Electrokinetic Treatment of Cu Contaminated Kaolin: Using an Fe/Cu Galvanic Cell

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In this work we present the results of a laboratory study to assess the possibility of Fe/C and Fe/Cu galvanic cell utilization for Cu removal from a kaolin model matrix as an electrokinetic treatment without electricity consumption. In addition, we examine improving the desorption of Cu ions from kaolin particles by acidification. Several experiments were conducted: conventional (ECC), Fe/C galvanic cell (GC1), Fe/Cu galvanic cell (GC2), Fe/C galvanic cell with kaolin acidification (GC3) and Fe/Cu galvanic cell with kaolin acidification (GC4). The following removal efficacies were achieved: 44% for ECC, 20% for GC1, 37% for GC2, 46% for GC3 and 45% for GC4. The Fe/Cu galvanic cell resulted in better removal efficacy as metallic Cu was deposited at the cathode. Acidification of kaolin prior to treatment contributed to Cu^{2+} desorption and thus improved removal efficacy, especially during GC3. This work demonstrates that an Fe/Cu galvanic cell can be used for electrokinetic treatment of Cu contaminated soil with no waste produced after treatment as the Cu is deposited at the cathode.
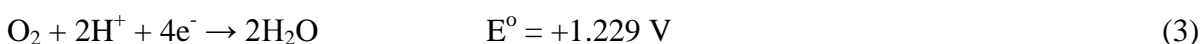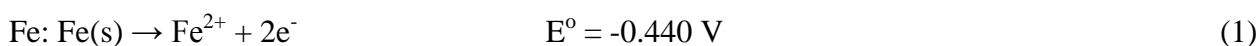
1. INTRODUCTION

There are numerous sites in Serbia where soils have been contaminated with heavy metals as a result of the disposal of toxic and hazardous wastes from domestic, agricultural, and industrial activities [1]. Although several soil remediation technologies have been developed within the last decade, many have proven to be either ineffective or costly for the remediation of clayey soils due to the low permeability.

Electrokinetic remediation is a developing technique that has significant potential for remediation of low permeability soils contaminated with heavy metals [2,3]. Electrokinetic remediation involves applying a low DC current or a low potential gradient to electrodes that are inserted into the ground and encompass the contaminated zone [3-5]. Two major processes influence the behaviour of heavy metals whilst a current is applied: water electrolysis and electromigration [6]. Electrolysis reactions generate hydrogen ions (H^+) and oxygen gas at the anode and hydroxyl ions (OH^-) and hydrogen gas at the cathode. The hydrogen ions in the anode migrate through the soil towards the cathode, whereas the hydroxyl ions in the cathode migrate towards the anode. Depending upon the extent of H^+ and OH^- migration, pH will vary across the soil. These pH changes affect major physico-chemical processes such as adsorption–desorption, precipitation–dissolution and oxidation–reduction, which dictate the removal of the contaminants in soils. Electromigration is the movement of ions and charged species towards the respective electrodes (anions moving towards the anode and cations moving towards the cathode) under an electric field. The removal of heavy metals during electrokinetic remediation depends on the polarity of the heavy metal, the type, the coexistence of other heavy metals, sorption affinity etc. [7-10].

There are a number of different techniques given in the literature to further the electrokinetic process, mostly engaged in improving the efficiency of removing substances of concern. During electrokinetic remediation electric power is consumed, so it is therefore important to develop techniques to reduce consumption, in order to make them applicable at full scale levels, especially in countries where the cost of electricity is high. Thus far, experimenters have taken a number of different approaches: pulsed technique [11-13], using bipolar electrodes [14,15], the application of solar energy [16] and galvanic cells [17,18]. The idea behind the application of galvanic cells is desirable because the system cleans itself. The only drawback would be that it is time consuming due to the low voltage generated. Applications of galvanic cells have shown good results [17,18]. A diagram of the process is presented in Figure 1. So far, an Fe/C galvanic cell was investigated. Iron (Fe) and carbon (C) are placed separately and connected with a conductive wire while the polluted medium is placed between them [17]. The following reactions take place:

$$Fe: Fe(s) \rightarrow Fe^{2+} + 2e^- \qquad\qquad E^o = -0.440 \text{ V} \qquad\qquad (1)$$

$$C: 2H^+ + 2e^- \rightarrow H_2 \qquad\qquad E^o = 0 \text{ V} \qquad\qquad (2)$$

$$O_2 + 2H^+ + 4e^- \rightarrow 2H_2O \qquad\qquad E^o = +1.229 \text{ V} \qquad\qquad (3)$$

