J Appl Electrochem (2010) 40:1101–1111
DOI 10.1007/s10800-010-0073-2

ORIGINAL PAPER

Removal of phosphate from agricultural soil by electrokinetic remediation with iron electrode

Jeong-Hee Choi · Sundaram Maruthamuthu · Hyun-Goo Lee · Tae-Hyun Ha · Jeong-Hyo Bae · Akram N. Alshawabkeh

Received: 30 August 2009 / Accepted: 4 January 2010

Abstract Phosphorus is considered the limiting nutrient in eutrophication of agricultural soil in Korea. This study evaluates the coupled application of electrokinetic process by iron and titanium electrodes for removal of phosphate from agricultural soils. Experiments were conducted to evaluate phosphate removal under the following conditions: (I) control; (II) 1% starch addition in the soil without EK; (III) 1% starch addition at the anolyte using a cast iron anode and a carbon cathode; (IV) no starch addition using a cast iron anode and a carbon cathode, and; (V) 1% starch at the anolyte using a titanium anode and a carbon cathode. When an iron anode was used under 0.5, 1.0 and 2.0 V/cm, the removal of phosphate was significant at 2 V/cm. The addition of starch also helps to remove nitrate significantly using an iron electrode. The results reveal that iron electrodes result in significantly more removal compared to titanium electrodes.

Keywords Phosphate · Electrokinetics · Iron · Titanium · Starch

---

J.-H. Choi · H.-G. Lee · T.-H. Ha · J.-H. Bae
Smart Power Facility Research Center, Smart Grid Research Division, Korea Electrotechnology Research Institute,
70 Boolmosangil, Changwon 641-120, Korea

S. Maruthamuthu (✉)
Corrosion Protection Division, Central Electrochemical Research Institute, Karaikudi 630 006, India
e-mail: biocorrcecri@gmail.com

A. N. Alshawabkeh (✉)
Department of Civil and Environmental Engineering,
Northeastern University, Boston, MA 02115-5000, USA
e-mail: aalsha@coe.neu.edu

1 Introduction

Excessive phosphorous loading from man-made sources is commonly linked to eutrophication of lakes and streams. This phenomenon is responsible for dramatic growth of algae in soil and water systems. In agricultural soil, the dumping of manure increases phosphate concentration in surface or ground water which is responsible for eutrophication in a closed water system. Phosphorus is extremely chemically active. Usually phosphorous occurs in the oxidized state, either as ions of inorganic orthophosphate (HPO_4^{2-}, $H_2PO_4^{-}$) or in organic compounds [1]. The quantities of phosphate delivered to surface waters from agricultural run-off and wastewater has led to legislation, such as those under the European Union Urban Waste Water Treatment Directive of 1991 that are designed to remove phosphorous from domestic and industrial water.

The broad categories of phosphate treatment and/or removal from soil/water systems include physical [2, 3], chemical [4], biological [5] and crystallization methods [6]. Chemical removal techniques are the most effective and well-established methods to date, and include phosphate precipitation with calcium, aluminum and iron salts [7–9]. The removal of phosphate compounds by sorption onto various sorbents has been extensively tested and discussed. Aluminum and aluminum oxides [10, 11], iron oxides [12–15], fly ash [16, 17], slag [18, 19], red mud [20, 21] bauxite [22], silicates [23, 24], active carbon [25] and anion exchange [26] were evaluated as adsorbents. Electrocoagulation has also been proposed to treat waste water. Electrocoagulation is a process that creates metallic hydroxide flocks within waste water by electrodissolution of soluble anodes, usually made of iron or aluminum [27, 28]. This is a simple system that is easy to operate, relatively fast, does not require additional chemicals and does not generate a significant amount of sludge. Other studies used iron oxide tailing for phosphate removal in aqueous solutions and were an effective adsorbent in removing soluble phosphorous [29] from solution.

Biological processes are also considered. In activated sludge process, biological phosphorous removal is achieved by introducing an anaerobic and/or anoxic zone ahead of an aerobic zone. A number of activated sludge-related processes have been developed, including main-stream or side-stream processes, and processes designed to also remove nitrogen [30]. These methods, while successful in treatment of wastewater have limitations in removal of phosphate from soil.

To address the problem of phosphate removal from soils, this study evaluates the use of electrokinetic processes (EK) for transport and removal of available phosphate from agricultural soil by employing iron anodes and carbon cathodes. Electrochemically generated metallic iron can undergo hydrolysis near the anode to produce a series of activated intermediates that are able to stabilize the finely dispersed particles in the soil/waste water to be treated. Iron anodes produce electrons through corrosion and simultaneously act as a reactive iron for phosphate transformation. Iron plate electrodes are relatively inexpensive, readily available and have been proven effective in treatment of waste water systems by electrocoagulation [31].

The process combines electrokinetic transport and electrocoagulation to induce transport followed by reactivity with iron for treatment of phosphate in soil. When iron electrodes are used, the following reactions occur:At the cathode

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

At the anode

$$Fe(s) \rightarrow Fe^{2+} + 2e^-$$

and with dissolved oxygen in solution,

$$4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8H^+$$

It is also reported that starch is a good organic nutrient for nitrate-reducing bacteria present in the Korean soil [32] where 21 *Bacillus* sp. were identified. The study will assess the effect of presence of organics (in the form of starch) in the anolyte on the removal of phosphate. Organic content (or humus) is not thought to retain or adsorb phosphorous in soils since it is normally present as negatively charged complexes. However, in association with cations such as iron, it is organic matter which is able to adsorb significant amounts of phosphorous [33]. Though the effect of organic content on the phosphate sorption is ambiguous, organic matter acts on phosphate sorption in two ways, either by sorbing phosphate or by blocking sorption sites on inorganic particles [1].

2 Materials and methods

2.1 Electrokinetic cell configuration and testing

Figure 1 shows a schematic of the laboratory EK reactor. The EK cell is made of acrylic sheet with dimension $24 \times 4 \times 6$ cm^3. It is divided into three compartments. The central compartment holds the soil sample and the others are reservoirs for catholyte and anolyte solutions. The length of the central compartment is 10 cm. Cast iron and graphite were used as anode and cathode, respectively. To avoid soil dispersion to the electrolyte reservoirs, nylon mesh [34] (mesh opening 149 μm) and filter paper (Whatman No. 2) were placed between the soil sample and each reservoir. The soil was silty loam. DC power supply (3A–30 V, ED Laboratory, ED-245B) was used for applying constant voltage gradients of 0.5, 1.0 and 2.0 V/cm for 7 days.

Five testing systems were conducted to evaluate phosphate removal. Before starting each experiment, 400 g of agricultural soil was air-dried for 24 h; mixed with deionized water or 1% starch solution to bring the soil to 30% water content; and carefully placed in the central compartment. The five systems varied in the type of treatment and applied boundary conditions. System I was maintained as a control without electric current application. System II was a control (no electric current) but with 1% starch addition to assess microbial transformation processes. System III was conducted using cast iron anode and carbon cathode with 1% starch solution as anolyte. System IV was conducted using cast iron anode and carbon cathode without starch addition. System V was conducted using titanium anode and carbon cathode with 1% starch solution as anolyte. The experiments were conducted in duplicates using duplicate cells. A summary of the experiments and testing conditions is presented in Table 1.

To examine the role of starch in the phosphate removal process, 1% starch solution was used as anolyte in Systems II, III and V. In EK experiments, voltage gradients of 0.5, 1 and 2 V/cm were maintained. Sterilized 1% starch solution was added daily into the anolyte compartment while maintaining a constant hydraulic gradient across the sample. In the systems with no added starch, distilled water was used as anolyte and catholyte and the same voltage gradients were maintained. The openings of the chambers were closed with UV-sterilized polythene paper to avoid external contamination of the soil. All the systems were maintained between 25 and 28 °C.

