INFLUENCE OF NICKEL SPECIATION ON ELECTROKINETIC SEDIMENT REMEDIATION EFFICIENCY

This article presents a bench-scale investigation of nickel removal during electrokinetic (EK) remediation of sediment, and the dependency of removal efficiencies upon the speciation of the metal, as influenced by the duration of the nickel-sediment interaction. The sediment used in this study was from the Grand Bačka canal (Vojvodina, Republic of Serbia). The sediment used is anaerobic and the nickel pollution has been aged for several years, so it is mostly sorbed by sulphides and organic matter (57%). In EXP I, conventional EK remediation was conducted on this sediment for 7 days, but was ineffective (0% removal). EXP II investigated the influence of the duration of nickel sorption onto the sediment, by contaminating the sediment with additional nickel. In this sediment, nickel appeared mainly in the most mobile, acid-soluble fraction, and was thus available for migration towards the cathode. Consequently, conventional EK remediation of this sediment resulted in significantly better nickel removal (23%) than EXP I. During EXP III, the same spiked sediment was investigated using an increased applied current density, with no significant increase in removal efficacy. This study demonstrates that metal-sediment interaction duration affects efficacy of metal removal during EK remediation.

Keywords: electrokinetics; remediation; sediment; nickel; speciation.

Many industrial and agricultural activities in Vojvodina (Republic of Serbia) have lead to canal, lake and river sediments, which are highly polluted with organic and inorganic pollutants. It has been shown that heavy metals are the main pollutants in some sites [1,2] with emphasize on nickel, cadmium and lead. Since contaminants from sediment can be released into water bodies by changes in conditions (temperature, redox potential, pH value, ionic strength, bioturbation, etc.) and consequently become available to aquatic organisms and humans [3], it is critical that sediment contamination is addressed quickly and the appropriate remediation treatment applied. The most common remediation method has been dredging the contaminated sediments followed by disposal in landfills. However, disposal of dredged sediments at landfills can create potential concerns such as contaminant exposure, slow dewatering and consolidation, high costs, and long-term liability. There are many techniques for treating sediments, including physical, chemical, or biological processes to remove or degrade contaminants or immobilize the contaminants within the sediment [4]. Among those, techniques which provide extraction of contaminants from the sediment are a better choice that those based on transformation of contaminants into more stable forms which are not available to organisms. Besides treatment efficiency, cleanup cost has to be considered and is the major constraint for the wider application of treatments in sediment remediation projects. Different treatments can be applied ex situ and in situ, with in situ techniques generally being seen as more desirable since they are cost-effective, technically possible, efficient and safe for the aquatic environment [5,6].

It is necessary to develop a simple, safe and cost-effective cleanup process for contaminated sediments. Essentially, electrokinetic (EK) remediation involves the installation of electrodes into the contaminated sediments (ex situ or in situ). After the electrodes are installed, an electric field is applied to create a flow of water in the inter-electrode space, facilitating the migration of contaminants towards the electrodes. The contaminants are then collected and treated, either in a separate process or directly in the sediment by chemical or biological reactions.

This study focuses on the influence of nickel speciation on the efficiency of electrokinetic remediation. It demonstrates that the duration of nickel-sediment interaction has a significant impact on the removal efficacy of the process. The results show that conventional EK remediation can be improved by increasing the applied current density, leading to a more effective removal of nickel from the sediment.

Keywords: electrokinetics; remediation; sediment; nickel; speciation.
are installed, a low electric potential is applied across the anodes and the cathodes. The application of an electric potential induces the following three major transport processes in the sediment: electroosmosis, the movement of interstitial water towards the cathode or anode; electromigration, the movement of ionic species to the oppositely charged electrode; and electrophoresis, the movement of charged colloids and particles to the oppositely charged electrode. In addition, electrolysis reactions occur at the electrodes which generate H⁺ at the anode and OH⁻ at the cathode. The electromigration of H⁺ and OH⁻ can reduce the sediment pH near the anode and increase the sediment pH near the cathode [7]. Electromigration and electroosmosis are important mechanisms in electrokinetic processing which remove contaminants from sediment. The advantages of this technology are its relatively low operating costs and its potential applicability to a wide range of contaminant types [8,9].