Electric current flows from Fe to C through the wire and from C to Fe through the medium because the electrode potential of Reaction 1 is more negative than that of the Reactions 2 and 3. As a consequence, positive ions move from Fe to C by electromigration and negative ions from C to Fe. Compared with EK technology using a power source, the galvanic cell uses inexpensive materials and the system produces the electric field itself, therefore greatly reducing electricity consumption.

This paper presents the results of a laboratory study to assess the possibility of galvanic cell utilization for Cu removal from kaolin as a model matrix. The objectives of the present study were: a)

to explore the feasibility of using a Fe/Cu galvanic cell to remove copper from kaolin and b) to enhance the treatment by improving Cu^{2+} ions desorption from kaolin particles by acidification. The use of Cu as the cathode was introduced due to (Figure 1):

$$Cu: Cu^{2+} + 2e^- \rightarrow Cu\ (s) \qquad\qquad E^o = +0.340\ V \qquad\qquad (4)$$
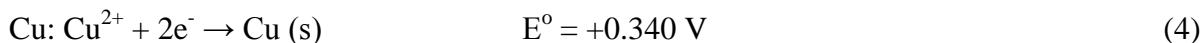
indicating that Cu^{2+} ions will be deposited on the Cu cathode surface. In this way there would be no waste produced after treatment.
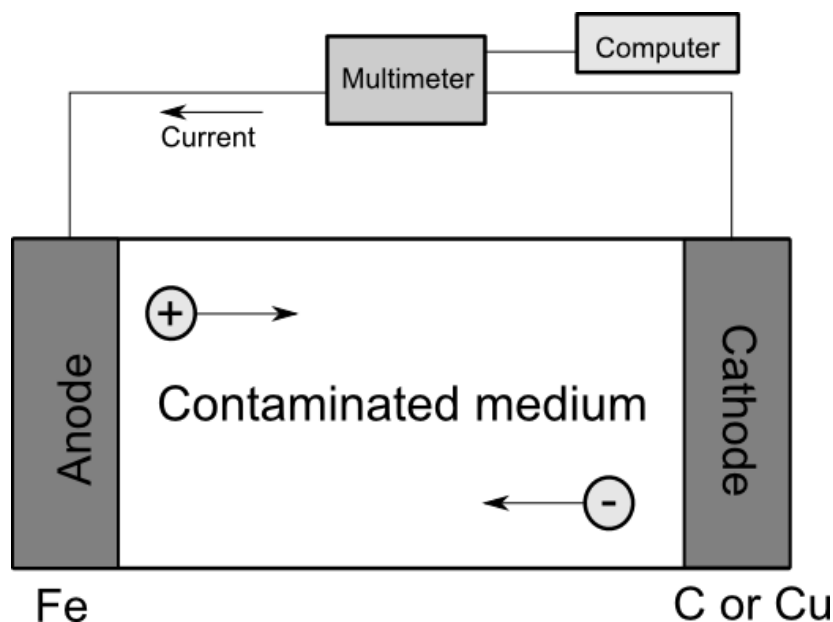

