Reactivity of Aluminum Lactate-Modified Nanoscale Iron Particles with Pentachlorophenol in Soils

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Abstract

Due to the hindered transport of nanoscale iron particles (NIP) in the subsurface caused by the agglomeration and adsorption of NIP during transport, the NIP surface has to be modified to improve the transport of NIP in the subsurface. This study assessed the effectiveness of surface-modified NIP for *in situ* degradation of contaminants using aluminum lactate as the modifying agent, where aluminum lactate had been earlier shown to be an effective dispersant for enhanced transport of modified NIP in the subsurface. The reactivity of bare-NIP and lactate-modified NIP (LM-NIP) was investigated using pentachlorophenol (PCP) as a representative chlorinated hydrophobic organic contaminant in kaolin and field sand as low permeability clayey soil and high permeability soil, respectively. Kaolin and field sand were spiked at 100 mg/kg PCP and at 89 mg/kg PCP, respectively. NIP dosages of 4, 10, 20, 50, 75, and 100 g/L were applied for a reaction period of 24 h. For the bare-NIP dosage of 100 g/L, PCP degradation of 98% and 99% was obtained in 24 h for field sand and kaolin, respectively. The effect of reaction time on reactivity of bare-NIP and LM-NIP was evaluated using a lower NIP dosage of 4 g/L for 1, 2, 4, 7, and 14 days. After 14 days, greater PCP degradation occurred in bare-NIP systems than in LM-NIP systems, where 95% and 99% degradation was obtained for field sand and kaolin with bare-NIP, respectively, whereas 90% and 91% degradation was obtained for field sand and kaolin with LM-NIP, respectively. Differences in PCP degradation between bare-NIP and LM-NIP diminished with time more rapidly for field sand than for kaolin. For both field sand and kaolin, nearly complete dechlorination of PCP to phenol occurred with bare-NIP with a more rapid dechlorination in field sand than in kaolin.

Key words: pentachlorophenol; nanoscale iron particles; aluminum lactate; kaolin; field sand; reactivity

Introduction

MANY SITES AROUND the globe are contaminated with chlorinated organic compounds such as pentachlorophenol (PCP), trichloroethylene, and trichloroethane. The contaminants can reside in the groundwater, surface water, or soils. PCP has been used extensively as a general biocide for a variety of purposes such as agriculture and timber preservation. Worldwide use of PCP has led to severe contamination problems particularly around former timber treatment plant sites. PCP was widely used as a wood preservative in the United States for several decades, and currently there are several Superfund sites (surface and subsurface soils) contaminated with PCP, which is considered a priority pollutant by the U.S. Environmental Protection Agency (USEPA) (Keith and Telliard, 1979). Various technologies for remediation of

PCP-contaminated soils include soil washing, chemical oxidation, and bioremediation; however, these methods are either ineffective or expensive for subsurface soils.

Nanotechnology has the potential to clean up PCP-contaminated soils and groundwater both *in situ* and *ex situ*. Nanotechnology for environmental remediation consists of the use of nanoscale zero-valent iron particles to react with organic and inorganic contaminants. The small size of the particles and a vast surface to volume ratio makes them more reactive and versatile. This is applicable to a wide variety of contaminants. The reactivity of organic compounds with nanoscale iron particles (NIP) is dependant on the dosage of NIP, initial concentration of compounds, and reaction time (Choe *et al.*, 2001; Okinaka *et al.*, 2005; Yang and Lee, 2005). Wang and Zhang (1997) indicated that NIP are able to remediate organic compounds faster than microscale zero-valent iron particles. Tratnyek and Johnson (2006) reported that iron nanoparticles possess high reactivity due to their high surface area, greater density of reactive sites, and higher intrinsic reactivity on reactive sites. The utility of zero-valent iron as an effective reductant for treatment of contaminants is due to the generation of several types of reducing species

