



Reactivity of lactate-modified nanoscale iron particles with 2,4-dinitrotoluene in soils

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ABSTRACT

This paper investigates the reactivity of nanoscale iron particles (NIP) and lactate-modified NIP (LM-NIP) with 2,4-dinitrotoluene (2,4-DNT), a representative munitions contaminant, in kaolin and field sand as representative low and high permeability soils, respectively. Aluminum lactate, a green compound, was selected as the modifier based on earlier studies which showed it to be an effective dispersant for enhanced transport of NIP in soils. Kaolin and sand were spiked at concentration of 920 and 740 mg/kg of DNT. Batch experiments were conducted with NIP and LM-NIP dosages of 1, 4, 10, 20, 50, 75 and 100 g/L for 24 h. The effect of reaction time was then evaluated using NIP and LM-NIP dosages of 4 g/L for 1, 2, 4, 7, and 14 days. Higher NIP and LM-NIP dosages resulted in greater degradation of DNT in both soils. The DNT degradation ranged from 68% to 99% and 67% to 98% in kaolin and sand, respectively, with bare NIP, and it ranged from 65% to 99% and 59% to 98% in kaolin and sand, respectively with LM-NIP. The highest degradation was attained after 14 days in both soils. The reactivity of LM-NIP improved with time to levels as high as the reactivity of bare NIP.

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1. Introduction

Many sites around the globe are contaminated with chlorinated organic compounds and nitroaromatic organic compounds such as pentachlorophenol (PCP), trichloroethylene (TCE), trichloroethane (TCA), dinitrotoluene (DNT) and trinitrotoluene (TNT). The contaminants can reside in the groundwater, surface water or soils. DNT is commonly found in soils and groundwater near former ammunition factories, TNT-DNT-production plants, and storage sites. DNT is mostly used to produce toluene diisocyanate which is employed in the making of polyurethane foam products, dyes and plastics, plasticizer, deterrent coating and burn rate modifier for propellant. DNT has been listed as a priority pollutant by the U.S. Environmental Protection Agency (USEPA) due to its acute toxicity and carcinogenicity [1–3]. DNT is toxic and a suspect carcinogen; symptoms of DNT poisoning include headache, methemoglobinemia, jaundice, anemia and cyanosis [4,5].

The conventional treatment of nitroaromatic pollutants such as DNT in soils includes incineration or landfilling, immobilization, thermal removal, biological degradation, and solvent extraction [6,7]. However, these methods are relatively expensive, slow and limited by the production of concentrated waste streams that pose disposal problems. Recently, nanotechnology using nanoscale

zerovalent iron particles has emerged as a potential technology to remediate soils and groundwater contaminated by a wide range of organic contaminants both *in-situ* and *ex-situ* in an effective manner within a short duration. However, nanoscale iron particles (NIP) are found to aggregate, limiting their transport in soils during *in-situ* remediation applications. Modification of NIP with dispersants is required to enhance transport in soils, but any such modification is generally believed to reduce the reactivity of NIP.

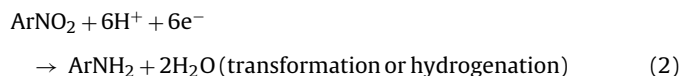
Modification of NIP with aluminum lactate was shown to enhance transport in soils [8,9]. In this study, the reactivity of aluminum lactate modified NIP (LM-NIP) with 2,4-dinitrotoluene (2,4-DNT) in soils as compared to that of bare NIP was investigated. The effects of NIP concentration, aluminum lactate and reaction period were examined.

2. Background

Nanotechnology has the potential to remediate DNT contaminated soils and groundwater both *in-situ* and *ex-situ*. Nanotechnology for environmental remediation commonly 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 large surface to volume ratio makes nanoscale iron particles more reactive than that of microscale zero valent iron particles. The reactivity of NIP with contaminants depends on the concentration of NIP, initial concentration of contaminants and reaction time [10–12].

