

Removal of Chromium Contaminated Soils by Electro-Kinetic Method

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ABSTRACT

Chromium-contaminated soil is a serious environmental problem that threatens human health and the environment. Electrokinetic technology is used as a promising solution to treat these soils, as it relies on applying an electric field to remove pollutants from the soil. In this study, four experiments were conducted, where experiments have shown that the use of wheat straw as an available, cheap, economical and efficient adsorbent material to prevent the occurrence of reverse osmosis. The results showed that the percentage of removal increased with the increase in the acidity of the medium, that is, as the pH decreased. This is due to an increase in the movement of pollutants as the soil particles become more positively charged, which enhances Attract negative heavy metal ions. This leads to increased movement of heavy metal ions into soil pores, making them more susceptible to transport under the influence of an electric field. The results proved that when using a disinfection solution with a pH of 2, it gave a higher result compared to pH 7 and 12, where the percentage of removal was 78.3%, 62.6 %, and 51.9% respectively. The dissolution of these metals can be enhanced by adding oxalic acid at a constant voltage gradient 1.2 v/cm and an initial concentration of 200 mg/kg. It was noted after the end of the experiment that the percentage of removal reached 81.9%, as the concentration of metals on the cathode side was higher than on the cathode side. The anode, and this is due to the migration of metals under the influence of electromigration to the cathode side, where the chromium concentration was 47 mg/kg at the cathode side, 27 mg/kg at the anode side.

Keywords: chromium, heavy metals, soil, wheat straw, oxalic acid, electro-kinetic.

INTRODUCTION

For the past 100 years, heavy metals have been a source of environmental contamination. This is a result of the industrialization and rapidly expanding economy. Residential waste, industrial effluent/wastes, agricultural tool waste, mechanic village scraps, and, more recently, electronic waste are some of the sources of these pollutants. Soil, subterranean water, rivers and streams, lagoons, and the sea serve as the receiving systems; the water eventually settles or accumulates in the ocean (Idera et al., 2014). The heavy metals present in soils can exist as soluble compounds in the form of ions or in interchangeable configurations. Primarily, these metals are stabilized by interacting with different soil compartments and fractures such as hydroxide, oxide, carbonate, and organic component (Srivastava et al., 2007). Precipitation, mining, waste treatment, industrial

waste, and fertilizers are the primary sources of cadmium in soil. Other non-point sources include atmospheric deposits and ecological contamination actions (Herngren et al., 2005; Hawal et al., 2021b). Chromium (Cr) is a major soil contaminant at superfund sites and industrial sites like tanneries, electroplating, and power plants. Chromium in polluted soils is trivalent (Cr(III)) or hexavalent (Cr(VI)). HCrO_4 (hydro-chromate), CrO_2 (chromate), and Cr_2O_2 are the primary environmental Cr(VI) ions. CrO_2 dominates above pH 6.5 in aqueous solutions, while HCrO_4 dominates below. In most natural environments, Cr(III) rapidly precipitates as Fe(III)–Cr(III) oxyhydroxides (FexCr1x(OH)_3) or sparingly soluble Cr(OH)_3 . Because Cr(VI) is more toxic to living things than Cr(III), which is nontoxic and immobile, and because of its high mobility in subsurface media, environmental and public health regulatory agencies are interested in remediating Cr(VI)

contaminated sites (Shariatmadari et al., 2009). According to (Hawal et al., 2023a), soil pollution is a critical environmental issue that affects environmental scientists worldwide. To remediate polluted areas, numerous techniques have been implemented, including chemical treatment, electrokinetic method, and biological treatment. It is theoretically possible to use these technologies both on- and off-site (Hawal, Omran, et al., 2023b; Hawal et al., 2021b). Out of all the technologies that were tried, the electrokinetic technology proved to be attractive, remarkable, and effective due to its on-site applicability electrokinetic remediation is a cost-effective and environmentally friendly technology that uses an electric field to migrate, separate, and remove pollutants in soil and sediment. It is also known as electrokinetic soil processing, electromigration, electrochemical, or electro reclamation. This method involves the use of electric currents to extract radionuclides, heavy metals, certain organic compounds, and mixed inorganic species and organic wastes from soils and slurries. EKR has been widely applied in the removal of various pollutants, including heavy metals like Cr, Cu, Pb, Zn, and Cd, as well as organic pollutants such as phenanthrene, thorium, triclosan, aniline, and phenol (Han et al., 2021, Hawal et al., 2023a).