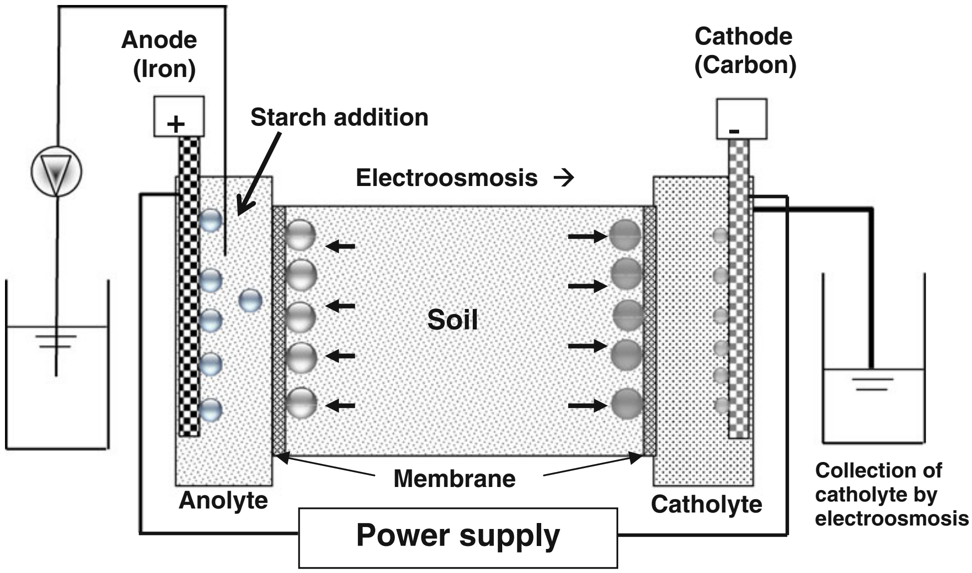

Fig. 1 Electrokinetic cell model

Table 1 Experimental systems conducted in the present study

Experiment	Anolyte	Catholyte	Anode	Cathode	Voltage gradient	Data collected	Remarks
System I (only soil)	–	–	–	–	–	Phosphate, nitrate, iron, pH, calcium, magnesium, heterotrophic bacteria, nitrate reducing bacteria, organic content	No EK
System II soil with 1% starch (water content 30%)	–	–	–	–	–	Phosphate	No EK
System III soil with 1% starch (water content 30%)	1% starch	Distilled water	Iron	Carbon	0.5 V/cm	pH, EC, EOF, Fe, Phosphate, nitrate	EK
					1.0 V/cm	pH, EL, EOF, Fe, Phosphate, nitrate	EK
					2.0 V/cm	pH, EC, EOF, Fe, Phosphate, nitrate	EK
System IV soil with deionized water(water content 30%)	distilled water	Distilled water	Iron	Carbon	0.5 V/cm	pH, EC, EOF, Fe, Phosphate, nitrate	EK
					1.0 V/cm	pH, EL, EOF, Fe, Phosphate, nitrate	EK
					2.0 V/cm	pH, EC, EOF, Fe, Phosphate, nitrate	EK
System V soil with 1% starch(water content 30%)	1% starch	Distilled water	Titanium	Carbon	2.0 V/cm	Phosphate	EK

The cast iron anodes (4 cm × 4 cm) were mechanically polished to a mirror finish and then degreased using trichloroethylene. After 7 days of treatment under 0.5, 1 and 2 V/cm, the electrodes were removed and placed in pickling solution (Hydrochloric acid with antimony trioxide and stannous chloride), washed in water and dried with an air drier. The final weight of the electrodes in each system was measured and the average corrosion rates were calculated. The standard deviation for each system is also evaluated.

2.2 Chemical analysis

Iron formation and migration as a result of electrolysis and electrokinetic transport is expected to impact the process. The mobility of iron in soil under voltage gradients of 0.5, 1.0, 2.0 V/cm was estimated based on iron concentrations in soil. To measure chemical concentrations, 5 g of soil was air-dried, mixed with 50 mL of 1 M ammonium acetate in a 100 mL flask and agitated for 30 min. The soil mixture was filtered with filter paper (Whatman 2) and the filtrate concentrations were measured by atomic absorption spectroscopy (AAS), model Analyst 800 (PerkinElmer). The soil pH was measured according to soil examination standards (Ministry of Environment, Korea). In each case, 5 g of soil was air-dried, mixed with 25 mL of distilled water in a 50 mL vial and agitated with a magnetic stirrer for 1 h at 300 rpm. The pH of the soil–water slurry was measured by pH meter (Istek Inc, Model 76P). Electrical conductivity (EC) was measured for the same slurry by EC meter (Istek Inc, Model 47 C). The average value of triplicate measurements is presented. In addition, pH and EC of both the anolyte and catholyte were measured by pH and EC meters during the EK experiment. Electroosmotic flow was estimated with time by measuring the volume of excess electrolyte collected at the cathode chamber.

Nitrate concentrations were measured in the soil after testing. Ten grams of air-dried soil samples were placed in 100 mL flask and 2 M potassium chloride was added. The mixture was agitated for 30 min and filtered using Whatman No 2 filter paper. The nitrate level of the filtered solution was estimated using a QuAAtro auto analyzer (BRAN + LUEBBE, Germany).

X-ray diffraction (XRD) was used to scan the corrosion products between 10° and $85^\circ{-}2\theta$ with copper K∞ radiation (Ni filter) at a rating of 40 kV, 20 mA. The dried corrosion product on steel surface was used for XRD analysis to determine the nature of corrosion oxides products.

The available phosphate was estimated using the Lancaster method [35]. Five grams of soil were extracted with 20 ml of 0.33 M CH_3CHOOH, 0.15 M lactic acid, 0.03 M NH_4F, 0.05 M $(NH_4)_2SO_4$ and 0.2 M NaOH at pH 4.25. The available phosphate of the soil extraction was analyzed using a UV–VIS spectrophotometer (Hitachi, Japan).

3 Results and discussion

3.1 Initial chemical analysis

The initial organic content of the agricultural soil used in testing was 25 g/kg. Calcium, potassium, and magnesium concentrations were 3.6, 0.9 g/kg and 0.5 g/kg respectively. Nitrate and ammonium concentrations were 800 mg/kg and 12 mg/kg, respectively. The concentration of available phosphate was between 1470 and 1780 mg/kg. The soil contained 8.7×10^6 CFU/g of heterotrophic bacteria and 5.5×10^5 CFU/g of nitrate-reducing bacteria.

3.2 pH of soil and electrolytes

Figure 2 shows the soil pH profiles during EK phosphate removal with and without starch (Systems III and IV). The pH values of anolyte and catholyte were respectively 4 and 12 throughout the experiments. The anolyte and catholyte pH affected soil near the electrodes but no significant pH changes were observed within the middle portion of soil under 0.5 and 1.0 V/cm. The higher pH in the middle area of the soil when compared to control (pH 5.8) may be due to the hydrolysis of iron hydroxide and low electroosmosis in the soil. Under 2 V/cm, the pH of the anode soil was 4 with starch and 4.7 without starch. This may be due to the higher electroosmotic flow at 2.0 V/cm. The middle portion of the soil pH was lower (4.5) when compared to 0.5 and 1.0 V/cm. The pH of the soil near the cathode was about 8 with and without starch. Using titanium anodes for nitrate removal under 2.0 V/cm reduced the pH of the soil to about 3 near the anode [32] and the pH change was correlated with electroosmosis. EK literature [36, 37] shows that the soil pH decreases to around 2 near the anode and increases to 8–12.1 near the cathode when inert electrodes are used. In this study, the pH did not drop to below 4, because electrolytic oxidation of iron was competing with water electrolysis at the anode, resulting in iron oxidation instead of water oxidation.