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Tratnyek and Johnson [13] reported that nanoparticles possess high reactivity due to their high surface area, greater density of reactive sites and higher intrinsic reactivity on reactive sites. Choe et al. [14] studied the degradation of nitrotoluene, nitrobenzene, dinitrobenzene and dinitrotoluene in aqueous solutions at ambient and anaerobic conditions using NIP. They predicted degradation of the nitroaromatic compounds by the following pathways:



All the nitroaromatic compounds were transformed within five minutes of reaction and produced different reaction products of the amine group. After 30 min of reaction, 100% aniline was produced from nitrobenzene, 85% of toluidine from nitrotoulene, 80% of benzene diamine from dinitrobenzene, and 70% of diamino toluene was produced from dinitrotoluene. Generally, the following steps take place during reaction of NIP: (a) movement of nitroaromatic compounds from the solution to the surface of the iron; (b) adsorption of compounds onto the surface of the iron; (c) reductive hydrogenation of compound on the surface of the iron; (d) the desorption of reduced products; and (e) the transfer of products to the bulk solution [15]. The presence of dissolved oxygen can affect the reactivity of NIP with the target contaminants [13]. The effect of ionic strength on the reactivity of NIP is minimal at high concentration of NIP [10]. Factors such as pH, ORP, temperature, anaerobic or aerobic conditions, type of organic compound, and dosage of NIP affect the reaction rate. The degradation of compounds with more complex functional groups results in less reaction rate with the NIP [14,16,17].

Due to agglomeration, transport of nanoscale iron particles in soils is extremely limited, making it difficult to distribute into the contaminated source zone during *in-situ* remediation [8,18–21]. Such characteristics of bare NIP compelled researchers to investigate different ways to modify the surface of bare NIP in order to overcome its negative transport characteristics [8]. Saleh et al. [21] studied ways to enhance the nanoscale iron particles for effective transport using three different modifiers (Tri-block polymer modified, surfactant modified and a commercially available polymer-modified nanoiron). Whenever the surface of NIP is modified with a polymer, its surface charge and stability change, which in turn change the hydrodynamic diameter of the particles.

Most of the reactivity studies with NIP were performed in aqueous environment using bare NIP, and only limited studies have focused on the reactivity of bare or modified NIP in soils [12–15,22–28]. The reactivity in soils is complicated as recalcitrant organic chemicals are sorbed to soil minerals and organic matter. For example, 90% of PCBs in aqueous solution was degraded as compared with 38% of PCBs degradation 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 [22]. Reaction rate in soils increases with increase in iron concentration and also by increasing reaction time [22–23]. Chang et al. [23] reported pyrene removal of 60% from soils in Taiwan by nanoscale iron, while microscale iron was able to reduce only 11%.

Though the transport in soils is improved, the reactivity of the modified NIP is shown to decrease as compared to that of bare NIP. A comprehensive research program was undertaken at the University of Illinois at Chicago (UIC) to optimize both transport and reactivity of modified NIP. Cameselle et al. [29] evaluated the effectiveness of different modifiers or dispersants. 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, β -cyclodextrin and hydroxyl propyl- β -cyclodextrin. The influence of the dispersants was found to vary significantly depending on the chemical nature of the dispersant and the electrical charge of the ions in solution. Several column experiments using NIP modified with different dispersants and field sand (representative porous media) were also conducted. The study showed that 10% aluminum lactate exhibited the highest (93%) elution of the modified iron from the soil media. Based on the column experiments and zeta potential measurement results, aluminum lactate was selected as suitable dispersant for NIP to enhance transport in soils. Lactate is considered as a green compound (environmentally benign) and inexpensive. Moreover, it may enhance the bioremediation of contaminants in soils, making it a favorable alternative for long-term residual treatment if relied on biodegradation.

Though the aluminum lactate modification is shown to improve the transport of NIP in soils, the extent of reduction in reactivity due to this modification was not quantified. In this study, a series of batch experiments was conducted to quantify the destruction and removal of 2,4-DNT using bare nanoscale iron particles and aluminum lactate modified NIP (LM-NIP). Based on the results, the effects of NIP concentration, aluminum lactate and reaction period on DNT destruction were evaluated.