MATERIALS AND METHOD

Soil

Baghdad's agricultural nursery provided the soil. It was dried by being exposed to the sun. To remove big lumps and get a uniform soil sample, then it sieved using a 2 mm sieve. After carefully measuring the system and the amount of soil that was suitable for it, three kilograms of soil was sorted for each condition. The soil was then contaminated with chromium in the laboratory in an even manner on the soil to ensure that the contamination occurred in all regions of the soil. Finally, the soil was placed in the EK cell. Table 1 shows the physical and chemical properties of soil

Wheat straw

Wheat straw was picked up from a farm in the Al-Qazaniya region of the barley Diyala Governorate. Subsequently, the straws were washed using distilled water and allowed to air dry in the

sun to eliminate any remaining moisture. The dried wheat straw was then processed in a ball mill for no more than a minute to produce a straw that was between one and two centimeters long. Lastly, the collected fractions were cleaned with distilled water and dried once more. The wheat straw that has been processed is placed in a bag that has holes in it and put inside a chamber that measures 5 by 12 by 14 cm.

Chromium contaminant

In order to generate a chromium solution with a concentration of 2000 mg/kg (PPM), a total of 15.9 g of $\text{Cr}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, which has a molecular weight of 400.15 grams per mole, was dissolved in 1000 milliliters of distilled water. for preparing 200, 400, 600 ppm of chromium to soil weight and initial moisture content equal to 30%, amount of 300, 600, and 900 ml of this solution was taken and added to 3 kg of dry soil. The purpose of this study was to investigate three simulated Pb contaminated soil samples. The samples were created at concentrations of 200 mg/kg, 400 mg/kg, and 600 mg/kg.

Electrokinetic test setup

The electro-kinetic cell used in this research is shown as a 3D diagram in Figure 1. The electrokinetic cell is constructed using glass. The inside dimensions of the cell are 50 cm in length, 12 cm in width, and 14 cm in height. The actual length of the soil specimen in this cell is 25 cm. In the electro-kinetic cell, wheat straw with a thickness of 5 cm was utilized as a barrier between the soil and the cathode compartment. The wheat straw

Table 1. Properties of soil

Property	Value
Particle size distribution (ASTM D 422)	
Sand (%)	97.12
Silt (%)	0.71
Clay (%)	2.12
Texture class	sand
Atterberg limits (ASTMD2487)	
Liquid limit (%)	ND
Plastic limit (%)	ND
Plasticity index (%)	ND
Specific gravity	2.66
Electric conductivity EC ($\mu\text{S}/\text{cm}$)	725
Organic content (%)	0.03
Primary pH	7.4
Porosity (n)	54.25

