Electrokinetically enhanced transport of organic and inorganic phosphorus in a low permeability soil

Goontaek Lee — *National Instrumentation Center for Environmental Management, Seoul National University, Seoul 151-921, Korea*

Heemyong Ro* — *School of Agricultural Biotechnology, College of Agriculture and Life Sciences, Seoul National University, Seoul 151-921, Korea*

Sukyoung Lee — *R&D, Environmental Engineering, Research Institute of Technology, Samsung Corporation, Seongnam, Gyeonggi-do 463-771, Korea*

Sangmo Lee — *National Instrumentation Center for Environmental Management, Seoul National University, Seoul 151-921, Korea*

ABSTRACT: The transport of P sources (organic and inorganic phosphorus) using electrokinetic process through a low-permeability soil was investigated. A series of batch experiments was conducted to construct the adsorption isotherms of KH_2PO_4 and triethyl phosphate (TEP) on kaolin soils. Approximately 60.3% of phosphorus from KH_2PO_4 was adsorbed within 24 hours, and the maximum adsorption (73%) was attained at 6 days after adsorption. In contrast, TEP showed no P adsorption in 7 days, thus suggesting an alternative P source that may maintain a favorable proportion of C:N:P through the effective delivery during *in situ* bioremediation in low permeability soils. Experiments using electrokinetic process were carried out with electrokinetic reactor having a hydraulic conductivity of 1.99×10^{-7} cm s^{-1} for a 0.01 M NaCl aqueous solution. TEP and KH_2PO_4 were used as organic P source and inorganic P source, respectively, and introduced individually into a chamber near the platinum anode and near the platinum cathode, respectively. Potassium dihydrogen phosphate was not distributed uniformly along the soil column and most of transported phosphorus was changed to water-insoluble aluminum phosphate after 12 days of treatment, indicating the decrease of bioavailability of the phosphorus. In case of TEP, the advancing P front progressed with time, resulting in uniform P distribution through the kaolin column. In terms of transport, organic phosphorus, TEP, would be a more effective P source than inorganic phosphorus, KH_2PO_4, in electrokinetic enhanced bioremediation.

Key words: bioremediation, electrokinetics (EK), phosphorus, soil contamination, triethyl phosphate (TEP)

1. INTRODUCTION

In situ bioremediation approach is an alternative method for the remediation of soils contaminated with organic compounds, particularly with petroleum hydrocarbons. Despite its well-known advantages, effectiveness of bioremediation is often limited by microbial and physicochemical conditions of the soils. In bioremediation, biological oxidation of organic substance requires transfer of electrons from organic contaminants to electron acceptors in soil (Thevanayagam and Rishindran, 1998). Oxygen functions as a primary electron acceptor for achieving efficient biodegradation of organic

substance. However, due to its low solubility and reduced diffusion in soil water, O_2 becomes depleted long before the bulk of hydrocarbons are degraded. When the soil O_2 is depleted, nitrate acts as an alternate electron acceptor, maintaining the redox potential near +280 to 220 mV (Brady and Weil, 2002).

At the same time, nutrients are also required to enhance soil microbial growth and metabolic activities. Moreover, the treatments of combinations of nutrients have a greater effect on biodegradation than that of single nutrients (West and Harwell, 1992). Therefore, it is very important to maintain a favorable proportion of C:N:P during bioremediation of organic substances (Smith et al., 1998). To satisfy such conditions, soil should have a reasonably high permeability to ensure the delivery of required electron acceptors and nutrients to the contaminated soil zone in a desired time, and thus the flow domain formed should cover the entire treatment zone. Due to technical difficulties of fluids injection through soils having relatively low permeability, application of bioremediation approach is presently limited to soils having permeabilities higher than 10^{-4} m s^{-1} (Thomas and Ward, 1994).