3.3 Electrical conductivity (EC) and electroosmotic flow (EOF)

No significant differences were detected (Fig. 3) in the EC values of the anolyte and catholyte under 0.5 and 1.0 V/cm. However, under 2.0 V/cm, the EC values of the catholyte were higher than the anolyte. Higher EC values were observed (Fig. 4) in the middle soil sections under 0.5 and 1.0 V/cm. The trend was different under 2 V/cm as the EC of the middle sections of the soil was lower than the anode and cathode sections. Up to 70% reduction in the EC was observed under 2.0 V/cm. The decrease in EC after EK treatment indicates removal of the soil salinity. In general, the EC value for soil should be lower than 2.0 dS/m for purposes of crop cultivation. Even though the whole soil sample under 0.5 and 1.0 V/cm did not meet this benchmark, application of 2.0 V/cm was sufficient for treating the soil salinity and restoring the soil. The influence of starch on EC of the soil is negligible because the concentration is relatively low and the electrolysis of acid/base chemistry dominates the medium.

Figure 5 shows the accumulated EOF with time under 0.5, 1.0 and 2.0 V/cm. The EOF under 0.5 and 1.0 V/cm were lower than those measured under 2.0 V/cm. When starch was applied under 0.5 and 1.0 V/cm, the EOF was insignificant when compared to the case without starch. However, under 2 V/cm, EOF was similar in both cases with and without starch application. The results again show that a minimum voltage gradient threshold (on the order of

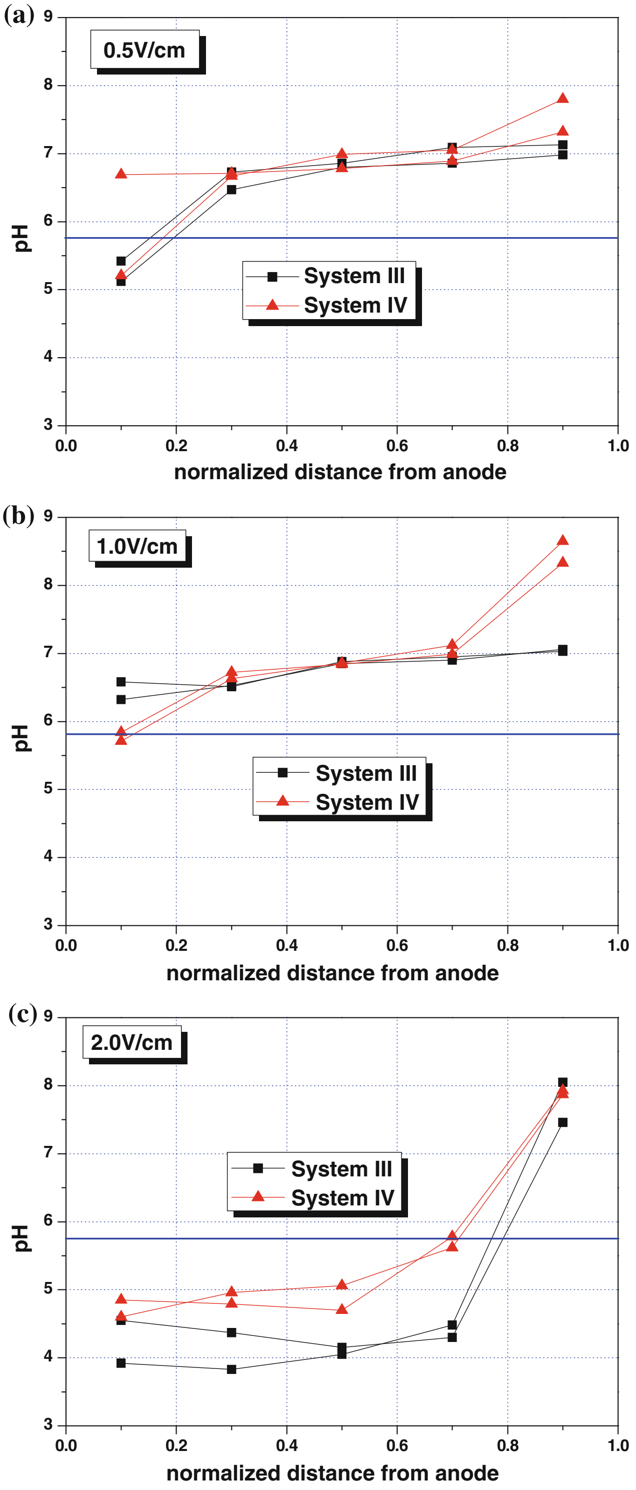

Fig. 2 pH profile of the soil at various voltage gradients 0.5 (**a**), 1.0 (**b**) and 2.0 V/cm (**c**) after completing EK with (System III) and without (System IV) starch addition

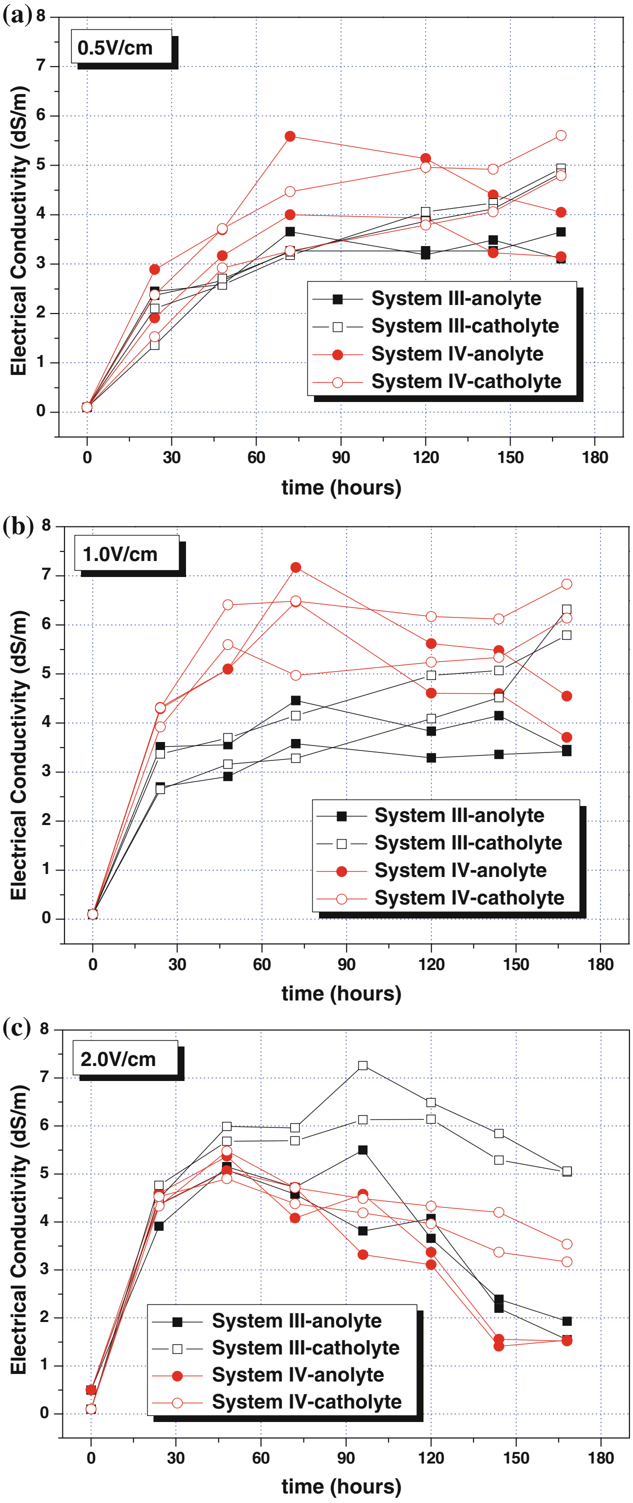

Fig. 3 EC of anolyte and catholyte at various voltage gradients 0.5 (**a**), 1.0 (**b**) and 2.0 V/cm (**c**) with (System III) and without (System IV) starch

2 V/cm for this soil) is needed to induce sufficient flow for treatment. The net transport of oxygen and H^+ ions through soil by EOF is higher at 2.0 V/cm when compared to 0.5 and 1.0 V/cm. It is expected that H^+ will affect the phosphate removal under EK. The oxygen may also help the formation of Fe^{3+} in the acidic–anodic area of the soil.