So far, little attention has been given to the influence of heavy metals speciation on the EK process and the influence of the conditions during the EK process on metals speciation [10]. To determine the nature of the chemical species present in the sediment and their relative mobilities, sequential extraction analysis has been suggested. Heavy metals present their highest bioavailability immediately after application in the sediment. This is ascribed to reactions between the metal ions and the sediment, which mainly include complexation, surface adsorption, exchange reactions, chelation, and precipitation of metal ions in the soil particle surface or diffusion into the mesopores and macropores of the sediment, leading to the conversion of highly soluble forms into less soluble ones [11]. If heavy metals exist as exchangeable or adsorbed forms on the surface of clay, organic matter and oxides with weak bonding strength, they tend to be easily moved and dispersed.

The purpose of this study was to investigate the influence of Ni speciation on EK removal efficiencies and Ni behavior in sediment during EK treatment. The experimental results are used to evaluate possible mechanisms for Ni removal efficiencies under an induced electric field during conventional EK treatments of sediment.

MATERIALS AND METHODS

Sediment sample

The sediment used in these experiments was collected from the Grand Bačka Canal in Vojvodina, Republic of Serbia, with an initial Ni concentration of 110 mg kg⁻¹. The sediment was then spiked with NiCl₂·6H₂O to achieve a Ni concentration of (mg kg⁻¹): 299±15 and 289±14. The mixture was standing for two days to let the adsorption and/or reaction of Ni with the sediment constituents. The idea was to create conditions where Ni ions would have less time to sorb onto sediment particles than was the case for the original sediment. In all experiments the sediment was used non-homogenized and with its initial water content (77%) in order to simulate the real sediment chemistry. The original sediment sample was labelled S1 and the spiked sediment samples after Ni addition as S2 (299±15 mg kg⁻¹) and S3 (289±14 mg kg⁻¹).

Electrokinetic setup

The EK setup (Figure 1) consisted of an electrokinetic cell, two electrode reservoirs connected to the cell with the polyethylene tube, a DC power source (0-30 V, 0-3 A) and a multimeter connected to the computer. The Plexiglas test cell consisted of the sample compartment (dimensions 16 cm×5 cm×10 cm) with the electrode chambers (working volume 495 ml) at the both sides and gas vents, isolated from the sample compartment by perforated Plexiglas plates. At both sides of the sample compartment two sheets of filter paper (pore size 2.5 μm) were inserted to prevent sediment particles from flowing into the electrode chambers. The graphite plate electrodes were 10 cm×7 cm×1 cm.

Chemicals and analytical methods

All the chemicals used were at least analytical-reagent grade. The sediment particle size was determined using ISO method 13317-2:2001. The pH and oxidation-reduction potential (ORP) of the contaminated sediment were measured on a pH meter (340i, WTW). The sediment pH measurements were carried out in deionized water (sediment:water = 1:5) with a
SenTix®21 electrode. Dissolved organic carbon (DOC) was measured in the supernatant after filtration through 0.45 μm cellulose nitrate filters, on a total organic carbon analyzer (liquiTOCII, Elementar, Germany). The ORP of the contaminated sediment was measured with a SenTix®ORP electrode placed directly in the sediment. The ammonium acetate method was used to measure cation exchange capacity (CEC). Acid neutralizing capacity (ANC) was measured and calculated according to the Gran method. The content of organic matter was determined by weighing the dried sample and then heating it in a furnace at 550 °C for 4 h.