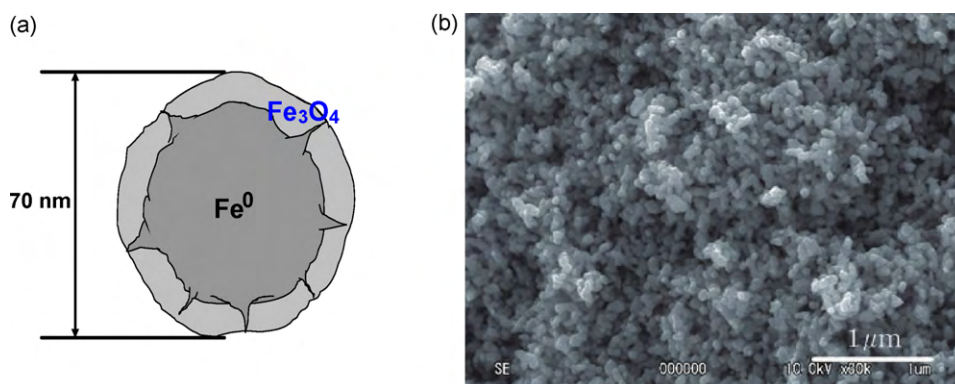


Fig. 1. Nanoscale iron particles (NIP) used in this study: (a) structure and (b) SEM.

Table 1
Properties of nanoscale iron particles.

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

3. Materials and methods

3.1. Characteristics of nanoscale iron particles

The NIP used in this study were obtained from Toda Kogyo (Japan). 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 $37.1 m^2/g$. The NIP consisted of an elemental iron core (α -Fe) and a magnetite shell (Fe_3O_4) as depicted in Fig. 1(a), with approximate 50 wt.% α -Fe core and 50 wt.% Fe_3O_4 . The average particle size determined with a scanning electron microscope (SEM) was 70 nm (Fig. 1(b)). The density of the aqueous NIP particle suspension was 1.27 g/mL at solids concentration of 25.6 wt.%. The sulfur content was approximately 4500 mg/kg which originates from the ferrous sulfate starting material used for the production of NIP. These particles are manufactured in bulk and are available presently (2010) at a cost of \$25 to \$30 per pound. Because of their nontoxic characteristics and relatively low cost, these particles are being used for subsurface contaminant remediation. The main properties of NIP are also summarized in Table 1. The NIP exhibit electromagnetic properties [10,24].

3.2. Chemicals used

2,4-DNT was used to spike the soils. DNT has a chemical formula of $CH_3C_6H_3(NO_2)_2$ and was obtained from Aldrich Chemicals (Milwaukee, WI). The aluminum lactate used for surface modification of NIP was obtained from Aldrich (CAS-18917-91-4). Aluminum lactate was chosen among other dispersants due to enhanced NIP transport in soils and also being an environmentally friendly (green) compound. Electrolyte was used to simulate groundwater conditions, and it contained 0.006 M of sodium bicarbonate, 0.002 M of calcium chloride, and 0.001 M of magnesium chloride. The pH, total dissolved solids and electrical conductivity of the electrolyte solution were 7.8, 500 mg/L and 1020 $\mu S/cm$, respectively (Table 2).

3.3. DNT-spiked soils

Field sand was used for this study to represent highly porous media, while kaolin was used to represent low permeability soil. The grain size distribution of field sand and kaolin are shown in

Table 2
Composition and properties of simulated groundwater (electrolyte).

Composition	
Sodium bicarbonate ($NaHCO_3$) (M)	0.006
Calcium chloride ($CaCl_2$) (M)	0.002
Magnesium chloride ($MgCl_2$) (M)	0.001
Properties	
pH	7.75–7.76
Conductivity ($\mu S/cm$)	1020
Total dissolve solids (TDS) (mg/L)	500

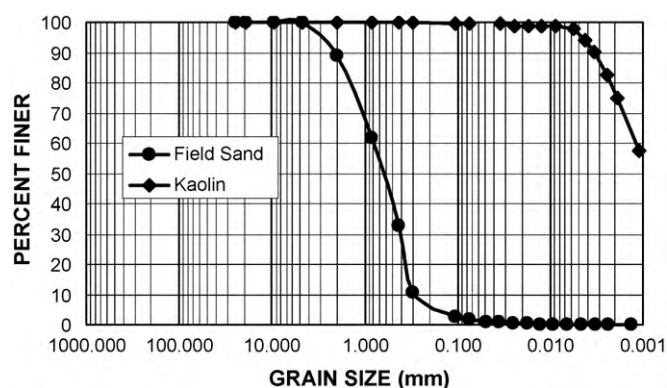
**Fig. 2.** Grain-size distribution of field sand and kaolin.

