Remediation of Nickel-Contaminated Clayey Soil by Electro-Kinetic Technology Coupled with Zeolite – a Permeable Reactive Barrier

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This study checks the effectiveness of using different purging solutions: acetic acid (AA), ammonium citrate (AC), ethylenediaminetetraacetic (EDTA), and sodium dodecyl sulphate (SDS), as purging solutions for saturating soil. The study also investigates the using a catholyte solution in the electro-kinetic (EK) process coupled with zeolite as a permeable reactive barrier (PRB). The nickel-contaminated clayey soil is loaded as positions I, II, III, IV, and V from the anode to the cathode. The PRBs/Zeolite are put in three regions: near the anode side, in the center, and near the cathode side (positions I, III, and V). Twelve different tests (Series-1 & Series-2) were conducted on clay soil spiked with nickel in concentrations of 250 mg/kg. These tests were conducted with a voltage gradient of 1.5V/cm and processing time of 4 days for the Series-1 and 3 days for the Series-2. The results indicate that the EK/PRB leads to a significant improvement in the efficiency of removal and in reducing the remediation duration. While the removal efficiency in tests when AA using as purging solution and zeolite–PRB was inserted at various positions (I, III, and V) was 51.6%, 57.12%, and 41%, respectively, the removal efficiency is greater than that in the test of the electro-kinetic process without a barrier (i.e. 34.4%) under the same conditions.

Keywords: nickel, electro-kinetic, zeolite, EDTA, acetic acid.
Introduction

Naturally, nickel occurs widely in the environment. It is released through both natural and anthropogenic sources. Nickel occurs naturally in the environment through sources such as forest fires, vegetation and volcanic emissions. However, the anthropogenic activities that cause the atmospheric accumulation of nickel include combustion of coal and diesel oil, incineration of waste and sludge, and other miscellaneous sources. Nickel content in soil varies widely and it is estimated to range from 3 to 1,000 ppm; for the world soils, the grand mean is calculated to be 22 ppm. Nickel can also exist in several forms in soil; these forms are adsorbed or complex on organic cation surfaces or on inorganic cation exchange surfaces, inorganic crystalline minerals or precipitates, water soluble, free-ion or chelated metal complexes in a soil solution. With the decreasing pH, the solubility and mobility of nickel increases; hence, soil pH is the major factor that controls nickel solubility, mobility and sorption, while clay content, iron-manganese minerals and the soil's organic matter are of secondary importance (Iyaka 2011).

Many studies have shown that the EK technology has possibility to remove heavy metals by horizontal or vertical DC in low permeability soils (Hamed et al. 1991, Reddy and Chinthamreddy 2003, Lee et al. 2003, Kim et al. 2003, Wang et al. 2007, Mascia et al. 2007, Al-Hamdan and Reddy 2008a, Maturi and Reddy 2008, Castellote et al. 2008, Ma et al. 2010, and Wei and Hui 2011). Removal of contaminants from porous media by EK process is accomplished by 3 main mechanisms: electro-migration, electro-osmosis and electrophoresis. Factors affecting contaminant extractability from soils in the EK process include soil type (Reddy and Saichek 2003), contaminant type and concentration (O’Connor et al. 2003), zeta potential of soil (Yeung and Hsu 2005), electrode spacing (Alshawabkeh et al. 1999) and enhancement techniques coupled (Reddy and Chinthamreddy 2003; Sawada et al. 2003), as cited by Yuan and Chiang (2007). One such enhancement involves integration of EK with other methods of subsurface environment remediation like permeable reactive barriers (PRBs). This concept was first studied at the University of Waterloo, with the first pilot-scale PRB installed in Ontario in 1991 as cited by (Saedidi et al. 2013). Yuan and Chiang (2007) proposed batch tests with permeable reactive barrier media of Fe (0) and FeOOH to estimate the arsenic removal from contaminated soil. They observed that the arsenic removal in EK/PRB systems was significantly affected by surface adsorption/precipitation on the permeable reactive barrier media than by the EK process. Saedidi et al. (2009) investigated the impact of incorporating an activated carbon barrier into the EK process on removal of nickel (Ni) from kaolinite clayey soil. The results showed that the coupling of the electro-kinetic technology with an activated carbon barrier could successfully stop the converse electro-osmotic flow, which has an opposing impact on the removal of nickel from soil. Furthermore, 20–50% of Ni migration to the cathode through the tests was achieved. Zanjani et al. (2012) studied the removal of nickel (500 mg/kg) from kaolinite clay by EK remediation coupled with an activated carbon barrier. The results show that the barrier could prevent the creation of reverse electro-osmotic flow, which had an opposing impact on the Ni (II) removal. Furthermore, application of an activated carbon barrier in the EK process caused an increase of Ni migration from 11% to 47%.