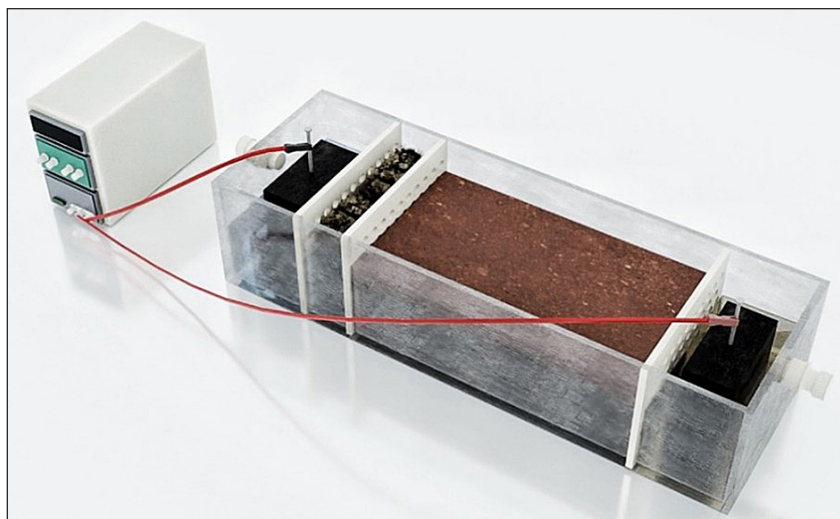


Figure 1. 3D diagram of electro-kinetic

barrier is 14 cm in height. Each electrode compartment, measuring $10 \times 12 \times 14$ cm, contained a valve positioned 10 cm above the bottom. This valve was used to regulate the flow within the cell and electrode. The electrodes were constructed in a cylindrical form using graphite material, with dimensions of 10 cm in height and 4 cm in breadth. The electrodes were punctured at the uppermost part to create a threaded structure for the purpose of facilitating electrical conduction. Perforated plastic plates were employed to create a barrier between the wheat straw and the earth at one end, and between the wheat straw and the cathode electrode at the other end. The plates measure 12×14 cm and include holes with a diameter of 6 mm. The holes are spaced 1 cm apart, measured from the center of one hole to the center of another. A Whatman 40 filter paper is placed in front of each perforated plastic plate. A DC power source (LDESTAR, LP 3005D) was utilized to provide the cell with a consistent voltage via the electrode. The electric current flowing through the soil during the trials was measured using a multi-meter.

Experimental work

At first, the cell was washed with distilled water to ensure the accuracy of the work. After that, filter papers were placed between the soil and water chambers the polluted soil was deposited into this compartment until it reached the maximum permissible limit and was then meticulously shaped using a tool to produce a consistent form. Subsequently, the soil was left undisturbed for a

duration of one day. A uniform solution level was maintained in the electrode chambers throughout the duration of the testing in order to avoid variations in hydraulic gradients inside the soil. Afterwards, the electrodes were placed in the designated chamber and connected to an electrical generator source under the application of a constant voltage 1.2 v/cm, then the system was turned on. In this study, tap water was chosen for use in all experiments. Four experiments were conducted to find the effect of changing values pH and the effect of adding organic acid (oxalic acid) on the process of removing heavy metals (chromium). In the first experiment, tap water with a pH of 2 and an electrical conductivity of $576 \mu\text{s}/\text{cm}$ was used in the electrode chamber, with a voltage of 1.2 v/cm and an initial concentration of 200 mg/kg. In the second experiment, the pH was set at 7 and EC $617 \mu\text{s}/\text{cm}$, while the concentration and voltage remained constant as in the first experiment. To conduct the third experiment, the same conditions were adopted in the first and second experiments, but with a pH of 12 and the EC of tap water was equal to $565 \mu\text{s}/\text{cm}$. As for the fourth experiment, it was similar to the first experiment, but by adding 100 ml of oxalic acid to the aqueous medium and maintaining Rest of the circumstances are the same. During the process of continuously monitoring the operation of the cell, it was found that the pH and EC values were constantly changing as a result of the electrolysis of water. To maintain the stability of the pH of the solution throughout the operation of the cell, it was necessary to add HCl acid and NaOH base to the cell continuously. After the end of each experiment, the soil was

divided into five parts, and the soil was extracted from each part and stored in a bottle in order to examine the concentration of remaining chromium. The wheat straw was extracted from the system and stored for examination. A 5 g sample was collected and combined with 12.5 ml of water in a bowl. The mixture was then stirred by hand for a few minutes before being left unstirred for an hour, allowing the soil particles to settle to the bottom. As a result, the pH and EC values of the sample were determined. Table 2 presents the specific parameters of the laboratory environment used in the removal process.

Analytic methodology

A mixture consisting of 5% nitric acid, 1% perchloric acid, and 3% hydrochloric acid was used. This specific acid combination is employed to digest materials in order to prepare them for chemical examination. After measuring the weight of one gram of the dehydrated sample, five milliliters of the acid mixture are introduced into the mixture. Subsequently, it is left unattended for the duration of the night. On the subsequent day, the substance is subjected to heat on a high-temperature surface until it reaches a state of near-dryness. It is then let to cool down, followed by the addition of a certain amount of purified water. The resulting mixture is filtered, and the final volume is adjusted to 25 milliliters. Subsequently, it is introduced into the atomic device. Subsequently, the instrument starts the process of quantifying the concentration of chromium.