Figure 1. Diagram of the electrokinetic galvanic cell system

2. EXPERIMENTAL

2.1. Materials and methods

All reagents used were of analytical grade. The pH was measured in deionized water (kaolin:water=1:5) with a SenTix®21 electrode on a pH meter (340i, WTW). The ammonium acetate method was used to measure the cation exchange capacity (CEC) [19]. Acid neutralizing capacity (ANC) was measured and calculated according to the Gran method [20]. The protocol for chemical extraction for determination of pseudo-total Cu content in kaolin was performed in accordance with USEPA Method 3051A [21]. Dry kaolin samples (0.5 g) were mixed with 10 mL of cc HNO_3 in Teflon beakers. Extraction was carried out by microwave oven (Milestone, Stare E microwave) using the following program: temperature increased over 5.5 minutes to 175°C, then held at 175°C for another 4.5 minutes. Cu^{2+} concentration was determined by flame atomic absorption spectrometry (PerkinElmer, AAnalyst 700) according to US EPA Method 7000b [22]. Samples for electrokinetic treatments were prepared by adding $CuCl_2$ solution to kaolin. To confirm the Cu deposition on the cathode scanning electron microscope (SEM) was used (Jeol, JSM-6460LV with INCA X sight

program). Besides using SEM we also measured electrode mass before and after the treatment to witness Cu deposition. The kaolin and the solution were stirred thoroughly so a water content of 50% was achieved. The mixture was then allowed to settle for about 24 h.

2.2.Electrokinetic setup

The treatment setup was made of a Plexiglas cell (14.5 cm long x 5 cm wide x 9.5 cm deep) as shown in Figure 1. Table 1 gives the experiment details. For the Fe/C galvanic cell system scrap iron and granulated carbon were placed at the two sides and connected with a conductive wire. The conditions in the cathode compartment (granulated carbon) were aerobic in order to gain higher voltage in the cell (Reaction 3). Perforated tubes were inserted into the granulated carbon to allow O_2 dissolution. For the Fe/Cu galvanic cell system, scrap iron and a set of 6 copper rods were used as the cathode and anode. The mass of the Cu electrodes was measured before and after the experiments in order to prove Cu deposition. The current and voltage were monitored by a multimeter connected to the electrical circuit. All the experiments were carried out in duplicate to ensure accuracy of the results, and were carried out at room temperature (25 ± 3°C).

pH and the pseudo-total content of Cu^{2+} ions were measured at the beginning and after the treatments at normalized distances from the anode, z/L (z=distance from anode; L=distance between electrodes): 0.1, 0.3, 0.5, 0.7 and 0.9. The overall treatment efficacies were calculated as follows:

$$\% = [(m_i - m_k)/m_i] \times 100 \qquad\qquad (5)$$

where m_i is the initial amount of Cu^{2+} ions in the kaolin [mg] and m_k is the amount of Cu^{2+} ions that remains in the kaolin after the treatments.

Table 1. Description of the experiments

Experiment assignation	Medium	Pre-treatment	Anode/ Cathode	Type	Duration
ECC	Kaolin	No	Graphite/ Graphite	Electrochemical cell (1 V cm^{-1})	7 days
GC 1	Kaolin	No	Fe/C	Galvanic cell	21 day
GC 2	Kaolin	No	Fe/Cu	Galvanic cell	21 day
GC 3	Kaolin	H_2SO_4/Initial pH 3.5	Fe/C	Galvanic cell	21 day
GC 4	Kaolin	H_2SO_4/Initial pH 3.5	Fe/Cu	Galvanic cell	21 day

3. RESULTS AND DISCUSSION

3.1. Sample characterization

The initial Cu^{2+} concentration was 190 mg/kg. This concentration indicates that the kaolin (soil) is contaminated and that remediation is necessary [23]. The initial kaolin pH value was 7.8, CEC

was 5.4 meq/100g and ANC was <0.5 meq/100g. This indicates that the kaolin is an appropriate medium for electrokinetic treatment (it allows acid front migration).

3.2. Changes in the current and voltage during the treatments

Figure 2 shows the changes in electric current and voltage during the treatments. The current passing through the system decreases during the EK process. This is due to the fact that content of ions migrating towards the electrodes declines during the treatment, decreasing the conductivity of the system. During GC3 and GC4, where the pH of the kaolin was low, the current was higher than in GC1 and GC2, since more ions were available for migration (due to the presence of H^+ ion and desorption of Cu^{2+} ions from the kaolin particles).

