INVESTIGATION OF NI AND CD ELECTROKINETIC REMOVAL FROM A SEDIMENT [†]

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Abstract. *In this paper we examine the efficacy of the enhanced electrokinetic remediation of a sediment from the Tamiš River contaminated with Ni and Cd. The moving anode technique and an increased cathodic compartment length were simultaneously used to enhance the technique. The removal efficacy increase appeared after the enhanced treatment for Ni (23%) and Cd (73%). The increased cathodic compartment length successfully prevented OH⁻ ions migration in the sediment. Finally, sediment classification according to different risk assessment methodologies indicates that further remediation is required even after the enhanced treatment. Here we indicate that enhanced electroremediation resulted in the removal of efficacy increase but it is highly influenced by sediment characteristics.*

Key words: *sediment, nickel, cadmium, electrokinetics, enhancing*

1. INTRODUCTION

Contaminated sediments affect human health and the environment and can cause the loss of important resources such as drinking water. For ecological and economic reasons, feasible technologies are urgently needed which can remove pollutants from contaminated sediments such that the sediments can be restored for beneficial use. Electrokinetic (EK) remediation is a technique for the decontamination and restoration of different porous solid mediums such as polluted soil, sludge and sediment [1-3]. Electrokinetic remediation involves applying a low DC current or a low voltage gradient to electrodes that are inserted into a medium. There are two major processes that influence the heavy metals' behavior whilst the current is applied: electromigration and water electrolysis. Electromigration is the movement of ions towards the respective electrodes (anions moving towards the anode and cations moving towards the cathode) under an electric field. Due to water electrolysis hydrogen ions (H^+) and oxygen gas are produced at the anode and

hydroxyl ions (OH⁻) and hydrogen gas at the cathode. Electromigration moves H^+ towards the cathode and an acid front generates in the medium. This enables metals to desorb from the particles and to be removed from the medium by electromigration. OH⁻ also migrate under the voltage so high pH values occur in the cathode region. This causes metals to precipitate and accumulate in this region and limits remediation efficacy. To enhance the removal of heavy metals from heterogeneous mediums, numerous methods have been reported in studies aimed at improving desorption of metals from medium particles, but only a few which improve the process without adding chemicals (organic and inorganic acids) into the system [4-6].

The objective of this work was to investigate the efficacy of EK remediation of sediment from the Tamiš River contaminated with Ni and Cd by using the moving anode method and increased cathodic compartment length.

2. MATERIALS AND METHODS

All the chemicals used were at least analytical-reagent grade. The sediment particle size was determined using ISO method 13317-2:2001 [7]. 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) [8]. Acid neutralizing capacity (ANC) was measured and calculated according to the Gran method [9]. The content of organic matter (OM) was determined by weighing the dried sample and then heating it in a furnace at 550 °C for four hours.

The protocol for chemical extraction for determination of pseudo-total Ni and Cd content in sediment was performed in accordance with USEPA Method 3051A [10]. Dry sediment sample (0.5 g) was mixed with 10 mL of cc 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 minutes to 175 °C, then held at 175 °C for another 4.5 minutes. 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 and Cd in the sediment, samples were sequentially extracted according to the BCR method, modified by *Arain et al. 2008* [11]. The Ni and Cd 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 and Cd were carried out using Flame Atomic Absorption Spectrophotometry (PerkinElmer, AAnalyst 700) in accordance with USEPA method 7000b [12].