The protocol for chemical extraction for determination of pseudo-total Ni content in sediment was performed in accordance with USEPA method 3051A. Dry sediment sample (0.5 g) was mixed with 10 mL of 6M nitric acid in Teflon beakers. Extraction was carried out with a microwave oven (Milestone, Stare E microwave) using the following programme: temperature increased over 5.5 min to 175 °C, then held at 175 °C for another 4.5 min. The term “pseudo-total” refers to the fact that the metals content incorporated in the silicates was not determined, as this metals fraction is not available to organisms and is therefore not of interest from an ecological point of view. To determine the speciation of Ni in the sediment, samples were sequentially extracted according to the BCR method, modified by Arain et al. [12]. The Ni species in the sediment are divided in three groups: 1) acid-soluble fraction (labile and carbonates-bound), 2) reducible fraction (Fe-Mn oxides-bound) and 3) oxidizable fraction (organic- and sulphide-bound). The first step of the extraction involved mixing 0.25 g of dry sample and 10 mL of 0.11 M acetic acid. The microwave extraction was then performed (Milestone, Stare E microwave). The second step of the extraction involved mixing 0.25 g of dry sample and 10 mL of 0.5 M hydroxylamine-hydrochloride followed by microwave extraction. The residue after the second step was mixed with 5 mL of hydrogen peroxide and heated at 85 °C for 1 h. This was repeated twice and followed by addition of 25 mL ammonia-acetate and microwave extraction. Each microwave digestion step lasted 120 s at 45 °C. The liquid after each step was separated from the solid particles by vacuum through a 0.45 μm filter and diluted to 50 mL. Analyses of Ni were carried out using Flame Atomic Absorption Spectrophotometry (Perkin Elmer, AAnalyst 700) in accordance with USEPA method 7000b.

Electrokinetic experiments

A non-homogenized sediment sample was measured for each experiment test and placed into the sample compartment of the electrokinetic cell. A constant voltage was applied to the system and the electrical voltage gradient was 1 VDC/cm. De-ionized water was used as anolyte and catholyte. The experiments lasted for 7 days.

The experimental conditions are summarized in Table 1.

<table>
<thead>
<tr>
<th>Test</th>
<th>Sample</th>
<th>Sediment dry mass, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXP I</td>
<td>S1</td>
<td>190</td>
</tr>
<tr>
<td>EXP II</td>
<td>S2</td>
<td>190</td>
</tr>
<tr>
<td>EXP III</td>
<td>S3</td>
<td>80</td>
</tr>
</tbody>
</table>

At the end of the process, the sediment sample was sectioned into five parts. Each part was assigned as the normalized distance zL (z = distance from the anode, L = the sediment bed length) from the anode: 0.19, 0.34, 0.49, 0.64 and 0.79. The pH, ORP, Ni pseudo-total concentrations and chemical forms of Ni of the initial sediment sample and in each of its sections were measured.

Quality assurance

Some precautions were taken in order to ensure the accuracy and repeatability of the test results. These precautions included: 1) soaking the apparatus, including perforated Plexiglas plates and tubing, in dilute nitric acid solution for 24 h and rinsing with tap water, followed by deionized water, to avoid cross-contamination between experiments and 2) washing all glassware and plastic material before use with dilute nitric acid and rinsing with tap water, followed by deionized water. In addition, for quality assurance of the sample analyses, duplicates were performed, and the calibration of the atomic absorption spectrophotometer was performed after every five samples.

The BCR extraction procedure was carried out on the certified reference material (BCR701) and there was a good correlation between the results. In our lab analysis of BCR701 (Ni certified concentration: 15.4±0.9 for acid soluble fraction, 26.6±1.3 for reducible fraction and 15.3±0.9 for oxidizable fraction) gave a Ni concentration of 15.5±0.78 (acid-soluble fraction), 24.6±1.2 (reducible fraction) and 17.7±1.3 (oxidizable fraction).

RESULTS AND DISCUSSION

Initial sediment properties

The physicochemical characteristics of the sediment used for EK experiments are shown in Table 2.
The Ni pseudo-total concentrations as well as the contents of different fractions in the sediment are presented in Table 3.