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during iron corrosion. The standard reductive potential of zero-valent iron is 447 mV [$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$; $E_h^0 = 447 \text{ mV}$]. Among possible reduction reactions involving iron and a halogenated organic compound, RX, dissolved in the aqueous phase, the predominant reaction between dissolved RX (e.g., PCP) and zero-valent iron is the heterogeneous reaction occurring at the surface of the metal rather than the reactions with hydrogen and ferrous iron in the aqueous phase:

Kim and Carraway (2000) found microscale zero-valent iron to be more efficient than other modified zero-valent iron used in their study for dechlorination of PCP, where nearly 50% of the PCP was removed in a few hours. Morales *et al.* (2002) showed the affinity of microscale zero-valent iron for the dehalogenation of chlorinated phenols. Cheng *et al.* (2006, 2008) showed that different isomers of chlorophenol (2-CP, 3-CP, and 4-CP) were dechlorinated by NIP and removal increased from 4-CP to 2-CP. The percent removal of 4-CP, 2-CP, and 3-CP was, respectively, 25.6%, 32.0%, and 39.9%, where the position of the halogens did have an effect on its removal rate. In addition, temperature affected the rate of removal and reaction pathway as dechlorination was predominant at higher temperature (30°C), whereas adsorption was the leading process at low temperature of 10°C. The presence of dissolved oxygen can affect the reactivity of NIP with the target contaminants (Tratnyek and Johnson, 2006). The effect of ionic strength on the reactivity of NIP is minimal at high concentration of NIP (Okinaka *et al.*, 2005). Factors such as pH, redox potential, temperature, anaerobic or aerobic conditions, type of organic compound, dispersed NIP, and dosage of NIP affect the reaction rate.

There have been limited studies on the reactivity of NIP with organic contaminants in soils. NIP can be injected directly into the soil to react with the contaminant *in situ*. For example, 90% of PCBs in aqueous solution was degraded as compared with 38% of PCBs, which were degraded in soils and the difference in reaction rate was due to the difficulty of the PCB in diffusing from the surface of the soil particles to the nanoscale iron surface for effective reaction (Varanasi *et al.*, 2007). Reaction rate in soils also increases with increasing iron concentration and with increasing reaction time and reaction temperature (Varanasi *et al.*, 2007). The potential of reaction with organic contaminants in soils is better for NIP than for microscale iron.

Surface-modified NIP

Due to agglomeration of the bare-NIP they have limited transport in soil, making it difficult to distribute into the source zone. Bare-NIP is not well dispersed, but modified NIP is more dispersed and homogeneous, and therefore a strong contender for *in situ* remediation (Kanel and Choi, 2007; Saleh *et al.*, 2007; Reddy *et al.*, 2008).

To directly assess the enhanced transport of NIP in soils, we conducted a systematic study to evaluate the effectiveness of different modifiers or dispersants (Cameselle *et al.*, 2008). Eight different dispersants (three types of lactate, two polymers, and three cyclodextrins) at different concentrations were tested. The dispersants tested were aluminum lactate, sodium lactate, ethyl lactate, polyacrylic acid, aspartic acid,

methyl β -cyclodextrin, beta-cyclodextrin, and hydroxyl propyl-beta-cyclodextrin. The zeta potential of NIP with various surface modifying agents was measured, showing that the zeta potential of bare-NIP was $41.7 \pm 2.3 \text{ mV}$. The influence of the dispersants was found to vary depending on the chemical nature of the dispersant and the electrical charge of the ions in solution. Aluminum lactate released Al^{3+} into the solution, resulting in a reduction of the modified NIP zeta potential from 37.7 ± 1.8 to $9.5 \pm 0.7 \text{ mV}$ for NIP modified with 2% and 15% aluminum lactate, respectively.