However, the electrokinetic process under direct current applied to the soil could enhance delivery of electron acceptors and nutrients in a low permeability soil having a heavy texture (Budhu et al., 1997; Zelina and Rusling, 1998). Therefore, *in situ* bioremediation incorporates electrokinetic processes such as electromigration, electroosmosis, and electrophoresis, depending on the electrolytes, molecules, or particles (Probstain and Hicks, 1993), to facilitate transport of a target ionized substance under the interaction of an electric field with negatively charged surface formed in the micropores of the soils. As consequences, overall transport of a target substance is determined as a result of electrokinetic flow of fluids due to interaction of the double layer with the electrical field, and diffusion and migration in the flowing fluids as well as hydrodynamic flow of fluids itself. The most important advantage of electrokinetically driven flow is to attain uniform delivery of a reasonable concen-

tration of the injected ions to contaminated zones of low permeability soils in a relatively short duration (e.g., a week) (Chilingar et al., 1970).

Since nitrate is negatively charged and has relatively high mobility in most soils, electrokinetic delivery of nitrate would not be a problem even in clay-rich soils (Thevanay-agam and Rishindran, 1998). However, inorganic forms of phosphate will not be transported through soil by conventional method because soil clay minerals have very high binding capacity for phosphate. Rapid immobilization of phosphates by Fe and Al hydrous oxides in soils was reported (Haynes, 1984). The process of P adsorption involves the transformation of water-soluble P to less soluble or insoluble phosphates through interaction with hydrolytic species of Al^{3+} and Fe^{3+}, and Ca^{2+} in the soil (Morel et al., 1989). This phenomenon suggests that inorganic phosphate compound such as KH_2PO_4 or K_2HPO_4, currently applied as P sources in *ex situ* bioremediation technologies, would not be suitable for *in situ* bioremediation technology in terms of nutrients delivery, and necessitates a testing of an alternative P source that may maintain a favorable proportion of C:N:P through the effective delivery during *in situ* bioremediation of organic pollutants. Therefore, TEP was chosen for comparison. Accordingly, the objective of this study was to evaluate the transport characteristics of inorganic and organic phosphorus in a low permeability soil using electrokinetic-testing module under the influence of electrokinetic gradient.

2. MATERIALS AND METHODS

2.1. Batch Adsorption Experiments of KH_2PO_4 and TEP on Kaolin Soils

Phosphorus sorption isotherms were generated by batch equilibration with standard phosphorus solutions using reagent-grade KH_2PO_4 or TEP in deionized water (18 MΩ). Standard P solutions ranged from 0 to 50.0 mg L^{-1} for KH_2PO_4 and TEP. To do so, five grams of kaolin soils were placed into a 250 mL conical flask containing 20 mL of each P standard solution, and shaken at 20 °C and 200 rpm on a mechanical shaking incubator (Vision Scientific Co., KMC8480) equipped with a temperature controller by shaking from 1 to 7 days. The amount of phosphorus adsorbed on kaolin was estimated by analyzing the remaining concentration in supernatants obtained by centrifuging at 3,000 rpm for 15 min. All the solution P measurements were carried out using inductively coupled plasma-atomic emission spectrometry (Shimadzu, 1000VI) (Soltanpour et al., 1979). Phosphorus equilibrium dada were fitted by the Langmuir adsorption isotherm equation (Sposito, 1989).

2.2. Preparation of Electrokinetic Reactor

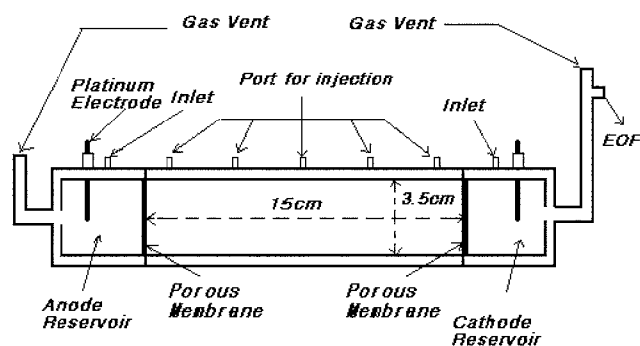Commercial kaolinite clay (kaolin), ground and passed