Fig. 2. The properties of sand and kaolin are also summarized in Table 3. The presence of about one percent organic matter was observed in the field sand, whereas kaolin did not contain any organic matter.

The field sand and kaolin were spiked with 2,4-DNT. For this, about 600 mL hexane was used to dissolve 1000 mg of solid DNT. To ensure all the DNT solids were dissolved, the DNT–hexane mixture was placed on a magnetic stirrer for about 45 min. The 1 kg soil was weighed in a large glass beaker. The hexane–DNT solution was added to the soil in the beaker and mixed well with a stainless steel spoon continuously for about 30 min to ensure that the DNT was distributed uniformly. The soil–hexane–DNT mixture was placed in a ventilation hood nearly 7 days for the mixture to dry. During the drying period, the soil was mixed regularly to ensure uniform spiking and drying. The final concentrations of DNT measured in the kaolin and field sand were 920 and 740 mg/kg, respectively. These levels of concentrations represent typical concentration of DNT in the field where *in-situ* remediation can be feasible [30,31].

3.4. Test variables, set-up and procedure

A series of batch experiments was conducted using the DNT-spiked kaolin and field sand. Different NIP dosages (1, 4, 10, 20, 50, 75 and 100 g/L) and different reaction times (1, 2, 4, 7 and 14 days) were selected to evaluate the effect of NIP concentration and reaction time on DNT degradation. The experiments were conducted in 50 mL bottles at a soil:liquid ratio of 1 g:5 mL. Thus, 25 mL

Table 3
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)	2.67×10^{-3}	1.0×10^{-8}
pH (ASTM 4972)	7.5	8.3
Organic content (%) (ASTM D 2974)	0.8	~0
USCS classification (ASTM D 2487)	SP	CL

NIP solution prepared was added to 5 g of spiked soil. The samples were placed in a rotating tumbler for their respective testing time intervals of 1, 2, 4, 7 and 14 days. In preparing the NIP solution without lactate, a specified amount of NIP slurry was weighed on the analytical balance and mixed with 1 L of electrolyte solution and shaken well to ensure homogeneous mixing. Aluminum lactate modified NIP was prepared by the addition of lactate to the NIP slurry; the mixture of NIP and lactate was then shaken with a vortex mixture for several minutes before adding to the electrolyte solution. After the reaction period, the NIP-soil slurry was centrifuged at 7000 rpm for 10 min to separate the solution from the soil. The supernatant solution and the soil were analyzed for DNT concentration. All experiments were conducted in triplicate to ensure repeatability and accuracy.

3.5. Chemical analysis

The soil was extracted with solvent for 24 h using 1:1 (v/v) mixture of acetone and acetonitrile [32]. The extracts were then analyzed for 2,4-DNT using gas chromatography according to the USEPA method 8091 [33] with 1-chloro-3-nitrobenzene as the internal standard. The aqueous supernatant solutions were filtered prior to analysis using GC after liquid–liquid extraction into hexane.

The mass of DNT in the soil prior to treatment was calculated. The mass of DNT in both the supernatant and the soil after the treatment was also calculated. The amount of DNT found in supernatant was attributed to solubilization, while the difference between the initial DNT mass in the soil and the sum of DNT mass found in supernatant and the soil after the treatment was attributed to degradation. In order to clarify the extent of solubilization and degradation of DNT, the results are presented in terms of (1) removal of DNT from the soil (solubilized and degraded DNT), and (2) degradation of DNT.

