Sorption, Desorption, Remediation and Fertility Characteristics of a Clay Soil

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Abstract: This study is conducted to investigate sorption and desorption characteristics of a clay soil of Medicine Hat, Alberta, Canada. Also, the soil fertility after the desorption tests was investigated. Sorption of copper by a clay soil was examined using copper solutions with concentrations from 1,000 mg/L to 5 mg/L. The influence of copper concentration and pH on desorption was also studied. Electrokinetic remediation was carried on soil specimen spiked with copper. Soil fertility parameters for specimens acidized by electrolysis reactions and nitric, hydrochloric, and citric acids were compared. From the results, the adsorption of copper by the soil is proportional to the concentration in the solution and Langmuir isotherm represents the data. Desorption of copper was found to increase with the increase of initial copper in the soil and the decrease of pH. At pH of 5.75 ± 0.25 , the maximum desorption was 16.5% of initial copper and the minimum was 4.2%. In tests with similar copper concentrations, the maximum desorption was 76.6% in the test with pH of 2. Electrokinetics reduced the pH of soil near the anode to 2.1 and removed 86% of copper. Soil specimen acidized by electrolysis reactions preserved favourable fertility parameters compared with specimens acidized by acids.

Key words: Sorption, desorption, electrokinetic remediation, fertility.

1. Introduction

The sorption and desorption characteristics of soil contaminated with heavy metals are crucial for understanding and evaluating the effectiveness of various remediation techniques. Heavy metals can be defined as elements with specific density greater than 5 g/cm^3 [1]. Contamination of soil with heavy metals poses threat to human and animal's health. The sorption capacity of a soil is essential in estimating fertility and amount of contaminant in the soil solids and that in the soil pore fluid [2, 3]. There are numerous sorption sites on the soils having a range of high and low binding energies [4]. For instance, when soil is contaminated with heavy metals of low concentration, the high-energy binding sites are occupied first, while at higher concentrations, the high-energy binding sites are completely occupied and

the lower-energy binding sites begin to fill, resulting in a decrease in the average metal-soil binding energy. In general, it is easy to remove certain amount of heavy metals from a highly contaminated soil compared with a low contaminated soil because less energy is required to remove contaminants from the former. The hysteresis phenomena in sorption-desorption can be attributed to the binding of heavy metals to the different energy sites [5]. The amount of contaminant adsorbed is also a function of the soil physiochemical properties such as organic matter and pH [6-8]. Contamination by heavy metals can affect the fertility of the soil [9]. For instance, high copper concentration in soil has an adverse effect in soil fertility by affecting nitrogen fixation [10, 11]. Desorption of heavy metals from soil matrix to pore fluid is a prerequisite for in-situ and ex-situ soil remediation. In a soil desorption study by Stone and O'Shaughnessy [6], tap water (equivalent to 20 pore volume) was used to leach heavy metals from contaminated soil. The results showed that only 50%

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of the heavy metals that was sorbed by the soil matrix can be removed. Most heavy metals tend to desorb from soil at low pH values [12]. A low pH is achievable by adding acids (organic or inorganic) to the soil or by electrolysis reactions associated with electrokinetics. However, a low pH environment may reduce the soil fertility and prevent maintaining the soil equilibrium [13].

Successful applications of electrokinetic remediation for soil contaminated with heavy metals require understanding of the adsorption and desorption characteristics of the soil for ranges of pH and metal concentration. The pH is known to be a dominant factor on the adsorption/desorption behavior of heavy metals by soils [14]. In electrokinetic remediation, electrolysis reactions change the soil pH and, thereby, influence the adsorption and desorption characteristics.

In this study, copper, a common heavy metal pollutant, was selected and used to investigate the adsorption and desorption characteristics of a clay soil from Medicine Hat, Alberta along with electrokinetic remediation of the soil. The influences of copper concentration and pH on desorption characteristics of the soil were investigated. The effect of the source of acidity on soil fertility was explored by comparing the fertility parameters for samples acidized by electrolysis reactions, nitric acid, hydrochloric acid and citric acid.