Instead of 1.669 V for Fe/C system and 0.720 V for Fe/Cu as voltages calculated from the half-reaction potentials these were lower during the experiments. For GC1 and GC3 the initial voltages were 1.554 V and 1.214 V, respectively. In the Fe/C system the electron donated by iron was accepted by H^+ with a standard potential of 0 V and by O_2 with a standard potential of 1.229 V in aerobic conditions, which indicated a standard voltage of 1.669 V. In this system, the container was open to air and perforated tubes were inserted into the granulated carbon, so O_2 could dissolve into the solution, so Reaction 3 was preferable. With respect to the cathodic reactions, H^+ and O_2 were gradually consumed, resulting in the cathodic potential becoming more negative. In addition, the voltage was influenced by the anodic and cathodic polarizations. Still, the voltage was more positive than reported by previous researchers [17], probably because more O_2 was dissolved due to the inserted perforated tubes. During GC3, where the H^+ content in the system was higher than in GC1, a slightly lower voltage was observed since Reaction 2 overcame Reaction 3.
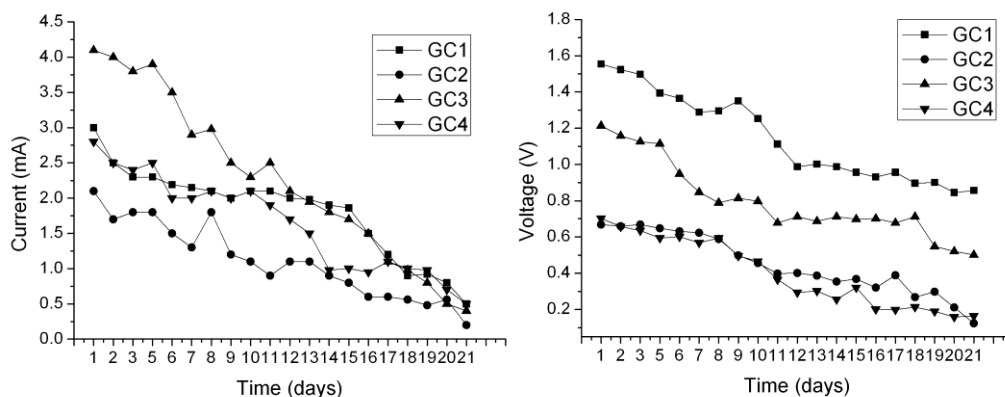

Figure 2. Current and voltage changes during the experiments

For GC2 and GC4, the initial voltage values were 0.668 V and 0.702 V, respectively. Slightly lower values than expected were observed due to the low content of Cu^{2+} in the kaolin available for

reaction (Reaction 4). In the Fe/Cu galvanic cell, the lower pH value caused a higher voltage to occur as more Cu^{2+} ions were desorbed from the kaolin particles.

Since iron was used as anode for both galvanic systems it can be assumed that the state of its surface can influences the voltage and current during the treatment. This is due to the anode corrosion which includes formation of different iron oxides and hydroxides (dictated by the availability of water and oxygen) and it is accelerated at low pH (which appears during the treatment, Figure 3).

3.3 Changes in the kaolin pH

The changes in the pH after the treatments are shown in Figure 3. The kaolin pH in decreased except from near the cathode where a slight increase in pH occurred during ECC, GC1 and GC2. The slight pH decrease after GC2, compared to ECC and GC1, is a consequence of the low voltage in the system. Although the kaolin pH values were not low, it is assumed that desorption of Cu^{2+} took place. As well as pH, the concentration of ions also has an important influence on ion desorption from kaolin particles. At higher concentrations desorption occurs at higher pH values than at lower concentrations [24]. So, Cu^{2+} was desorbed even though the pH values were not lower than pH=4.9. The cathode compartment was 5 cm long so a small amount of OH^- could penetrate into the kaolin (Figure 3) [25]. This explains the pH values near the anode and consequently in the kaolin. This suggests that by optimizing the cathode and anode length, the pH value can be controlled.

