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Effect of electric potential on nanoiron particles delivery for pentachlorophenol remediation in low permeability soil

Effet du potentiel électrique sur la livraison de nanoparticules ferriques pour l'assainissement de sols à faible perméabilité contaminés par pentachlorophénole

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ABSTRACT

This paper examines the delivery of nanoscale zero valent iron particles (nanoiron) under different electric potentials for the remediation of a low permeable kaolin soil spiked with pentachlorophenol (1000 mg/kg of dry soil). Bench-scale electrokinetic experiments were conducted using nanoiron suspension (50-300 nm particle size; 5 g/L and 10 g/L concentrations) in the anode and applying different electric potentials (1 and 2 VDC/cm). The iron concentrations in the soil increased with increased nanoiron concentration from 5 g/L to 10 g/L in the experiments conducted with 1 VDC/cm voltage gradient for a total duration of 427 hours. The iron concentrations in the soil were further increased with higher voltage gradient (2 VDC/cm) and increased operating duration (938 hours). As the testing progressed, the transport of nanoiron particles was limited by their aggregation, settlement and partial oxidation within the anode. The electrical current and electroosmotic flow were higher in the experiments conducted with 1 VDC/cm as compared to that of experiments with 2 VDC/cm, possibly due to the combined effects of faster acidification of the soil and rapid oxidation of nanoiron particles under higher voltage gradient. PCP was partially reduced (40-50%) in all of the experiments. PCP was completely reduced near the cathode due to abiotic reductive dechlorination within the cathode. Improved strategies are needed to prevent aggregation, settlement and oxidation of nanoiron particles for enhanced remediation of PCP in soils.

RÉSUMÉ

Ce document examine la livraison de particules de fer zéro valent (nanoiron) sous différents potentiels électriques pour l'assainissement de sol kaolin à faible perméabilité contaminés par pentachlorophénole (1000 mg/kg de sol sec). Des expériences électrocinétiques ont été réalisées en laboratoire en utilisant des suspensions de particules nanoferriques (taille des particules : 50-300 nm; concentrations : 5 g/L et 10 g/L) dans l'anode et en appliquant des potentiels électriques différents (1 et 2 VDC/cm). Les concentrations de fer dans le sol ont augmenté avec l'augmentation de la concentration des particules nanoferriques à partir de 5 g/L jusqu'à 10 g/L dans les expériences menées avec 1 VDC/cm de gradient de tension, pour une durée totale de 427 heures. Les concentrations en fer dans le sol ont été de nouveau augmenté avec un gradient de tension plus élevée (2 VDC/cm) et l'augmentation de la durée d'application (938 heures). Durant la progression de l'essai, le transport de particules nanoferriques a été limitée par leur agrégation, leur tassement et leur oxydation partielle au sein de l'anode. Le courant électrique et le flux électroosmotique étaient plus élevés dans les expériences menées sous 1 VDC/cm par rapport à celles menées sous 2 VDC/cm, peut-être due aux effets combinés de l'accélération de l'acidification des sols et de l'oxydation rapide des particules nanoferriques sous un gradient de tension plus élevé. La teneur en PCP a été partiellement réduite (40-50%) dans toutes les expériences. La teneur en PCP a été complètement réduite à proximité de la cathode en raison de la déchloration réductrice abiotiques à l'intérieur de la cathode. L'amélioration des stratégies sont nécessaires pour empêcher l'agrégation, le tassement et l'oxydation des particules nanoferriques pour améliorer l'assainissement des sols contaminés en PCP.

Keywords : soil pollution, electrokinetic remediation, chlorinated organic compounds, nanoiron, clays, chemical reduction, solubilization

1 INTRODUCTION

Pentachlorophenol (PCP) was extensively used in the past for the preservation of wood and wood products, and its release into the environment caused extensive contamination of subsurface soils. PCP is relatively resistant to biodegradation, creating a persistent environmental problem. PCP aqueous solubility varies between 10 to 20 mg/L and it increases with increasing pH. PCP is toxic to humans and may target and/or damage the liver, kidney, and hematopoietic, pulmonary and central nervous systems. The toxicity and persistence of PCP in contaminated soils poses a long-term threat to public health and the environment; therefore, PCP has been listed as a priority pollutant in many countries including the USA (Keith and Telliard 1979). The remediation of sites contaminated by PCP has been a major challenge to the environmental professionals.