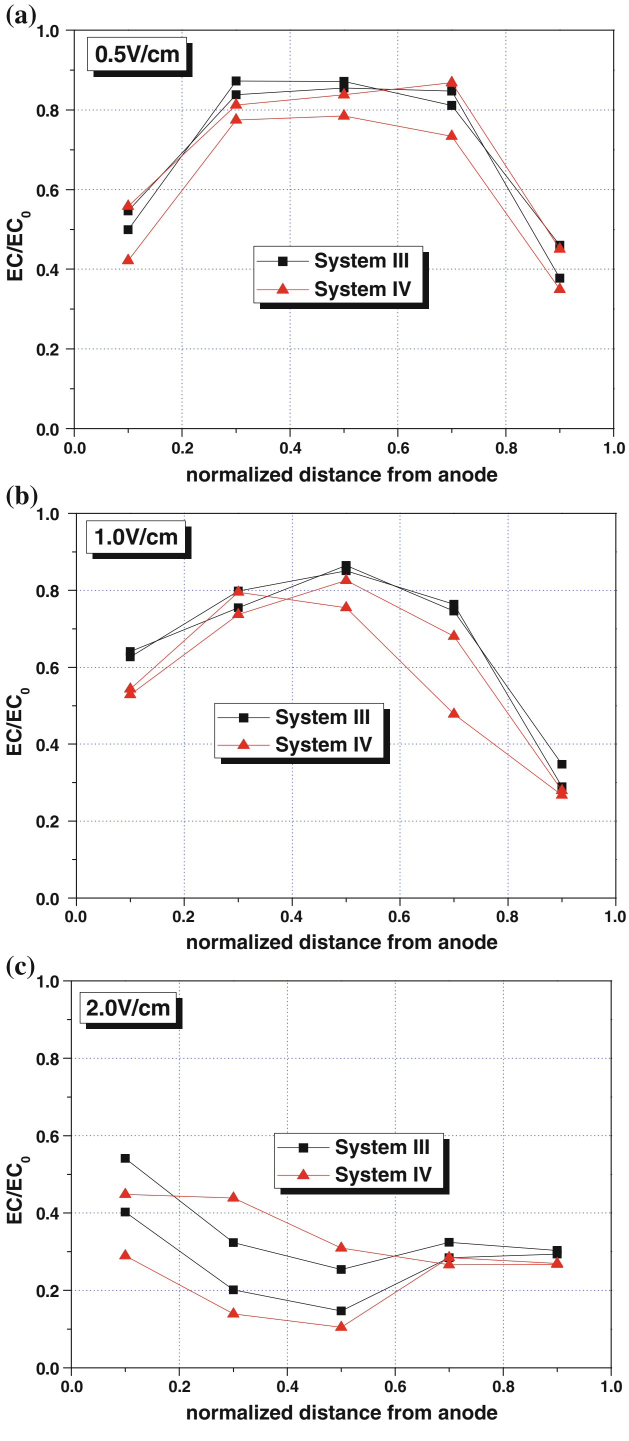

Fig. 4 EC of the soil at various voltage gradients 0.5 (**a**), 1.0 (**b**) and 2.0 V/cm (**c**) after completing EK with (System III) and without (System IV) starch without (System IV) starch (initial EC of the soil: 5.6 dS/m)

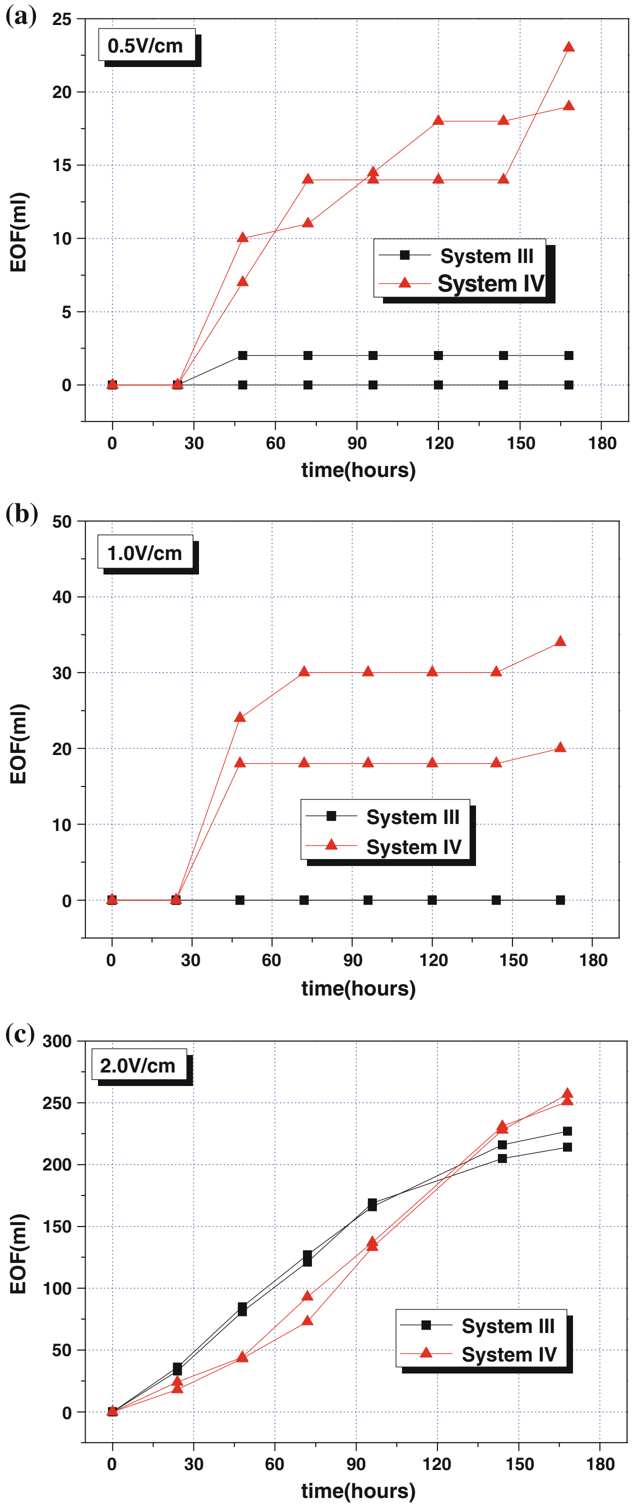

Fig. 5 Accumulated EOF at various voltage gradients 0.5 (**a**), 1.0 (**b**) and 2.0 V/cm (**c**) during EK with (System III) and without (System IV) starch addition

3.4 Fe fate and transport

The concentration profiles of iron in soil after treatment are presented in Fig. 6. The concentration of iron was about one order of magnitude higher after treatment under 2.0 V/cm when compared to 0.5 and 1.0 V/cm. The distribution of iron at the anode and cathode soil areas was higher than the middle area of the soil. This may be due to the migration of iron in the soil by EK. Under 2.0 V/cm, the distribution of iron was higher at the anodic area when compared to the cathode. The change in the mass of iron anodes after EK is presented in Table. 2. The decrease in mass of the electrode was higher in the absence of starch, indicating that starch has slightly inhibited dissolution of the anode, possibly by formation of an organometallic complex on the metal surface. The decrease in mass was also higher under 2.0 V/cm when compared to other systems, causing higher iron accumulation in soil under 2.0 V/cm, thus facilitating phosphate removal.