Influence of pH

In this study, the pH of the solution clearly affected the removal process, as shown in Figure 2. The soil was contaminated with chromium at a concentration of 200 mg/kg. The remaining concentrations were 29 and 73 mg/kg near the anode, and between 59 and 118 mg/kg near the cathode. Upon completion of the test, it was found that the chromium content was higher at the cathode than at the

chromium electrode, and this is a result of the movement of charges towards the cathode electrode. Figure 3 shows a difference in the pH value in the soil sample. The results show that the soil pH is high at the cathode and low near the anode. Because the H^+ ions are constantly moving, but the OH^- ions are bound close to the cathode. It is known that an increase in OH^- ions correspond to an increase in deposited metal pollutants; Hence, it obstructs the passage of the contaminant to the cathode. The reason why the acid front moves more quickly than the basic front is that H^+ may migrate more quickly than OH^- ions (Acar and Alsha-wabkeh, 1993). While Figure 4 shows a difference in EC values throughout the soil section, ranging between 2.14 and 2.78 $\mu s/cm$ the nearby anode and approximately 1.07 to 1.29 $\mu s/cm$ the adjacent cathode. This is due to the increase in current passing through the soil over time. Additionally, the pH value of the solution affected the electric current with a change in physical and chemical characteristics, as in the case of the dissolution and chemical precipitation of heavy metals and so forth. Thus, because of the migration and high solubility of heavy metals, the electric current tended to increase when the pH started to drop (Hamed and Bhadra, 1997). The chromium contamination was well adsorbable by the wheat straw. Returned via reverse osmosis; the efficacy of the salt ions with chromium ions in the soil section has left a certain amount of chromium on the surface of this medium (rice husks). Throughout all tests, wheat straw absorbed between 30 and 39 mg/kg of chromium ions.

Influence of oxalic acid

In the EKR process, the high pH created by water electrolysis at the cathode may precipitate heavy metal cations flowing toward it. This is termed the “focusing effect” and reduces removal efficiency. Creating soluble heavy metal complexes with boosting agents is one way to avoid the concentrating effect and promote heavy metal dissolution. Due to their high heavy metal removal effectiveness, synthetic chelating agents. Chemical chelating agents are

Table 2. Operational conditions

EX. NO.	Chromium concentration (mg/kg)	Remediation duration (in days)	Voltage (V/cm)	pH of solution	Objective of the experiment
EX-1	200	5	1.2	2	pH impact
EX-2	200	5	1.2	7	pH impact
EX-3	200	5	1.2	12	pH impact
EX-4	200	5	1.2	2	OX impact