Several soil column experiments using NIP modified with the above-mentioned dispersants were conducted using field sand as the porous media. The study showed that 10% aluminum lactate-modified NIP (LM-NIP) exhibited the highest (93%) elution of the modified NIP from the field sand. On the basis of the results from column experiments and zeta potential measurements, 10% aluminum lactate was selected as suitable dispersant for NIP to enhance transport in soils. Lactate is considered a green compound (environmentally benign) and is relatively inexpensive (Subramanian *et al.*, 2010). Moreover, it may enhance the bioremediation of contaminants in soils, making it a favorable alternative for long-term residual treatment if relied on biodegradation.

In this study the degradation of PCP was investigated using bare-NIP and aluminum LM-NIP. The effects of NIP dosage, reaction period, soil type, and aluminum lactate on reactivity of NIP with PCP were examined.

Materials and Methods

Characteristics of NIP

The NIP used in this study was obtained from Toda Kogyo. The particles had an average diameter of 70 nm (with a range of 50–300 nm), pH of 10.7, and BET surface area of $37.1 \text{ m}^2/\text{g}$. On the basis of X-ray diffraction, the NIP are found to consist of an elemental iron core (α -Fe) and a magnetite shell (Fe_3O_4) with $\sim 50 \text{ wt}\%$ α -Fe core and $50 \text{ wt}\%$ Fe_3O_4 . The average particle size determined with a scanning electron microscope is 70 nm. The density of the aqueous NIP particle suspension is 1.27 g/mL at solids concentration of $25.6 \text{ wt}\%$. The sulfur content is $\sim 4,500 \text{ mg/kg}$ and it originates from the ferrous sulfate starting material used for the production of NIP. These particles are manufactured in bulk and available presently at a cost of \$25 to \$30 per pound. Because of the characteristics of NIP as relatively environmentally benign, NIP have been deemed suitable for subsurface contaminant remediation. The main properties of these are summarized in Table 1. These

TABLE 1. PROPERTIES OF NANOSCALE IRON PARTICLE

Coercive force (Hc)	408 Oe
Mass magnetization (σ_s)	149.6 emu/g
σ_p/σ_s (ratio of ferromagnetism and antiferromagnetism)	0.152
pH	10.7
Surface area (BET)	$37.1 \text{ m}^2/\text{g}$
Electrical conductivity	$2.29 \times 10^2 \mu\text{S}/\text{cm}$
Particle size	50–300 nm
Aqueous suspension	20–30 wt%
Density of aqueous slurry	1.2–1.3 g/mL

Data provided by TODA Kogyo (Japan).

NIP possess electromagnetic properties (Liu *et al.*, 2005; Okinaka *et al.*, 2005).

Chemicals

PCP was used to spike the soils. PCP [MW = 266.5] was obtained from Aldrich Chemicals. PCP [C_6Cl_5OH] is a hydrophobic organic compound with a log K_{ow} of 5.0 and an aqueous solubility of 14 mg/L at 25°C. The aluminum lactate [$C_9H_{15}AlO_9$; MW = 294] used for surface modification of NIP was obtained from Aldrich Chemicals. A simulated groundwater solution was prepared in the laboratory using de-ionized water; this solution contained sodium bicarbonate (0.006 M), calcium chloride (0.002 M), and magnesium chloride (0.001 M). The pH, total dissolved solids, and electrical conductivity of the simulated groundwater solution were 7.8, 500 mg/L, and 1,020 $\mu S/cm$, respectively.

PCP-spiked soils

As mentioned earlier, field sand was used for this study to represent highly porous media and kaolin was used as low permeability soil. The properties of field sand and kaolin are shown in Table 2. The field sand had an organic content of 0.8%, whereas the kaolin had no organic content. About 600 mL hexane was used to dissolve 100 mg of solid PCP. To ensure all the PCP solids were dissolved, the PCP-hexane mixture was placed on a magnetic stirrer for about 45 min. Then, 1 kg of soil was weighed in a large glass beaker. After mixing the soil-PCP-hexane mixture for 30 min, the mixture was placed in a ventilation hood nearly 7 days for the mixture to dry. During the drying period the soil mixture was mixed regularly to ensure uniform drying.

