Injection of nanoscale Fe$_3$O$_4$ slurry coupled with the electrokinetic process for remediation of NO$_3^-$ in saturated soil: Remediation performance and reaction behavior

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**ABSTRACT**

This work aimed to investigate the remediation performance and reaction behavior of the injection of nanoscale Fe$_3$O$_4$ slurry coupled with the electrokinetic (EK) process for remediation of NO$_3^-$ in a saturated soil with the texture of sandy clay. First, 0.8 wt% of polyacrylic acid (PAA) was added to the laboratory-prepared nanoscale Fe$_3$O$_4$ to yield the nanoscale Fe$_3$O$_4$ slurry. Thus prepared slurry was then injected into the anode reservoir of the EK set-up for remediation of nitrate-contaminated soil ([NO$_3^-$] = 69.39–71.65 mg/kg) in the soil compartment (L: 25 cm; Φ: 10 cm). Application of an electric field of 1 V/cm and daily injection of nanoscale Fe$_3$O$_4$ slurry at a dose of 5 g/L were practiced during the test period of 12 d. The remediation results indicated that residual NO$_3^-$ concentration of 1.35 mg/L in the anode reservoir was found to be lower than Taiwan EPA’s Pollution Control Standards for Type I Groundwater Quality. In addition, a very low residual NO$_3^-$ concentration in soil was detected. It indicates that the hybrid technology employed in this work is effective for remediation of nitrate in the subsurface following the adsorptive reduction model. The relevant reaction behavior was discussed.

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1. Introduction

Nitrites and nitrates are commonly found in surface water and groundwater. Elevated concentrations of these substances, in general, could pose a threat to both organisms in the water bodies and human health [1,2]. When nitrate is reduced to nitrite, it might oxidize the hemoglobin in blood cells to methemoglobin, thereby preventing the transport of oxygen to the body tissues. Severe methemoglobinemia can result in brain damage and death. A high level of methemoglobin would lead to blue-tinged blood for babies under six months old in particular, namely so-called “blue baby syndrome” [3]. Under low gastric acidity conditions, nitrate would also react with nitrosatable compounds in the human mouth and stomach to form N-nitroso and other carcinogenic compounds [4]. Therefore, many countries have regulated the concentration of nitrate in drinking water. The US EPA has established a maximum contaminant level (MCL) of 10 mg/L of NO$_3^-$–N for drinking water. In Taiwan, the regulatory thresholds for NO$_3^-$–N and NO$_2^-$–N in drinking water sources are set as 10 mg/L and 0.1 mg/L, respectively. The same MCLs apply to the drinking water quality as well [5].

Traditionally, nitrate in water can be removed by various technologies including biological denitrification [6], ion exchange [7], reverse osmosis [3], and chemical reduction [8–10]. Electro dialysis and catalytic de-nitrification are also promising technologies for nitrate removal [3]. In the literature, EK processing and a combined EK/iron wall process for in situ remediation of nitrate-contaminated groundwater have been reported [11]. Yang et al. [12] further reported their results of using the hybrid technology of the EK process and nanosized zero-valent iron wall for treatment of nitrates in the subsurface environment. The same research group has also reported their work on removal of nitrate in a saturated soil using the combined processes of the injection of nanoiron slurry and EK remediation [13,14]. Very recently, a study on reaction behavior of nanoscale magnetite and nitrate ions in simulated groundwater has been reported by Yang and Chen [15] at the 239th ACS (American Chemical Society) National Meeting in San Francisco. In that work, it was found that nitrate ions were first chemically adsorbed onto the surface of Fe$_3$O$_4$ nanoparticles and then were reduced to NO$_2^-$ and NH$_4^+$ at an initial pH of 3 in the simulated groundwater. Thus, the model of adsorptive reduction was proposed and Fe$_3$O$_4$ nanoparticles were considered as the nanoscale adsorbent in this context.