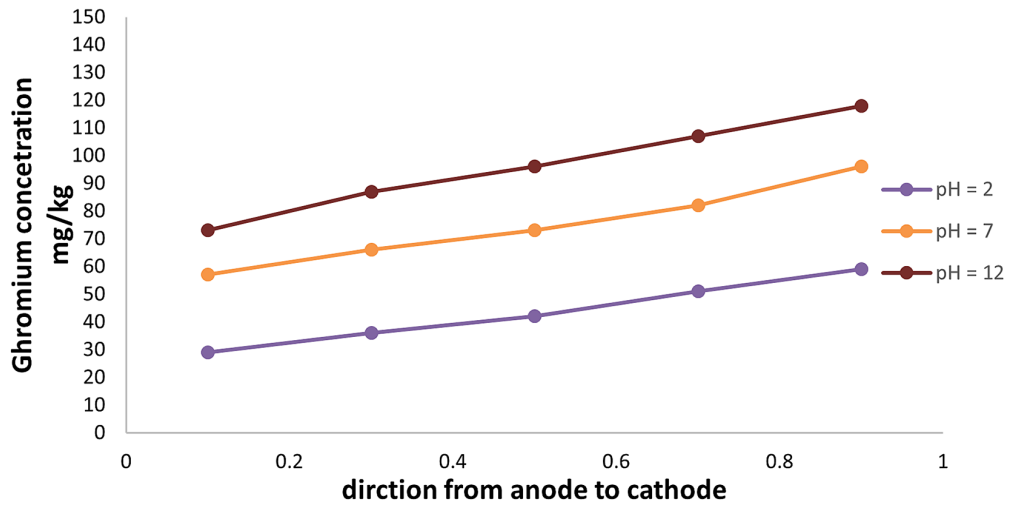


Figure 2. Chromium concentrations (mg/kg) of soil at different pH values

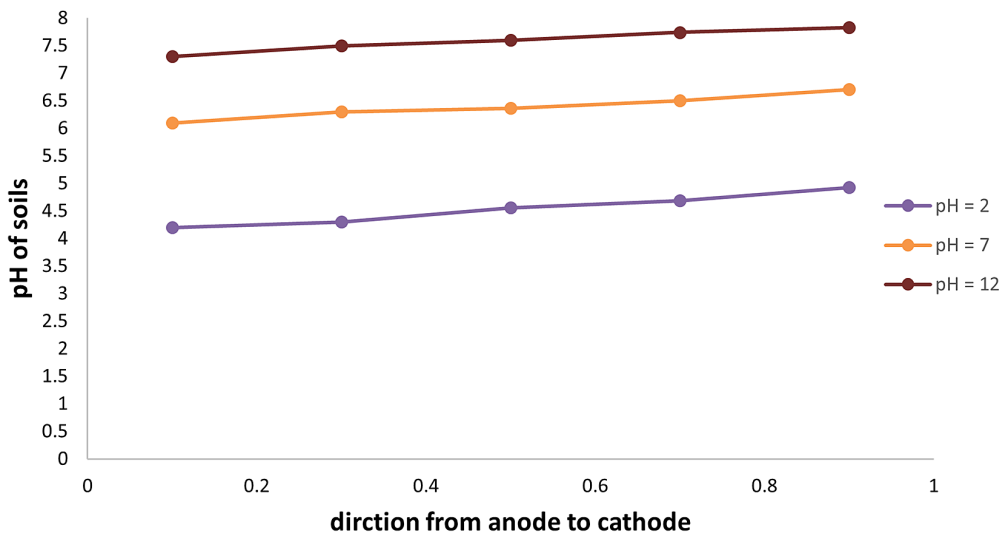


Figure 3. Soil pH versus at different pH values.

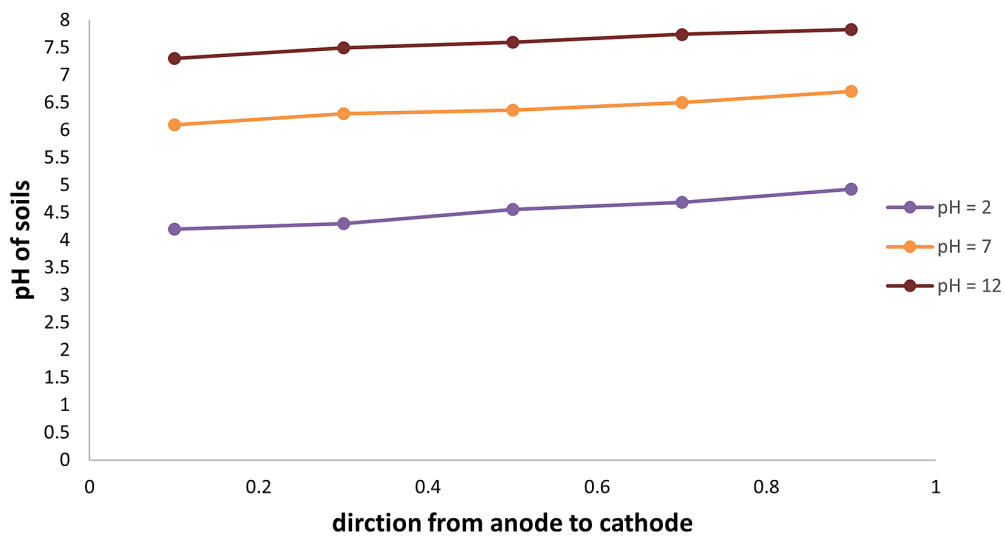


Figure 4. Soil EC versus at different pH values.