Fig. 1. Schematic diagram of electrokinetic reactor.

through a 0.5 mm sieve, was used for the packing material, which was intended to simulate a low permeable soil. The kaolin had a pH of 7.7, CEC of 8.9 cmol kg^{-1}, organic matter of 0.1 g kg^{-1}, 65.0 mg total-P and 0.01 mg Bray-1P kg^{-1}. The contents of total-N, NH_4-N and NO_3-N were 0.1 g kg^{-1}, 0.8 mg kg^{-1} and 4.5 mg kg^{-1}, respectively. The contents of exchangeable Al, Ca and Fe were 7.5, 1461.8 and 108.0 mg kg^{-1}, respectively. The total population of microorganism was 5×10^2 colony-forming unit (CFU) g^{-1}.

Schematic diagram of electrokinetic reactor was shown in Figure 1. The plexi-glass electrokinetic reactor is 15 cm long and 3.5 cm in diameter. Platinum electrode was inserted into each of the anode and cathode reservoir to apply a constant voltage across the column, and it was connected to each of electrode reservoirs. A 200 g of kaolin was mixed with 120 mL of distilled water and shaken vigorously. The kaolin suspension was centrifuged at 2500 rpm for 10 min and the supernatant was decanted for prevention of over-saturation and for heavy compaction. Kaolin was compacted by tapping the cell wall. The water content of the kaolin fraction separated from aqueous suspension was about 0.3 kg kg^{-1}. Kaolin specimen had a bulk density of 1.39 Mg m^{-3}, porosity of 46.5%, pore volume of 67.07 mL, and hydraulic conductivity of 1.99×10^{-8} cm s^{-1} measured by a 0.01 M NaCl aqueous solution. Electrical potential (direct current, 1 Vcm^{-1}) was applied across the electrokinetic reactor with change of time (from 3 to 12 days). In order to maintain proper pH value for bioremediation, 0.0033 M Na_2CO_3 buffer solution was used to purge the anode reservoir where hydrogen ions are generated and 0.25 M H_2SO_4 was used to purge the cathode reservoir where hydroxyl ions are generated. There was no hydraulic gradient across the glass electrokinetic reactor.

The KH_2PO_4 as inorganic P source was injected at the cathode inlet based on electro-migration theory which means that a negatively charged ion introduced near the cathode moves toward the anode and vice versa for a positively charged ion (Yeung and Mitchell, 1993), while TEP as organic P source was injected at the anode inlet based on electro-osmosis theory which means that a kind of water flow, usually having a direction toward cathode, is made when an

electrical potential is applied across a wet soil mass (Mitchell, 1993). The KH_2PO_4 and TEP solution having theoretically attainable P concentration of 100 mg kg^{-1} was injected to each electrokinetic reactor.

2.3. Fractionation of Soil Phosphorus

After completion of electrokinetic process, kaolin sample in electrokinetic reactor was divided into five parts along the normalized distance from anode. The phosphorus in each kaolin sample was fractionized following the procedures of Chang and Jackson (1956). A 1 g sample of kaolin was placed in a 100 mL centrifuge tube and extracted with 50 mL of 1 M NH$_4$Cl for 30 min on a mechanical shaker. The suspension was centrifuged and the supernatant solution was discarded for the determination of the soluble and loosely bound phosphorus. A 50 mL of neutral 0.5 M NH$_4$F is added to a 100 mL centrifuge tube again and the suspension extracted on a mechanical shaker for 1 hour.