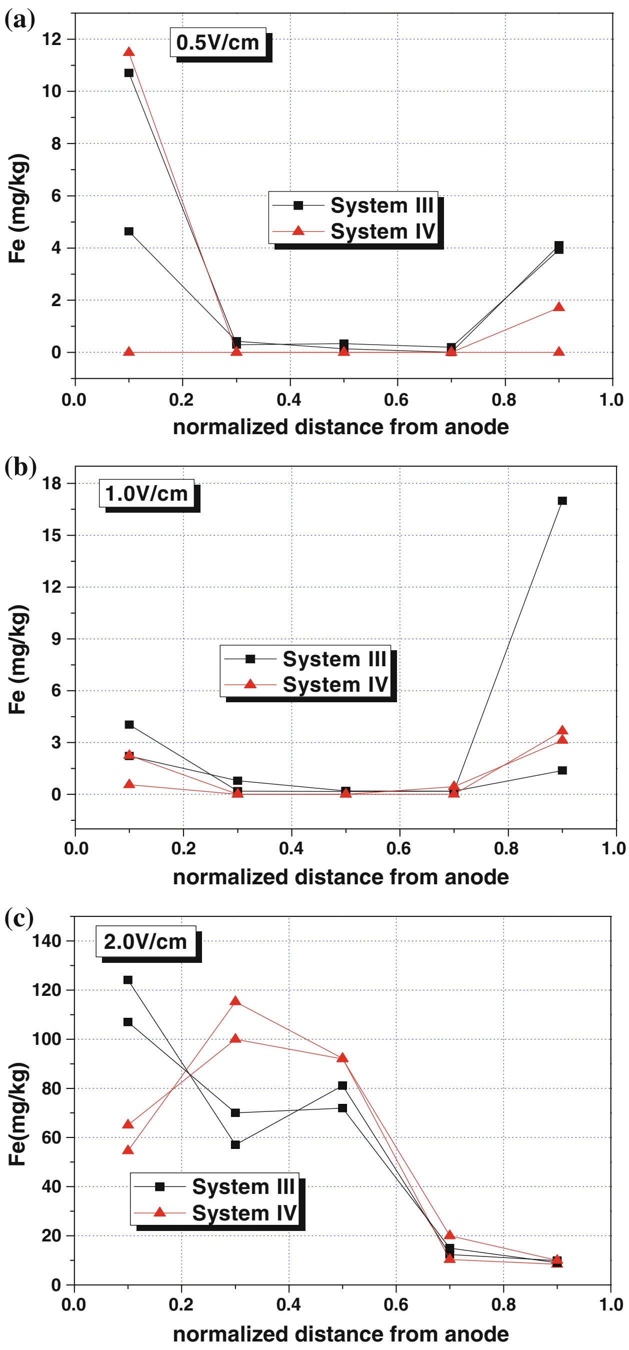

Fig. 6 Distribution of iron at various voltage gradients 0.5 (**a**), 1.0 (**b**) and 2.0 V/cm (**c**) after completing EK with (System III) and without (System IV) starch addition

Figure 7 presents the details of XRD data corresponding to the phases present in the corrosion products collected from the iron electrode at 2.0 V/cm. XRD reveals the presence of iron oxylate, Fe_2O_3, Fe and FeOOH on steel during EK. A broad peak between 10 and 30 2θ indicates the adsorption of organic content on the metal surface. It reveals that the starch adsorbs on the anodic surface and enhances the intensity of Fe, FeOOH and Fe_2O_3 peaks. It can be concluded that the corrosion products of Fe, FeOOH and Fe_2O_3 affect the phosphate removal process. The phosphate adsorption of different iron oxides was studied by Parfitt et al. [38], using the same inorganic phosphate used in this study. They reported that phosphate adsorption capacity (mg P/g adsorbent) at pH 3.5 was higher with FeOOH. The amorphous iron oxides appeared to have a higher phosphate adsorption capacity than the crystalline iron oxides. Zeng et al. [28] also reported that FeOOH (amorphous hydrous iron oxide) adsorbed more phosphate than Fe_2O_3. Recht and Ghassemi [39] reported that homogeneously generated iron(III) is a more efficient phosphate precipitant than iron(II) added from an external

Table 2 Weight loss of Fe anode during EK process

System (V/cm)	With starch (mg/cm^2)	Without starch (mg/cm^2)
0.5	14.86 ± 1.2	14.91 ± 0.9
1.0	19.00 ± 0.5	22.00 ± 1.3
2.0	58.57 ± 0.7	64.29 ± 1.5

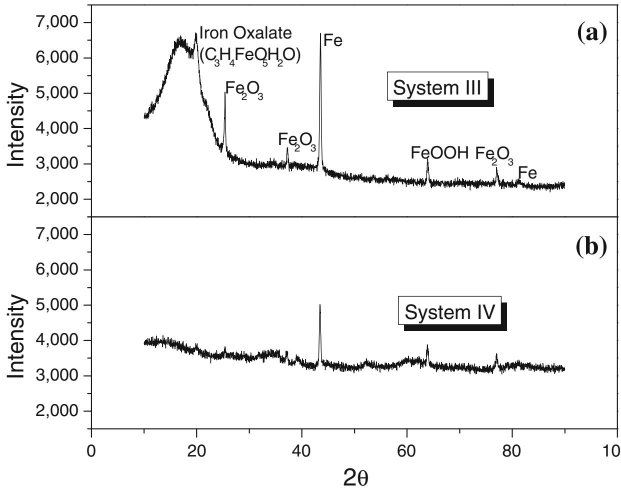

Fig. 7 XRD observations of corrosion product on steel electrode at voltage gradient 2.0 V/cm with (System III) and without (System IV) starch

source. The iron(II) salt precipitated orthophosphate to the same extent as the iron(III) salt only in the pH range 7–8. At other pHs, the iron(II) salt was considerably less effective [40]. It can be assumed that lower pH at 2.0 V/cm encourages the ferric activity and phosphate removal.

3.5 Removal of phosphate

The removal of phosphate in EK system is presented in Fig. 8 (a–c). Available phosphate concentration in the agricultural soil was between 1470 and 1780 mg/kg (System I). No removal was detected in System II with starch addition (Fig. 8c). While using iron anode at 0.5 and 1.0 V/cm, the phosphate concentration in soil near the anode was 250 mg/kg and cathode soil contained between 1300 and 1400 mg/kg. Under 2.0 V/cm (Systems III and IV), the available phosphate was 200 and 500 ppm at the anode and cathode soil respectively. While using titanium (System V) as the anode at 2.0 V/cm (Fig. 8 c), no significant reduction in phosphate concentration was detected at any point within the soil. There was 750 ppm of available phosphate at the cathode. The reduction of phosphate at the cathode is due to the electromigration of phosphate from the cathode to the anode, which is also supported by the large quantity of phosphate (between 1250 and 2700 mg/kg) detected at the anodic area of System V. Due to its negative charge, the ionic mobility of phosphate caused its transport toward the anode. The results reveal that an iron electrode results in significantly higher removal of phosphate under 2.0 V/cm compared to a titanium electrode, and that an iron electrode encourages coagulation of phosphate in the soil. The results also show that a minimum voltage gradient threshold of 2.0 V/cm is required for sufficient removal of phosphate from soil. It also reveals that starch does not affect removal of phosphate in agricultural soil, at least within the time frame of the experiments (a few days).