expensive, not biodegradable, and potentially harmful. Therefore, ecologically benign and economically effective alternatives must be sought. Oxalic acid is found in root exudates, microbial secretions, and plant and animal breakdown leftovers in soils. these Low molecular-weight organic acids are biodegradable, ecologically friendly, and commercially accessible for soil remediation; therefore, they increase heavy metal removal. Many studies have shown that the aforementioned acid improves soil pH conditioning and heavy metal extraction (Ge et al., 2022). Figure 5 confirms the use of oxalic acid enhancement had a substantial impact on the elimination process, as seen by the observed final concentrations of the treated soil, which varied from 29 mg/kg in close proximity to the anode, to 59 mg/kg in close proximity to the cathode. Figures 5, 6, and 7 show the chromium concentration, pH, and EC along the soil specimen after the electro-kinetic testing is completed. According to Figure 5, the highest effectiveness in removing

chromium was achieved when oxalic acid was utilized as the purging solution. Therefore, it reached around 81.9%, in contrast to the use of tap water with a pH of 2, which is around 78.3% for the sandy soil.

Percentage of removal

The percentage of removal were determined using the provided equation. The elimination efficiency is determined by Equation:

$$\eta\% = \frac{\text{initial chromium conc.} - \text{residual conc.}}{\text{initial chromium conc.}} \quad (1)$$

The using of ox had the highest percentage of removal about 81.9% when used as the purging solution in EX-4. The percent of contaminants removed in the first three trials was 78.3% in EX-1, 62.6% in EX-2, and 51.9% in EX-3. The results of the study of chromium percentage of removal for each experiment are shown in Figure 8.

