

Electrokinetic removal of Cr(VI) from contaminated soil matrices: a comparative study with soil and kaolin samples

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Abstract

In the present study electroremediation was evaluated as an option for the remediation of Cr(VI) contaminated soils. The experimental work was carried out in two samples, a contaminated soil sample, collected from Asopos River basin, and a kaolin sample, used as typical inert material. The tests were conducted applying a voltage of 30 Volt to a cylindrical electrokinetic cell of 30 cm length and 4 cm diameter. Initial experiments were conducted using 0.01 M Na₂SO₄ as inert electrolyte and allowing free pH evolution. Additional tests were carried out increasing the concentration of inert electrolyte to 0.04 M and using Mg(OH)₂ in the anolyte to neutralize the produced acidity. In the initial tests, Cr(VI) content of treated materials was diminished by 41% in the kaolin and 54% in the soil sample. In the second series of tests the removal of Cr(VI) was improved to 61% for kaolin and 69% for soil. Mass balance calculations, based on the detailed analyses of treated soil/kaolin samples and anolyte/catholyte solutions, indicated that in the case of soil the decrease of Cr(VI) concentration is partially due to the reduction of Cr(VI) in the trivalent state, Cr(III), probably due to the presence of organic matter in the soil sample. In the case of kaolin, the removal of Cr(VI) is primarily due to the electromigration of chromate anion in the anolyte.

Keywords: Chromate, Electroremediation, soil, kaolin

1. Introduction

Chromium is a frequent pollutant in groundwater and in soils alike due to its wide use in industry and broad range of applications. In the environment chromium exists both in trivalent and hexavalent state. Unlike trivalent chromium Cr(III) which is a trace element essential to human health hexavalent chromium Cr(VI) is carcinogenic and mutagenic (Sawada *et al*, 2004). Hence its presence in industrial sites is an issue of great importance that needs to be carefully addressed. Some of the remediation methods used in contaminated soils throughout the years are solidification/stabilization, bioremediation, soil washing, phytoremediation and electrical remediation. Electrical remediation is based on the phenomena that take place when an electrical field is applied to the soil through electrodes (Page and Page, 2002). The primary phenomenon is electromigration where the ionic contaminants are moving due to the electric field towards the electrodes of opposite charge. The second is

electroosmosis where the contaminants are moving as a result of the motion of pore water, usually towards the cathode, by cause of the application of the electric field. The third is electrophoresis where the electric field moves the charged colloids. Electrophoresis takes place usually in sludge processing. In the present study two couples of comparative tests were carried out using a calcareous soil from Asopos River basin, Central Greece, and a kaolin sample as typical inert material from Milos Island.

2. Materials and Methods

2.1 Materials

The main characteristics of soil and kaolin are presented in Table 1. The soil has a calcareous matrix with neutralizing potential equivalent to 206 g of CaCO₃ per kg. On the contrary the kaolin does not contain any CaCO₃ and the neutralizing potential is slightly negative. Based on their texture the soil is characterized as sandy clay loam and kaolin as clay. Soil's content in total chromium is 1284 mg/kg, due to the high geochemical background of Asopos area in Cr-rich minerals. Kaolin's content in total chromium is 93 mg/kg. Chromium (VI) was below detection limit in both samples indicating that all Cr is in the trivalent state. It is noted that Cr(VI) in the soil was determined with the alkaline digestion method (USEPA SW 846 Methods 3060A), while in the kaolin it was measured with the method of exchangeable chromium (Bartlett and James, 1996). The different procedure was followed because preliminary experiments indicated that the alkaline digestion method was inaccurate in the case of kaolin, due to interference of co-dissolved SiO₂. Experiments with standard additions of Cr(VI) indicated satisfactory recovery of Cr(VI) (>93%) with the method of exchangeable chromium. Characterization of solids with X-ray diffraction showed quartz, calcite, muscovite and clinochlorite as major phases in soil, and kaolinite and quartz in kaolin.

