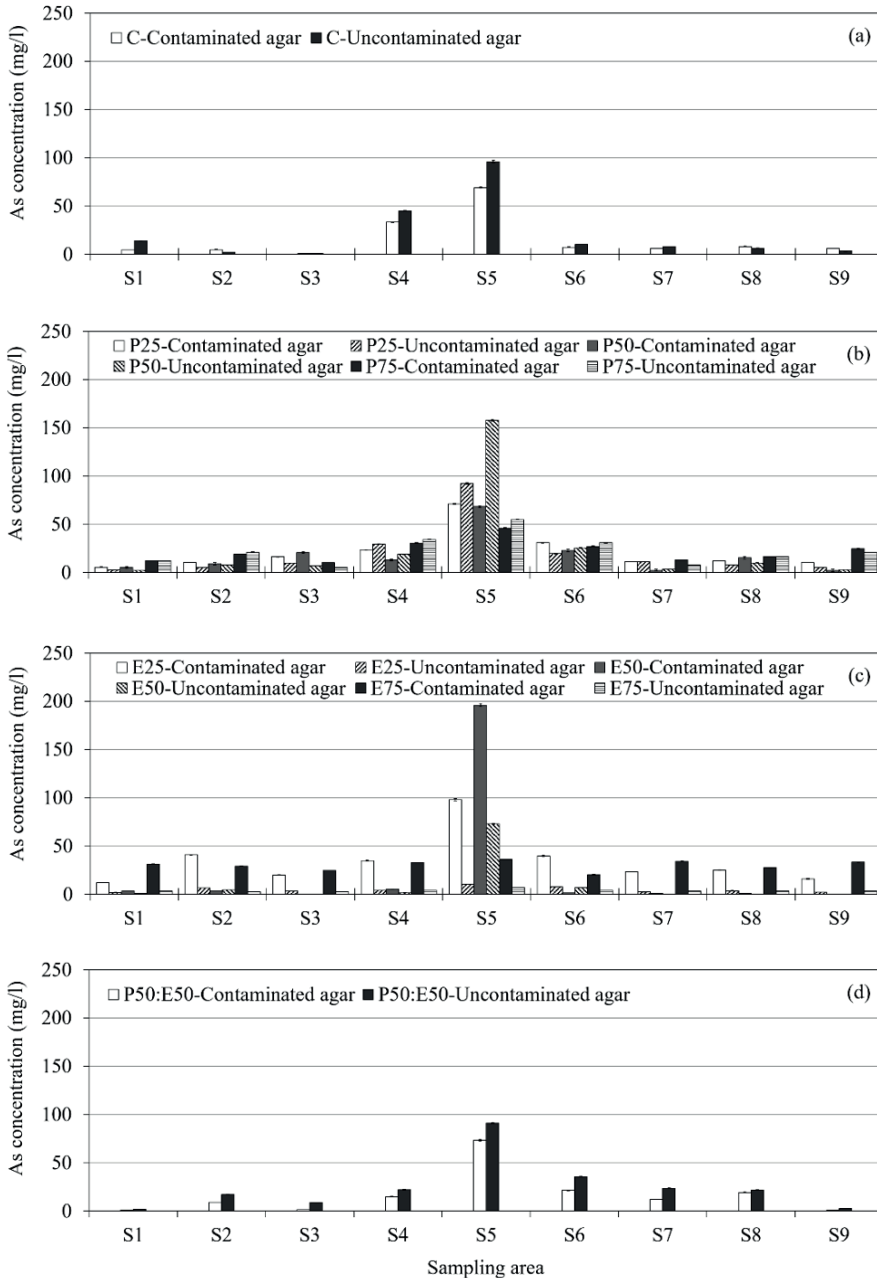


Figure 3. Distribution of As in the agar matrix after EKR treatment in the (a) control, and in the presence of (b) P25, P50, and P75, (c) E25, E50, and E75, and (d) P50/E50 in the uncontaminated and contaminated agar layer. The EKR was run continuously for 72 h at a constant electric DC field or at 2 V/cm.