During the Fe/Cu experiment, no OH^- is produced at the cathode compartment, so no pH increase appeared in system. This is of great importance since alkaline conditions near the cathode cause metal precipitation and accumulation in this region. After GC3 and GC4, where the initial pH value was adjusted to 3.5, the pH remained low.
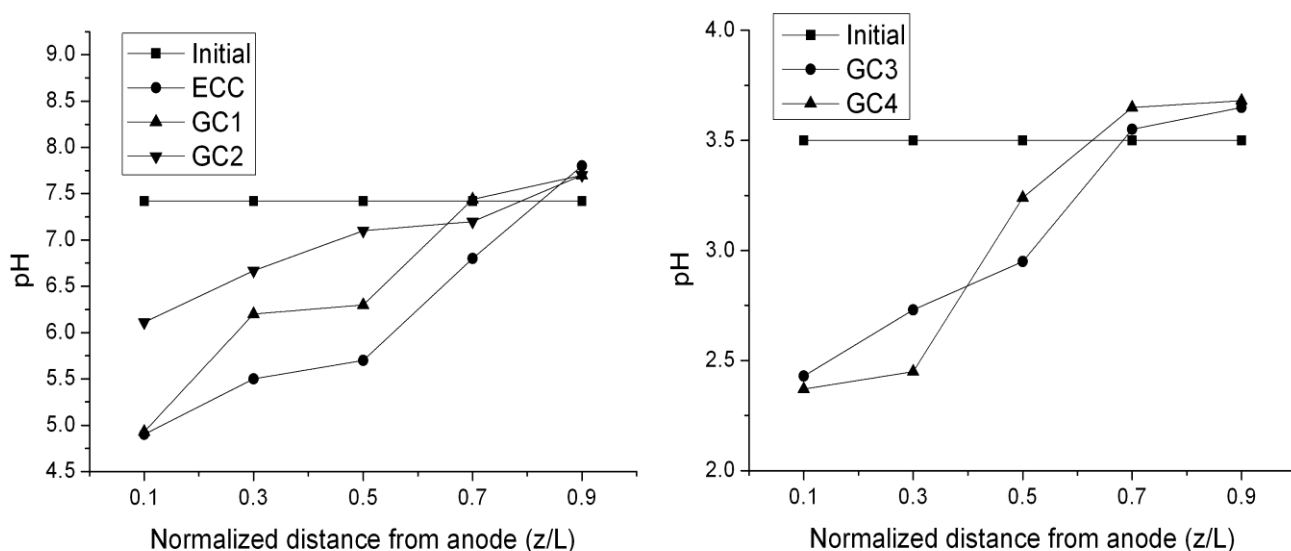