The objectives of this work were 2-fold: (1) to study the feasibility of combining the injection of nanoscale Fe$_3$O$_4$ slurry and the EK process for remediation of NO$_3^-$ in a saturated soil; and (2) to ver-
ify the relevant reaction behavior in the said remediation system fit the proposed adsorptive reduction model.

2. Experimental

2.1. Materials and chemicals

Soil studied in this work was collected from an abandoned farmland in central Taiwan, where there has been no agricultural activity for over a decade. After collection, soil was first air dried for several days, during which time plant roots and debris were removed. Then the soil was subjected to various characterization methods before it was spiked potassium nitrate to yield a contaminated soil having a NO$_3^-$ concentration of $70.0 \pm 2.0$ mg/kg.

Chemicals used were all reagent grade: ferric chloride (97–102% in purity) from Panreac; ferrous sulphate (99% in purity) from Riedel-de Héan; sodium hydroxide (96% in purity) from SHOWA; potassium nitrate (98% in purity) from SHOWA; polyacrylic acid (average $M_W = 2600$ g/mol) form DHUCHEM (a Taiwanese manufacturer); and humic acid sodium salt from Sigma-Aldrich. Fe$_3$O$_4$ nanoparticles were prepared using the co-precipitation method based on the following reaction equation [16]:

$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$$

During the synthesis process 0.8 wt% of polyacrylic acid (PAA) was added to yield the stabilized nanoscale Fe$_3$O$_4$ slurry.

2.2. Methods and equipment

The schematic diagram of the experimental set-up for the EK remediation system is shown in Fig. 1. It was composed of a direct-current power supply, an assembly of EK test compartments with two graphite rod electrodes, and a peristaltic pump to maintain the water level of the anode compartment. The Pyrex glass EK test compartments include the anode compartment ($L$: 10 cm; $\Phi$: 10 cm), soil compartment ($L$: 25 cm; $\Phi$: 10 cm), and cathode compartment ($L$: 10 cm; $\Phi$: 10 cm). The electrolytes contained in both electrode reservoirs were simulated groundwater, which was prepared according to the formulations reported by Yang et al. [17]. Details of the experimental conditions employed by the EK remediation system are given in Table 1. After each test, the soil specimen in the soil compartment was pushed out and cut into five equal sections along the longitudinal axis for determinations of the soil pH and residual NO$_3^-$ concentration.

3. Results and discussion

3.1. Characterization of the soil specimen

The soil specimen was determined to be of a sandy clay texture (see Table 2). Its pH was 8.17. It contained only 50.11 mg/kg NO$_3^-$.

3.2. Characterization of the prepared nanoscale Fe$_3$O$_4$ and its slurry

Based on the XRD pattern (see Fig. 2), the black tiny particles prepared were identified as Fe$_3$O$_4$. FE-SEM image (not shown) has illustrated that a majority of Fe$_3$O$_4$ particles were in the size range of 10–30 nm, but in aggregate forms. The results of ESEM-EDS (see Fig. 3) show that the synthesized particles contained Fe, O, and Cl, where Cl was due to the residual of ferric chloride. The EDS results indirectly proved that the synthesized particles were Fe$_3$O$_4$. Based on the above results, it

Fig. 1. Schematic diagram of the experimental set-up of the EK remediation system.

Table 1

<table>
<thead>
<tr>
<th>Operating conditions of the EK system</th>
<th>Test designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial soil pH</td>
<td>7.12</td>
</tr>
<tr>
<td>Weight of saturated soil (kg)</td>
<td>2.95 ± 0.05</td>
</tr>
<tr>
<td>Initial pH of anolyte and catholyte</td>
<td>7.00 ± 0.5</td>
</tr>
<tr>
<td>Initial NO$_3^-$ concentration in saturated soil (mg/kg)</td>
<td>69.39</td>
</tr>
<tr>
<td>Daily dose of nanoscale Fe$_3$O$_4$ slurry injected into the anode reservoir (g/L)</td>
<td>0</td>
</tr>
<tr>
<td>Electrical potential gradient (V/cm)</td>
<td>1</td>
</tr>
<tr>
<td>Remediation time (d)</td>
<td>12</td>
</tr>
</tbody>
</table>