The suspension was centrifuged and the supernatant solution was decanted for determination of aluminum phosphate. The kaolin sample saved after the extraction of aluminum phosphate was washed twice with 25 mL of saturated NaCl solution. It was then extracted with 50 mL of 0.1 M NaOH on a mechanical shaker for 17 hours. The kaolin suspension was centrifuged for 15 min at 2400 rpm and centrifuged again, if necessary, to obtain a clear solution that was decanted into another centrifuge tube for determination of iron phosphate. The decanted supernatant was added with 2 mL of 1 M H$_2$SO$_4$ and one or a few drops of concentrated H$_2$SO$_4$ until onset of flocculation of organic colloids. The suspension was then centrifuged and the clear solution was collected. The kaolin sample after extracting iron phosphate was washed with two successive aliquots of 25 mL of saturated NaCl solution. It was then extracted with 50 mL of 0.25 M H$_2$SO$_4$ for 1 hour on shaking machine. The suspension was centrifuged and the clear supernatant solution is decanted for determination of calcium phosphate. The ICP-AES was used for determination of P in the supernatant solutions that were obtained previous steps. Determination of phosphorus originated from TEP was also carried out. A 1 g sample of kaolin was placed in a 100 mL centrifuge tube, and extracted with 50 mL of 1 M NH$_4$Cl for 30 min on a mechanical shaker. The suspension was centrifuged and the supernatant solution discarded for the determination of phosphorus. The ICP-AES was also used for the determination of phosphorus in the supernatant solution.

3. RESULTS AND DISCUSSION

3.1. Batch Adsorption Experiments of Phosphorus

Variations of phosphorus concentration in supernatant were shown in Figure 2. Approximately 60.3% of phosphorus
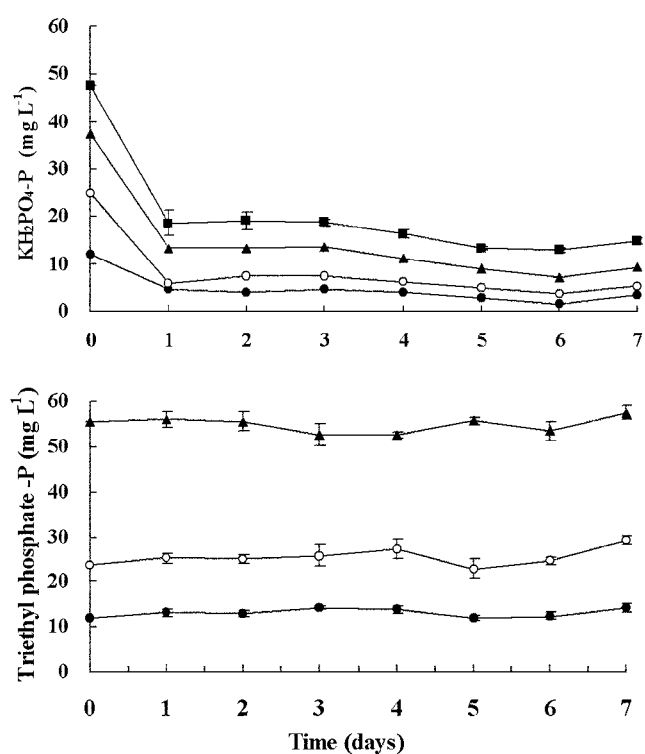

Fig. 2. Changes in phosphorus concentration in supernatant with time.

from KH_2PO_4 was adsorbed within 24 hours, and the maximum adsorption was attained at 6days after adsorption (73%). The process of sedimentary adsorption of P involves the transformation of water-soluble form of P to less soluble or insoluble one bound to cations on the soil solid phase, especially with Al^{3+}, Fe^{3+} and Ca^{2+}. Concentrations of Fe^{3+} and Al^{3+} in sediments affect the amount and rate of P adsorption (Morel et al., 1989).