2. Materials and Methods

2.1 Gravimetric Composition

Copper(II) chloride dihydrate, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (molar mass of 170.48 g/mol), was used as the source of copper in the tests. Sodium nitrate, NaNO_3 (84.99 g/mol), was used as background electrolyte. Hydrochloric acid (HCl), citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and nitric acid (HNO_3) were used in the soil fertility tests. Solutions with different pH were prepared by the addition of dilute HNO_3 and/or NaOH solution to water. Deionized water was used in adsorption and

desorption tests, and tap water was used in electrokinetic test. Inorganic clay soil obtained from plainsman clay in Medicine Hat, Alberta was used for all the tests. Kaolinite is the predominant clay mineral of the plainsman clay soil. The USCS (unified soil classification system) group symbol for the soil is CL (lean clay). The main properties of the soil are summarized in Table 1. The chemical composition of the soil is shown in Table 2.

2.2 Electrokinetic Remediation

The application of a DC (direct current) electric field between two electrodes (i.e., anode and cathode) inserted in a moist soil mass establishes an electric potential gradient between the electrodes. This results in electroosmotic flow of water in the soil pores from the anode to the cathode. In addition, it initiates electromigration of ionic species available in the pore fluid towards the oppositely charged electrode.

Along with electroosmosis and electromigration, electrolysis reactions of water occur at the electrodes in an electrokinetic process. The reactions result in

Table 1 Properties of the plainsman clay soil.

Properties	Values
Liquid limit	41
Plastic limit	19
Sand (%)	0
Silt (%)	58
Clay (%)	42
Specific gravity	2.64
Cation exchange capacity	8.9 meq/100g

Table 2 Chemical composition of the plainsman clay soil.

Properties	Values
BaO	0.4
CaO	0.2
K ₂ O	2.2
MgO	0.5
Na ₂ O	0.1
TiO ₂	0.6
Al ₂ O ₃	15.6
P ₂ O ₅	0.0
SiO ₂	72.7
Fe ₂ O	1.2
MnO	0.0
LOI	6.5%

oxidation at the anode generating an acid front and reduction at the cathode producing a base front:

The pH near the anode is reduced due to the generation of hydrogen ions (H^+), whereas, in the vicinity of the cathode, the pH is increased by the formation of the hydroxyl ions (OH^-). The H^+ ions have smaller size than OH^- ions. Accordingly, by electromigration transport, H^+ ions travel a longer distance towards the cathode than the distance advanced by OH^- ions towards the anode. Further, H^+ ions also travel by electroosmosis towards the cathode resulting in an acid-base meeting closer to the cathode. The sorption of the cations (Me) with the clay soil surface (S) can be represented by Eq. (3):

3. Procedures and Equipment

3.1 Adsorption of Copper by Soil

In the adsorption tests, 0.01 M (mole/liter) NaNO_3 solution was prepared by adding 0.85 g of NaNO_3 to one liter deionized water. The mixture was thoroughly agitated until NaNO_3 was completely dissolved. The 0.01 M NaNO_3 solution was used as background electrolyte in the adsorption tests.

Copper solution of concentration 1000 mg/L was prepared by mixing 0.268 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 100 mL of the previously prepared 0.01 M NaNO_3 solution in 250 mL Erlenmeyer flask. Six additional solutions with copper concentrations of 500, 250, 100, 50, 20 and 5 mg/L were prepared by successive dilution of the 1,000 mg/L copper solution. The concentrations of copper solution were selected to achieve a wide range of copper adsorption (60 mg to 3,700 mg of copper per kg of dry soil). Seven stopper 50 mL Erlenmeyer flasks were used in the adsorption tests. A dry soil sample of 1 g was weighed into each flask. From each of the prepared copper solutions, 14 mL was measured and added to one of the seven soil samples in the Erlenmeyer flasks.