X-ray diffractometry (XRD; PANalytical X’Pert PRO, Japan) was employed for identification of the crystalline structure of the prepared solid particles. The relevant morphology and particle size were examined by TF field emission scanning electron microscopy (SEM; JEOL JSM-6330F, Japan). An energy dispersive X-ray spectrometer (EDS) incorporated into an environmental scanning electron microscope (ESEM; FEI QUANTA-200, Czech Republic) was used for quantitative analysis of elements in the synthesized particles.
Table 2
Characteristics of the raw soil specimen.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil texture</td>
<td>Sandy clay</td>
</tr>
<tr>
<td>Particle size distribution (%)</td>
<td>&lt;2 μm: 45.02</td>
</tr>
<tr>
<td></td>
<td>2–50 μm: 0.91</td>
</tr>
<tr>
<td></td>
<td>50–2000 μm: 54.07</td>
</tr>
<tr>
<td>pH</td>
<td>7.23</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>1.54</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.15</td>
</tr>
<tr>
<td>Organic matter content (%)</td>
<td>1.29</td>
</tr>
<tr>
<td>Cation exchange capacity (meq/100 g)</td>
<td>12.02</td>
</tr>
<tr>
<td>Total Fe (mg kg⁻¹)</td>
<td>31174.56</td>
</tr>
<tr>
<td>NO₃⁻ (mg kg⁻¹)</td>
<td>50.11</td>
</tr>
<tr>
<td>Total Fe (mg kg⁻¹)</td>
<td>31174.56</td>
</tr>
</tbody>
</table>

Fig. 2. The XRD pattern of the prepared black tiny particles.

was verified that the prepared solid particles were nanoscale Fe₃O₄. The stability of nanoscale Fe₃O₄ slurry in various solution media was also appraised by visual observation and UV–vis spectrophotometry set at a wavelength of 345 nm. From Table 3, PAA was found to be a good dispersant to stabilize nanoscale Fe₃O₄ in the tested solution media. This is ascribed to the synergistic effect of electrostatic repulsion and steric hindrance yielded by PAA molecules. Table 3 shows that the existence of humic acid in the solution medium further enhanced the stabilization of the said slurry. This was due to the negative charge associated with humic acid in the solution. It was also noted that the effects of various anions and cations in the simulated groundwater on stabilization of the slurry was insignificant in this work.

3.3. Performance evaluation of NO₃⁻ removal in the EK system with or without the injection of nanoscale Fe₃O₄ slurry

3.3.1. Cumulative electroosmotic flow quantity

Fig. 4 shows the variation in cumulative electroosmotic (EO) flow quantity as the time elapsed for remediation of nitrate ions in saturated soil. As compared with the EK-alone test (i.e., EN-Blank Test), Test EN-1 yielded a slightly greater amount of EO flow starting from Day 6 throughout the end of the test period.

3.3.2. Residual NO₃⁻ concentration in the anode reservoir

In view of the residual NO₃⁻ concentration in the anode reservoir, it was found to increase as the remediation time elapsed for the EK-alone test (Fig. 5). This is self-explanatory because NO₃⁻ migrated from the soil compartment into the anode reservoir and remained there without subjecting to adsorption or chemical reduction. On the other hand, very low concentrations (<5.98 mg/L) of nitrate ions in the anode reservoir were observed throughout the
Table 3 Comparison of the stability of nanoscale Fe₃O₄ slurry prepared under various conditions.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Solution medium</th>
<th>Humic acid (mg/L)</th>
<th>Polyacrylic acid (wt%)</th>
<th>Visual stabilization (after 48 h)</th>
<th>UV₃₄₅ absorbance (after 48 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Simulated groundwater</td>
<td>0</td>
<td>0.8</td>
<td>Good</td>
<td>2.011</td>
</tr>
<tr>
<td>S2</td>
<td>Simulated groundwater</td>
<td>10</td>
<td>0.8</td>
<td>Good</td>
<td>2.311</td>
</tr>
<tr>
<td>S3</td>
<td>Simulated groundwater</td>
<td>10</td>
<td>0.8</td>
<td>Good</td>
<td>2.312</td>
</tr>
</tbody>
</table>