4. Results and discussion

4.1. Effect of NIP concentration

Results from the batch experiments conducted on field sand and kaolin using different concentrations of NIP solution (1, 4, 10, 20, 50, 75 and 100 g/L) are shown in Fig. 3(a) and (b), respectively. All the experiments were performed for a reaction period of 24 h. The percent DNT removal is calculated based on the final and initial mass of DNT in the soil. The difference between the initial DNT mass in the soil and the total DNT mass in the soil and effluent found after the treatment is attributed to degradation by NIP, and this degraded mass divided by the initial mass in the soil resulted in percent DNT degradation.

The results show that most of the DNT in the soil was degraded. The degradation of DNT occurs primarily at the surface of NIP. The desorption of DNT into the NIP slurry results in the release of DNT from the soil matrix into the aqueous phase where the DNT will be exposed to the reactive surface of NIP, and degradation of DNT will then occur at the NIP surface. The degradation of DNT in both soils increased with increasing NIP concentration. It was found that about 67–98% DNT was degraded in field sand while about 68–99% was degraded in kaolin using bare NIP. In all cases, the degradation was greater at higher concentration of NIP. For instance 1 g/L NIP resulted in 67% degradation of DNT in field sand, whereas increased concentration of 100 g/L NIP resulted in nearly 98% degradation of DNT. The highest degradation was observed for high concentrations of NIP (100 g/L) and similar results were obtained by Reddy and Karri [25] for the degradation of PCP in soils.

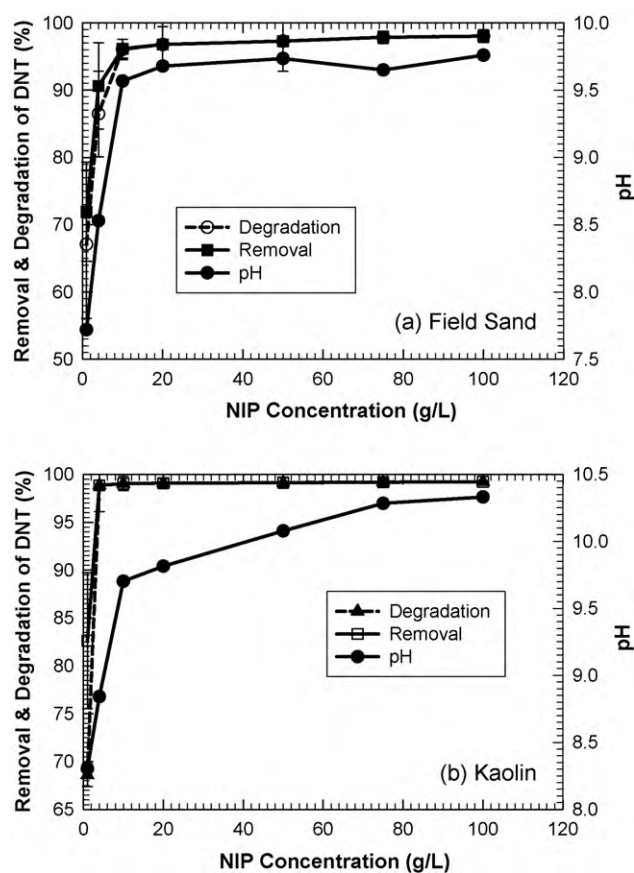


Fig. 3. Effect of NIP concentration on DNT degradation in soils: (a) field sand and (b) kaolin.

Fig. 4(a) and (b) shows the effect of concentration of lactate-modified NIP (LM-NIP) on the degradation of DNT. About 60–98% of DNT degraded and the highest degradation was obtained with 100 g/L LM-NIP. In all the tests, the reactivity of NIP in kaolin was higher than that in sand. This might be due to the presence of about one percent organic content which inhibits the desorption of DNT from sand. The soil organic matter may compete with the contaminants for reaction sites on the surface of the iron nanoparticles. Tratnyek et al. [26] reported that the reduction of nitrobenzene (NB) and trichloroethylene (TCE) was subdued by the presence of natural organic matter (NOM).