The soil-solution mixtures were equilibrated at room temperature ($21 \pm 1^\circ\text{C}$) for 24 h in a shaking table at 120 rpm. The pH of the soil-solution suspensions was adjusted to 5.75 ± 0.25 with nitric acid (HNO_3) and/or sodium hydroxide (NaOH). The pH was measured every 2 h to 3 h and readjusted when needed. The soil and solutions were then poured into 20 mL centrifuge tubes. The tubes with the soil and equilibrated suspensions were placed in centrifuge and rotated at 4,000 rpm for 10 min. After that, 1 mL of the supernatant from each tube was drawn and placed in 20 mL plastic tube. The solution in each tube was diluted by adding 9 mL deionized water. The concentrations of the diluted solutions were determined using the ICP-OES (inductively coupled plasma-optical emission spectrometry). Each adsorption test was carried out in triplicate.

3.2 Desorption of Copper from Soil

Two sets of tests were conducted to investigate copper desorption from the soil. In the first set, the effects of initial copper concentration on desorption were studied with similar pH. The second set investigated the effects of the pH on desorption of copper from soil samples with identical initial copper concentration. The selected pH values were from 2 to 10, a range that is typically encountered in electrokinetic processes.

3.2.1 Influence of Copper Concentration on Desorption

Desorption tests were performed using soil samples containing different amounts of adsorbed copper with similar pH. The amount of copper desorbed from each soil sample was obtained and compared with the initial amount adsorbed into the sample.

After decanting the solutions from the centrifuge tubes in the adsorption tests as discussed in Section 3.1, the soil samples were used for the desorption tests. For each soil sample (contained 1 g of dry soil), 14 mL of 0.01 M NaNO_3 solution was added and then the soil and the solution were equilibrated for 24 h in a

shaking table at 120 rpm in room temperature (21 ± 1 °C). The pH of the soil-solution suspensions was adjusted to 5.75 ± 0.25 with nitric acid (HNO_3) and/or sodium hydroxide (NaOH). The pH was measured and readjusted every 2 h to 3 h. After 24 h, the tubes with the soil and the solution mixture were centrifuged at 4,000 rpm for 10 min. From each tube, 1 mL from the supernatant was drawn and poured in a 20 mL plastic tube. The solution in the tube was diluted by adding 9 mL deionized water. The concentrations of copper in the diluted solutions were then determined using ICP-OES. Each test was carried out in triplicate.

3.2.2 Influence of pH on Copper Desorption

Desorption tests were conducted using soil samples with identical copper concentration and different pH values. The amount of copper desorbed at each pH was obtained and compared with the initial copper concentration.

The clay soil sample was initially contaminated with 355 mg of copper per kg of dry soil with water content 41% (the same copper concentration and water content of the soil specimen used in the electrokinetic remediation test). The soil sample was air-dried for 72 h and then ground. Five soil samples of 1 g each were weighted into five Erlenmeyer flasks of 50 mL volume. 14 mL of 0.01 M NaNO_3 solution was added to each soil sample in the Erlenmeyer flasks. The soil samples with the solution were equilibrated for 24 h in a shaking table (120 rpm) in room temperature (21 ± 1 °C). The pH of the soil-solution suspensions were controlled at values of 2, 4, 6, 8 and 10 with the addition of nitric acid (HNO_3) and/or sodium hydroxide (NaOH). The pH was measured every 2 h to 3 h and readjusted when needed. The soil and solution was transferred to 20 mL plastic centrifuge tubes. The tubes with the soil and solution mixture were then centrifuged at 4,000 rpm for 10 min. After that, 1 mL of the supernatant from each tube was drawn and placed in 20 mL plastic tube. Then the solution in each tube was diluted by adding 9 mL deionized water. The concentrations of

the diluted solutions were determined using ICP-OES. Each experiment was repeated three times.

3.2.3 Electrokinetic Remediation

Electrokinetic cell was designed and fabricated for the soil remediation test. The electrokinetic cell, constructed of clear plexiglas plates 15 mm in thickness, has inner dimensions of 385 mm $\times$ 125 mm $\times$ 250 mm (length $\times$ width $\times$ height). The cell is composed of upper part, base and two movable rectangular perforated plexiglas plates (250 mm length $\times$ 125 mm width). The upper part forms an outer boundary to accommodate the soil sample. The rectangular plexiglas plates can be used to adjust the soil sample length between 200 mm and 320 mm. The base of the cell is detachable to allow for easy recovery and minimum disturbance of the soil specimen that is to be used for subsequent parametric studies. At the base far ends, two drainage valves were installed and used to collect water during the remediation process. Fig. 1 shows the electrokinetic remediation cell.