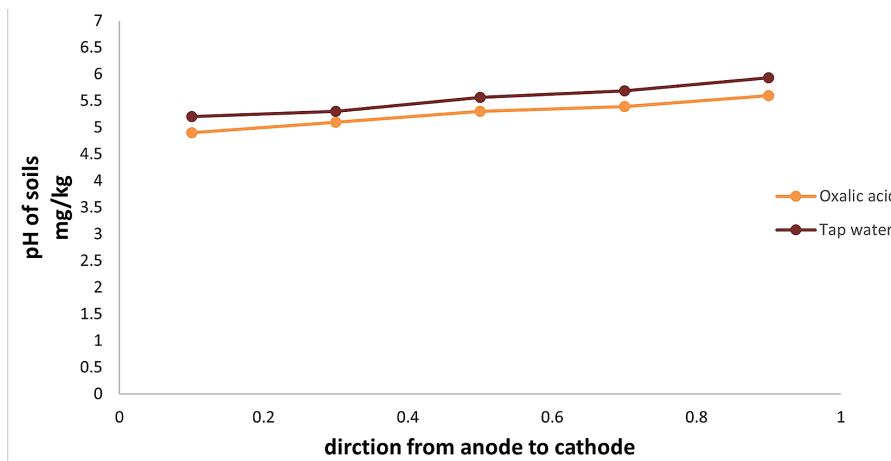


Figure 5. Chromium concentrations (mg/kg) of soil at enhanced condition OX

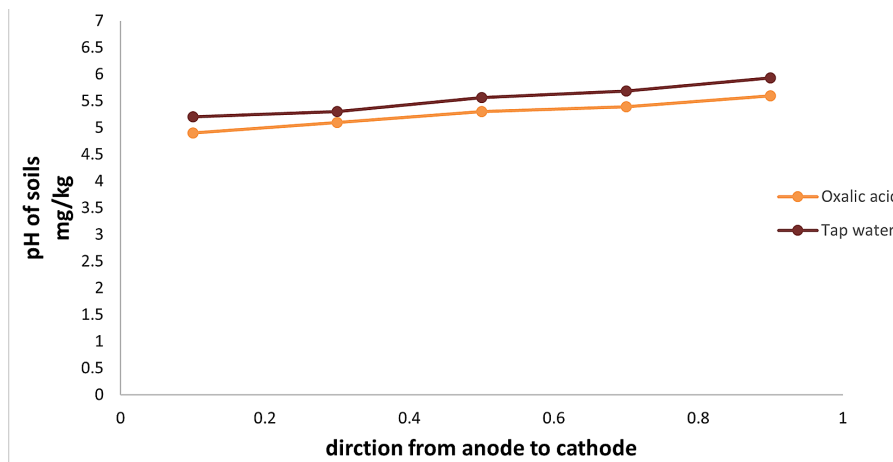


Figure 6. Soil pH versus at enhanced condition OX

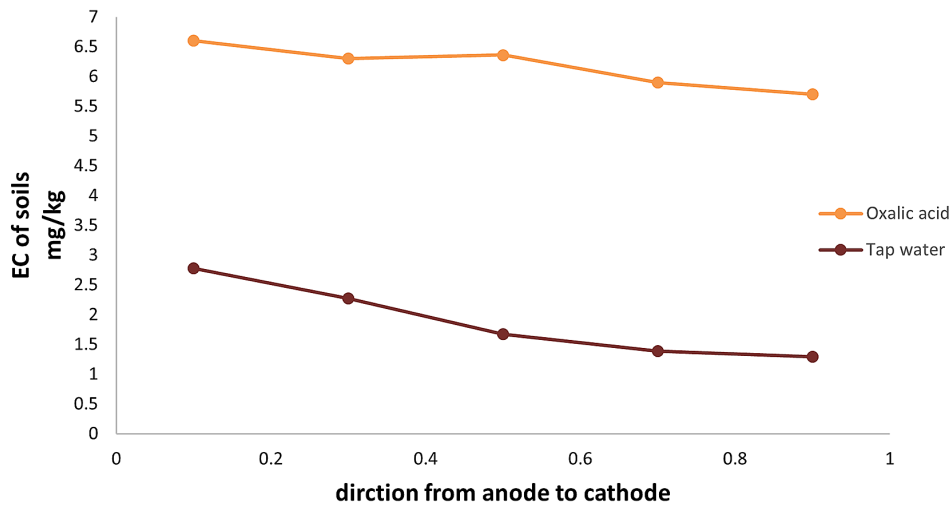


Figure 7. Soil EC versus at enhanced condition OX

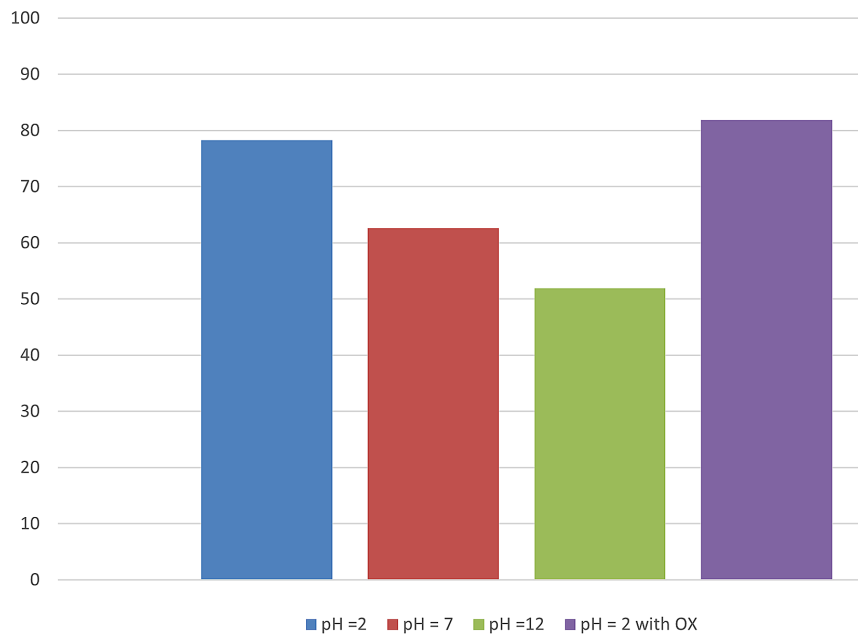


Figure 8. Percentage of chromium removal

CONCLUSIONS

The experiments in this study demonstrated that the presence of enhancing agents (oxalic acid) has a significant Influence on the treatment process. The results showed that the removal efficiency increased in the presence of oxalic acid compared to the other three experiments that were conducted under the same conditions, but with the exception of the presence of the enhancing agent, where the percentage of removal was for the first three experiments 78.3% at pH 2, 62.6% at pH 7, and 51.9 at pH 12, the removal

efficiency for the fourth experiment in the presence of oxalic acid was 81.9% at pH 2 The presence of wheat hulls in the cell as a cheap and available adsorbent material has proven its efficiency in combating reverse osmosis.

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