Various methods considered to remediate PCP in contaminated soils include soil washing, chemical oxidation,

and bioremediation; however, these methods are found either ineffective or expensive, particularly when dealing with low permeability soils. One method considered to degrade PCP is via its reaction with metallic iron. Kim and Carraway (2000) used zero valent iron and bimetallics for the dechlorination of PCP, and they concluded that zero valent iron showed the maximum affinity for the dechlorination of PCP as compared to other selected modified zero-valent iron. Nearly 50% of PCP was removed in few hours. Morales et al. (2002) reported the feasibility of using zero valent metals (Fe and Mg) for the dehalogenation of various chlorinated phenols. Marshall et al. (2002) investigated the effect of temperature and catalyst on the dehalogenation of PCP. Several other laboratory and field studies used zero valent iron (Fe^0) as an effective media to remediate certain groundwater pollutants. In recent years, research has concentrated on the potential use of nanoscale zero valent iron particles (NIP), also known simply nanoiron. The advantage of nanoiron as compared to micro-size iron or iron

filings is that it can be directly injected into the contaminated soils *in situ*. Recently, Reddy and Karri (2008a) investigated the efficiency of nanoiron to promote the reductive degradation of pentachlorophenol (PCP) in kaolin. A series of batch experiments was conducted using kaolin that was spiked with PCP at 1000 mg/kg with different contact times (1, 2, 8, 12, 24 and 48 hours) and different nanoiron concentrations (1, 2, 4, 5, 8, 10, 20, 40, 60, 80 and 100 g/L). These results showed increase in PCP reduction from 50% to 78% at one hour contact time to 40% to 90% at 24 hours contact time for different nanoiron concentrations. The PCP reduction increased with increase in concentration of nanoiron with 30% at 1 g/L to 98% at 100 g/L. There appears to be an optimal nanoiron concentration beyond which benefits are diminished. However, for *in situ* remediation applications, it is only feasible to inject dilute nanoiron slurries (below 10 g/L).

The success of *in situ* remediation using nanoiron will depend on the extent of its distribution in the soil. The delivery of nanoiron is challenging due to agglomeration and settlement of these particles as well as ineffective hydraulic delivery in low permeability soils. Electrokinetics has been investigated as a developing technology for the *in situ* removal of both organics and heavy metals as well as for the delivery of reactive agents and nutrients in low permeability soils (Reddy, 2009). Electrokinetics essentially involves applying a low electric potential across the soil, causing the contaminants transported into the electrodes due to electromigration, electroosmosis and electrophoresis processes and subsequently removed. Recently, Reddy and Karri (2007, 2008b) investigated the transport of bare nanoiron slurry in soil under electric potential and also investigated the effects of combining nanoiron with cosolvent or surfactant on the efficiency of using a nonionic surfactant and a cosolvent on enhanced stability and transport of nanoiron. Kaolin soil was used as a model low permeability soil and it was artificially spiked with PCP (1000 mg/kg). Laboratory electrokinetic experiments were conducted using deionized water and nanoiron of 50-300 nm particle size at slurry concentrations of 5 g/L and 10 g/L at the anode. Two additional experiments were conducted with 5 g/L NIP in 5% Igepal CA720 (nonionic surfactant) and 5 g/L NIP in 5% ethanol (cosolvent), respectively. All experiments were conducted at a constant voltage gradient of 1 VDC/cm. The experimental results showed that the transport of nanoiron in the soil was limited by aggregation and settlement of nanoiron in the anode. Additionally, nanoiron may have oxidized into Fe^{3+} ions under the oxygenated and low pH conditions that existed at the anode and prevented their transport into the soil. The effects of surfactant and cosolvent were insignificant. Nanoiron did not transport and contribute to PCP degradation; however, 47% to 55% of PCP was found degraded within the cathode by reductive dechlorination process.