The soil specimen for electrokinetic remediation test was prepared in batches. For each batch, 5 kg of dry plainsman clay soil was weighed into a plastic pail. 2,050 mL of tap water (required for water content of 41% similar to the liquid limit of the soil) was poured into a container. To investigate the effectiveness of electrokinetics in remediating soil contaminated with a heavy metal, the plainsman clay soil was spiked with copper at concentration of 355 mg/kg of dry soil. 4.77 g of copper(II) chloride dehydrate was thoroughly mixed with the water in the container. The dry soil and the copper solution were mixed using a mechanical mixer. Additional batches were similarly prepared. The soft contaminated soil was poured into a thick plastic bag and placed in a pail with airtight cover. The soil was stored to allow for copper adsorption by soil to take place and reach equilibrium. 72 h after preparing the pre-contaminated soil, the soil was placed into the electrokinetic cell in three layers for a total height of 165 mm. Each layer was rodged

Fig. 1 Schematic diagram for electrokinetic cell.

25 times using steel rod, 16 mm in diameter and 600 mm long with a hemispherical shaped tip, to prevent the entrapment of air pockets. The high water content of the soil and the thorough rodding during placement insured that the soil specimen was nearly, if not fully, saturated. A surcharge load of 12.8 kg (corresponding to a pressure of 5 kPa) was applied to the soil via the loading plate in four increments over a period of four days. The first surcharge load was 0.6 kg, followed by 3 kg, 5 kg, 7.8 kg and 12.8 kg. Graphite (nonmetallic) was selected as electrode material to avoid/minimize adverse reactions by-products of metallic electrode. Two perforated graphite electrodes, one serving as anode and the other as cathode with dimensions of 200 mm × 125 mm × 3 mm (height × width × thickness), were placed in direct contact with the soil. A geotextile filter was wetted by tap water and placed between the electrode and the plexiglas. The electric field was provided by a solar cell panel with peak outputs of 41 V and 5 A connected to the graphite electrodes in the electrokinetic cell. The

corresponding applied voltage gradient across the cell was 205 V/m. The experiment was carried out in July 3, 2010 for a period of seven days.

3.3 Soil Fertility

Tests were carried out to compare the effect of acidification by electrolysis reactions and by the addition of acidic chemical compounds on the fertility characteristic of the plainsman clay soil. In the chemical compound tests, the pH of the soil was lowered to 2.25 ± 0.25 , similar to the pH values encountered near the anode in an electrokinetic remediation process. The chemical compounds used in the tests were hydrochloric, citric and nitric acids. Three soil samples contaminated (355 mg of copper per kg of dry soil) were acidified using the acids. The acidified soil samples along with soil sample near the anode in the electrokinetic test were analyzed at the FoReST (Forest Recourse and Soil Testing) Laboratory, Lakehead University for fertility characteristics. OMAFRA (Ontario Ministry of

Agriculture, Food and Rural Affairs), fertilizer recommendations chart to optimize plant growth was used to obtain the amount of lime required for the soil.

4. Results and Discussion

4.1 Adsorption of Copper

Adsorbed copper was calculated as the difference between the amount initially present in the solution and the amount remaining in solution after equilibration. The results were used to determine the parameters for both Langmuir and Freundlich sorption models. The Langmuir isotherm was found to best represent the data. Langmuir equation is given by Langmuir [15]:

$$\frac{C_e}{S} = \frac{1}{K_L M_L} + \frac{C_e}{M_L} \quad (4)$$

where, C_e (mg/L) is the equilibrium copper concentration in the supernatant, S (mg/g) is the amount of copper adsorbed by the soil, K_L (L/mg) is the Langmuir constant and M_L (mg/g) is the Langmuir maximum adsorption capacity of the soil.