### Table 2. Composition and properties of the sediment used in the electrokinetic experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size, %</td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>90.7</td>
</tr>
<tr>
<td>Silt</td>
<td>13.1</td>
</tr>
<tr>
<td>Clay</td>
<td>3.8</td>
</tr>
<tr>
<td>Water content, %</td>
<td>77</td>
</tr>
<tr>
<td>pH</td>
<td>7.4</td>
</tr>
<tr>
<td>CEC, meq/100g</td>
<td>17</td>
</tr>
<tr>
<td>ANC, meq/100g</td>
<td>146</td>
</tr>
<tr>
<td>OM, %</td>
<td>20.3</td>
</tr>
<tr>
<td>DOC, %</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The particle size composition of the sediment used in this study was determined as: sand (90.7%), silt (13.1%) and clay (3.8%). The sediment has a high OM content (20.3%) which is mainly responsible for the high CEC value (17 meq/100g), since the clay content is relatively low. This indicates that Ni can be sorbed by organic matter in a high percentage. Also, since there is high content of DOC (1.2%) in the sediment, Ni could exist in metal-organic complexes. The high ANC value indicates that the sediment cannot easily be acidified, which is an important parameter in predicting EK metal removal.

### Table 3. Initial concentrations of Ni and its contents in different fractions in S1, S2 and S3 (mg kg⁻¹)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid-soluble</td>
<td>8.53±0.42</td>
<td>89.7±4.5</td>
<td>139±7</td>
</tr>
<tr>
<td>Reducible</td>
<td>7.02±0.35</td>
<td>73.9±3.7</td>
<td>55.4±2.8</td>
</tr>
<tr>
<td>Oxidizable</td>
<td>61.9±3.1</td>
<td>117±6</td>
<td>74.4±3.7</td>
</tr>
<tr>
<td>Pseudo-total</td>
<td>108±5</td>
<td>299±15</td>
<td>289±14</td>
</tr>
</tbody>
</table>

The results in Table 3 indicate that in S1 the Ni mostly appeared in the oxidizable fraction which is a stable form of the metal. In S2 and S3 a high percentage of the Ni appeared in the oxidizable fraction, but there is also a large amount in the acid-soluble fraction.

### Changes in the current density, pH and ORP in the sediment during the EK experiment

Figure 2 shows the overall current densities of the cross-sectional area between the electrodes, measured every 1 h for each experiment. There were no significant changes in the current density during the experiments. The increased current density during EXP II compared to EXP I can be explained by the higher amount of ions in the pore water. During EXP III there is a much higher current density which was accomplished by lowering the cross-sectional area. There was no significant decrease in the current after seven days of experiment, since some Ni remained in the acid-soluble fraction of the sediment. Besides, there was probably a certain amount of other naturally occurring cations (Ca²⁺, Na⁺, Mg²⁺, etc.) and the corresponding anions.

![Figure 2. Changes of current density during EK experiments.](image)

After the EK removal experiment, the pH in the sediment compartment was measured at the different normalized distances from the anode (Figure 3). The overall pH in the sediment did not decrease significantly because of the high CEC and high buffer capacity (ANC) of the sediment [13,11], which decreased the dissolution and desorption rates of the adsorbed and/or complexed species in the sediment. However, the pH in the region close to the cathode (z/L = 0.79) did show an increase during this study.

The ORP showed a significant movement to more negative values in the sediment bed during the experiment with increasing distance from the anode (Figure 4), and it highly affected the Ni speciation. Such behaviour probably occurred due to hydrogen evolution at the cathode during the EK process [13]. The somewhat more positive ORP near the anode can be ascribed to oxygen generation.