3.3 Variation in the pH, Eh, and EC in the mine tailing during EKR

The initial pH of the mine tailings was 8.35 ± 0.05 and this changed during EKR as a result of water electrolysis that caused basification at the cathode and acidification at the anode. The OH^- generated at the cathode caused a basic front that migrated towards the anode, while the H^+ generated at the anode caused an acid front that migrated towards the cathode, resulting in a pH gradient between the cathode and anode as well (Kim *et al.*, 2012b, 2014). Figure 4(a) shows the tailing pH after EKR treatment for 72, 120, and 168 h at the cathode, in-between, and anode sampling points. After EKR, all the treatments showed a similar trend in the pH, being increased at the cathode (8.44–9.10), clearly decreased at the anode (2.41–4.40) and tending to be decreased in-between the anode and cathode (7.48–8.05). Note that the transport of H^+ is approximately two-fold faster than the transport of OH^- (Acar *et al.*, 1995). However, the P50 and E50 supplemented tailings showed a lower pH at the cathode than the control tailings, which likely reflected that KH_2PO_4 and $\text{Na}_2\text{-EDTA}$ can be deprotonated and so decreased the effect of the basic front from OH^- (Kim *et al.*, 2005, 2014). In the same way, the PO_4^{3-} and EDTA anions generated at the anode will reduce the acidification from H^+ and so the pH value at the anode of the P50 and E50 supplemented tailings was higher than in the control. In contrast, the P50/E50 tailing tended to have a pH value similar to the control. Presumably, the large amount of OH^- and H^+ generated from the electrolysis of water and dissociation of the respective enhancing agents still caused a basic front at the cathode and acid front at the anode.

The Eh is a parameter that identifies the ability of oxidation-reduction reactions, and is related to the amount of oxygen in the tailing. At the end of the EKR, the Eh of the tailing in every treatment showed a similar tendency in the direction of change (Figure 4(b)). The variation in Eh is related to the reducing condition at the cathode from the electrolysis of water, which decreased the Eh value from the movement of OH^- to the anode by electromigration and increasing the amount

of H_2 . Moreover, the increasing amount of O_2 at the anode results in an oxidizing condition and increases the Eh value (Cameselle, 2015). At the cathode, the Eh ranged from 151.48–243.31 mV and tended to increase at the anode and in-between the cathode and anode, ranging between 277.23–503.67 and 208.33–308.03 mV, respectively.

The change in the pH and Eh implied that Fe (26,943 mg/kg), Al (14,390 mg/kg), and Mn (1,194 mg/kg), which are the main components in the mine tailing, could dissociate into the ionic form, especially in the low pH and oxidizing condition at the anode. In an oxidizing condition, Fe can exist as Fe(II) at a pH <8 and Fe(III) at a pH <4, while Al will be in the form of Al(III) at a pH <4 and Mn will be in the form of Mn(II) at a pH <9 (Brookins, 1988). The dissociation of these main elements then affected the increasing EC of the tailings. The EC values at the anode ranged from 3.61–12.72 dS/m, as shown in Figure 4(c). The increasing EC in the EKR of the As-contaminated soil is related to the movement of H^+ and OH^- from the hydrolysis of water, the ion of the added enhancing agent, and the dissociation into ionic form of the existing elements in the soil (Kim *et al.*, 2005).

3.4 Effect of EKR on the As distribution in the mine tailing in the presence of PO_4^{3-} or EDTA

As(V) is the main As species present under an oxidizing condition and exists as an oxyanion (H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-}). In EKR, As(V) migrates from the cathode to the anode by electro-migration. However, the movement of water from the anode to cathode by electro-osmosis will counter the migration of As(V) from the cathode to anode, with the net movement reflecting the balance between these opposing forces (Baek *et al.*, 2009; Yang *et al.*, 2014). Table 2. shows the amount of As that accumulated in the mine tailing at the cathode, in-between, and anode after 72, 120, and 168 h of applied EKR. The control treatment at 72 h showed that As tended to accumulate at the cathode, then migrated to accumulate in-between the cathode and anode, attaining a significantly higher concentration than at the cathode or anode after 120 h of applied EKR. Finally, after 168 h of applied