$$C_{e1} = \frac{C_{e1} + C_{e2} + C_{e3}}{3} \quad (5)$$

$$S = \frac{(C_i - C_e)}{(M_s)} \times 14 \text{ mL} \times \frac{1 \text{ L}}{1,000 \text{ mL}} \quad (6)$$

where, C_{e1} , C_{e2} and C_{e3} (mg/L) are equilibrium copper concentration in the supernatant in Tests 1, 2 and 3, and C_i (mg/L) is the initial copper concentration in the solution (e.g., 1,000 mg/L) and M_s is the mass of dry soil in grams.

Langmuir equation parameters were obtained from Fig. 2 which shows C_e/S (ratio of copper concentration in the supernatant to copper adsorbed into the soil) vs. copper concentration in the supernatant (C_e). Fig. 2 also shows the amount of adsorbed copper (S) vs. copper concentration in the supernatant (C_e). From Fig. 2, S increased with the increase of the C_e . The results obtained from this test showed similar adsorption behavior to that reported by Yuan et al. [14] on kaolin clay.

Fig. 2 Ratio of copper concentration in the supernatant to copper adsorbed into the soil (C_e/S) and copper adsorbed into the soil (S) vs. copper concentration in the supernatant (C_e).

Table 3 Langmuir isotherm equation.

Regression equation	Coefficient R^2	K_L L/mg	M_L mg/g
$C_e/S = 0.25 C_e + 19.22$	$R^2 = 0.988$	0.013	3.98

Table 3 presents Langmuir equation, Langmuir constant (K_L) and the maximum adsorption capacity of the soil (M_L). From the results of the adsorption test, the Langmuir equation for the soil is given by:

$$\frac{C_e}{S} = 19.22 + 0.2508 C_e \quad (7)$$

4.2 Desorption of Copper

4.2.1 Effect of Copper Concentration on Desorption

The amount of copper desorbed from the soil was calculated as follows:

$$D_e = \frac{(D_{ave} - C_i) \times VI}{(M_s)} \times \frac{1,000 \text{ g}}{\text{kg}} \quad (8)$$

$$D_{ave} = \frac{D_1 + D_2 + D_3}{3} \quad (9)$$

where, D_e (mg/kg) is the desorbed copper, D_{ave} (mg/L) is the average desorption equilibrium copper concentration in the supernatant, D_1 , D_2 and D_3 (mg/L) are desorption equilibrium copper concentrations in the supernatant in Tests 1, 2 and 3, respectively, C_i (mg/L) is the initial copper concentration in the solution (C_i in the sodium nitrate solution was zero), and VI (L) is the volume of sodium nitrate solution added to the soil sample ($VI = 0.014 \text{ L}$).

The desorbed copper (D_e) was plotted against the initial adsorbed copper (S) in Fig. 3. The experiments covered a range of the adsorbed copper between 60 mg and 3,700 mg per kg of dry soil (Table 4). For the range tested, Fig. 3 shows that the desorbed copper increases with the increase of the initial adsorbed copper. The highest copper desorbed (670 mg/kg) was obtained for the adsorbed amount of 3,700 mg/kg. For adsorbed copper < 1,000 mg/kg of dry soil, the slope of desorption profile is somewhat flat, whereas, for initial adsorbed copper > 1,000 mg/kg, the profile slope is steeper. The percentage of desorbed copper to the initial adsorbed copper was calculated for each test and Fig. 4 shows ratio (in percentage) of desorbed copper to the initial adsorbed copper (D_e/S) vs. initial adsorbed copper (S). As seen in Fig. 3 in general, D_e/S increases with the increase of S . The highest and lowest D_e/S percentages were 16.5% and 4.2% reported

Fig. 3 Desorbed copper (D_e) vs. initial adsorbed copper (S) at pH of 5.75 ± 0.25 .

Table 4 Sorption test results.