Reactivity experiments

A series of batch experiments was conducted using kaolin and field sand soils spiked with PCP at 100 and 89 mg/kg, respectively. Different NIP dosages (4, 10, 20, 50, and 100 g/L) and different reaction times (1, 2, 4, 7, and 14 days) were

applied to evaluate the effect of NIP dosage and time on PCP degradation in soils. The experiments were conducted in 50 mL bottles at a soil:solution mixing ratio of 1 g:5 mL. Thus, 25 mL NIP solution was added to 5 g of spiked soil. The samples were placed in a rotating tumbler for 1, 2, 4, 7, and 14 days. In preparing the bare-NIP solution, a certain amount of NIP slurry was weighed on the analytical balance and mixed with 1 liter of the groundwater solution and shaken well to ensure homogeneous mixing. Aluminum LM-NIP were prepared by the addition of solid aluminum lactate to a known weight of NIP slurry to achieve a 10% concentration (w/w) of aluminum lactate; the mixture of NIP and aluminum lactate was then shaken with a vortex mixture for several minutes before addition to the groundwater solution. After the reaction period, the NIP-soil slurry was centrifuged at 7,000 rpm for 10 min to separate the solution from the soil. The supernatant solution and the soil were analyzed for PCP and phenol. All experiments were carried out in triplicates.

Chemical analysis

After separation of soil and solution, the soil was extracted with solvent for 24 h using 1:3 (v/v) mixture of water and ethanol (Khodadoust *et al.*, 1999). The extracts were then analyzed for PCP using gas chromatography (GC) according to USEPA method 8041 (USEPA, 1996). The aqueous supernatant solutions were filtered and acidified with HCl to less than pH 2 before liquid-liquid extraction into hexane followed by injection into GC. The extracts and supernatant solutions were also analyzed for phenol using GC according to USEPA method 8041.

Results

The degradation of PCP as a function of bare-NIP dosage is shown in Fig. 1a and b for field sand and kaolin, respectively. These results show that greater degradation of PCP occurred in 24 h with increasing dosage of bare-NIP from 4 to 100 g/L. The degradation in field sand increased from 87% for 4 g/L NIP to 98% for with 100 g/L NIP. The degradation in kaolin increased from 85% with 4 g/L NIP to 99% with 100 g/L NIP. For both field sand and kaolin, nearly complete degradation of PCP was obtained with 100 g/L bare-NIP; similar results were obtained by Reddy and Karri (2008), who reported that higher NIP concentrations increased the removal of PCP from soil, where near 100% destruction of PCP in kaolin was obtained with 100 g/L bare-NIP. The reactivity of bare-NIP with PCP was greater by 2%–3% for kaolin than for field sand at higher dosages of NIP. For both field sand and kaolin, there was a greater increase in reactivity from 4 to 20 g/L dosage of NIP followed by a lesser increase in reactivity from 20 to 100 g/L of bare-NIP. The pH values of the field sand and kaolin systems are also shown in Fig. 1a and b, respectively. The pH data show that the application of larger dosages of bare-NIP led to higher pH values for both field sand and kaolin. For field sand, the pH increased from 7.67 at 4 g/L NIP dosage to 8.84 at 100 g/L NIP dosage. For kaolin, the pH increased from 8.19 at 4 g/L NIP dosage to 9.59 at 100 g/L NIP dosage. The pH of the kaolin system was greater than the pH of the field sand system.

To compare the reactivity of the smallest dosage of NIP with reaction time to the higher reactivity of the larger dosages of NIP in 24 h, the reactivity of NIP with PCP was

TABLE 2. PROPERTIES OF FIELD SAND AND KAOLIN

Property	Field sand	Kaolin
Mineralogy	Quartz	Kaolinite: 100%, Muscovite: trace, Illite: trace
Particle size distribution (ASTM D 422):		
Gravel (%)	0.1	0
Sand (%)	98.1	4
Silt (%)	1.7	18
Clay (%)	0.1	78
Specific gravity (ASTM D 854)	2.71	2.52
Hydraulic conductivity (cm/s) (ASTM D 2434 and ASTM D 5084)	2.67×10^{-3}	1.0×10^{-8}
pH (ASTM 4972)	7.5	4.9
Organic content (%) (ASTM D 2974)	0.8	~0
USCS classification (ASTM D 2487)	SP	CL