Figure 3. Changes of kaolin pH value after treatment

3.4. Distribution of Cu in kaolin after treatment

The distribution of Cu^{2+} in the kaolin after the treatments is shown in Figure 4. Overall treatment removal efficacies (Equation 5) were 44% after ECC, 20% after GC1, 37% after GC2%, 46% after GC3 and 45% after GC4. The Cu^{2+} concentration required to indicate that the soil is not contaminated (<100 mg kg^{-1}) was achieved after ECC and GC3 (except at z/L=0.9) and after GC4 (except at z/L=0.3 and 0.5). The high efficacy of ECC is due to the high voltage gradient applied to the system (1 V cm^{-1}). It should be noticed that even though a higher voltage is formed during GC1, and the kaolin pH value is lower than in GC2, the latter treatment was more efficient.
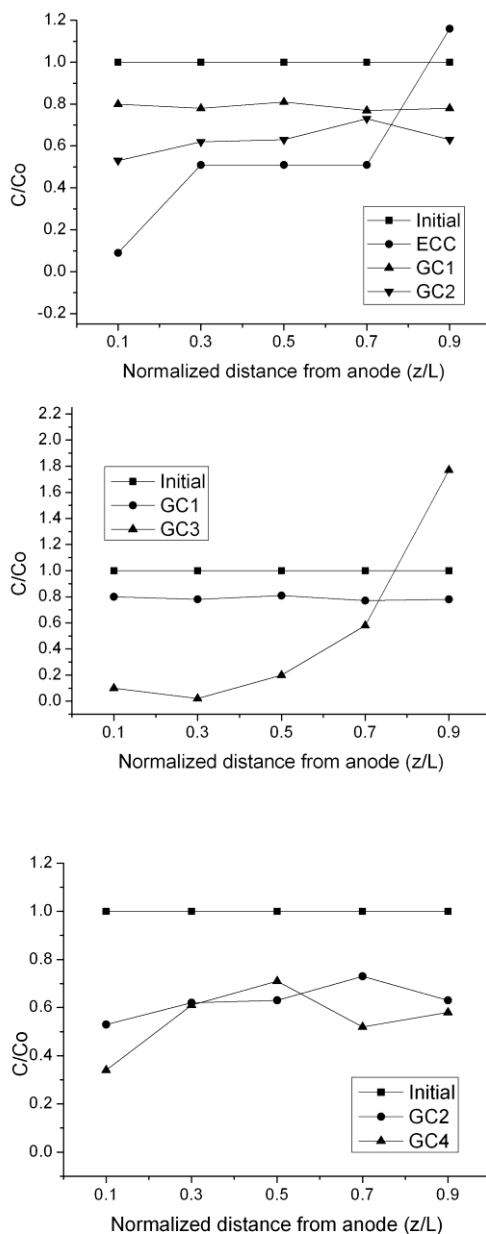

Figure 4. Distribution of Cu in the kaolin after the treatments

Cu^{2+} ions are driven by diffusion and electromigration towards the cathode, but in the case of GC2 the formation of metallic Cu is preferable. There was a deposit of 14 mg at the Cu electrodes used in GC2, which corresponds to the amount of Cu^{2+} ions extracted from the kaolin. The distribution of Cu^{2+} ions in the kaolin is similar during these treatments (Figure 4a). This is due to the fact that the low voltage present during the galvanic cell experiments enables diffusion of H^+ to desorb Cu^{2+} and diffusion of Cu^{2+} due to the concentration gradient [15]. Overall, GC1 and GC2 had low efficacies since desorption of Cu^{2+} from the kaolin was limited (due to pH behaviour). The lack of accumulation of Cu in the kaolin after GC1 and GC2 at z/L=0.9 is probably due to the pH behaviour. During GC1, a small amount of copper was extracted from the kaolin and was precipitated in the granulated carbon compartment.