Initial Cu concentration (mg/L) C_i	Equilibrium Cu concentration (mg/L) $C_{ave} = C_e$	Amount adsorbed (mg/kg) S
1,001.00	735.70	3,710
511.20	304.10	2,900
274.50	126.83	2,070
96.21	26.76	970
48.43	10.96	520
21.70	3.19	260
5.33	0.80	60

Fig. 4 Ratio (in percentage) of desorbed copper to the initial adsorbed copper (D_e/S) vs. initial adsorbed copper (S) at pH of 5.75 ± 0.25

with the tests with initial adsorbed copper of 3,700 mg/kg and 60 mg/kg, respectively.

4.2.2 Effect of pH on Copper Desorption

Fig. 5 shows the amount of desorbed copper at different pH values. The figure shows that the amount of desorbed copper decreases as the pH increases. For instance, for soil sample with pH of 2, the amount of desorbed copper was 270 mg/kg of dry soil compared to 180 mg/kg at pH of 4. Fig. 5 shows that very little or no copper was desorbed at pH ≥ 8 . Fig. 6 shows the ratio in percentages of copper desorbed to the initial copper in the soil (355 mg copper per kg of dry soil) at different pH values. At low pH values (i.e., pH of 2 and 4), the percentages of copper desorption were 76.6% and 50%, while at pH > 8 (alkaline medium), virtually no copper was desorbed from the soil.

It has been reported in the literature that, in general, the rise of pH results in more adsorption of heavy metals by soils and vice versa [14, 16, 17]. Therefore, it can be concluded that, for the clay soil and the range of copper concentrations tested in this study, desorption of copper increases with the decrease of pH. The maximum desorbed copper was 76.6% of the initial concentration reported in the test with pH of 2. In an electrokinetic remediation process, the desorbed copper will be free in the pore fluid and available to be removed from the soil by electroosmosis and electromigration.

Fig. 5 Desorbed copper (D_e) vs. pH for soil samples with initial copper concentration of 355 mg/kg.

Fig. 6 Ratio (in percentage) of desorbed copper to initial copper in soil (D_e/C_0) vs. pH for soil with C_0 of 355 mg/kg.

4.3 Electrokinetic Remediation

After the electrokinetic remediation test, the soil in the electrokinetic cell was divided into four equal sections. Fig. 7 shows the pH along the soil after the test. D is the horizontal distance between the mid of the soil section and the anode. D_0 is the total length of the soil sample (200 mm). Thus, $0.1 D/D_0$ is the soil section near the anode while $0.9 D/D_0$ is the section near cathode. As shown in the figure, 60% of the soil reported pH < 3.5 (i.e., acidic) with the lowest pH near the anode (2.1). The remaining 40% of the soil had pH > 7 and the highest pH was 8.9 near the cathode. The pH profiles are in agreement with the electrolysis reactions at the electrodes and the distance travelled by the H^+ and OH^- ions.

Fig. 8 shows the ratio (in percentage) of the copper

concentration after the electrokinetic test to the initial concentration of 355 mg/kg of dry soil along the electrokinetic cell. The concentrations are presented for the total copper in the soil, copper in soil solids and copper in pore fluid. The figure clearly shows that electrokinetics was generally effective in moving copper from the soil near the anode towards the cathode. The movement of copper was due to the combined effects of electroosmosis and electromigration along with the change in the soil pH during the process. The lowest ratio of the copper concentration after the test to the initial concentration was 14% in the soil section near the anode ($0.1 D/D_0$). Thus, 86% of the initial copper was removed from the soil near the anode. The copper concentration increased toward the cathode with the maximum concentration of 256% at $0.7 D/D_0$ (the soil section the

Fig. 7 pH of the soil vs. normalized distance between the anode and cathode (D/D_0).

Fig. 8 Ratio of copper concentration at the end of test to initial copper concentration (C/C_0) vs. normalized distance between the anode and cathode (D/D_0).

acid and base fronts met). As seen in Fig. 8, the highest ratio of copper in the pore fluid was observed near the anode and the ratio decreased towards the cathode. This resulted from the low pH near the anode which promotes copper dissolution while the high pH at the cathode caused copper precipitation.