The purpose of the present study is to investigate the effects of increased electric potential on delivery of nanoiron into low permeability soil. Bench-scale electrokinetic experiments were conducted using kaolin soil spiked with PCP at two different voltage gradients (1 and 2 VDC/cm). The experimental results were analyzed to assess the electric current, electroosmotic flow, iron transport, and PCP removal/reduction during the electric potential application. The test results helped to assess if any beneficial effects can be realized with increasing the voltage gradient on enhanced nanoiron transport and PCP remediation under electric potential.

2 EXPERIMENTAL METHODOLOGY

All experiments were conducted in electrokinetic setup that consisted of an anode reservoir, an electrokinetic cell, a cathode reservoir, a power source, and a multimeter. The electrokinetic cell was made of Plexiglas and it had an inside diameter of 3.1 cm and a total length of 12.9 cm. Each electrode compartment consisted of a valve to control the flow into the cell, a slotted

graphite electrode, and a porous stone. Small holes in the electrode compartment contained the electrode pins, and filter paper was placed between the soil sample and the electrode. The electrode reservoirs were 1.0 cm inner diameter Plexiglas tubes and were connected to the electrode compartments using Tygon tubing. There were exit ports in the electrode compartments to which thin tubes were attached to allow the escape of gas and condensate. Any condensate from these tubes was redirected to the reservoir. A power source was used to apply a constant voltage to the electrodes, and a multimeter was used to monitor the voltage and measure the current during the testing.

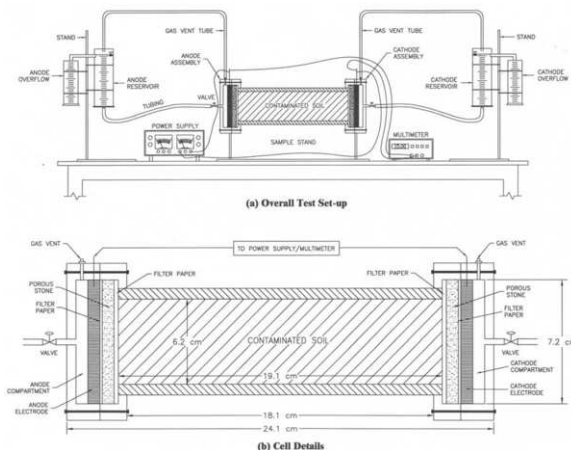


Figure 1. Schematic of electrokinetic test setup.

All of the experiments were conducted on kaolin spiked with PCP with a target concentration of 1000 mg per kg of dry soil. To spike the soil, hexane (500 mL) was used to dissolve solid PCP (1.5 g). This hexane-PCP mixture was slowly added to 1500 g of kaolin soil. Additional hexane was added so that the soil-hexane-PCP mixture could be easily stirred and blended homogeneously. The mixture was stirred with stainless steel spoons, and all mixing operations were performed within glass beakers. The purpose of this mixing technique was to distribute PCP evenly throughout the soil. The soil-hexane-PCP mixture was then placed beneath a ventilation hood for nearly a week until the hexane completely evaporated and the contaminated soil was dry. The dry soil was then mixed with 35% deionized water to mimic natural moisture condition and was compacted into the electrokinetic cell in uniform layers using hand-held compactor. After packing the cell, filter paper, graphite electrodes and porous stones were placed on both sides of the sample along with electrode compartments. The weight of all cell components was recorded before and after packing wet spiked soil.