FIG. 1. Degradation of PCP as a function of bare-NIP dosage in (a) field sand and (b) kaolin. NIP, nanoscale iron particles; PCP, pentachlorophenol.

evaluated as a function of reaction time for up to 14 days using a bare-NIP dosage of 4 g/L. The same testing was performed using 4 g/L LM-NIP. The results of reactivity of NIP with PCP as a function of time and surface modification are shown in Fig. 2a and b for field sand and kaolin, respectively. The PCP degradation data presented in Fig. 2a and b show that greater destruction of PCP in both soils was obtained with bare-NIP than with LM-NIP. The PCP degradation with LM-NIP after 1 day was less than the reactivity with bare-NIP, but the PCP degradation increased after 14 days for both field sand and kaolin. For field sand the degradation with LM-NIP was 79% after 1 day but increased to 90% after 7 days, whereas the degradation with bare-NIP increased from 87% after 1 day to 93% after 7 days. Thus, the difference in reactivity between NIP and LM-NIP was larger initially but diminished after 7 days for the field sand systems. For kaolin, although the degradation with LM-NIP increased with time, it was appreciably less (10% to 12%) than the degradation with bare-NIP from 2 to 14 days of reaction. There was no significant increase in PCP degradation in field sand for both bare-NIP and LM-NIP systems from 4 to 14 days, whereas there was no significant increase in PCP degradation in kaolin for bare-NIP system from 7 to 14 days. Thus, the difference in reactivity between bare-NIP and LM-NIP did not diminish as much with time for kaolin.

The pH of the soil-NIP systems was measured as a function of time. The pH data are shown in Fig. 3a and b for field sand and kaolin, respectively. The pH data show that the pH values

FIG. 2. Degradation of PCP as a function of reaction time using 4 g/L bare-NIP and modified NIP in (a) field sand and (b) kaolin.

for the bare-NIP systems were higher than the pH values for the LM-NIP systems for both field sand and kaolin. The data also show that the difference in pH values between the bare-NIP and LM-NIP systems were greater for kaolin than for field sand, where the bare-NIP-kaolin systems had the largest pH values (>8) and the LM-NIP-kaolin systems the lowest pH values (<6.5). For both field sand and kaolin systems with LM-NIP, the pH values increased between 1 and 4 days but remained relatively unchanged between 4 and 14 days. For field sand-bare-NIP system, the pH increased from 1 to 2 days, decreased from 2 to 4 days, and remained constant thereafter. For kaolin-bare NIP system, the pH decreased slightly from 1 to 2 days, and remained relatively unchanged thereafter. For all pH readings, the variation in pH of the triplicate samples was quite small; therefore, no error bars have been shown for pH.

Discussion

Effect of bare-NIP dosage on PCP degradation

The data in Fig. 1 show that degradation of PCP increased with increasing bare-NIP dosage.

For bare-NIP dosages, the greater reactivity of NIP at higher NIP dosages was due to the presence of greater NIP

FIG. 3. pH as a function of reaction time using 4 g/L bare-NIP and modified NIP in (a) field sand and (b) kaolin.