An existing soil pollution problem in Iraq is that the sites are contaminated with nickel and contaminants vary from 72.63 to 85.32 mg/kg. The observed values are higher than the world average concentration of Ni in soil, which is around 20 mg/kg as reported by (Al-Obaidy and Al-Mashhadi 2013, Al-Dabbas et al. 2014). The present study aims to explore the possibility of applying an electro-kinetic treatment technique coupled with zeolite/PRB to remove nickel from low permeable contaminated soil in Iraq. Batch EK/PRB-zoelite tests were conducted under a potential gradient of 1.5 v/cm for 3 days duration, and chelating agents acetic acid (AA), ethylene diamine tetraacetic acid (EDTA), ammonium citrate (AC), and anionic surfactant as sodium dodecyl sulphate (SDS) were used as purging solutions (PS) to evaluate the removal of nickel from contaminated soil and to assess the effect of the location of the PRB.
Materials and method

Soil

The clay soil used in this study was taken from an unpolluted agriculture field near Al-Shamiyah, west of Diyaniya city in Iraq. The properties of this soil are presented in Table 1. To simulate the soil’s nickel contamination, a solution of Ni (NO$_3$)$_2$.6H$_2$O was prepared (1.6 g of Ni (NO$_3$)$_2$.6H$_2$O dissolves in 500 mL of distilled water) and added to 1 kilogram of dry soil to reach the desired nickel concentration of 250 mg/Kg and 40% moisture content was achieved. The feature of Iraqi soil is that it contains a high proportion of calcium carbonate (i.e., 29%), which is responsible for the soil’s high buffering capacity. This buffering capacity is measured at about 0.397 M, according to the method used by Reddy et al. (2010). Preliminary analyses of the background nickel content of the soil was about 4.5 mg kg$^{-1}$.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size distribution (ASTM D 422)</td>
<td></td>
</tr>
<tr>
<td>Sand (%)</td>
<td>15</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>62</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>23</td>
</tr>
<tr>
<td>Carvel (%)</td>
<td>0</td>
</tr>
<tr>
<td>Atterberg limit (ASTM D 2487)</td>
<td></td>
</tr>
<tr>
<td>Liquid limit (%)</td>
<td>42.10</td>
</tr>
<tr>
<td>Plastic limit (%)</td>
<td>27.48</td>
</tr>
<tr>
<td>Plasticity index (%)</td>
<td>14.62</td>
</tr>
<tr>
<td>Compaction text</td>
<td></td>
</tr>
<tr>
<td>Max dry density (gm/cm$^3$)</td>
<td>1.74</td>
</tr>
<tr>
<td>O.M.C. %</td>
<td>18.5</td>
</tr>
<tr>
<td>pH</td>
<td>7.7</td>
</tr>
<tr>
<td>CaCO$_3$, (%)</td>
<td>29</td>
</tr>
</tbody>
</table>

Zeolite

The reactive barrier consisted of zeolite manufactured by Dwax Company for synthetic zeolite with a diameter of 35.96 mm. The resins were washed with 1M of NaOH and 1M of HCl in order to remove possible organic impurities, and then they were washed with distilled water in order to remove all excess and basic. Finally, the resins were dried for 24 hours. A 2-mm thick reactive was installed at a number of regions (near the anode side, at the centre, and near the cathode side).