The sample for these experiments was surface sediment from Tamiš River (Vojvodina, Republic of Serbia) near Pančevo additionally contaminated with nickel and cadmium so that the corrected concentrations according to the Dutch standard [13] were 250-290 mg kg^{-1} and 12-15 mg kg^{-1}, respectively (indicating that sediment remediation is necessary). The conventional experiment was denoted e1 and the enhanced treatment e2. The conventional treatment was performed in set up previously given in *Rajić et al. 2010* [14]. The enhanced treatment was conducted in device as shown in Fig. 1. Perforated graphite electrodes were inserted into the sediment for e2 and switched on stepwise for 24h of operating time. An increased cathodic compartment length including a cation exchange membrane was used. A non-homogenized sediment sample was measured for each experiment test and placed into the sample compartment of the electrokinetic cell. A constant voltage gradient (1 Vcm^{-1}) was maintained during the experiments. pH and nickel and cadmium contents were measured after treatment at different normalized distances from the anode (z/L): 0.19, 0.64, 0.49, 0.64 and 0.79, and conclusions on remediation efficacy were made according to the Dutch standard [15], risk assessment code [16], logistic regression model [17] and ERL (effect range-low) and ERM (effect range-median) [18, 19].
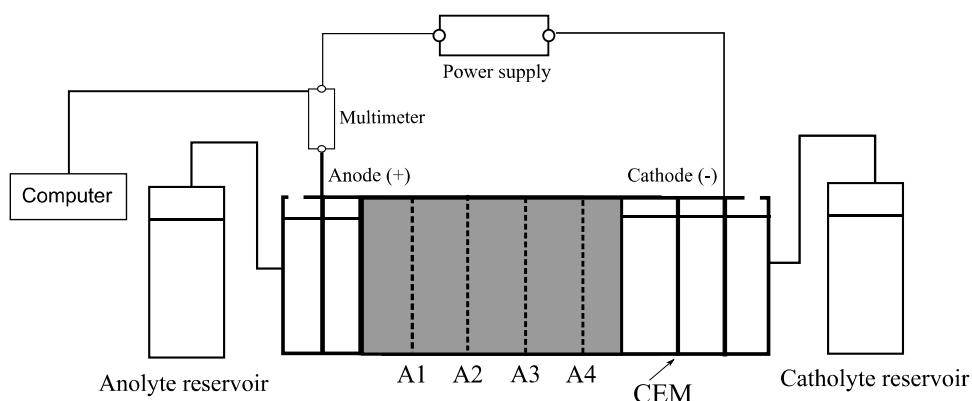
Fig. 1 The electrokinetic setup

3. RESULTS AND DISCUSSION

3.1. Sediment characterization

The sediment characteristics are shown in Table 1. The organic matter and clay content contribute to the low sediment CEC. ANC is low so an acid front is expected to migrate through the sediment. The high Ni content in the oxidizable fraction appears due to the negative redox potential leading to sulphide formation.

Considering the sediment characteristics (mainly ANC), the moving anode technique was chosen for the enhanced EK treatment. Additionally, using the anode moving tech-

nique is cost effective [4]. The increased cathodic compartment length was simultane-ously employed to prevent OH⁻ ions penetration into the sediment and consequent metals accumulation.

Table 1 Sediment characteristics

Parameter	Value
Particle size distribution (%)	
Sand	80
Silt	15.8
Clay	4.2
Moisture content (%)	56.6
pH	7.17
CEC (meq 100 g⁻¹)	0.75
ANC (meq 100 g⁻¹)	11.7
Organic matter (%)	7.5
Dissolved organic matter (%)	0.5
Ni content in sediment fractions (%)	
Acid-soluble	35
Reducible	19
Oxidizable	46
Cd content in sediment fractions (%)	
Acid-soluble	39
Reducible	28
Oxidizable	33

### 3.2. Conventional and enhanced sediment treatments

Fig. 2 shows the current density changes during the experiments and sediment pH changes after treatments. During the conventional and enhanced treatments, the current density decreased over time. The higher current density values at the beginning of e2 appeared since the system is more conductive due to:

1. more H^+ ions present formed at the surfaces of the implemented anodes (Fig. 1) and
2. increased metal ions content in pore water due to desorption from sediment particles.

Note that there was no change in the sediment pH value (Fig. 1) after the conventional treatment, despite the low ANC (11.7 meq 100g⁻¹) and CEC (0.75 meq 100g⁻¹) values. This may be a consequence of H^+ neutralization by OH⁻ ions which penetrate into the sediment, as well as the possible presence of anions which contribute to the buffer capacity besides carbonates, hydrocarbonates and hydroxides: borates, phosphates, silicates and organic acids anions. Using the moving anode method resulted in a slight pH decrease compared to e1 due to H^+ ions formation at the implemented anodes, while increasing the cathodic compartment length successfully prevented OH⁻ ions migration in the sediment. The Ni and Cd distributions in the sediment (presented as normalized concentration C/Co) are given in Fig. 3. Overall removal efficacies after e1 are 13% for Ni and 6.6% for Cd while after e2 it is 17% for Ni and 24% for Cd. Removal efficacies are according to effective ionic mobilities (7.4 x 10⁻⁹ m² V⁻¹s⁻¹ for Ni and 7.82 x 10⁻⁹ m² V⁻¹s⁻¹ for Cd). Additionally, Ni is not available for migration since it has small ionic radius so it is primarily sorbed on particles [20]. The slight increase of overall Ni removal efficacy after e2 can be ascribed to the pH behaviour in the sediment (Fig. 1). Generally,