The phosphate concentration in sections close to the anode was significantly reduced under 0.5 and 1.0 V/cm in experiments with iron anodes. The low EOF and high pH of soil do not favor removal of phosphate from other areas of the soil during EK. The efficiency of phosphate removal with and without starch is presented in Fig. 9 (a and b). The experimental data show that removal percentage in the zones of the soil at pH 4 ranges from 68 to 81% whereas the percentage at pH 8 was 66%. Low pH and improved EOF with iron anodes enhance the removal of phosphate from the soil. The highest removal percentage was observed near the anode, between 75 and 81% removal of available phosphate at 2.0 V/cm. Irdemez et al. [41] reported the highest efficiency of phosphate removal from wastewater using iron plate electrodes by electrocoagulation were 86% for pH 3, 71% for pH 6, and 64% for pH 9 after 20 min. Fytianos et al. [8] reported the highest value of 63% removal at pH 4.5. Zeng et al. [29] observed that phosphate adsorption on the iron oxide tailings tends to decrease with pH increase. Since the highest phosphate removal efficiency was observed under 2.0 V/cm, the EC value was lower at all the points of the soil compared to other systems.

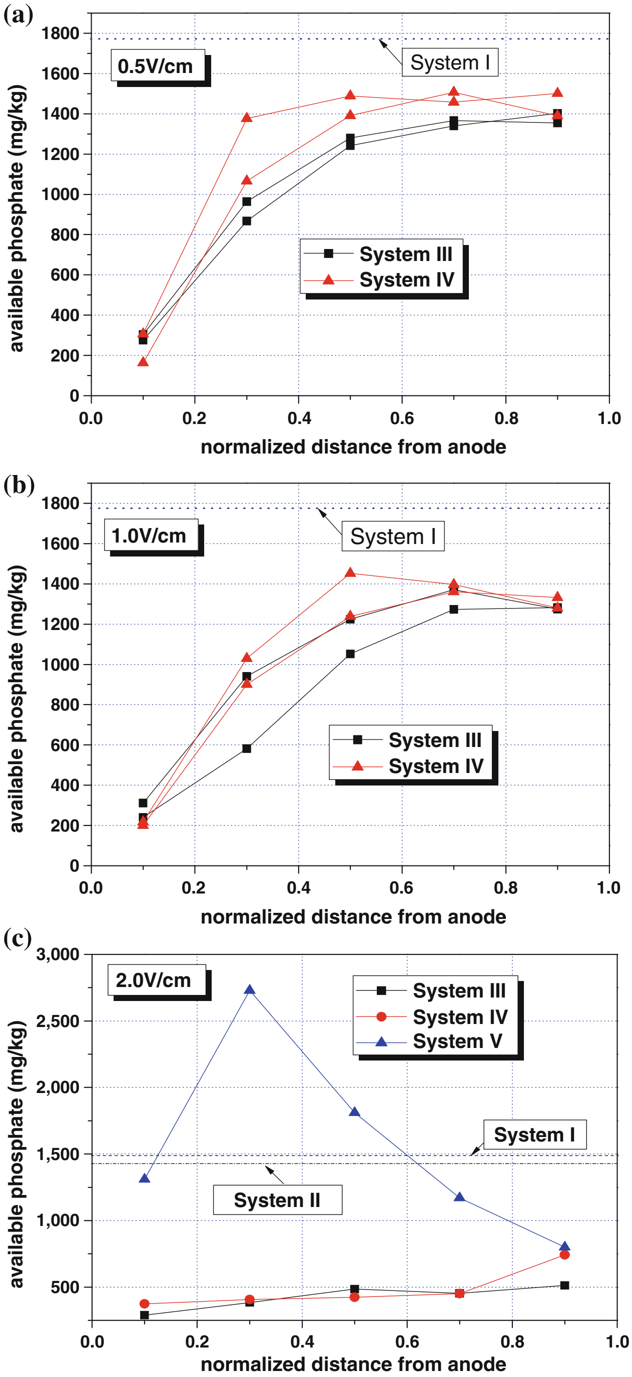

Fig. 8 The available phosphate distribution in soil at various voltage gradients 0.5 (**a**), 1.0 (**b**) and 2.0 V/cm (**c**) after completing EK Experiments

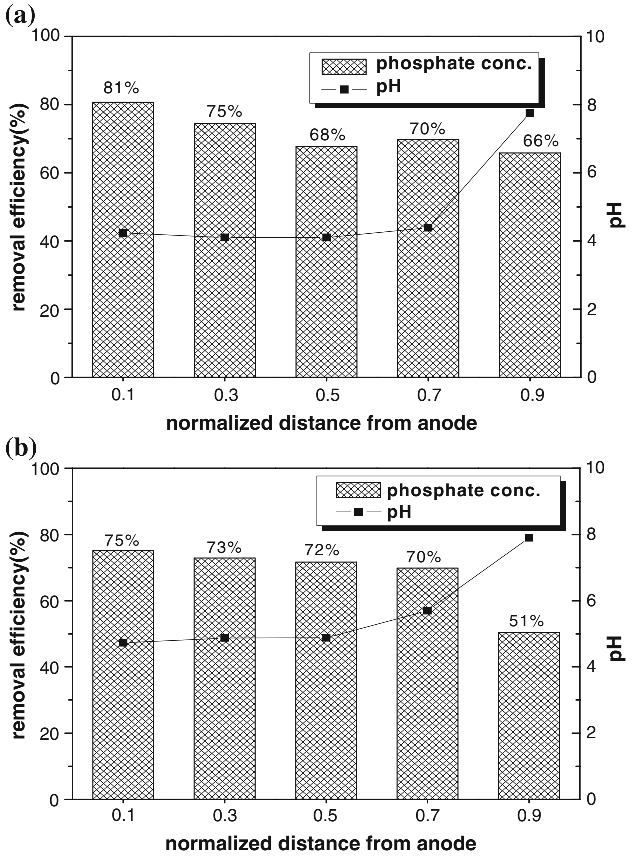

Fig. 9 The efficiency of phosphate removal with iron anode in soil at voltage gradient 2.0 V/cm with (**a**) and without starch (**b**) after completing EK

3.6 Role of iron on phosphate removal

A clear solution of starch in the anolyte indicates that organic species can prevent crystallization of Fe-hydroxides. It was expected that the presence of starch may increase the phosphate sorption [42]. No significant differences in phosphate removal were detected between the cases with and without starch addition during EK. The results (System II) indicate that starch does not influence phosphate removal without EK application for the time scale of the experiments. Starch is also a good nutrient for nitrate reducers [32], leading to significant nitrate removal at the anodic and cathodic areas of the soil with iron electrode under 2.0 V/cm (Fig. 10). The present study supports the observation made by Choi et al. [32], who noticed that nitrate was removed by both bacterial (denitrification) reduction and electromigration by EK while using titanium as an anode in an EK system at 2.0 V/cm. XRD results reveal the presence of iron oxylate, Fe_2O_3, FeOOH and Fe on the electrode surface. The electrode undergoes corrosion and the product is:

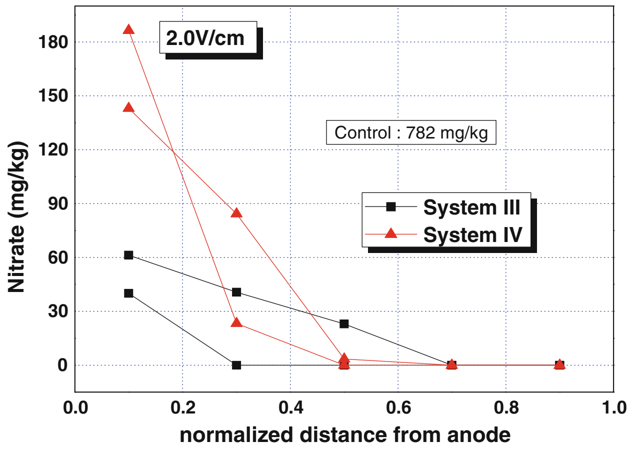

Fig. 10 Nitrate reduction by EK at 2.0 V/cm with and without starch

$$2Fe^0 + O_2 + 2H_2O \leftrightarrow 2Fe^{2+} + 4OH^-$$

Subsequently the precipitation of ferrous iron produces hydrogen ion

$$4Fe^{2+} + O_2 + 10H_2O \leftrightarrow 4Fe(OH)_3(s) + 8H^+$$

The addition of starch acts to adsorb organic ligand exchange reactions and releases OH^- into solutions from the corrosion product of $Fe(OH)_3$ and FeOOH. Hence, the pH of the electrolyte is relatively high in the anolyte when an iron anode is used compared to a passive electrode [43]. In the present study, heterotrophic bacteria and nitrate-reducing bacteria were enumerated in the soil where the existing nitrate reducers were identified in the previous work [32]. The soil microflora capable of reducing iron will be greater than that of the microflora capable of reducing nitrate [44] because iron is a co-factor for nitrogenase enzyme. The following are the possible reactions on iron reduction by bacteria.

$$C_6H_{10}O_5 + 3H_2O \rightarrow 2CH_3COO^- + 2CO_2 + 8H^+ + 10e^-$$

$$2FeOOH + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 4H_2O$$

$$Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$$

The reactions will lead to availability of Fe^{2+} and Fe^{3+} in the soil due to corrosion of the iron electrode during the EK process. It is expected that Fe^{3+} is higher at a lower pH near the anode area while Fe^{2+} concentration may be higher in the alkaline area of cathode soil. Overall, the availability of iron was higher at the anodic area at 2.0 V/cm. This supports the observation that low oxygen and low pH result in poor conversions of iron(II) to iron(III) [40].

With decreasing pH, there is less dissociation of H_2PO_4 and less release the phosphate ions. But with increasing pH, there is stronger competition between the hydroxide ion and phosphate for iron reactivity [40]. Both scenarios may impact the formation of iron phosphate [45]. The efficiency of orthophosphate removal with iron(II) is strongly pH–dependent, with maximum removal obtained in the vicinity of pH 8 [39]. It is suggested [39] that orthophosphate removal increases from 7 to 94% by increasing pH from 6 to 8 under 1:1 iron : phosphate ratio. In the present study at 2.0 V/cm, the removal percentage was between 51 and 81% within a pH range of 4.5–8, and the highest removal percentage occurred between pH 4 and 4.5. Gillbert et al. [46] investigated the influence of pH on precipitation of orthophosphates when adding metal salts and hydroxides produced from the different salts. At most pH values, more orthophosphate was precipitated by adding the metal salts to solutions of orthophosphate than by adding metal hydroxides. Iron(II) salt precipitated orthophosphate to the same extent as the iron(III) salt within a pH range of 7–8. At other pH levels, iron(II) salt was considerably less effective. Fytianos et al. [8] modeled phosphorous removal from aqueous and waste water samples using ferric ion. The highest removal was observed at pH 4.5 with Fe:P > 1:1 M ratios. Karargeorgiou et al. [47] observed that pH is an important factor in orthophosphate adsorption onto calcite. Orthophosphate was completely removed from solution in the basic pH region around 12. Vasudevan et al. [28] reported that the maximum removal of phosphate was 98% at pH 6.5 by employing an iron electrode in the electrocoagulation process in drinking water. It can be concluded that the availability of Fe^{3+} at low pH and mobility of phosphate ions by electroosmosis and electromigration determine the removal process in agricultural soil. The controversy about removal of phosphate in various pH levels is due to the extent of availability of Fe^{2+} and Fe^{3+}. The possible formation of a high quantity of Fe^{3+} in low pH determines the removal of phosphate which is due to the availability of oxygen and H^+ at 2.0 V/cm.

Fytianos et al. [8] suggested that when ferric salts were added into water or waste water for removal of phosphate ions, a large number of products, including complexes, polymers and precipitates were formed. The following reactions were proposed to develop an equilibrium phosphate—precipitation model, using ferric iron addition.

$$H_3PO_4 \rightarrow H_2PO_4{}^- + H^+$$

$$H_2PO_4{}^- \rightarrow HPO_4{}^{2-} + H^+$$

$$HPO_4{}^{2-} \rightarrow H^+ + PO_4{}^{3-}$$

$$Fe^{3+} + HPO_4{}^{2-} \rightarrow FeHPO_4{}^+$$

$$Fe^{3+} + H_2PO_4{}^- \rightarrow FeH_2PO_4{}^{2+}$$

In addition, four solid phases were considered in the model and their formation was tested [8] with the experimental data. These phases were $FePO_4(s)$, $Fe_{2.5}PO_4(OH)_{4.5}(s)$, $Fe_{1.6}H_2PO_4(OH)_{3.8}(s)$ and am. FeOOH. The first phase was considered in a chemical equilibrium model by Kavanaugh et al. [48], the second and fourth in a similar model by Luedecke et al. [49], and the third and fourth by Jenkins and Hermanowiez [50]. In the present study, it can be assumed that $H_2PO_4{}^-$, $HPO_4{}^{2-}$ and OH^- move toward anode as the first step. The chemical reaction taking place will be dependent on the affinity of the metal ion toward OH^- and $PO_4{}^{3-}$ ions. The equilibrium constants show that OH^- has a stronger affinity for Fe^{3+} than does $HPO_4{}^{2-}$ or $PO_4{}^{3-}$. However, the extent of chemical interactions of Fe^{3+} with $HPO_4{}^{2-}$ or $PO_4{}^{3-}$ depends on the ratio $(HPO_4{}^{2-})/(OH^-)$ or $(PO_4{}^{3-})/(OH^-)^3$, respectively [51]. Under 2.0 V/cm, the pH was lower (about 4.5) and iron content in the soil was higher. Hence, it can be suggested that iron (high quantity of Fe(III) at low pH) moves from the anode due to electromigration at low pH [8] and forms as $FeHPO_4{}^+$ and $FeH_2PO_4{}^{2+}$. Furthermore, the positively-charged complex moves to the catholyte by electroosmosis and electromigration as the second step. The solubility of iron phosphate has also increased with increasing pH [52]. On the basis of the present study, the removal of available phosphate has been explained in Fig. 11. It suggests that the process of phosphate removal in the soil is significant at 2.0 V/cm.