The Langmuir adsorption isotherm was fitted to calculate the maximum P adsorption and the value of Langmuir constant, which were 204 mg P kg^{-1} and 0.178 L mg^{-1}, respectively (Fig. 3). The blast furnace slag, one of the industrial by-products, showed P adsorption capacity of 44,200 mg P kg^{-1} slag and the clinoptilolite material (zeolite), which is used to remove ammonium ion from wastewater, was found to have a P adsorption capacity of 2,150 mg P kg^{-1} (Sakadevan, 1998). Phosphate in soil solutions interacts extensively with soil constituents and is immediately decreased to a very low concentration due to either precipitation or adsorption. Recent experimental evidence, however, shows that hydrolytic species of Al^{3+} and Fe^{3+} are involved in the precipitation in acidic soils (Ro and Cho, 2000). On the other hand, another line of evidence suggests that phosphorus adsorbs to hydrous oxides of Fe and Al of soil particles (Haynes, 1984). In contrast, TEP showed no P adsorption in 7 days, thus suggesting useful characteristics in terms of nutrients delivery in low permeability soils.
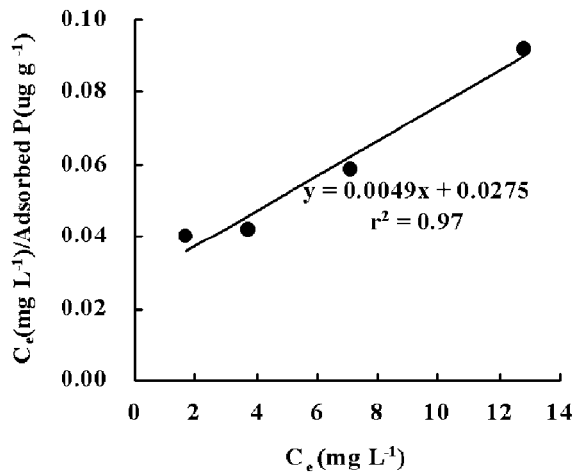
Fig. 3. Phosphorus adsorption data plotted according to the Langmuir isotherm with KH_2PO_4. The maximum adsorbed amount was 204 mg kg^{-1}, and a constant related to the binding strength was 0.178.

Fig. 5. Fractionation of phosphorus originated from KH_2PO_4 after electrokinetic process.

3.2. Electorkinetic Transport of Phosphorus

Distributions of inorganic phosphorus (KH_2PO_4) in electrokinetic reactor were shown in Figure 4. Inorganic P was not distributed uniformly along the electrokinetic reactor and most of transported phosphorus was changed to water-insoluble aluminum phosphate after 12 days of treatment, suggesting the decrease in phosphorus bioavailability. Presence of various pairs of phosphate with aluminum or iron combinations is theoretically probable, since the valences of hydroxy-aluminum or iron with orthophosphate complex species in aqueous system are variable depending on the pH of the system (Ro and Cho, 2000). Up to 9 days of elec-
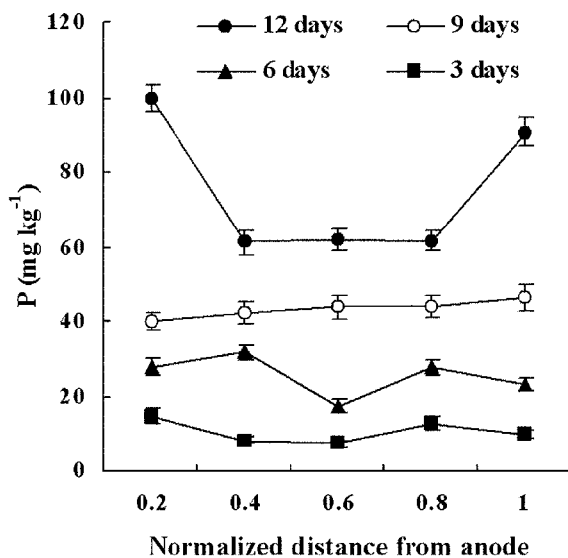
trokinetic process, calcium phosphate was the major form of inorganic P phase, and thereafter aluminum phosphate was the major form of inorganic P phase (Fig. 5), suggesting that KH_2PO_4 was not a favorable P source as a microbial nutrient in soil.