EKR the As had accumulated at the cathode and in-between the cathode and anode at a significantly higher concentration than at the anode. The pH and Eh of the control tailings indicated that As would be in the protonated form of HAsO_4^{2-} at the start of the EKR and was changed into the less charged form of

H_2AsO_4^- by the end of the EKR treatment (Brookins 1988). Therefore, it is possible that the oxyanion of As was influenced more by the movement of water from electro-osmosis than by electromigration towards the anode and so accumulated at the cathode and in-between the anode and cathode.

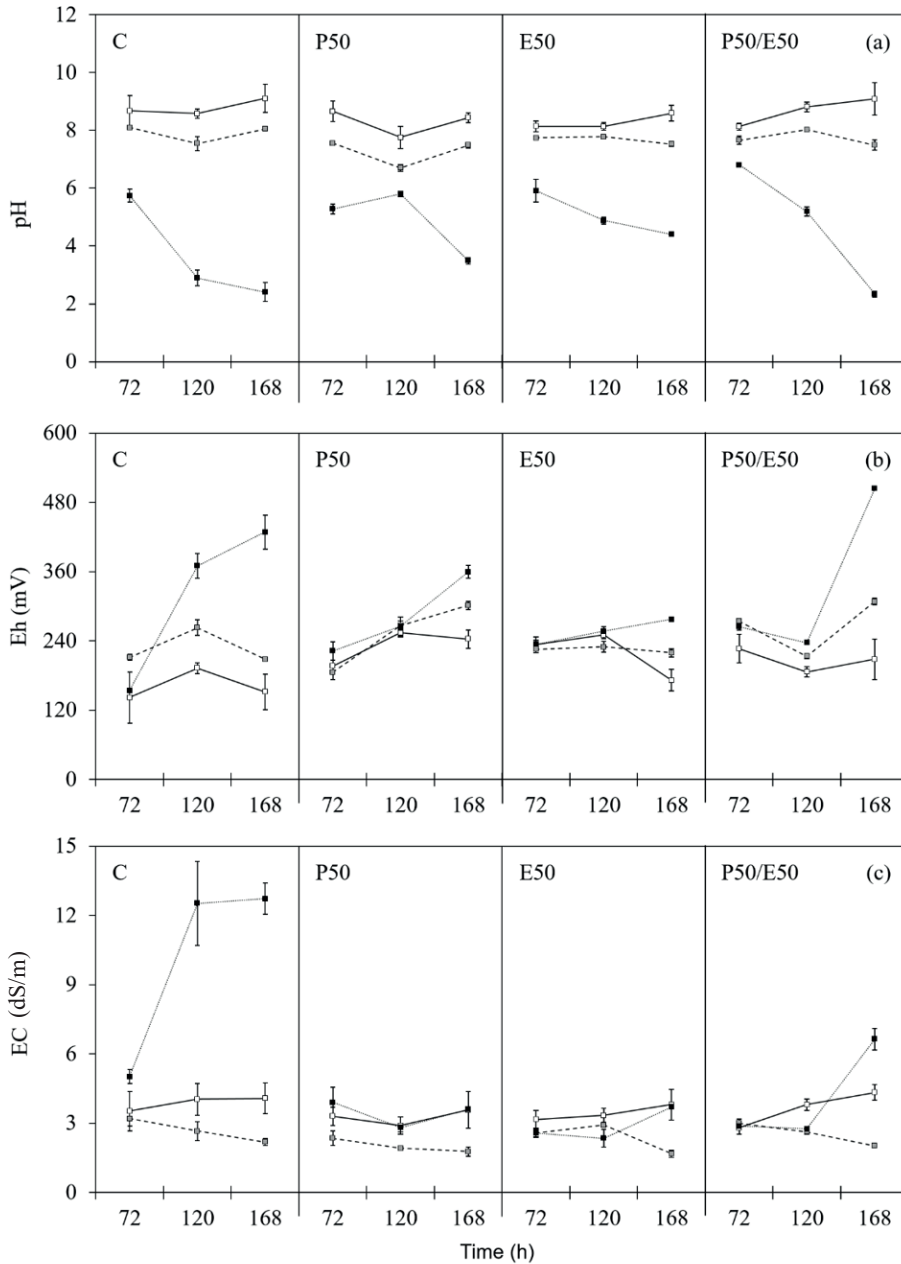


Figure 4. Variation in the (a) pH, (b) Eh, and (c) EC of the mine tailings after 72, 120, and 168 h of EKR at a constant 2 V/cm electric field at the cathode (□), in-between the cathode and anode (○), and at the anode (■) of the control and the P50, E50, and P50/E50 supplemented tailings.

Table 2. Summary of As concentration in the mine tailing after EKR treatment for different times with or without the addition of 50 mg/L of PO₄³⁻ and/or EDTA.

Time (h)	Sampling point	As concentration (mg/kg)			
		C	P50	E50	P50/E50
72	Cathode	64.15 ± 1.63 ^k	60.64 ± 2.74 ^{fg hij}	61.57 ± 1.30 ^{hijk}	61.16 ± 0.98 ^{hij}
	In-between	60.92 ± 2.13 ^{fg hij}	61.54 ± 0.35 ^{hijk}	62.07 ± 1.03 ^{hijk}	60.75 ± 0.28 ^{fg hij}
	Anode	62.51 ± 2.28 ^{ijk}	55.72 ± 1.56 ^{abc}	61.88 ± 0.87 ^{hijk}	61.67 ± 1.41 ^{hijk}
120	Cathode	59.04 ± 0.61 ^{defgh}	57.94 ± 1.08 ^{cdef}	60.52 ± 1.11 ^{fg hij}	61.03 ± 0.81 ^{ghij}
	In-between	63.07 ± 1.60 ^{jk}	58.08 ± 0.80 ^{cdefg}	59.90 ± 0.48 ^{efghi}	60.38 ± 1.07 ^{fg hij}
	Anode	57.52 ± 1.16 ^{bcde}	59.79 ± 1.96 ^{efghi}	60.41 ± 2.65 ^{fg hij}	63.00 ± 0.97 ^{jk}