Enhancements to the solution (purging solution)

The removal efficiency of heavy metals from contaminated soil relies up on the extraction solution (i.e., PS) used. Hence, the present study focused on using 3 selected PS, based on previous studies such as Ginnis et al. (2007), Kim et al. (2008), Saeedi et al. (2013) and Rashid (2015), (which comprise 1 M acetic acid (AA), 1 M ammonium citrate (AC), and a mixture of 0.1 M (ethylenediaminetetraacetic (EDTA) + sodium dodecyl sulphate (SDS)).

Electro-kinetic/permeable reactive barrier system

Experimental test setup

Figure 1 shows the experimental system of the EK treatment coupled with zeolite as a permeable reactive barrier utilized in this study. The schematic diagram of this system contains an electro-kinetic cell made of plates of glass with inner dimensions of 10 cm D×10 cm W× 30 cm L as the same dimensions used by Rashid (2015), including 2 electrode compartments, 5 soil sections, 2 interface purging solutions, and DC power supply. The real length of the soil sample in this cell is equivalent to 14 cm. The soil sections were branded as regions I, II, III, IV and V from the anode to the cathode, according to Cang et al. (2009) and Spiga (2010). The PRBs/zeolite are put into the soil cell in diverse locations (positions I, III and V), whereas the clean soil was added after the barrier. The upper side of the cell was opened to the air in order to permit the emission of the electrolysis gases created at the cathode (H$_2$) and the anode (O$_2$). Perforated plastic mesh was used to separate the different segments inside the cell and filter paper was used to prevent the soil in the cell from heading for the electrode compartments. The length and the diameter of the cylindrical electrode in the cathode were 11 and 5 cm, respectively. Additionally, a sheet of graphite (7 cm W, and 8 cm D) was used as the working anode electrode. A (DC) power supply was utilized in order to apply a constant voltage to the electrodes.
Experimental design

In the present study, 2 series of tests (Series-1 and Series-2) were carried out with different locations for the zeolite/PRBs within the soil column, as listed in Table 2. Series-1 included tests EK-1, EK-2, EK-3 and EK-4 in order to study the removal of nickel from contaminated soil by using the EK process without a barrier coupled with different types of PS: 1 M AA, 1 M AC and 0.1 M (MEDTA+SDS). The series-1 tests were conducted under potential gradient 1.5 V/cm for 4 days. Series-2 included tests EK-5, EK-6, EK-7, EK-8, EK-9, EK-10, EK-11 and EK-12 in order to study the nickel removal from contaminated soil by using the EK process coupled with using zeolite as a permeable reactive barrier at a different location in the cell (positions I, III and V). The anode compartment influent and cathode compartment effluent were filled with distilled water and different types of PS (1 M AA, 1 M AC and 0.1 (MEDTA+SDS)) to the same level and the hydrostatic levels were kept constant throughout the experiment; this ensured that the water flow through the soil was caused by electro-osmosis. The EK-PRB/zeolite experiments are running under potential gradient 1.5 V/cm for 3 days with PRBs located at 3 regions: near the anode side (I), in the center (III), and near the cathode side (V) from the anode side. Thus, in EK-5 regions II, III, IV and V of the volume cell were filled with contaminated soil. Region I of the cell volume was filled with clean soil and zeolite of 2 cm in length. Filter paper was also put between the contaminated and the uncontaminated soil. In EK-6, regions I, II, IV and V of the cell volume were filled with contaminated soil. Region III of the cell volume was filled with clean soil and zeolite of 2 cm in length. For EK-7, regions I, II, III and IV of the cell volume were filled with contaminated soil, whereas region V near the cathode compartment was filled with zeolite of 2 cm in length and the remaining volume of the region was filled with clean soil (control test), according to the practical method is adopted by Cang et al. (2009) and Spiga (2010) (as shown in table 2, experiment scheme). However, in the tests using 1 M AC and 0.1 M (EDTA+SDS), a permeable reactive barrier was arranged as the reverse of the test using 1 M AA as purging.
Table 2
Experimental design of EK-PRB treatments