2.2 Electrokinetic set-up

The experimental set-up is shown in the Figure 1. It consists of three cylindrical compartments (4 cm internal diameter). The central compartment (30 cm length) containing the soil and kaolin samples is placed between the two electrode compartments (anodic and cathodic) (5 cm length). The solutions applied to the anode and cathode were recirculating using a peristaltic pump. The electrodes

used in anode and cathode consisted of titanium and graphite respectively. Experiments were carried out applying a constant voltage of 30 V.

Table 1. Characteristics of soil and kaolin samples

	Soil	Kaolin
pH	8.02	7.08
NP ^(a) (g CaCO ₃ /kg)	206	-5.56
Organic carbon ^(b) (%)	0.67	<0.01
Texture ^(c)		
Sand, %	51.16	33.34
Silt, %	28.3	23.3
Clay, %	20.54	43.36
Elemental analyses ^(d)		
(%)		
SiO ₂	40.8	65.72
Al ₂ O ₃	6.93	19.42
CaO	13.6	0.07
MgO	4.73	0.08
FeO	4.31	0.09
MnO	0.095	0.002
K ₂ O	1.45	0.03
Na ₂ O	0.85	0.99
Chromium (mg/kg)		
Cr ^(d)	1284	93
Cr(VI)	< 0.24 ^(e)	< 0.02 ^(f)

^(a)NP: Neutralizing Potential, ^(b) Walkley-Black (1934), ^(c) Bouyoucos (1962), ^(d) Analyses carried out with X-ray fluorescence (XRF) ^(e) USEPA SW 846 Methods 3060A and 7196A, ^(f) Exchangeable Cr (Bartlett and James, 1996)

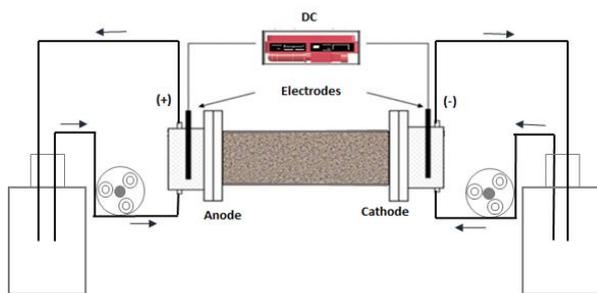


Figure 1. Schematic diagram of electrokinetic set-up

2.3 Procedures and analyses

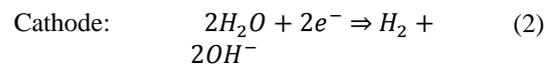
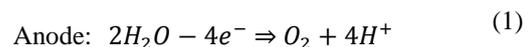
Before each electrokinetic test the solid samples were artificially contaminated in order to obtain a concentration of Cr(VI) equal to 500 mg/kg on dry basis. The artificial contamination was carried out by mixing each solid with an aqueous solution containing Cr(VI) and Na₂SO₄ as inert electrolyte. Due to the fact that dry kaolin was able to absorb a much higher amount of water compared to soil, the ratio ‘milliliters of aqueous solution per gram of dry solid’ (ml/g), was different for the two solids. Namely in

the case of soil the ratio was 0.24 ml/g and in the case of kaolin 0.64 ml/g. The moist samples were kept covered for 2 days in order to avoid evaporation and then were transferred to the electrokinetic cell. Filling of the cylinder was carried out by layers of 2 cm, which were gently packed with an appropriate piston to obtain homogenous distribution of the material. The final amount of solids transferred to the cell was ~770 g wet weight (~640 g dry weight) in the case of soil and ~630 g wet weight (~390 g dry weight) in the case of kaolin. The average duration of the electrokinetic tests was 160 hours. Two samplings were taking place daily from the electrode solutions. The parameters measured in each sampling were pH, electrical conductivity (EC), hexavalent and total chromium. The weight of the electrode solutions was also measured so as to determine the extent of the electroosmotic flow. When the tests were completed the soil/kaolin was removed from the tube using the piston and divided into 6 slices. The measurements in each slice included determination of pH and analysis of hexavalent and total chromium. Two sets of tests were carried out. In the first two tests (one with soil-S1 and one with kaolin-K1), the concentration of inert electrolyte Na₂SO₄ was 0.01M and the pH of the solutions in the anolyte and catholyte compartments was left free to evolve without any adjustment. In the two following tests (one with soil-S2 and one with kaolin-K2), the concentration of Na₂SO₄ increased to 0.04M and Mg(OH)₂ was added in the anolyte in order to neutralize the acidity produced from the electrolysis of water.