Therefore, incorporation of inorganic phosphorus form could be a limiting factor because of rapid and extensive P fixation via precipitation with Ca, Fe, or Al and low solubility and bioavailability of the products (Rubeiz et al., 1992). In contrast, the distribution of phosphorus derived from organic phosphorus (e.g., TEP) in electrokinetic reactor was quite different (Fig. 6). The advancing P front progressed with time, resulting in uniform P distribution through the kaolin column with P concentration of 100 mg kg^{-1} at 8 days. This concentration was approximately the same as the value estimated when TEP had been applied.
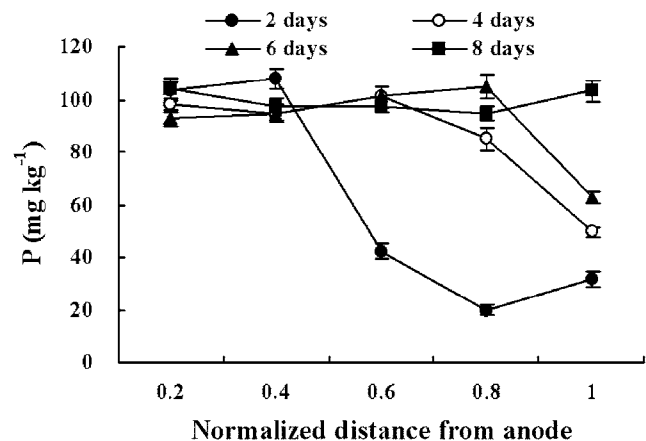

Fig. 4. Distribution of phosphorus originated from KH_2PO_4 along the electrokinetic reactor.

Fig. 6. Distribution of phosphorus originated from TEP along the electrokinetic reactor.

Unlike KH$_2$PO$_4$ TEP was delivered along the electrokinetic reactor without loss, thus suggesting that TEP would be favorable P form for efficient and uniform nutrients delivery into the biologically active zones. The excessive dosing coupled with the shortcomings of the transport processes can result in nutrient-rich areas with excessive biological growth (biofouling). Biofouling adversely impacts system implementation due to reduced conductivity by microbial growth plugging the flow paths (Rabbi et al., 2000). The uniform and efficient introduction of additives into the biologically active zones has been a bottleneck for successful implementation of *in situ* bioremediation (Suflita and Sewell, 1991).

If the input of phosphorus into the subsurface is disproportionate to that of contaminated organic compounds, phosphorus limitation could greatly reduce the ability of microbes in the lower soil profile to attenuate pollutants during their transit to the underlying groundwater, assuming that oxygen or another electron acceptor is not limiting (Environmental Protection Agency, 1985). In terms of transport, organic phosphorus such as TEP would be a more effective P source than inorganic phosphorus not only in conventional *in-situ* bioremediation but also in electrokinetic enhanced bioremediation.

4. CONCLUDING REMARKS

Batch adsorption experiments showed that approximately 60.3% of P from KH$_2$PO$_4$ was adsorbed within 24 hours, and the maximum adsorption was attained at 6 days after adsorption (73%). In contrast, TEP showed virtually no P adsorption even in 7 days, thus suggesting an alternative P source that may maintain a favorable proportion of C:N:P through the effective delivery during *in situ* bioremediation in low permeability soils. The results of electrokinetic experiment suggested that TEP, an organic P, would be transported through low permeability soils like clays without P loss. Inorganic P was not distributed uniformly along the electrokinetic reactor and most of P transported was immobilized to water-insoluble aluminum phosphates, while organic P such as TEP was delivered uniformly along the electrokinetic reactor. In terms of transport, organic P such as TEP would be a more effective P source than inorganic phosphorus not only in conventional *in-situ* bioremediation but also in electrokinetic enhanced bioremediation.

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