<table>
<thead>
<tr>
<th>Series</th>
<th>Experiment designation</th>
<th>Soil saturation</th>
<th>PS (pH)</th>
<th>PRB located at</th>
<th>Experiment scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>anode</td>
<td>cathode</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>EK-1</td>
<td>DW</td>
<td>DW</td>
<td>DW (~7)</td>
<td>without</td>
</tr>
<tr>
<td></td>
<td>EK-2</td>
<td>1 M AA</td>
<td>DW</td>
<td>1 M AA (~3)</td>
<td>without</td>
</tr>
<tr>
<td></td>
<td>EK-3</td>
<td>1 M AC</td>
<td>DW</td>
<td>1 M AC (~9)</td>
<td>without</td>
</tr>
<tr>
<td></td>
<td>EK-4</td>
<td>0.1 M (EDTA + SDS)</td>
<td>DW</td>
<td>0.1 M (EDTA + SDS) (~ 6)</td>
<td>without</td>
</tr>
<tr>
<td></td>
<td>EK-5</td>
<td>1 M AA</td>
<td>DW</td>
<td>1 M AA (~3)</td>
<td>Region I</td>
</tr>
<tr>
<td></td>
<td>EK-6</td>
<td>1 M AA</td>
<td>DW</td>
<td>1 M AA (~3)</td>
<td>Region III</td>
</tr>
<tr>
<td></td>
<td>EK-7</td>
<td>1 M AA</td>
<td>DW</td>
<td>1 M AA (~3)</td>
<td>Region V</td>
</tr>
<tr>
<td></td>
<td>EK-8</td>
<td>1 M AC</td>
<td>DW</td>
<td>1 M AC (~9)</td>
<td>Region I</td>
</tr>
<tr>
<td></td>
<td>EK-9</td>
<td>1 M AC</td>
<td>DW</td>
<td>1 M AC (~9)</td>
<td>Region III</td>
</tr>
<tr>
<td></td>
<td>EK-10</td>
<td>1 M AC</td>
<td>DW</td>
<td>1 M AC (~9)</td>
<td>Region V</td>
</tr>
<tr>
<td></td>
<td>EK-11</td>
<td>0.1 M (EDTA + SDS)</td>
<td>DW</td>
<td>0.1 M (EDTA + SDS) (~ 6)</td>
<td>Region I</td>
</tr>
<tr>
<td></td>
<td>EK-12</td>
<td>0.1 M (EDTA + SDS)</td>
<td>DW</td>
<td>0.1 M (EDTA + SDS) (~ 6)</td>
<td>Region V</td>
</tr>
</tbody>
</table>

DW – distilled water  Clean soil  Barrier  Contaminated soil  A – Anode  C – Cathode

Results and discussion
Electro-kinetic experiments without using a permeable reactive barrier

Figure 2 shows the variation for current as the function of time in EK systems without PRB for tests of EK-1, EK-2, EK-3 and EK-4 that were conducted with the enhanced purging solution; the initial current was within the range 15–55 mA for tests EK-1 through EK-4, then was increased to 53–141 mA within approximately
18–36 hours, and then decreased to become stable values between 25 and 28 mA. This result was consistent with Saeedi et al. (2013) who reported that the reduction of electrical current through soil during the tests relates to increasing resistance of the soil matrix electrical due to precipitation of ions as insoluble products, particularly next to the electrodes. The time differences for the initial increase of electric current between EK-1 and EK-2, EK-3 and EK-4 may be due to the presence of AA, AC and EDTA+SDS in soil pores.