3. Results and discussions

3.1 Evolution of pH in anode and cathode fluids and pH profiles in treated soil and kaolin

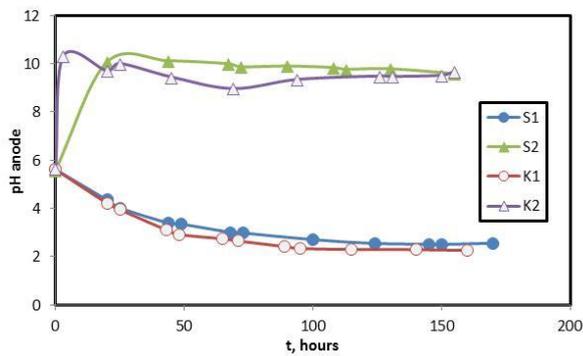
The evolution of pH in the anode and cathode compartments for all tests is shown in Figure 2. As seen in Figure 2a, the pH of the anode was constantly dropping in tests S1 and K1, due to the generation of H⁺ according to reaction (1). In tests S2 and K2, the pH was stabilized in values 9.5-10 due to the addition of Mg(OH)₂.



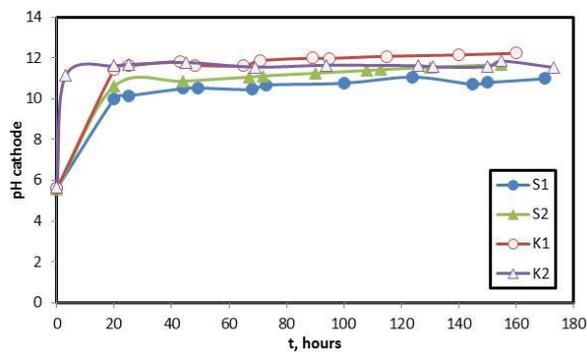
The pH in the cathode in all tests was steadily increasing (Figure 2b) due to the production of OH⁻ from the electrolysis of water.

The pH profiles in treated soil and kaolin samples are shown in Figure 3. As seen in the figure, the pH of soil in test S1 remains almost constant at all distances between anode and cathode, with values in the range 7.9 to 8.4. Even close to the anode, where the final pH of anolyte is 2.5, soil pH is maintained at alkaline values. This is due to the fact that soil has a high buffering capacity related with the high CaCO₃ content, as seen in Table 1. On the contrary, the profile of kaolin in test K1 is acidic, i.e. 2.7, close to the anode, and increases up to the value 9.2 close to the cathode. In tests S2 and K2 which were carried out with pH adjustment at the anode compartment, there was an increase in the measured pH values. In the case of soil (test S2) the pH varied between 9.0 close to the anode and 8.4 close to cathode. In the kaolin sample the pH was 7.2

in the vicinity of anode, decreased to 6.0 at the distance of 12.5 cm and increased to 9.8 close to cathode.



(a) Anode



(b) Cathode

Figure 2. Evolution of pH in the anode and cathode compartments. S1, S2 soil, K1, K2 kaolin. S1, K1 0.01 M Na_2SO_4 , S2, K2 0.04 M Na_2SO_4 and $\text{Mg}(\text{OH})_2$ in anode