The nanoiron used for this study was produced using the patented method by Uegami et al. (2003) and they consisted of an elemental iron core (α -Fe) and a magnetite shell (Fe_3O_4) in approximately same amounts by weight. The aqueous nanoiron suspension with 25.6% (by weight) solid concentration had density of 1.27 g/mL. The average particle size and surface area of nanoiron particles were 70 nm (0.07 μ m) and 28.8 m^2/g , respectively. The nanoparticles have slight negative surface charge. Tests 1 and 2 were conducted with 5 g/L and 10 g/L, respectively, under voltage gradient of 1 VDC/cm, while Tests 3 and 4 were the same as Tests 1 and 2 except that higher voltage gradient of 2 VDC/cm was used for these tests. Anode reservoir was filled with nanoiron, while cathode reservoir was initially filled with deionized water. Equal liquid levels within cathode and anode reservoirs were maintained during testing to avoid hydraulic gradient across the soil sample.

During the application of electric potential, current and electroosmotic flow were measured regularly. At the end of each test, aqueous solutions from the anode and cathode

reservoirs and the electrode assemblies were collected separately and the volumes were measured. The soil specimen was extruded and divided into five sections using a mechanical extruder. Each section was weighed and placed in a separate glass jar. The pH of the soil sections and electrode solutions were measured according to USEPA (1986). The PCP concentration in the soil was determined using the Soxhlet procedure as per the USEPA test method 3540C followed by gas chromatography (USEPA, 1986). The iron concentration in the soil was determined by the acid digestion as per the USEPA 3050 procedure followed by atomic absorption spectrophotometry.

3 RESULTS AND ANALYSIS

The electric current increased rapidly during the first few hours in all the four tests, and then decreased over a period of time (Figure 2). The initial higher current values are due to high concentration of ions in the pore water as a result of dissolution of salts attached with the dry soil particles. As the ions electromigrated towards the electrodes, their concentration in pore water decreases, resulting in a decreased current. During initial stages of testing (<100 h), lower current was measured in higher voltage experiments which may be attributed to rapid oxidation of nanoiron at the anode. However at later stages, the current values were similar and gradually decreased with time in both 1 VDC/cm and 2 VDC/cm tests.

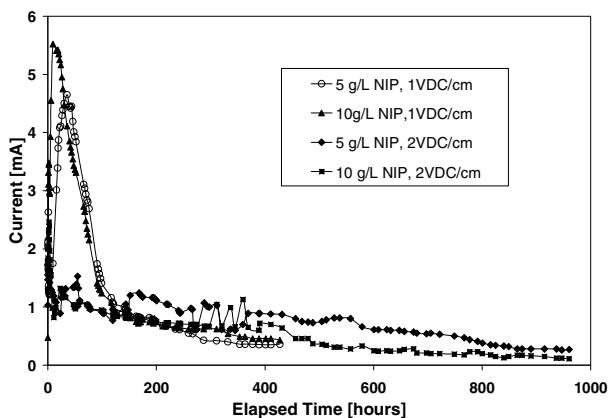


Figure 2. Current measured during testing.

Figure 3 presents the cumulative electroosmotic flow for all tests conducted. Both Tests 1 and 2 conducted with 5 and 10 g/L NIP, respectively, under 1 VDC/cm resulted in higher flow rate with approximately 2 pore volumes of flow within 427 days, while the Test 3 conducted with 5 g/L NIP and Test 4 conducted with 10 g/L NIP, both under 2 VDC/cm, resulted in lower flow rate with approximately 1 and 1.5 pore volumes of flow even after longer test duration of 937 hours. These results are consistent with the measured current values. The higher voltage gradient causes faster production of H^+ ions, leading rapid decrease in the soil pH which results in reduction in electroosmotic flow. The low flow under higher voltage gradient also attributed to faster oxidation of nanoiron in the anode and clogging of soil pores near the anode by the nanoiron particles.

Figure 4 shows the pH distribution in the soil after the completion of the experiments. The normalized distance is defined as the distance to the center of soil section from the anode divided by the total length of the soil sample. Generally, the electrolysis of water results in the formation of H^+ ions (low pH solution) at anode and OH^- ions (high pH solution) at cathode, and, primarily due to electromigration, these ions tend to migrate towards the oppositely charged electrode(s). Thus, Figure 4 illustrates that a strong acidic front of solution was generated by the electrolysis reaction at the anode and its

transport into the soil caused significant decrease in pH in all sections except in the section closer to the cathode. The higher flow in the low electric potential tests assisted in increased transport of acid base towards the cathode, leading to lower pH values as compared to that of the high electric potential tests.