As shown in Figure 4b, removal efficacy increased significantly (from 20% to 46%) after acidification of the kaolin. There was intensive Cu^{2+} ions removal from z/L=0.1, 0.3 and 0.5 and a negligible removal efficacy increase at z/L=0.7 compared to GC1. An accumulation of copper occurred at z/L=0.9 after GC3. Since the pH is low near the cathode it can be assumed that accumulated copper exists in soluble form, but there was no diffusion due to the electromigration process. When the removal efficacy is calculated without the copper content at z/L=0.7 and 0.9 the removal efficacy is high (94%). Since the accumulated copper is in soluble form it would be possible to further remove it using the moving anode method. Using a larger granulated carbon compartment should enable Cu penetration and accumulation into the granulated carbon instead of the kaolin. Since the kaolin pH is low, a large amount of Cu^{2+} ions is excepted to be desorbed from the particles, so it can be easily removed. Lowering the pH did not significantly enhance Cu^{2+} ions removal using the Fe/Cu system (8%), which was as expected since the Cu electrode dissolved in acidic conditions. 20% more Cu^{2+} ions was removed from z/L=0.1 and 0.7 after GC4 then GC2. There was a deposit of 17 mg at the Cu electrodes used in GC2, which again corresponds to the amount of Cu^{2+} ions extracted from the kaolin.
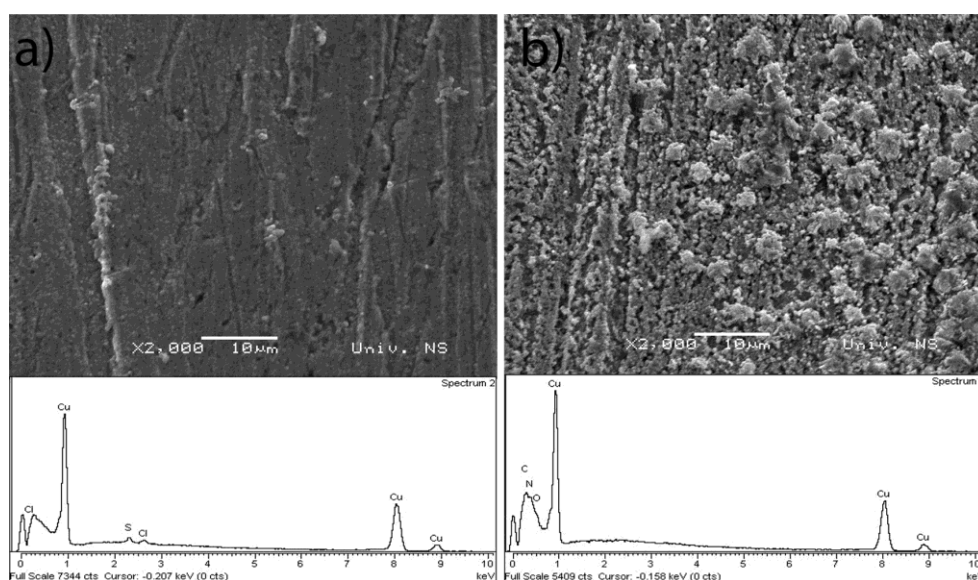

Figure 5. Scanning electron microscope image of the Cu cathode a) before and b) after EK treatment

In order to confirm the Cu deposition on the cathode SEM was used. Figure 5 shows the image of the Cu cathode before and after GC2. It can be concluded that deposition of Cu appears after treatment. The spectrum (Figure 5b) is the evidence that the surface of Cu rods were covered with Cu particles. It shows that deposited particles contains mainly Cu.

4. CONCLUSIONS

In this study we investigated using a galvanic cell for electrokinetic treatment of copper contaminated soil. Kaolin was used as a model matrix. The use of Fe/C and Fe/Cu galvanic cells was investigated, as well as the influence of acidifying the kaolin. The following can be concluded based on the results given above:

- Generally, using a galvanic cell is a cost effective method since relatively cheap materials (scrap iron, granulated carbon) are used and no electric power is consumed. The required clean up level (<100 mg Cu kg^{-1}) was achieved after the GC3 and GC4 treatments.

- The lack of Cu accumulation in the kaolin after GC1 at z/L=0.9 is probably due to the following: the cathode compartment was 5 cm long so a small amount of OH^- could penetrate into the kaolin. This indicates that the pH may be controlled by optimizing the cathode and anode length.

- Using the Fe/Cu system has numerous advantages over the Fe/C galvanic cell: no hydroxyl ions are produced at the cathode so no copper is accumulated in the cathode region of the kaolin, but is instead deposited at the cathode in metallic form, resulting in a removal efficacy increase (GC2 17% better than GC1); the deposition of Cu on the cathode in metallic form means the cathode may be used again after treatment, meaning no waste is produced by the treatment. It is important that the metals exist in a soluble form for using the Fe/Cu galvanic cell.

- Acidification of the initial sample (GC3 and CG4) resulted in significantly better removal efficacy (46%) after GC3, but lead to the accumulation of Cu in the cathode region. When the removal efficacy is calculated without the Cu content at z/L=0.7 and 0.9, the removal efficacy is high (94%). Since the accumulated Cu is in a soluble form, it would be possible to further remove it by moving anode method or using a larger granulated carbon compartment, to enable Cu^{2+} ions penetration and accumulation into the granulated carbon instead of the kaolin. Further galvanic cell method development is required.

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