surface area. The efficiency of PCP degradation relative to the dosage of bare-NIP depends on the available NIP reactive surface area. The degradation of PCP normalized to the dosage of NIP is shown as a function of NIP dosage in Fig. 4a and b for field sand and kaolin systems, respectively. The results presented in Fig. 4 show that the efficiency of NIP for PCP degradation decreased markedly for both soils with increasing dosage of NIP. The results indicate that for both field sand and kaolin, the rate of PCP degradation relative to NIP dosage declined appreciably from 4 to 20 g/L NIP followed by slow decline between 20 and 100 g/L NIP. The drastic decline between 4 and 20 g/L NIP indicates that PCP degradation was most efficient at 4 g/L NIP dosage among the applied NIP dosages. The slow decline between 20 and 100 g/L NIP indicates that the application of NIP above the 20 g/L dosage is inefficient. The nonlinear regression of data using a first-order exponential decay equation was carried out as follows:

$$\{(C/C_0)/D\} = \{(C/C_0)/D\}_{\max} [e^{-k_{\text{eff}} D}]$$

where D (g/L) and k_{eff} (L/g) were the bare-NIP dosage and the degradation efficiency coefficient, respectively. The k_{eff} values were 0.1268 ± 0.0089 and 0.1667 ± 0.0090 L/g for field sand and kaolin, respectively, and the $\{(C/C_0)/D\}_{\max}$ values

FIG. 4. NIP dosage normalized degradation of PCP in (a) field sand and (b) kaolin.

were 0.0512 and 0.0766 for field sand and kaolin, respectively. The results indicate that the decrease in efficiency of PCP degradation relative to bare-NIP dosage was greater for kaolin than for field sand.

Effect of pH on PCP degradation

For equivalent mass of bare-NIP (equivalent bare-NIP surface area), the data shown in Fig. 1 indicate that PCP degradation was greater for kaolin than for field sand. The effect of pH on reactivity is another factor in addition to the availability of greater reactive surface (sites) of NIP at higher NIP dosages. For an equivalent dosage of bare-NIP in field sand and kaolin systems, the PCP degradation was affected by the pH of the soil-NIP systems. PCP is an ionizable organic compound with a pK_a value of 4.7 that dissociates with respect to pH; hence, the desorption and the subsequent degradation of PCP were affected by pH. Greater desorption of PCP would lead to greater degradation. The bare-NIP solution was very alkaline with a pH of 10.7. The pH of the NIP-kaolin systems was higher than the pH of the NIP-field sand systems, whereas the pH of the kaolin soil was acidic (pH 4.9) and lower than the pH of the field sand, which was neutral-alkaline (pH 7.5) as shown in Table 2. The higher pH observed

in NIP-kaolin systems was due to the low buffering capacity of the kaolin, which upon contact with the alkaline bare-NIP solution increased to pH values between 8.19 and 9.59, whereas the pH of NIP-field sand systems ranged from 7.67 to 8.84 (versus a field sand pH of 7.5). The higher pH of the NIP-kaolin systems would be conducive to a greater desorption of PCP from kaolin.

The PCP degradation data in Fig. 2a and b and the pH values presented in Fig. 3a and b show that greater degradation occurred for systems with higher pH values; more degradation was observed for bare-NIP-kaolin system (higher pH) than for the bare NIP-field sand system (lower pH), whereas more degradation was observed for LM-NIP-field sand system (higher pH) than for LM-NIP-kaolin system (lower pH). The pH of the bare-NIP solution was high (10.7), whereas the pH of the LM-NIP slurry was much lower due to the acidity of aluminum lactate. Two factors may have contributed to the effect of pH on the reactivity of NIP with PCP, whereas the lower pH setting increased the corrosion rate of NIP; thus, generating more electrons for reductive dechlorination of PCP, the desorption, and subsequent degradation of PCP were favored at higher pH values, as evidenced by the greater degradation of PCP with bare-NIP in kaolin (higher pH) rather than in field sand (lower pH). The difference in reactivity between bare-NIP and LM-NIP diminished after 7 days for field sand, whereas the difference in reactivity between bare-NIP and LM-NIP did not diminish with time for kaolin. The smaller difference in pH values of the bare-NIP and LM-NIP systems for field sand (7.6 vs. 7.0) and the larger difference in pH values of the bare-NIP and LM-NIP systems for kaolin (8.0 vs. 6.5) may have attributed to the smaller and the large differences in PCP degradation with time for the field sand and kaolin systems, respectively.