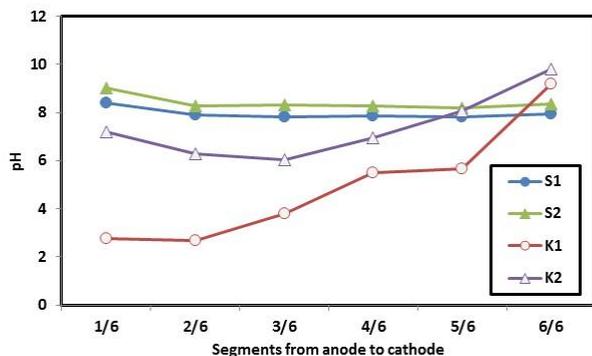
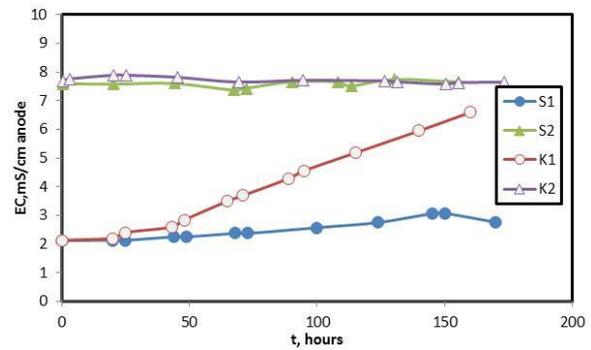


Figure 3. pH of soil and kaolin segments at increasing distances from the anode

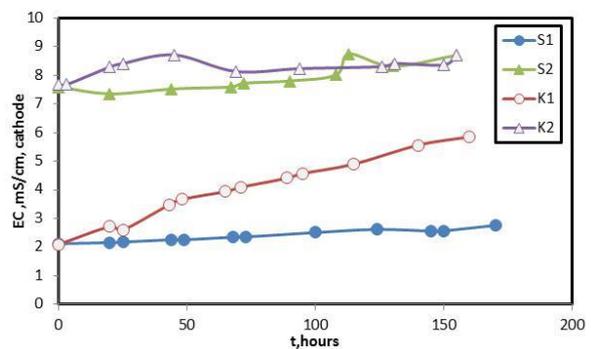
3.2 Evolution of electrical conductivity

The electrical conductivity (EC) in test S1 remained almost constant, with initial value 2.12 mS/cm and final 2.76 mS/cm, both in the anode and cathode compartments (Figure 4a). On the contrary, in test K1 EC increased constantly from the initial value 2.12 to 6.59 mS/cm in the anode and 5.85 mS/cm in the cathode. Increase of conductivity indicates that dissolution processes were taking place during the electrokinetic treatment of kaolin, resulting in the enrichment of aqueous phase with

dissolved cations and anions. As seen in Figure 3 kaolin slices in K1 have a very acidic pH 2.7-2.8 close to the anode and alkaline pH 9.8 close to cathode. The strong acidic



(a) Anode



(b) Cathode

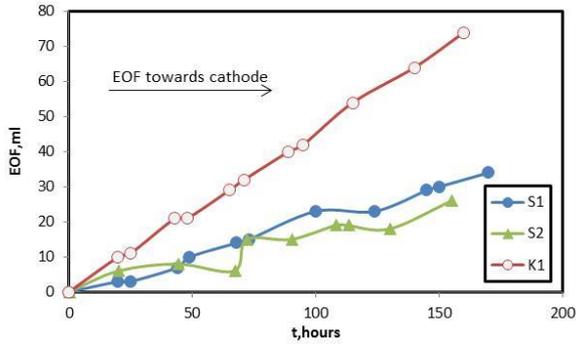
Figure 4. Evolution of electronic conductivity (EC) in the anode and cathode compartments. S1, S2 soil, K1, K2 kaolin. S1, K1 0.01 M Na_2SO_4 , S2, K2 0.04 M Na_2SO_4 and $\text{Mg}(\text{OH})_2$ in anode

and alkaline conditions established in the edges of kaolin sample can explain the observed increases of EC values. Dissolution was not observed in the case of soil (test K1) and this can be attributed to the buffering capacity of soil. The electrical conductivity in tests S2 and K2 (Figure 4b) is significantly higher than in S1 and K1 both in anolyte and in catholyte, with values ranging between 7.6 and 8.7 mS/cm. This is due to the fact that the experiments were carried out using a higher concentration of the inert electrolyte.