The production of nitrate was monitored during the removal of DNT from soils. A small concentration of nitrate was detected in the aqueous solutions after separation of solution from the soil–NIP slurry. This concentration of nitrate corresponded to about 1–3% degradation of DNT. In general, there was no correlation between the removal of DNT and production of nitrate. However, for both sand and kaolin, the concentration of nitrate was greater in the systems which reacted with lactate-modified NIP than with bare NIP. In the case of kaolin and NIP, the production of nitrate increased slightly with increasing concentration of NIP and degradation of DNT. Thus about 2.67 mg/L nitrate was obtained for 1 g/L, this increased to about 2.92 mg/L for 100 g/L NIP. In the other test conditions, although there was some production of nitrate, this could not be correlated with the removal of DNT.

4.2. Effect of contact time

The concentration of 4 g/L for bare NIP and LM-NIP solutions was selected to conduct the kinetic experiments to evaluate the effect of reaction time on the reactivity of NIP and LM-NIP with DNT. The

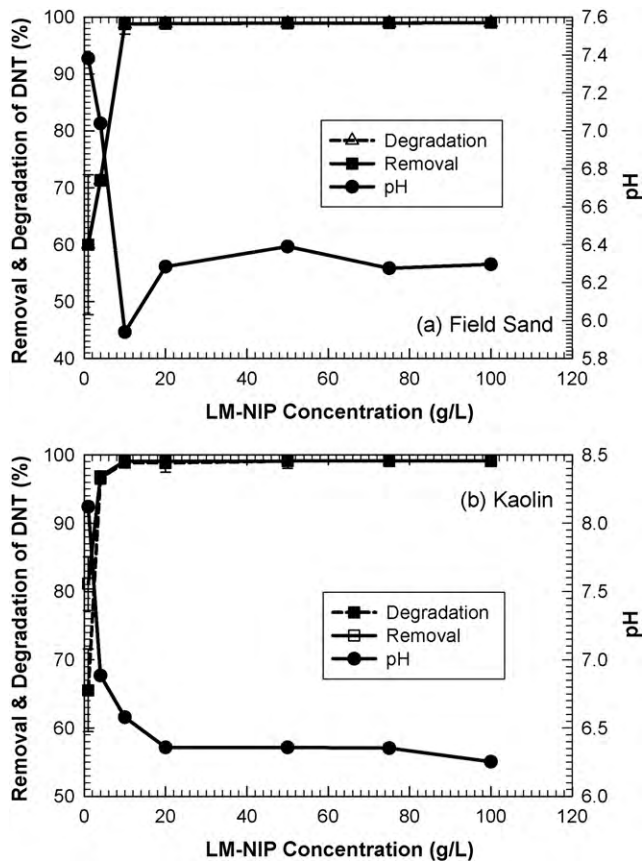
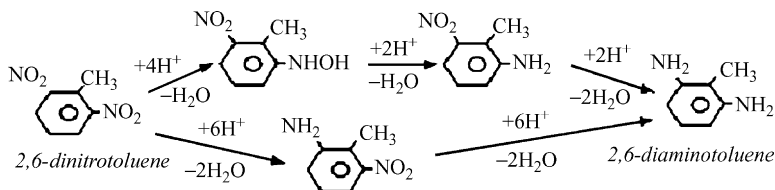


Fig. 4. Effect of LM-NIP concentration on degradation of DNT: (a) field sand and (b) kaolin.

results for the degradation and removal of DNT with time are shown in Fig. 5(a) and (b) for sand and kaolin, respectively. Degradation increased with increasing reaction time, with almost 99.4% DNT degraded in kaolin after 14 days of reaction with bare NIP. Similarly when LM-NIP was used, 96% of DNT was degraded after 1 day and about 99% degradation was achieved after 14 days. In similar fashion, 86% and 96% of DNT were degraded in sand after 1 day and 14 days of reaction with bare NIP, respectively. The results show that increasing the contact time increased the degradation of DNT in soils. Choe et al. [14] reported the complete degradation of DNT in aqueous solution after 30 min of contact time. The initial concentration of DNT used by these researchers was 10 mg/L and degradation increased with time. The researchers reported that the following reaction pathway with major final product of diaminotoluene:



Nishino et al. [28] also reported diaminotoluene as the final product after biological degradation of DNT.