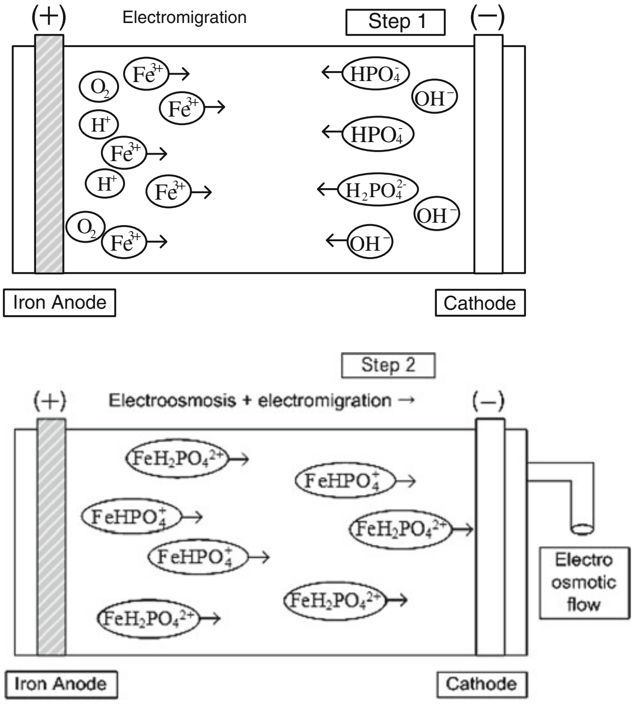

Fig. 11 A proposed hypothesis on removal of phosphate by EK at 2.0 V/cm

4 Conclusions

Using iron as an anode is a feasible approach for the removal of phosphate from agricultural soil by electrokinetic remediation. At a threshold voltage gradient (2 V/cm in this study) soil pH near the anode decreases to between 4 and 5 and the final EC values relatively decrease. It is concluded that a minimum voltage gradient (on the order of 2.0 V/cm for this study) is required for effective removal of phosphate by producing and transporting sufficient quantity of iron by electroosmosis and electromigration. The high percentage of removal of phosphate at the anode soil under 2.0 V/cm is due to the relatively low pH with a sufficient concentration of Fe(III). While iron electrode results in a significant removal of available phosphate, titanium electrode was ineffective.

Acknowledgements The second author S. Maruthamuthu is grateful to the Korean Federation of Science and Technology Societies, Korea, for the award of a Brain Pool Fellowship to carry out this work and also thanks Central Electrochemical Research Institute (CSIR), India for granting deputation to KERI, South Korea.

References

1. Holtan H, Kamp-Nielsen L, Stuanes AO (1988) Hydrobiologia 170:19
2. Omoike AI, Vanloon GW (1999) Water Res 33:3617
3. Clark T, Stephenson T, Pearse PA (1997) Water Res 31:2557
4. Ruixia L, Jinlong G, Hongxiao TJ (2002) J Colloid Interface Sci 248:268
5. Stensel HD (1991) Principles of biological phosphorus removal. In: Sedlak RI (ed) Phosphorus and nitrogen removal from municipal wastewater-principles and practice, 2nd edn. H. K. Lewis, London
6. Moreno EC, Varughese K (1981) J Cryst Growth 53:20
7. Boisvert JP, To TC, Berrak A, Jolicoeur C (1997) Water Res 31:1939
8. Fytianos K, Voudrias E, Raikos N (1998) Environ Pollut 101:123
9. Yeoman S, Stephenson T, Lester JN, Perry R (1998) Environ Pollut 49:183
10. Tang W-P, Shima O, Ookubo A, Ooi K (1997) J Pharm Sci 86:230
11. BJohnson B, Ivanov AV, Antzutkin ON, Forsling W (2002) Langmuir 18:1104
12. Hongshao Z, Stanforth R (2001) Environ Sci Technol 35:4753
13. Lin SH, Kao HC, Cheng CH, Juang RS (2004) Colloids Surf A 234:71
14. Juang RS, Chung JY (2004) J Colloid Interface Sci 275:53
15. Huang X (2004) J Colloid Interface Sci 271:296
16. Tsitouridou R, Georgiou JA (1987) Toxicol Environ Chem 17:129
17. Ugurlu A, Salman B (1998) Environ Int 24:911
18. Yamada H, Kayama M, Saito K, Kara M (1986) Water Res 20:547
19. Oguz E (2005) J Colloid Interface Sci 281:62
20. Koumanova B, Drame M, Pogangelova M (1997) Resour Conserv Recycl 19:11
21. Akay G, Keskinler B, Cakici A, Danis U (1998) Water Res 32:717
22. Altundogan HS, Tümen F (2001) J Chem Technol Biotechnol 77:77
23. Kasama T, Watanabe Y, Yamada H, Murakami T (2004) Appl Clay Sci 25:167
24. Shin EW, Han JS, Jang M, Min SH, JK Park, RM Rowell (2004) Environ Sci Technol 38:912
25. Bhargava DS, Sheldarkar SB (1993) Water Res 27:303
26. Yoshida H, Galinada WA (2002) AlChE J 48:2193
27. Bektas N, Akbulut H, Inan H, Dimoglo A (2004) J Hazard Mater 106B:101
28. Vasudevan S, Sozhan G, Ravichandran S, Jayaraj J, Lakshmi J, Sheela SM (2008) Ind Eng Chem Res 47:1735
29. Zeng L, Li X, Liu J (2004) Water Res 38:1318
30. Bowker RPG, Stensel HD (1990) Phosphorus removal from water. Noyes Data Corporation, New Jersy
31. Irdemez S, Deircioglu N, Yildiz YS (2006) J Hazard Mater B137:1231
32. Choi JH, Maruthamuthu S, Lee HG, Ha TH, Bae JH (2009) J Hazard Mater 168:1208
33. Wild A (1950) J Soil Sci 1:221
34. Chang JH, Liao YC (2006) J Hazard Mater B129:186
35. RDA (Rural Development Administration, Korea) (1988) Methods of soil chemical analysis. Agricultural Science and Technology, RDA, Suwon (in Korean)
36. Reddy KR, Chinthamreddy S (2003) J Geotech Geoenviron Eng ASCE 129:263
37. Acar YB, Alshawabkeh AN (1993) Environ Sci Technol 27:2638
38. Parfitt L, Atkinson J (1975) Soil Sci Am Proc 39:837
39. Recht HL, Ghassemi M (1971) Phosphate precipitation with iron(II) iron, Water Pollution control Series, 17010 EKI 09/71
40. Thistleton J, Berry TA, Pearce P, Parsons SA (2002) Trans Inst Chem Eng 80:265
41. İrdemez Ş, Demircioğlu N, Yıldız YŞ, Bingül Z (2006) Sep Purif Technol 52:218
42. Stuanes AO (1982) Phosphorus sorption by soils : a review. In: Eikum AS, Seabloom RW (eds) Alternative waste water treatments. Low-cost small systems, research and development. Proceedings of conference, Oslo, Norway, 7–10 Sept, 1981. D. Reidel Publishing, Norway, p 145
43. Szpyrkowicz L, Daniele L, Radanelli M, Specchia S (2006) Appl Catal B Environ 66:40
44. Johnson DB, McGinness S (1991) Appl Environ Microbiol 57:207
45. Hsu PH (1976) Wat Res 10:903
46. Gillbert L, Nilsson D, Akesson M (1996) The influence of pH when precipitating orthophosphate with aluminium and iron salts, in chemical water and waste water treatment IV. Spriner-Verlag, Berlin
47. Karageorgiou K, Paschalis M, Anastassakis GN (2007) J Hazard Mater A139:447
48. Kavanaugh MC, Krejci V, Weber T, Eugster J, Roberts PV (1978) J Water Pollut Control 50:216
49. Luedecke C, Hermanowicx SW, Jenkins D (1989) Water Sci Technol 21:325
50. Jenkins D, Hermanowicz SW (1991) Principles of chemical phosphate removal. In: Sedlak R (ed) Phosphorus and nitrogen removal from municipal wastewater. Principles and practice, 2nd edn. Lewis Publishers, Raton, pp 91–108
51. Stumm W, Morgan JJ (1970) Aquatic chemistry. Wiley Interscience, New York
52. Eilbeck WJ, Mattack G (1987) Chemical processes in wastewater treatment. Wiley, Chichester