**Fig. 2**
Variation in the current of electro-kinetic process without PRB as function of time for experiments EK-1 –EK-4

Figure 3 shows the current through the soil specimen for tests of EK 5–7 coupled with zeolite-BRP; these experiments were enhanced by acetic acid. In addition, these experiments were conducted for a total of 72 hours as compared with the test of EK-2 at the end of the treatment time (which was conducted for 96 hours). The current increased to high values of 120, 113 and 118 mA in 36 hours for tests of EK-5, EK-6 and EK-7, respectively, at the end of treatment time for 72 hours. It is clear that the current for test EK-2 was higher than those for tests EK 5–7. Furthermore, as it can be seen in the same figure, the difference in the current was significantly related to the PRB positions and the trend of the current in the present study the same as reported by Yuan and Chiang (2007). The initial increase in the current was largely because of the ability of acetic acid to desorb different conductive ions, in an aqueous environment. Then, a gradual decrease in the current reached stable values for different reasons, according to Yuan and Chiang (2007), where the clogging of precipitates in the soil pores resulted in a low current density at the end.

**Fig. 3**
Current variations with different regions of BRP in the EK/ zeolite system

Figure 4 (a, b, c and d) shows the distribution of Ni\textsuperscript{2+} within the soil matrix with pH values at the end of 96 hours treatment time. The pH profiles for soil after treatment are shown in Figure 4 (a). In test EK-1, distilled water was used as PS. The pH for soil near the anode reduced from 7.7 for the initial soil to around 7.3, while the pH for soil close to the cathode compartment increased to about 10.6 at the end of the treatment time. Here, pH for soil was observed to be increasing from the anode towards the cathode region and, consequently, nickel concentration values increased to about 245 mg/kg in the cathode region; this may have been due to the precipitation of nickel as hydroxide salts that occurred within the soil matrix. In contrast, it decreased in the anode region to about 221 mg/kg. The concentration profile in the same figure indicates that removals of nickel from the soil system in this test are below the initial concentration, which was 250 mg/kg. Therefore, the final achieved removal efficiency was 5.36%.

Figure 4 (b) illustrates the nickel concentration profile, and the movement trend soil pH within the soil specimens after the end of the electro-kinetic treatment period. Test EK-2 used 1 M acetic acid (AA). Here, in
this test front movement of the acidic towards the cathode occurred, because the technique of saturating the soil for about 24 hours before electro-kinetic treatment was used, according to Paramkusam et al. (2015). This resulted in a low pH in all parts of the soil matrix relative to the initial soil pH 7.7, i.e., the addition of acetic acid may have been limiting base front propagation from the cathode, as observed from the residual nickel concentration results and also shown in the same figure. This means that the part of nickel would migrate toward the cathode and the final achieved removal efficiency was 34.4%, the test result of the present study are similar as reported by Rashid (2015). Figure 4 (c) displays the profile for soil pH and distribution of nickel concentration in all parts of the soil after the electro-kinetic process for test EK-3 (i.e., using ammonium citrate (1 M) for saturating the soil and in the cathode compartment, with pH adjusted to become about 9). Figure 4 (c) shows that the pH values in all parts of the soil were found to be higher than the initial pH value for nickel-contaminated soil, where the soil pH was equal to 7.8 in the part near the anode side but was equal to 9.6 in the part near the cathode side. In addition, it was found that the residual nickel concentration in the cathode region was 163 mg/kg, while it was 241 mg/kg in the anode region. Therefore, it might be said that nickel migrated towards both sides of the electrode compartments, but all nickel concentrations were observed below the initial concentration at all parts (i.e., no accumulation

**Fig. 4**
Residual nickel distribution in soil after the 96-hour electro-kinetic process without PRB treatment. Electro-kinetic experiment using a permeable reactive barrier.
within any parts of the soil). The removal efficiency achieved was equal to 19.4%. In other words, Ni\(^{2+}\) was transported towards both the anode and the cathode electrode during the experiment because the complexes with ammonia and with the citric part were formed. Similar results have also been reported by Rashid (2015) and Paramkusam et al. (2015).