Rogers and Bunce [34] found that under reductive potentials, 2,4-DNT in aqueous solution was electrochemically transformed to diaminotoluene compounds. Doppalapudi et al. [35] found that under various anoxic and oxic conditions in electrochemical reactors, 2,4-DNT was transformed into solid phase dimer and other nitroaromatic compounds that precipitated from solution.

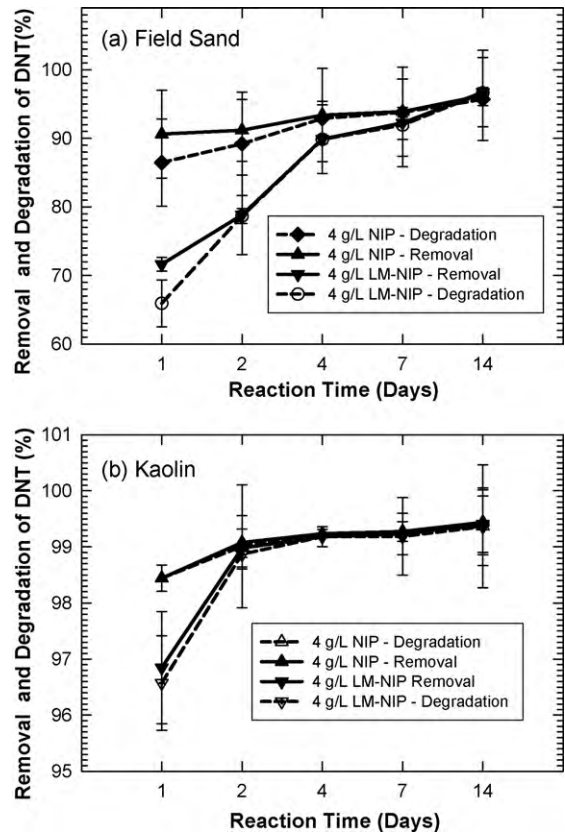


Fig. 5. Effect of reaction time on degradation of DNT in: (a) field sand and (b) kaolin.

This study did not investigate for the reaction products, but analyzed for the destruction of DNT. Most of the degradation of DNT occurred within the first 24–48 h of contact time and then the reaction rate decreased thereafter. The decrease in the reaction rate might be due to oxidation of the nanoparticles after sometime or due to saturation of the surface sites. The oxidation can be confirmed by the measurement of ORP in the system which indicates that the medium was initially reducing, but becomes oxidized after sometime. The initial ORP was about -500 mV but this increased to about $+200$ mV after 7 days of reaction.

4.3. Effect of aluminum lactate modification

In this study, aluminum lactate was selected among other dispersants because it enhances transport of NIP and also it is environmentally friendly [9,29]. Figs. 3–5 show the effects of lactate on the degradation of DNT in soils. It is clearly seen that the higher

amount of DNT was degraded in the absence of lactate; the addition of lactate reduced the amount of DNT degraded in both soil types. In the case of kaolin, the degradation of DNT with bare NIP varied from 98% to 99%; however, this decreased to 96–99% when LM-NIP was used. In the case of sand, degradation decreased from 86% to 65% when NIP was modified with aluminum lactate. The decrease in reactivity may be attributed to the lactate forming a thin film layer around the particles thereby reducing its surface area for reactiv-

ity. The lactate may also have blocked the reaction sites where the contaminants should have been absorbed for effective reaction to take place. Other authors have reported similar trends whereby the addition of dispersant decreased the rate of reactivity [21,27].

This study shows that, despite the decrease in reactivity with the addition of aluminum lactate, the reaction improved with time. Thus, the difference in reactivity between NIP and LM-NIP was large initially but diminished after seven days. For instance the degradation of DNT in kaolin after 24 h was 98% and 96% with NIP and LM-NIP, respectively. However after 14 days, the degradation was almost 99% for both NIP and LM-NIP. This can be due to the fact that aluminum lactate was protecting the NIP from easily getting oxidized or passivated. The thin film surrounding the NIP particles probably breaks off with time, thereby making them still reactive where by that time the NIP might have passivated or oxidized which reduces the reactivity. This indicates that aluminum lactate-modified NIP has a strong potential for remediation of soils contaminated with DNT in addition to enhanced transport in soils.