the low removal efficacy (after e1 and e2) can be explained by reorganization of Ni^{2+} ions among sediment fractions during the treatment [14] as it shown in Table 2. It can be noticed that small amount of Ni^{2+} ions is removed from acid-soluble fraction when e1 and e2 are compared. Also, content of Ni in reducible fraction increased at z/L=0.19, 0.34 and 0.49 due to O_2 production at anode (more positive redox potential). Content of Ni in reducible fraction decreased at z/L=0.64 and 0.79 while its content in oxidizable fraction increased. It is due to H_2 production at cathode which resulted in more negative redox potential [14].

After the enhanced treatment, Cd removal efficacy increased compared to e1 at each normalized distance except at z/L=0.19. Cd mostly exists in the acid–soluble and reducible fraction (Table 1) and so the slight pH decrease during e2 resulted in more Cd ions extracted from the sediment that Ni. Contents of Cd in different sediment fractions are presented in Table 2. Its behaviour after treatments is similar to Ni.
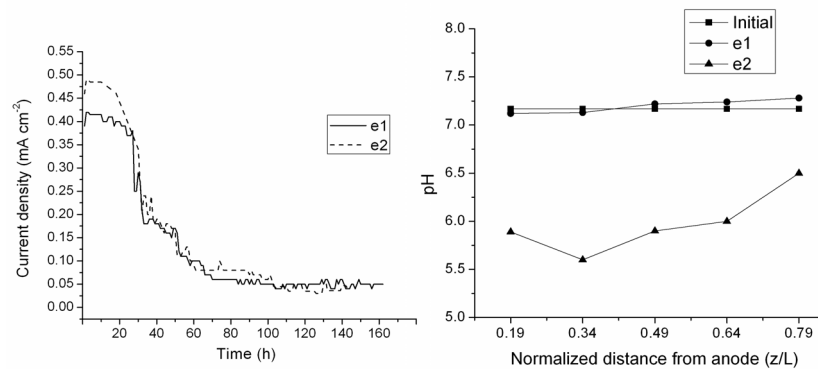
Fig. 2 Current density changes during the EK experiments and sediment pH values before and after EK experiments
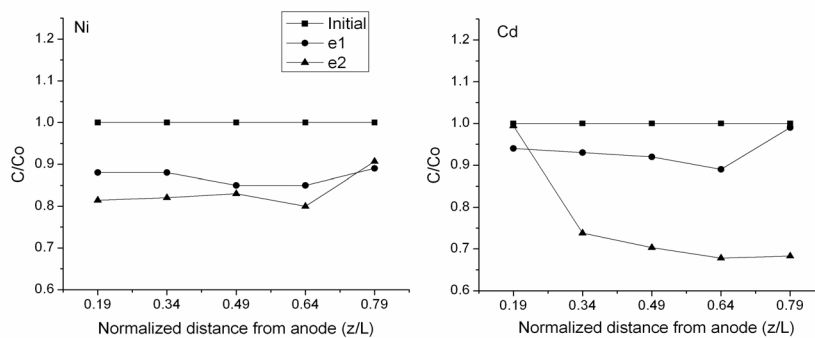
Fig. 3 Ni and Cd distribution in sediment after EK treatments