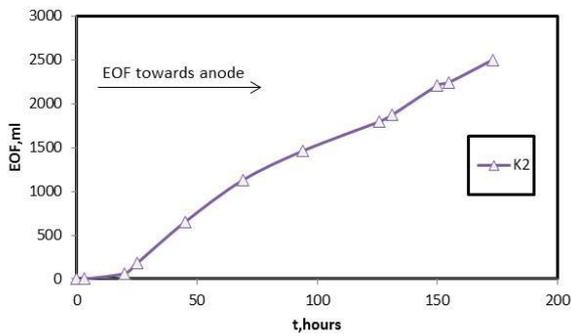
3.3 Electroosmotic flow

The electroosmotic flow (EOF) in tests S1, S2 and K1 is moving towards the cathode (Figure 5a). This is in agreement with the findings of the majority of electrokinetic studies. Many soil minerals and clay particles have a negative surface charge. The cations which are loosely bound to the solids by electrostatic forces, under the influence of an external electric field move towards the anode drawing with them all hydration and neighboring water molecules. EO flow in test K1 is higher indicating more negative surface charge and more numerous exchangeable cations in the kaolin sample compared to soil in S1 and S2. However in test K2 a massive reverse electroosmotic flow was observed (Figure

4b). A similar phenomenon of reverse EOF during electrokinetic studies has been reported by Weng *et al.* (2007) and Genc *et al.* (2009), but it was not fully explained.



(a)



(b)

Figure 5. Cumulative EO flow vs time. Collected in (a) cathode reservoir, (b) anode reservoir

Yukselen and Kaya (2003) studied the effect of alkali, alkaline earth and hydrolysable metal ions on the zeta potential of kaolinite. They showed that in the presence of hydrolysable divalent metals and when precipitation of hydroxides occurs, the zeta potential becomes positive. Similar phenomena may take place during test K2 with kaolin. In this test we have used $Mg(OH)_2$ for pH control in the anode. This procedure resulted in the enrichment of aqueous solution with Mg^{+2} all along the electrokinetic cell. XRF analyses of kaolin slices after the completion of electrokinetic tests showed increased Mg levels compared to the initial material. The presence of $Mg(OH)_2$ may have caused the development of a positive zeta potential on the kaolin sample explaining the observed reverse direction of EOF towards the anode.

3.4 Migration and removal of Cr(VI)

The cumulative transfer of Cr(VI) in the anode compartment per kg of treated material is shown in Figure 6. As seen in the figure the recovery of Cr(VI) in the anode during the treatment of soil was very limited, i.e. close to 35 mg/kg or 7% of the initial amount after 160 hours of treatment. The increase of Na_2SO_4 and the use of $Mg(OH)_2$ for pH neutralization did not improve the transfer to anode. Higher recoveries of Cr(VI) in the anode were recorded during the treatment of kaolin. In test K1 the final recovery

was 143 mg/kg and in test K2 280 mg/kg, corresponding to 28.5% and 55.9% of the initial amount respectively.

The distribution of Cr(VI) in the six segments of treated soil and kaolin is shown in Figure 7. Residual Cr(VI) in the segments of kaolin from test K2 varies between 13 and 280 mg/kg, indicating a removal rate of more than 50%, which is in agreement with the amount of Cr(VI) recovered in the anode.