Using a single and combined solution of the chelating agent, Olusegun and Oluwafemi (2012) investigated the removal of heavy metals from the soil collected from a foundry site. The soil samples were shaken with different chelating agents. Nickel, cadmium and manganese were removed from the contaminated soil at 88.24%, 85% and 82%, respectively, using a mixture of 0.2 M EDTA, 1.0 M citrate, 0.5 M oxalate and 1% SDS. This proved that a combination would be highly effective in the removal of all metals to an appreciable amount. Finally, Figure 4 (d) shows the distribution of nickel versus the normalized distance in a soil cell after test EK-4 for 4 days, which was performed under 0.1 M (EDTA+ SDS) for saturation of soil and also using the same purging solution in the cathode compartment according to the method used by Paramkusam et al. (2015). The results for test EK-4 show migration of nickel throughout the soil specimen to the anode region. There is an increased nickel concentration (277.5 mg/kg), i.e., accumulation, in the part near the anode side, but a significant decrease in the part near the cathode side (90 mg/kg) because of the increasing soil pH compared with the initial concentration of nickel (250 mg/kg). At this point using EDTA as a purging solution, precipitation of nickel occurred between the cathode and the anode. Then EDTA-nickel complexes flowed through the soil column and entered the cathode reservoir and then the pH of the soil specimens became greater than 7.7 or further dissociated EDTA to a species EDTA\(^{4-}\). Consequently, the EDTA-nickel complexes became negatively charged and began to migrate back toward the anode as cited by (Hosseini et al. 2011).

Figure 5 illustrates the soil pH profile through the soil specimen after EK/PRB. The profile shows the acid front generated at the anode compartment cross through the soil specimen, which decreased the soil pH from 7.7 to 5.3–6 near the anode side for tests EK 5–7. Although the pH in the cathode compartment was kept within the value about 3.0, the pH in the soil at position V (near the cathode) reached a value between 7.2 and 7.4 for all tests. From the general trend for the soil pH profile within the soil specimens for tests EK/zeolite-PRB no relation is seen between soil pH and PRB regions. These results consistent with Yuan and Chiang (2007) who reported that there was no evident relationship between pH and PRB positions.

Depending on the same arrangement adopted by Yuan and Chiang (2007) Table 3 shows, the electro-osmotic permeability coefficient observed over the entire experiment duration was calculated to be 2.9*10\(^{-6}\) cm\(^2\)/V.s for EK-5, 3.03*10\(^{-6}\) cm\(^2\)/V.s for EK-6, and 3.34*10\(^{-6}\) cm\(^2\)/V.s for EK-7; and these values are lower than the value of the test of EK-2, which was 4.01*10\(^{-6}\) cm\(^2\)/V.s. However, soil pH in tests EK-5 and EK-6, when zeolite-PRB was set in position I and III, reduced from 7.7 (initial soil pH) to 5.4–6.3. Also, as shown in Table 3, where adsorption capacity for zeolite of Ni\(^{2+}\) was 96.75 and 118.1 mg/kg for tests EK-5 and EK-6, when zeolite-PRB was set in position I and III, reduced from 7.7 (initial soil pH) to 5.4–6.3. Also, as shown in Table 3, where adsorption capacity for zeolite of Ni\(^{2+}\) was 96.75 and 118.1 mg/kg for tests EK-5 and EK-6, respectively, which was higher than that for test EK-7 (53.45 mg/kg), and because of that less concentration of nickel was removed by EO flow or electro-migration, this result can be proved through the lowest amount of salts accumulated on the surface of the cathode electrode at the end of EK-5 test.
Table 3
Fractional nickel distributor in EK/zeolite (initial concentration of nickel= 250 mg/kg)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>PRB located at</th>
<th>Ke cm²/V.s</th>
<th>Qe Cm³/s</th>
<th>Fractional Ni²⁺ residual mg/kg</th>
<th>Fractional Ni²⁺ sorbed onto zeolite mg/kg</th>
<th>Fractional Ni²⁺ Removal be EO mg/kg</th>
<th>Fractional Ni²⁺ in soil for clean mg/kg</th>
<th>Fractional removal of Ni²⁺ by sorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EK-2</td>
<td>-</td>
<td>4.01×10⁻⁶</td>
<td>6.02×10⁻⁴</td>
<td>159.8</td>
<td>-</td>
<td>90.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EK-5</td>
<td>I</td>
<td>2.9×10⁻⁴</td>
<td>4.47×10⁻⁴</td>
<td>121</td>
<td>96.75</td>
<td>25</td>
<td>7.25</td>
<td>75</td>
</tr>
<tr>
<td>EK-6</td>
<td>III</td>
<td>3.03×10⁻⁴</td>
<td>4.55×10⁻⁴</td>
<td>106.8</td>
<td>118.1</td>
<td>17.1</td>
<td>8</td>
<td>79.9</td>
</tr>
<tr>
<td>EK-7</td>
<td>V</td>
<td>3.34×10⁻⁶</td>
<td>5.01×10⁻⁴</td>
<td>145.2</td>
<td>53.4</td>
<td>14.9</td>
<td>9.5</td>
<td>51</td>
</tr>
</tbody>
</table>