Fig. 5. Variation in residual NO₃⁻ concentration in the anode reservoir for the EK tests with or without the injection of nanoscale Fe₃O₄ slurry for the remediation of NO₃⁻ in a saturated soil.

test period in Test EN-1 because NO₃⁻ was presumably adsorbed and chemically reduced by nanoscale Fe₂O₄ in intimate contact. By converting such NO₃⁻ concentrations to NO₃⁻–N concentrations, they were all below 1.35 mg/L. This value meets Taiwan EPA’s regulatory threshold for Type I Groundwater Quality (i.e., NO₃⁻–N = 10 mg/L). Further analysis of the results of EN-Blank Test showed that an average of 26.16 mg/L of NO₃⁻ migrated into the anode reservoir for the first 6 d as compared with the corresponding mean value of 11.48 mg/L for Days 7–12. To calculate the average daily removal of NO₃⁻ in the anode reservoir by the said remediation system, it was assumed that 26.16 mg/L of NO₃⁻ migrated into the anode reservoir on a daily basis. By subtracting the residual NO₃⁻ concentration in the anode reservoir in Test EN-1 from 26.16 mg/L, an average daily removal of 22.02 mg/L of NO₃⁻ was obtained for the first 6 d of the remediation period.

3.3.3. Residual NO₃⁻ concentration in the soil compartment

The residual NO₃⁻ concentration in the soil compartment is another key indicator to evaluate the performance of the said remediation system. Fig. 6 shows the residual mass fractions of nitrate ions in various soil sections for the EK tests with or without the injection of nanoscale Fe₂O₄ into the anode reservoir. As expected, NO₃⁻ in the soil compartment moved toward the anode reservoir as a result of electromigration. Thus, a much higher NO₃⁻ concentration in the soil section near the anode end than that of near the cathode end was observed in both tests. For each soil section with a normalized distance from anode reservoir greater than 0.6 in Test EN-1, its residual mass fraction of nitrate was determined to be less than 5%. It is about one-third of the residual mass fraction of nitrate in the corresponding soil section in the EK-alone test. This might be indirect evidence that the injected Fe₂O₄ nanoparticles were transported into the soil compartment by EO flow, resulting in adsorption and chemical reduction of NO₃⁻ in intimate contact. Accordingly, it is reasonable to assume that a prolonged remediation with the same practice would completely transform nitrate ions into innocuous end products.

3.4. Reaction behavior of NO₃⁻ removal in the EK system with the injection of nanoscale Fe₃O₄ slurry

Based on the remediation performance obtained above, the relevant reaction behavior can be deliberated from various fundamental aspects given below.

3.4.1. From the aspect of H⁺ concentration requirement

As the EK remediation time elapsed, pH values of the anode reservoir and cathode reservoir decreased to about 2 and 12, respectively (figure not shown) as a result of the electrolysis of water next to the electrodes. A further calculation shows that greater than 3.6 × 10⁻³ mol of H⁺ was generated in the anode reservoir starting from Day 1 in both tests. A study by Yang and Chen [15] has indicated that at least 1.94 × 10⁻³ mol of H⁺ is required to chemically reduce 20 mg/L of NO₃⁻. Based on that finding, stochiometrically, there was no need to add extra acid to the EK remediation system to achieve the goal in the present study. Therefore, in the EK test coupled with the injection of nanoscale Fe₃O₄ slurry, the following reaction occurred:

8Fe²⁺ + NO₃⁻ + 10H⁺ → 8Fe³⁺ + NH₄⁺ + 3H₂  \( E^0 = 0.11 \text{ V} \)

where Fe²⁺ is originated from Fe₃O₄ comprising FeO and Fe₂O₃.