In the treated kaolin of test K1, residual Cr(VI) is low in the three slices close to the anode and cathode, but in the middle slices the concentrations range between 414 and 445 mg/kg. The concentrations of residual Cr(VI) were unexpectedly low in the samples of treated soil, ranging between 108 and 280 mg/kg in test S1 and 38 and 248 mg/kg in test S2. In both tests the residual Cr(VI) in soil was less than 50% compared to the initial concentration, despite the fact that the amount recovered in the anolyte is close to 7%. The overall mass balance of Cr(VI) and total Cr in the four tests is summarized in Table 2. As seen in the table, the mass balance of total chromium after the EK treatment of both soil and kaolin is in reasonable agreement with total chromium in initial samples. However the mass balance of hexavalent chromium is highly deficient in the case of soil, i.e. the final amount of Cr(VI) corresponds to 54% and 40% of the initial amount in tests S1 and S2 respectively. This suggests that an important percentage of Cr(VI) is reduced to Cr(III) during the

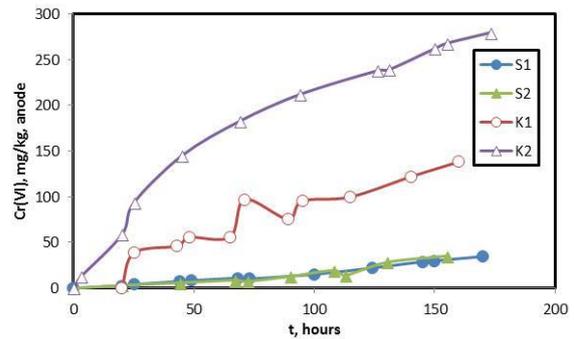


Figure 6. Cumulative transfer of Cr(VI) in anode (mg per kg of treated material)

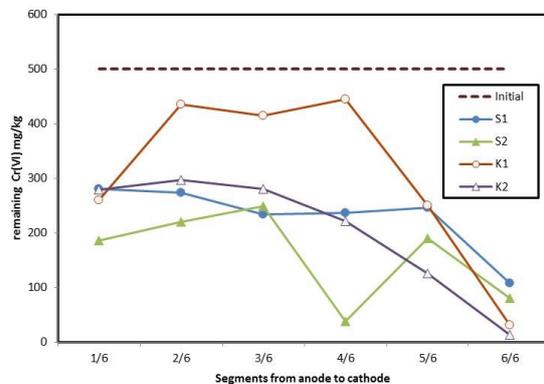


Figure 7. Residual Cr(VI) in the segments of treated soil/kaolin

Table 2. Overall mass balance of Cr(VI) and total Cr

	S1		S2		K1		K2	
	Cr(VI)	Cr(t)	Cr(VI)	Cr(t)	Cr(VI)	Cr(t)	Cr(VI)	Cr(t)
Initial, mg/kg	500	1784	500	1784	500	593	500	593
Anolyte, mg/kg	34.7	35.5	35.2	33.1	142.6	142.9	279.4	299.9
Catholyte, mg/kg	3.9	4.4	0.8	1.5	0.3	0.8	0.2	0.4
Treated soil, mg/kg	231.7	1880.0	162.6	1787.6	293.1	409.7	200.4	260.4
Total final, mg/kg	270.3	1919.9	198.5	1822.3	436.0	553.3	480.0	560.7
Total final/Initial, %	54.1	107.6	39.7	102.1	87.2	93.3	96.0	94.5

EK treatment of soil, and Cr(III) precipitates inside the soil as Cr(OH)₃, due to the high levels of soil pH in both tests S1 and S2. The same phenomenon had been observed by other researchers (Reddy *et al.*, 2003). Reduction of Cr(V) to Cr(III) was less clear in the case of kaolin. The reductive capacity of soil and the different behavior of kaolin is probably related with the presence of organic carbon, which is close to 0.67% in soil and less than 0.01% in kaolin.

4. Conclusions

In the present study four different electrokinetic tests were carried out, two on soil and two on kaolin. The maximum obtained removal of Cr(VI) 69% for soil and 61% for kaolin and was achieved using 0.04M Na₂SO₄ as inert electrolyte and g(OH)₂ for pH adjustment in the anolyte. Mass balance calculations, indicated that in the case of soil the decrease of Cr(VI) concentration is partially due to the reduction of Cr(VI) in the trivalent state, Cr(III), probably due to the presence of organic matter in the soil sample. In the case of kaolin, the removal of Cr(VI) is primarily due to the electromigration of chromate anion in the anolyte.

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