(with zeolite-PRB), as compared with a huge amount of salts that accumulated on the surface of the cathode at the end of EK-2 test (without PRB), as shown in Figure 6. Also, it can be seen from Table 3 that the concentration of Ni²⁺ was lower amount in the clean soil, that was placed after zeolite-PRB, because of the largest proportion of nickel was removed by adsorption on zeolite-PRB.

Fig. 6
Accumulation of salts on the surface of the cathode electrode at the end of the test of (a) EK-5 (with zeolite-PRB) and (b) EK-2 (without barrier), respectively

![Image](image.png)

The nickel distribution profile is shown in Figure 7, where an application of 1 M acetic acid for saturating soil and the purging solution in the cathode compartment was achieved for EK-2 test. In contrast, when enhancements were made to the electro-kinetic process by the addition of a permeable reactive barrier, when zeolite-PRB was located at region I (for EK-5), the residual concentration of nickel in the contaminated soil migrated towards the cathode, albeit, the nickel concentration at Region I was equal to 105 mg/kg. However, Regions III and IV had high values (151 and 150 mg/kg, respectively) compared to position II and position V, which were equal to 99 and 100 mg/kg, respectively. However, when the zeolite-PRB was put at position III (for EK-6), the concentration of nickel in the contaminated soil was decreased towards the cathode, i.e., it decreased in positions IV and V as compared to Regions I and II, where it increased. In general, the results of removal efficiency for tests when zeolite-PRB was inserted at Region I, III and V (for EK-5, EK-6, and EK-7) were 51.6%, 57.12% and 41%, respectively, which are greater than the electro-kinetic test without the barrier (for EK-2), which was equal to 34.4%. These results of the present study are consistent with Yuan and Chiang (2007), who reported that a best performance for removal of arsenic from contaminated soil was found in system with
FeOOH layer (PRB) located in the middle of electrokinetic cell (i.e. in the center of cell).

The nickel distribution profile is shown in Figure 8 for tests EK 8-10, which were coupled with zeolite-PRB. The lowest proportion of nickel was removed by adsorption, whereas the largest proportion of nickel was removed by the electro-migration mechanism. When a zeolite-PRB was loaded in position I in test EK-8, the Ni$^{2+}$ moved up to positions II, III, IV and V from the cathode side, where it precipitated and accumulated to become about 245, 238, 171 and 153 mg/kg, respectively, higher than those at the same region in test EK-3. While the tests EK-9 and EK-10, when zeolite-PRB was put at positions III and V. It was seen that the residual concentration of nickel in position V was lower than that the residual concentration of nickel in Region I. Finally, The removal efficiency of nickel for EK-8, EK-9, and EK-10, when zeolite-PRB was put at the same region was 20.64%, 19.56% and 17%, respectively. In deed, the difference in removal efficiency between EK tests 11 and 12, the pH of the soil was low relatively to the initial soil pH. The results reveal that the loaded zeolite/PRB did not greatly affect the pH difference, also similar results have also been reported by Yuan and Chiang (2007). Figure 9 shows the residual concentration profile of nickel for both tests: EK-11 (when zeolite-PRB was loaded in Region I) and EK-12 (when zeolite-PRB was loaded in Region V), where an application of 0.1 M (EDTA+SDS) for saturating soil and the purging solution in the cathode compartment. Here, it can be noted that most of the nickel concentration migrated from the soil section near the cathode and accumulated from all sections in Region I (section near the anode). The removal efficiency of nickel in Region V was higher than that in Region I. This may be because the EDTA formed effectively a complex with Ni$^{2+}$ (in particular in alkaline circumstances), resulting in more mobilization of Ni$^{2+}$ from the soil towards region I. The results of the present study (where the trend of migration for nickel occurred toward the anode) are consistent with that reported by Saeedi et al. (2013) and Rashid (2015).