In the electrokinetic test, the high copper removal (86% of initial copper) from soil section at 0.1 D/D_0 coincided with lowest soil pH reported in the soil (2.1). On the other hand, in the desorption test at approximately the same pH (2), the amount of desorbed copper was 76.6% of the initial copper. This means that the copper removal by electrokinetic was higher than that by the desorption test. This is attributed to the electromigration. The dominance role of electromigration is removing copper which is in agreement with previous studies by Page and Page [18] and Probst and Hicks [19]. Acar et al. [20] had successfully removed cadmium without electroosmosis flow. Therefore, any copper removal higher than 76.6% achieved by electrokinetic remediation can be attributed to removal by electromigration. As per the results, for clay soil contaminated with copper at 355 mg/kg, the use of conventional soil flushing with solution 14 times the mass of the soil, pH of 2 and 24 h of agitation, can remove 76.6% of the initial copper. Obviously, this will be very expensive and impractical for full-scale applications.

4.4 Soil Fertility

The results of the fertility parameters of the soil

after acidification are shown in Table 5. For a soil with high acidity ground, limestone is added to raise the pH to make the soil suitable for plant growth. In OMAFRA (Ontario Ministry of Agriculture, Food and Rural Affairs), fertilizer recommendations chart to optimize plant growth was used to obtain the amount of lime required for the soil. The results show that, according to OMAFRA fertilizer recommendations chart, the following amounts of limestone 2 kg, 2 kg and 1.9 kg per m^2 of soil should be added to the soil acidified with electrokinetic, hydrochloric and nitric acids, respectively. The soil acidified with citric acid needs significantly higher amount of lime. More important, the results showed that the amount of phosphorus on the soil treated with electrokinetics was 11.7 $\mu\text{g/g}$ compared with 3.5 $\mu\text{g/g}$ and 6.6 $\mu\text{g/g}$ hydrochloric acid and nitric acid, respectively. A highly phosphorous content is beneficial for soil fertility and plant growth. Despite the higher amount of phosphorus in soil acidified with citric acid (14.4 $\mu\text{g/g}$), substantially larger amount of lime is required for the soil to achieve the optimum pH for plant growth. The lower amount of K, Mg, Na and Ca in the soil treated with electrokinetic remediation can be attributed to the movement of these cations by electroosmosis and electromigration. It worth mentioning that there was no copper removal from the soil samples treated with acids. Therefore, it can be concluded that the soil treated with electrokinetic remediation is likely to regain more of its fertility characteristics compared to the soil samples treated with acids.

Table 5 Parameters for soil fertility and plant growth.

Soil treated by	pH	Buffer pH	Limestone (kg/m^2)	Olsen P ($\mu\text{g/g}$)	Ammonium acetate extractable ($\mu\text{g/g}$)			
					K	Mg	Na	Ca
Hydrochloric acid	2	4.7	20	3.5	156.9	487.7	193.8	875
Citric acid	2.3	3.1	>> 20	14.4	164.3	400.9	153.8	718
Nitric acid	2.5	5.4	19	6.6	163.4	470.1	188.4	855
Electrokinetics	2	5	20	11.7	70.4	40.4	20.9	139

5. Conclusions

This experimental study investigated the adsorption and desorption characteristics of plainsman clay soil using copper. Desorption and removal of copper by electrokinetic remediation was also investigated and discussed. The fertility parameters for soil acidized with electrolysis reactions and three acids were compared. The results show that:

(1) Adsorption of copper by the soil is proportional to the copper concentration in the solution and Langmuir equation represents the adsorption isotherm of the soil;

(2) Desorption of copper from the soil increases with the increase of copper concentration in the soil and the decrease in pH;

(3) Electrolysis reactions reduced the pH of the soil near the anode to 2.1 and increased the pH at the vicinity of the cathode to 8.9;

(4) Electrokinetic remediation removed 86% of copper from soil near the anode (pH of 2.1), while 76.6% of copper was removed in the desorption test with pH of 2;

(5) The fertility and plant growth characteristics of soil near the anode after electrokinetic remediation were superior to characteristics of soil samples acidized with acids.

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