168	Cathode	61.33 ± 1.85 ^{hijk}	56.36 ± 0.49 ^{abc}	60.73 ± 2.51 ^{fg hij}	60.55 ± 0.74 ^{fg hij}
	In-between	62.43 ± 1.53 ^{ijk}	55.05 ± 2.81 ^{ab}	60.96 ± 3.62 ^{ghij}	60.44 ± 0.59 ^{fg hij}
	Anode	53.60 ± 2.45 ^a	60.70 ± 2.41 ^{fg hij}	60.81 ± 2.66 ^{fg hij}	59.16 ± 1.50 ^{efgh}

Note: Results are shown as the mean ± SD (Cathode; n = 6, In-between and Anode; n = 3). Means with a different lowercase superscript letter between groups are significantly different ($p \leq 0.05$).

The addition of 50 mg/L PO₄³⁻ and/or EDTA, equal to 0.003 mg/kg, has the different results. In the presence of 50 mg/L PO₄³⁻ (P50), the As tended to accumulate at the cathode and in-between the cathode and anode at a significantly higher concentration than at the anode after 72 h of applied EKR, but thereafter started to accumulate at the anode and had a significantly higher concentrations at the anode than at the cathode or in-between after 168 h of EKR. The most likely cause was that at the anode As can be dissolved by acid dissolution, while at the cathode As(V) was desorbed to bulk moisture by phosphate ion as anion exchange, therefore enhance As(V) electromigration (Yang *et al.*, 2014). As a result, As migrated efficiently to the anode by electromigration. Kim *et al.*, (2005) reported that when using KH₂PO₄ as a catholyte in EKR, the As removal efficiency increased from 44.7% to 88.8% in kaolinite and from 9.96% to 27.3% in the tailing-soil from a gold mine. In addition, Isosaari and Sillanpää (2012) reported that PO₄³⁻ decreased the As concentration at the cathode by more than 25% and caused an increased As accumulation in the area in-between the cathode and anode. Moreover, Yang *et al.*, (2014) reported that applying H₃PO₄ in contaminated soil increased