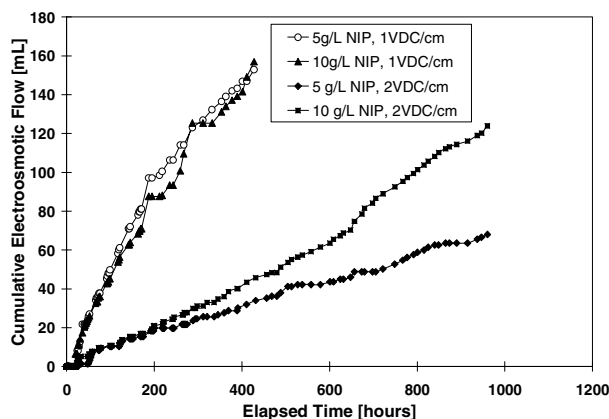


Figure 3. Electroosmotic flow measured during testing.

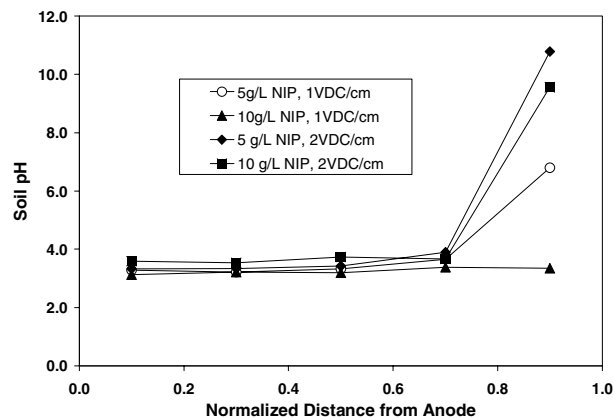


Figure 4. Final soil pH after testing.

Effluent samples were collected at different time intervals for all the four tests and were analyzed for iron and PCP concentrations. These results revealed that no significant masses of iron and PCP were found. After the completion of experiments, the soil samples were sectioned into five equal parts. The iron concentrations determined for each of these sections are plotted together in order to elucidate the delivery of nanoiron within the soil using electrokinetics. Figure 5 shows these residual iron distributions in the soil after the completion of electrokinetic tests. Results show that the residual iron concentrations in the soil are higher near the anode and they decrease with distance from the anode.

The variation in iron concentrations shows that some nanoiron was transported into the soil at least during the initial stages of testing when nanoiron was stable and not oxidized. The initial higher electroosmotic flow rate may also have promoted the transport of nanoiron. At later stages of testing, nanoiron may be oxidized at the anode into Fe^{+3} ions which cannot electromigrate from the anode.

Figure 6 shows the distribution of PCP remaining in the soil after the testing. Before applying the electric potential, the initial concentration of PCP in the soil for all the tests was 815 mg/kg in the soil. It should be noted here that the targeted PCP concentration was 1000 mg/kg, but some of PCP evaporated with hexane during spiking and drying procedure resulting in a lower PCP concentration. At the end of the testing, PCP concentration was lower than the initial value throughout the soil in all the tests except in test with 10 g/L NIP with 1

VDC/cm in which concentration was higher than the initial value. In general, PCP concentration decreased from anode towards the cathode end. PCP was not detected in the last soil section near the cathode in all the tests.