### Efficacy of EK removal and speciation of Ni

The efficacy of EK removal was assessed by determining the pseudo-total content of Ni in the sediment before and after the treatment. Figure 5 shows the distribution of pseudo-total Ni concentration remaining in the sediment after EXP I, EXP II and EXP
III. In order to understand Ni behaviour during the EK process, sequential extraction was performed and the results presented in Figure 6. The removal of Ni from sediment during EXP I was negligible, for several reasons. First, since the sediment has a low redox potential (-231 mV) and the Ni pollution has aged for several years, the Ni mostly exists in the oxidizable fraction and the residual fraction (61.9 and 30.3 mg kg^{-1}, respectively). Ni can also precipitate as hydroxide since the initial sediment pH value is high (8.3) [13]. Metals in these fractions are stable and are not available for migration under an electric field [11]. In addition, the sediment has a high CEC and buffering capacity (ANC), so an acid front, which could dissolve Ni sorbed onto sediment particles, did not occur in the sediment (Reddy et al. (2006)).

The EK removal of Ni from sediment during EXP II was significantly better (23%) than EXP I. This is probably because during the 48 h of Ni-sediment interaction, a large amount of Ni appeared in the highly mobile acid-soluble fraction (33.3%), and was thus available for electromigration towards the cathode, even though the sediment had a high pH value and high buffer capacity [14]. This is a consequence of the short interaction time between Ni and sediment as well as the presence of a high amount of dissolved organic matter which results in Ni complexation [11]. During the EK process, the acid-soluble Ni fraction decreased for 36, 7, 17, 10 and 33% at different distances from the anode, with significant reductions of this fraction only observed at the anode (z/L = 0.19) and at the cathode region (z/L = 0.79). Only dissolved metals can be removed during electrokinetic remediation. Besides dissolved metals the acid-soluble fraction includes metals sorbed on carbonates [15]. Since removal of sorbed metals is limited it affects the remediation efficiency. It means that some percentage of metals in acid-soluble fraction remains in sediment after remediation. The behaviour of the reducible fraction is probably due to the desorption of Ni from Fe-Mn oxides which were reduced (10, 87, 69, 78 and 75% at different distances from the anode) in the reducing conditions arising in the sediment during the EK process (Figure 2) [16]. These can explain the overall behaviour of the acid-soluble fraction since Ni probably rearranged in the acid-soluble fraction from reducible fraction and recovered the extracted amount of Ni. There is no dissolution at z/L = 0.19 since there is no significant pH decrease. There were no significant changes in the oxidizable Ni fraction during the process due to the reducing conditions in the sediment and the absence of an acid front in the sediment bed. Only at the z/L = 0.19 does the oxidizable fraction decrease significantly (37%), due to the oxygen produced at the anode [17]. Although the pH value increased in the sediment bed near the cathode, there was no increase in Ni concentration in that region. The absence of Ni(II)-hydroxide formation and the overall increase in the Ni concentration at z/L = 0.79 may be due to complexation of Ni with dissolved organic matter resulting in the formation of anionic Ni complexes [18,19] as well as high solubility product of Ni(II) hydroxide.

The degree of overall Ni removal during EXP III was greater than EXP I (14%), but not outdo the efficacy of EXP II (Figure 5). The acid-soluble fraction values (Figure 6) remain mostly the same due to the dissolution of the reducible fraction, except at z/L = 0.19 where the ORP shows a slightly more positive value and so the reducible fraction increased (62%). This is in agreement with the current density behaviour during treatment (Figure 2). Additionally, there is an increase of the oxidizable fraction in the sediment due to the increasingly reducing conditions, except at z/L = 0.19 where it showed a decrease due to the presence of oxygen.
Although EXP III has a greater current density than EXP II, no corresponding increase in removal efficacy was observed. This is explained by the fact that increasing the current density can only increase the removal rate to a certain limit which is dependent on the maximum speed the Ni ions can move [5]. The lower overall removal efficacy during EXP III is probably a consequence of the greater OH⁻ production (Figure 3) resulting in Ni(II)-hydroxide precipitation. Variations in Ni speciation after EXP II and EXP III could be ascribed to the different current density which affects redox conditions in the sediment (different production integrity of O₂ and H₂) as well as the heterogeneous nature of the sediment.