the As migration to the anode, resulting in a 30% higher As removal efficiency.

On the other hand, the addition of E50 showed different results to P50, since the EDTA can chelate metal cations (Maketon *et al.*, 2008), especially the oxides of Fe, Al, and Mn, with a large specific surface area that act as a natural source of As (Bowell *et al.*, 2014; Khalid *et al.*, 2016). Thus, with E50 addition the As concentration in each area did not significantly differ from each other over time due to the pH and Eh values in the mine tailings. In the case of Fe, the highest metal concentration element in the tailings, it would principally be in the uncharged Fe(OH)₃ form at the cathode (Brookins, 1988), which has a high affinity for As adsorption. This caused a decreased As electromigration from the cathode to anode. Moreover, Fe²⁺/Fe³⁺ at the anode (Brookins, 1988) can readily form a complex with As(V) as the concentration of EDTA in this study did not reach a 1:1 molar ratio of cations to EDTA. As a result, As at the anode had a low mobility and could not migrate to the cathode by electro-osmosis. The results of the addition of P50/E50 was similar to those with E50. However, at the end of the EKR treatment (168 h), the concentration of As at the anode tended to decrease, which

likely reflected that the EC value at the anode was higher with the E50/P50 addition than in the presence of E50 or P50 alone. The increasing EC indicated the higher rate of water electrolysis that decreased the pH and caused the increased level of uncharged species, especially H_3AsO_4 . Even though the addition of E50 or the co-addition of P50/E50 inhibited the electromigration of As, they also reduced the As migration to the cathode by electro-osmosis.

4. Conclusions

The application of EKR has the ability to cause the movement of As to the anode by electromigration. Both PO_4^{3-} and EDTA are attractive enhancing agents, which have different effects on the As migration in EKR. As PO_4^{3-} has chemical forms that are analogous to those of As(V) it enhanced the migration into the upper (uncontaminated) layer at the anode by water evaporation. On the other hand, EDTA inhibited the upwards migration of As, due to its large molecular structure with a higher molecular mass. Within the agar, the addition of PO_4^{3-} or EDTA at 50 mg/L (P50 and E50, respectively), but not at higher concentrations, gave the highest As accumulation at the anode, while the co-addition of both (P50/E50) showed a similar trend to the control (no addition of PO_4^{3-} or EDTA). Variation in the pH, Eh, and EC in the mine tailing affected the migration of As by electro-osmosis and electromigration. At the end of the 168-h EKR treatment, in the presence of P50 the As was still in an anionic form which migrated to accumulate at the anode by electromigration. This is different to the control, where As has subsequently been changed into less charged species and then migrated to accumulate at the cathode and in-between the cathode and anode by electro-osmosis. The As concentration in the presence of E50 or P50/E50 during the EKR treatment did not differ significantly between each area or over treatment time, which likely reflected the high concentration of Fe, Al, and Mn in the tailings. Thus, the concentration of EDTA was imbalanced compared to the concentration of these cation metals in the mine tailings. However, E50 and P50/E50 could reduce the As migration to the

cathode by electro-osmosis. Therefore, it is possible that increasing the concentration of EDTA may induce increasing As accumulation at the anode. Additionally, EKR with the addition of PO_4^{3-} or EDTA could be applied in combination with several technologies, such as phytoremediation. However, the pH, Eh, and EC of the mine tailings needs to be considered to ascertain if appropriate for the chemical form of As in combination with plant growth.

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