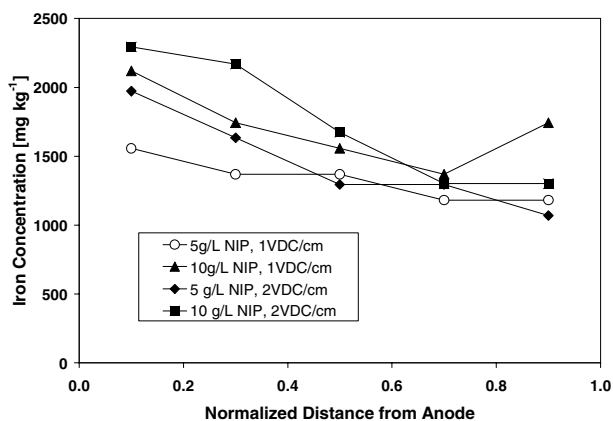


Figure 5. Iron concentrations in soil after testing.

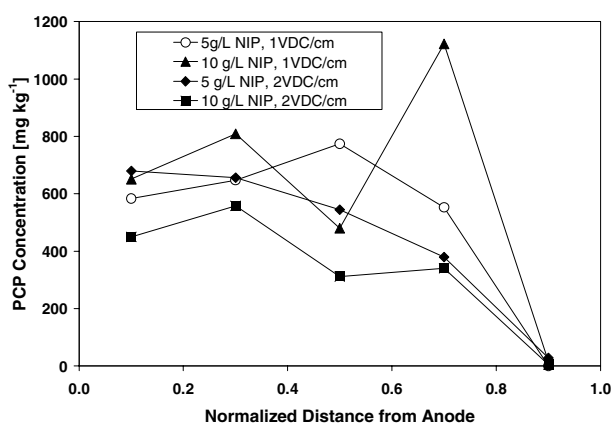


Figure 6. PCP concentrations in the soil after testing.

These results indicate that PCP transported towards the cathode due to electroosmotic advection. The extent of transport depends on the solubility of PCP. The solubility of PCP decreases with decrease in soil pH. The decreased pH due to the application of electric potential may have lowered the solubility of PCP. Under the applied electric potential, soil pH changes spatially and temporally from the anode to the cathode resulting in non-uniform distribution of soluble PCP in the soil. More PCP is expected to be present near the cathode due to relatively high pH conditions, allowing the transport of PCP into the cathode. At the beginning of the testing, the soil pH was high and PCP was soluble near the anode, causing the transport of PCP towards the cathode. However, as the low pH conditions were generated due to electrolysis reactions, the solubility of PCP was reduced, retarding the transport of PCP towards the cathode. Once the PCP is transported into the cathode, it undergoes reductive dechlorination.

Overall, this study showed that approximately 40-50% of PCP was degraded due to reductive dechlorination near the cathode in all the tests. In all of the tests, dechlorination due to nanoiron appears to be minimal. Most of the PCP degradation is attributed to dechlorination in the cathode and the extent of dechlorination was dependent on the amount of PCP transported into the cathode. Therefore, new strategies are needed to enhance stability and delivery of nanoiron into the soil and also to enhance transport of PCP into the cathode through sustained electroosmotic flow. Such improved electrokinetic system is being investigated in an on-going study.

4 CONCLUSIONS

Based on the experimental results of this study, the following conclusions may be drawn: (1) Increased voltage gradient resulted lower current and low electroosmotic flow. Nevertheless, substantial electroosmotic flow was induced in the low permeability soil by applying electric potential even when nanoiron slurry is placed in the anode; (2) The transport behavior of nanoiron with 1 or 2 VDC/cm was similar, but higher amount of iron was transported under higher voltage gradient. Nanoiron transport was observed near the anode regions of the soil in all of the tested conditions; however, it was limited by the aggregation and settlement as well as partial oxidation under oxygenated and low pH conditions in the anode; (3) The soluble PCP in the soil migrated towards the cathode due to electroosmotic advection. However, the low soil pH conditions resulting from the applied electric potential may have reduced the solubility and migration of PCP in the soil. PCP migrated into cathode was degraded due to reductive dechlorination.; and (4) Because of low transport of nanoiron and low PCP removal and degradation, new strategies to design electrokinetic delivery system to prevent agglomeration, settlement and oxidation of nanoiron are needed.

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