Mass balance

On the basis of the experimental results, the Ni mass balance was calculated as follows:

\[
\text{Mass balance} = \frac{[\text{Ni amount in the catholyte}] - ([\text{initial amount of Ni in sediment}] - \text{residual amount of Ni in sediment after treatment})}{100}
\]

The Ni mass balances were 96.4, 97.5 and 101.2% for EXP I, EXP II and EXP III respectively. Small amounts migrated into the anode chamber (around 3%) due to the formation of anionic Ni complexes [11]. The diffusion of dissolved Ni may also be partially responsible for some of the Ni detected in the anode region.

Energy consumption

Calculating the energy consumption is essential for choosing the most efficient technique for remediation. Even if the efficacy of one technique is higher than the other, it may not be the better solution for application on real contaminated sediments if it consumes more energy and therefore shows lower efficiency.

\[
\text{Eu} = \frac{1}{ms} \int VIdt
\]

where \(ms\) is the mass of sediment processed, \(V\) is the voltage difference between the electrodes, \(I\) is the current and \(Eu\) is energy consumption (as in KWh/t). The cumulative energy consumption for EXP I was...
1.10 kWh/t, EXP II was 1.23 kWh/t and EXP III was 3.00 kWh/t, after 7 days of EK remediation. Thus, as well as removing the largest amount of Ni, EXP II can also be described as satisfactory according to energy consumption.

CONCLUSIONS

This study shows that the duration of the Ni-sediment interaction influences its speciation and consequently the EK Ni removal efficacy. The EK remediation of Ni contaminated sediment which has aged over several years was not effective, due to the high buffering capacity (ANC) and CEC of the sediment, as well as Ni appearing mostly in the oxidizable fraction. With a short-time interaction (2 days) between Ni and sediment, a large amount of the Ni appears in the acid-soluble fraction, which is the most mobile fraction of metals in sediment. Consequently, under an electric field, Ni is electro-migrated towards the cathode and is extracted from the sediment (23%). Applying an increased current density does not increase the removal rate since it is limited by the maximum Ni ion velocity.

This investigation shows that understanding the behaviour of metal in sediments is essential for choosing the most efficient sediment remediation technique. It also indicates that conventional EK remediation can be effectively performed depending on the sediment chemistry and metal speciation.

Acknowledgement

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REFERENCES

UTICAJ SPECIJACIJE NIKLA NA EFKASNOST ELEKTROKINETIČKE REMEDIJACIJE SEDIMENTA

U ovom radu je ispitivana mogućnost uklanjanja nikla iz sedimenta primenom elektrokinetičke remedijacije kao i uticaj specijacije nikla na efikasnost njegovog uklanjanja. Za ispitivanja je korišćen sediment iz Velikog bačkog kanala (Vojvodina, Republika Srbija). Korišćeni sediment je bio anaeroban i na duži period zagađen Ni (nekoliko godina), pa je pretežno vezan za organsku materiju i u obliku sulfida (57%), što ga je činilo stabilnim i teško dostupnim za elektromigraciju. U EXP I vršena je konvencionalna elektrokinetička remedijacija navedenog sedimenta, ali nije bila efikasna (0%). U EXP II korišćen je sediment dodatno zagađen Ni, kako bi se ispitao uticaj dužine trajanja interakcije Ni i sedimenta, a time i specijacije Ni, na efikasnost remedijacije. U ovom slučaju Ni se nalazio uglavnom u kiselo-rastvornoj frakciji (mobilni oblik), pa je bio dostupan za elektromigraciju prema katodi. Kao posledica toga, nakon EXP II, znatno je povećana efikasnost uklanjanja (23%) u odnosu na EXP I. U EXP III korišćen je isti sediment kao u EXP II uz primenu veće gustine struje, ali nije došlo do povećanja efikasnosti tretmana. Ovim ispitivanjem je utvrđeno da trajanje interakcije metala i sedimenta utiče na efikasnost uklanjanja metala primenom elektrokinetičke remedijacije.

Ključne reči: elektrokinetička remedijacija; sediment; nikl; specijacija.