Table 2 Ni and Cd content in different sediment fractions after treatments

Normalized distance from anode	Acid-soluble fraction [%]	Reducible fraction [%]	Oxidizable fraction [%]	Acid-soluble fraction [%]	Reducible fraction [%]	Oxidizable fraction [%]
		e1			e2	
			Ni			
0.19	39.5	18.8	41.7	31.5	29.8	37.7
0.34	37.6	15.9	46.5	31.0	27.0	41.0
0.49	37.3	15.4	47.2	30.0	24.0	43.0
0.64	36.9	17.3	45.8	31.0	15.3	50.8
0.79	35.2	19.2	45.6	29.0	14.2	53.6
			Cd			
0.19	47.0	18.3	33.8	37.9	28.0	33.8
0.34	44.7	19.0	35.3	34.0	28.0	35.3
0.49	32.8	22.0	41.7	32.0	23.0	43.0
0.64	29.8	23.0	45.0	25.0	21.0	49.0
0.79	39.6	11.9	48.5	29.0	8.50	58.0

3.3. Mass balance

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

$$M_b = [m_c / (m_i - m_r)] \times 100$$

where M_b is mass balance, m_c are metals amount in the catholyte, m_i is an initial amount of metal in sediment and m_r is residual amount of metal in sediment after treatment. The Ni mass balances were 97.3% and 98.9% for e1 and e2, respectively while Cd mass balances were 98.3% and 96.9% for e1 and e2, respectively.

3.4. Risk assessment

Although, enhanced electroremediation resulted in more Ni and Cd ions extracted from sediment, final decision on treatment efficacy should be made according to risk assessment methodology. Table 3 shows the sediment classification according to the previously mentioned risk assessment methodologies. It should be noted that the sediment requires further remediation even after the enhanced treatment.

Table 3 Sediment risk assessment after enhanced treatment

Sample	Dutch standard		Risk assessment code		Logistic regression model		Risk assessment based on ERL and ERM values	
	Ni	Cd	Ni	Cd	Ni	Cd	Ni	Cd
Initial	Class 4		H[1]		Class 1		H[1]	
0.19	Class 3	Class 4	H[1]	H[1]	Class 1	Class 1	M[2]	H[1]
0.34	Class 3	Class 3	M[2]	H[1]	Class 1	Class 1	M[2]	H[1]
0.49	Class 3	Class 3	M[2]	H[1]	Class 1	Class 1	M[2]	H[1]
0.64	Class 3	Class 3	M[2]	M[2]	Class 1	Class 1	M[2]	H[1]
0.79	Class 3	Class 3	M[2]	M[2]	Class 1	Class 1	M[2]	M[2]

[1]High
[2]Medium

4. CONCLUSION

In this work we examined the efficacy of EK remediation of sediment from the Tamiš River contaminated with Ni and Cd, using the moving anode method and an increased cathodic compartment length. The removal efficacy increase appeared after enhanced treatment for Ni (23%) and Cd (73%). The increased cathodic compartment length successfully prevented OH^- ions migration in the sediment. Negligible pH decrease occurred which means that low ANC values do not necessarily indicate a low buffer capacity since there is the possibility for the presence of anions which contribute to the buffer capacity besides carbonates, hydrocarbonates and hydroxides. Here we indicate that enhanced electroremediation resulted in removal efficacy increase but it is highly influenced by sediment characteristics.

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ISPITIVANJE UNAPREĐENOG ELEKTROKINETIČKOG UKLANJANJA NI I CD IZ SEDIMENTA

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U ovom radu je ispitivana efikasnost unapređene elektrokinetičke remedijacije sedimenta reke Tamiš zagađenog Ni i Cd. Simultano korišćenje tehnike pomeranja anode i povećane dužine katodnog prostora predstavljalo je unapređenu tehniku elektroremedijacije. Efikasnost uklanjanja Ni i Cd nakon unapređenog tretmana je povećana u odnosu na konvencionalni tretman 23% odnosno 73%, redom. Povećana dužina katodnog prostora sprečila je prodor OH- jona u sediment. Na osnovu različitih metodologija za procenu rizika sedimenta utvrđeno je da je sediment i nakon unapređenog elektrokinetičkog tretmana opasan po životnu sredinu. Unapređena tehnika rezultovala je povećanjem efikasnosti uklanjanja Ni i Cd, ali je kompleksna struktura sedimenta onemogućila postizanje željenih koncentracija.

Ključne reči: *sediment, nikl, kadmijum, elektrokinetika, unapređenje*