3.4.2. From the aspect of reaction product

Fig. 4 further reveals that the cumulative EO flow quantities for EN-Blank Test and Test EN-1 up to Day 6 were all greater than
665 mL, which was the pore volume of soil in the soil compartment. Assuming that injected Fe$_3$O$_4$ nanoparticles were actually transported by EO flow into the cathode reservoir via the soil compartment and they did act as an adsorbent and reducing agent for NO$_3^-$ in the remediation system, then NH$_4^+$ would be detected as a reaction product in the cathode reservoir starting from Day 6. Indeed, 30.05 mg/L of NH$_4^+$ in the cathode reservoir was determined on Day 6 and the NH$_4^+$ concentration continued to rise (see Fig. 7). This finding was ascribed to the synergistic effect of chemical reduction of NO$_3^-$, EOF, and electromigration. Moreover, this finding is also in accord with the adsorptive reduction model proposed by Yang and Chen [15]. According to this model, nitrate ions were first chemically adsorbed onto the surface of Fe$_3$O$_4$ nanoparticles and then were reduced to NO$_2^-$ and NH$_4^+$ under strong acid conditions. In the present study, the required strongly acidic conditions were provided as a result of the acid front in the remediation system.

3.4.3. From the aspect of current density

The magnitude of current density in Test EN-1 was found to be greater than that of EN-Blank Test, as shown in Fig. 8. Based on the calculation of standard reduction potentials, the reaction of electromigrated NO$_3^-$ and H$^+$ (either in the anode reservoir or along with the acid front in the soil compartment) to occur was theoretically impossible in EN-Blank Test. In the EK-alone test, nitrate ions electromigrating toward the anode either entered the anode reservoir or still remained in the soil compartment (see Figs. 5 and 6). Thus, the electrical conductivity of the soil specimen dropped grad-
ually. In Test EN-1, as shown in the above reaction equation, \( \text{NO}_3^- \) electromigrated into the anode reservoir was chemically reduced to \( \text{NH}_4^+ \). Inversely, this positively charged species moved toward the cathode reservoir by electromigration again. This phenomenon, as compared with the phenomenon observed in EN-Blank Test, compensated the decrease of the electrical conductivity of soil in the soil compartment due to migration of \( \text{NO}_3^- \) into the anode reservoir. Bearing in mind that part of \( \text{NO}_3^- \) in soil was chemically reduced to \( \text{NO}_2^- \), which might also contribute to some extent of the electrical conductivity of soil. Therefore, the current density in Test EN-1 was greater than that of EN-Blank Test over the course of test period. A decrease of current density during Days 6–8 in Test EN-1 was also noted. It was postulated that during its transport process \( \text{NH}_4^+ \) accepted electrons encountered and then transformed into \( \text{N}_2 \) and \( \text{H}_2 \). Although \( \text{N}_2 \) and \( \text{H}_2 \) were not monitored in the present study, this hypothesis was supported by the study reported by other researchers [18].

4. Conclusion

The coupling of the injection of nanoscale \( \text{Fe}_3\text{O}_4 \) slurry into the anode reservoir and the electrokinetic process was found to be a viable technology for remediation of \( \text{NO}_3^- \) in saturated sandy clay soil to meet Taiwan EPA’s regulatory thresholds for groundwater pollution control. The relevant reaction behavior in the present study is in line with the adsorptive reduction model proposed by the same research group of this study. More specifically, nitrate ions were first chemically adsorbed onto the surface of \( \text{Fe}_3\text{O}_4 \) nanoparticles and then the comprising \( \text{Fe(II)} \) donated electrons for chemical reduction of \( \text{NO}_3^- \) in the remediation system.

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References


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