4.4. Effect of pH

Fig. 6(a) and (b) shows the variation of pH in sand and kaolin with reaction time during the destruction of DNT by NIP. In both cases, the pH with aluminum lactate was lower than that of NIP without lactate. This is due to the fact that aluminum lactate is acidic and lowers the pH. The average pH of NIP was about 8 and that of LM-NIP is about 6.3. The results indicate that pH reduces with time during the process for both sand and kaolin. Figs. 3 and 4 also show the variation of pH with NIP and LM-NIP concentration.

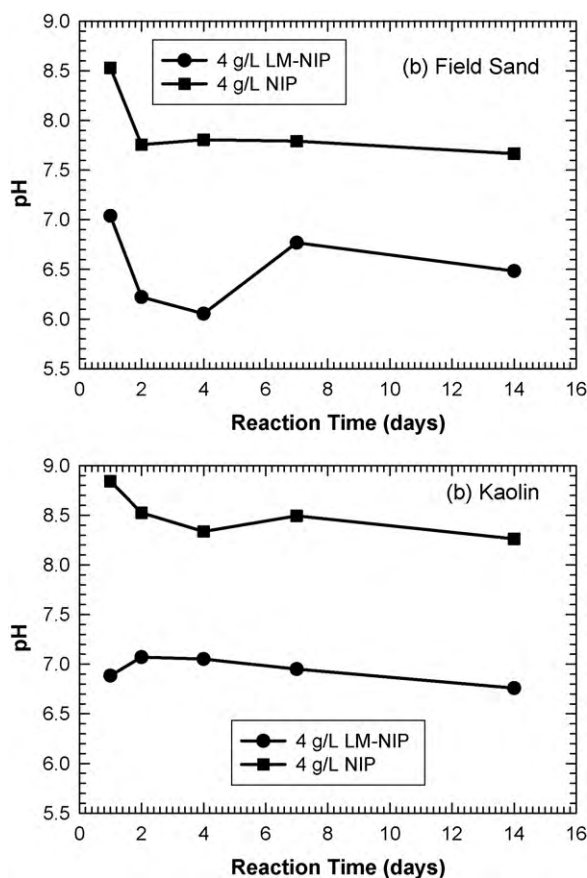


Fig. 6. Variation of pH with time in presence of bare and modified NIP in soils: (a) field sand and (b) kaolin.

The results showed a decrease in the pH from about 8.5 to about 6.2 for LM-NIP concentrations of 4 and 100 g/L, respectively. This is due to the acidity of the aluminum lactate.

The redox potential (ORP) for both NIP and LM-NIP was measured during the removal of DNT from sand to determine the variation of ORP with reaction time. The ORP for NIP was about -500 mV after 1 day but increased after 14 days to $+200$ mV. In the case of LM-NIP it ranged from -500 to about $+100$ mV. In all cases, the system was very reducing for the first two days but became more oxidative with time. This can be attributed to the decrease in reaction rate after 2 days. It is worth noting that after 14 days, the ORP of the LM-NIP was lower (100 mV) than that of NIP (200 mV) which indicates the lactate medium was still comparatively in a reducing state. This confirms that the reactivity of LM-NIP continues to increase with time as compared to that of bare NIP. Thus, the aluminum lactate protected the NIP from easily getting oxidized.

5. Conclusion

The aim of the study was to investigate the reactivity of aluminum lactate modified NIP with DNT as compared to that of bare NIP. The results indicate that reactivity of bare NIP with DNT increases with increasing NIP dosage. Degradation of DNT was achieved with bare NIP at lower dosage (4 g/L) but near complete destruction was obtained at a higher dosage (100 g/L). Reactivity was found to increase with increasing reaction time. Although the reactivity was less compared to bare NIP initially, the aluminum lactate modified NIP become as effective as bare NIP with increasing reaction time.

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