Effect of dispersant and reaction period on PCP degradation

The PCP degradation data presented in Fig. 2a and b for field sand and kaolin, respectively, show that PCP degradation in general increased with time. The degradation in field sand did not increase appreciably from 4 to 14 days with bare-NIP and LM-NIP, whereas the degradation in kaolin continued to increase from 4 to 7 days with bare-NIP and continued to increase from 7 to 14 days with LM-NIP. The continued degradation of PCP in the kaolin/LM-NIP system indicate that degradation was hindered by the surface desorption of PCP from kaolin at lower pH. The longer contact time allowed for the continued desorption and degradation of PCP in the kaolin/LM-NIP system.

The oxidation-reduction potential (ORP) for both NIP and LM-NIP was measured for NIP-field sand systems with reaction period. The ORP for the bare-NIP systems was about -480 mV for 1 day and increased to $+200$ mV within 4 days, whereas the ORP for the LM-NIP systems was about -500 mV after 1 day and increased to about $+100$ mV after 4 days. Both systems were very reducing for the first day but became much less reducing within 2 days. This increase in ORP may have contributed to the decrease in reaction rate after 2 days in field soil systems. The ORP of the LM-NIP system was lower (100 mV) than that of bare-NIP system (200 mV) for the period from 4 to 14 days, indicating that the presence of aluminum

lactate in the NIP solution led to moderately greater reducing conditions after the initial rapid reaction period of the first 2 days. The coating of the NIP surface with aluminum lactate also hindered the reactivity of LM-NIP despite the lower pH setting in the presence of aluminum lactate. Other authors have reported similar trends whereby the addition of dispersant decreased the rate of reactivity (Saleh *et al.*, 2007; Yang *et al.*, 2007). Tratnyek *et al.* (2001) reported that the reduction of nitrobenzene and trichloroethylene was subdued by the presence of field organic matter.

Phenol production and PCP dechlorination

The degradation of PCP occurred via reductive dechlorination (Khodadoust *et al.*, 1997), where the higher chlorinated compound is reduced to lower chlorinated compounds. For PCP (penta-CP), the general dechlorination pathway is as follows:

In our study, the production of phenol was monitored with time to determine the dechlorination activity for bare-NIP and LM-NIP systems for field sand and kaolin. While phenol was detected in all samples, no tetra-CPs and tri-CPs were detected. The production of phenol per mole of PCP degraded as a function of time is shown in Fig. 5a and b for field sand and kaolin systems, respectively, using 4 g/L NIP. The phenol production data presented in Fig. 5a and b show that nearly complete dechlorination of PCP occurred in both the field sand and kaolin systems after 14 days, where the ratio (mole phenol/mole PCP) becomes nearly 1.0 . The data also indicate that the nearly complete dechlorination of PCP occurred faster in the field sand systems (within 4 days) than in the kaolin systems (within 14 days).

The data were fitted to a first-order rate equation for the increase in the production of phenol with time:

$$[C_{\text{phenol}}/C_{\text{PCP}}](t) = [C_{\text{phenol}}/C_{\text{PCP}}]_{\text{max}}(1 - e^{-kt}),$$

where $[C_{\text{phenol}}/C_{\text{PCP}}]$ is the mole of phenol produced per mole of PCP degraded and k is the first-order rate constant. The rate constants were 0.792 ± 0.032 and 1.138 ± 0.119 d^{-1} for bare-NIP and LM-NIP in field sand systems, respectively, and 0.402 ± 0.084 d^{-1} for bare-NIP in kaolin system. At a 95% confidence interval, comparison of the rate constants for field sand systems resulted in a p -value of 0.021 (<0.05), indicating that the rate of phenol production was significantly faster for LM-NIP than for bare-NIP in field sand systems. Similarly, at a 95% confidence interval, comparison of the rate constants for kaolin and field sand systems with bare-NIP resulted in $p = 0.006$, indicating that the rate of phenol production was significantly faster in field sand than in kaolin.