Fig. 8
Residual nickel distribution of treated soil in the EK/zeolite system

![Figure 8](image)

Conclusions
In this research, a remediation method for Ni (II) contaminated soil was investigated that combined an EK-PRB system with zeolite as a permeable reactive barrier (PRB). In test EK-1(without a barrier), in which distilled water was used as the electrolyte in the anode and cathode compartments, the removal efficiency of Ni$^{2+}$ was low for soil to about 5.36%, because...
high pH values for soil were observed from the anode towards the cathode region and, consequently, nickel concentration values increased to 245 mg/kg in the cathode region. This may have been due to the precipitation of nickel as hydroxide salts that occurred within the soil matrix. In contrast, it decreased in the anode region to about 221 mg/kg. The removal efficiency for tests when zeolite-PRB was inserted at positions I, III and V (for EK-5, EK-6 and EK-7), where an application of 1 M acetic acid for saturating soil and the purging solution in the cathode compartment was 51.6%, 57.12% and 41 %, respectively, which is greater than the test of the electro-kinetic process without a barrier (for EK-2), which was equal to 34.4%.

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References


Nikeliu užteršto molingo dirvožemio išvalymas elektrokinetikos technologijomis, susietomis su ceolitu – naudojant reaktyvų barjerą

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Šis tyrimas įvertina skirtingų valymo tirpalų naudojimo efektyvumą: acto rūgštį (AA), amonio citratą (AC), etilenidarmetronato rūgštį (EDTA) ir natrio dodecilio sulfatą (SDS) kaip valymo tirpalai dirvožemiui prisoti. Tyriime taip pat analizuojama, kaip elektrokinetikos (EK) procesas kartu su ceolitu yra pralaidus reaguojantis barjeras (PRB) naudojant katolito tirpalą. Nikeliu užterštas molio dirvožemis pakraunamas kaip I, II, III, IV ir V padėtis nuo anodo iki katodo. PRB / ceolitas yra padalintas į tris pozicijas: šalia anodo pusės (I, III ir V pozicijos). Dyvlika skirtingų bandymų serijų (serija-1 ir serija-2) buvo atliekami ant molingo dirvožemio, kuriame nikelio buvo 250 mg/kg. Šie bandymai buvo atliekami su 1,5 V/cm įtampos gradientu ir serijos - 1 serijos, 1 ir 3 dienų trukmės, 4 dienų apdorojimo serija - 2. Rezultatai rodo, kad EK/PRB žymiai pagerina nikelio nuimimą iš dirvožemio, kuriame nikelio buvo 250 mg/kg. Šie bandymai buvo atliekami su 1,5 V/cm įtampos gradientu ir serijos - 1 serijos, 1 ir 3 dienų trukmės, 4 dienų apdorojimo serija - 2. Rezultatai rodo, kad EK/PRB žymiai pagerina nikelio pašalinimo efektyvumą ir mažina valymo trukmę. Nors pašalinimo efektyvumą bandymuose, kai AA, naudojant valymo tirpalą ir ceolitą-PRB, buvo atliekami įvairiose pozicijose (I, III ir V), buvo atitinkamai 51,6%, 59,12% ir 41,76%. pašalinimo efektyvumas yra didesnis nei tas, kuriame esant tokiomis sąlygomis atliekant elektrokinetikos procesą be kliūties (t. y. 34,4%), bandymas.

Raktiniai žodžiai: nikelis, elektrokinetika, ceolitas, EDTA, acto rūgštis, dirvožemis.