A possible factor for the more rapid dechlorination in field sand systems would be the faster desorption of PCP, which would have led to the faster reaction of desorbed PCP in the aqueous phase with the surface of NIP in field sand systems, indicating that the reaction of dissolved PCP with NIP was possibly more mass transfer limited in the kaolin systems than in the field sand systems. Kaolin clay particles have a much larger surface area with smaller particle size, whereas sand

FIG. 5. Production of phenol and PCP dechlorination rate using 4 g/L NIP in (a) field sand and (b) kaolin.

FIG. 6. Transmission electron microscopy images for (a) bare-NIP and (b) lactate-modified NIP.

FIG. 7. Transmission electron microscopy/X-ray electron diffraction system elemental analysis of lactate-modified NIP.

FIG. 8. Scanning electron microscopy micrographs for field sand (a) without NIP, (b) with bare-NIP, and (c) with modified NIP.

particles have larger particle size with less surface area. Although we hypothesize that a more rapid desorption of PCP from field sand would have been conducive to the more rapid dechlorination of PCP in field sand systems, further study on sorption kinetics is required to explain the difference between the field sand and kaolin systems.

Surface analysis

The surface analysis of bare-NIP and LM-NIP systems was carried out using electron microscopy. Transmission electron microscopy (TEM) analysis was conducted to investigate the differences in the physical and chemical characteristics of the bare-NIP and the LM-NIP. The representative TEM images of bare-NIP and LM-NIP are shown in Fig. 6a and b. The TEM analysis shows that the bare-NIP particles appear faceted with particle size ranging from 100 to 300 nm. X-ray Electron Diffraction System (XEDS) shows that the bare-NIP sample contains not just iron and oxygen, but also minute concentrations of aluminum. The micrograph from the LM-NIP sample shows that some of the NIP particles (faceted) are bounded by a blurry, featureless medium. The elemental

analysis obtained from XEDS for the LM-NIP is shown in Fig. 7. XEDS on this medium revealed high concentration of aluminum; electron diffraction indicates that it was amorphous, which seems to suggest that this blurry medium was likely to be aluminum lactate. The amorphous nature of the aluminum lactate might allow for the penetration of the target organic compound into the LM-NIP matrix and subsequent reaction on the surface of NIP.

Scanning electron microscopy (SEM) analysis was carried out for field sand-NIP systems. The SEM micrographs are shown in Fig. 8a–c for field sand particles without NIP, coated with bare-NIP, and coated with LM-NIP, respectively. The SEM micrographs shown in Fig. 8 indicate a distribution of bare-NIP on the surface of the soil particles, whereas there was a more uniform distribution of LM-NIP on the surface of the sand particles. Elemental analysis carried out by XEDS on all soil samples indicate the presence of iron on the surface of soil samples with bare-NIP and LM-NIP. Although XEDS indicates the presence of aluminum on the sand surface for both bare-NIP and LM-NIP, there was much more aluminum on the surface of samples coated with LM-NIP. The aluminum-to-iron mass ratio for LM-NIP samples was several times greater than the same ratio for bare-NIP samples due to the application of 10% aluminum lactate in the LM-NIP slurry. This means that an appreciable proportion of aluminum lactate remained on the NIP surface after contact between the LM-NIP and the field sand.

Conclusions

The LM-NIP have the potential to transform PCP in soils and groundwater. Degradation of PCP was achieved at lower bare-NIP dosages, but nearly complete destruction was obtained at the highest dosage of 100 g/L bare-NIP. The results indicate that reactivity increased with increasing NIP dosage. At lowest dosage of 4 g/L NIP, higher degradation was observed with increasing reaction time. The LM-NIP was effective for the degradation of PCP in both field sand and kaolin. Although the reactivity was less than that of bare-NIP, the LM-NIP became as effective as bare-NIP with time. Nearly complete dechlorination of PCP was obtained for both field sand and kaolin with bare-NIP.

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Author Disclosure Statement

No competing financial interests exist.

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