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Chromium Elimination from Contaminated Soil by Electro-Kinetic Remediation, Using Garlic Peels Powder

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ABSTRACT

In this paper, an electro-kinetic technique was applied to remove chromium from contaminated soil. This technique is appropriate for the soils with low permeability. Various experiments were carried out under different operating conditions, including various purging solutions. Garlic peels powder (GPP) was used in this study as a cheap adsorbent substance to avert the flow of reverse osmosis, which may affect the removal percentage. The results proved that the removal percentage increased as the pH of the purging solutions decreased. The first three experiments were performed with purging solution at pH of 4, 6, and 8 respectively. The highest removal percentages were 53.3% and 49.7%, respectively. This paper showed that the percentage of chromium removal decreased along with the voltage. The removal percentage at 1.5 V/cm was 66.3%, while at 1 V/cm was 61%. Garlic peels powder (GPP) is considered as an effective adsorbent material to avert the reverse osmosis flow. Therefore, the use of this material in this study will give a new impression on the application of these products as an absorbent medium.

Keywords: chromium, soil, electro-kinetic, removal percentage, garlic peels powder

INTRODUCTION

Soil contamination is a serious environmental problem for environmentalists around the world. There are different types of contaminants that threaten soil such as heavy metals and organic pollutants. The existence of heavy metals in the soil is a major concern for human health. Many techniques have been developed for soil purification, based on biological, physicochemical, and thermal techniques (Sharma and Reddy, 2004). Among the different techniques investigated, the electro kinetic technique has been shown as interesting and effective, due to its on-site applicability (Rosestolato et al. 2015, Ferrucci et al. 2017). It has more environmentally friendly nature compared to other techniques (Vocciante et al. 2016). An electro kinetic method has become a promising technology to remediate the soils contaminated with chromium.

Electro-kinetics is a technique that extracts and separates heavy metals from saturated or unsaturated soils. The application of the electro-kinetic method to remove contaminants may vary according to type of the soil and type of the pollutants in the soil (Virkutyte et al. 2002, Reddy and Cameselle 2009). An electro kinetic technique has been developed to overcome the limitations of the on-site treatment methods and fine-grained soil. Electro kinetic remediation is a simple method. Two electrodes are installed in the soil and an electrical current is applied across them, considering one as a cathode and the other as an anode. This electric current generates a path that the ions can travel through. The direction and amount of contaminant movement is affected by the kind and structure of the soil, contaminant concentration, the metal ions movement and the purging solution conductivity (Acar and Alshawabkeh 1993, Ayad et al. 2017).

There are many positive aspects to using this method such as: (1) it needs little equipment, (2) it can be used to eliminate the organic compounds, metals, and mixture of this contaminants, (3) it is safer for a worker and the people near work locations, (4) it needs low electrical power which results in lower total cost, (5) it can be utilized on-situ or ex-situ, (6) it can be applied for soils, groundwater, sediments, and sludge (Tiwari and Ramudu 2007).

Chromium is broadly used in several industries. Therefore, large quantities of waste contaminated with chromium are generated, which contaminate the water, soil, and atmosphere (Bellu et al. 2008, Gallios and Vaclavikova 2008, Kannan and Thambidurai 2008, Ali et al. 2014, Villacis et al. 2015). Commonly, the concentrations of chromium are low when created as a result of usual process, but up to a point, these concentrations are inclined to be in contaminated areas close to the industries that utilize chromium and its compounds (Laith et al. 2021). The soil contaminated with chromium has become a major concern around the world (Duan et al. 2016, Gao and Xia 2011). According to the soil quality standards specified by the World Health Organization, the maximum permissible concentration of chromium in Iraqi soils is 93 mg/kg.

The aim of this paper was to examine: (1) ability of electro-kinetic process to remove chromium from the contaminated soil, (2) influence of changing pH values of purging solutions on removal process (3) influence of changing voltage gradient on removal process (4) ability of using garlic peels powder, as a barrier material joined with electro kinetic system, to avert reverse osmosis flow.

EXPERIMENTAL PROGRAM AND MATERIALS

Soil

In this paper, soil was utilized as a porous medium in all tests. It was taken from an agricultural nursery in the city of Baghdad. The soil was washed, dried and sifted by (2 mm, sieve) to obtain the required uniformity. After that, it was laboratory contaminated with chromium. Table 1 explains the soil properties.

Table 1. Soil properties

Property	Value
Distribution of particle size (ASTM D 422)	
Sand (%)	73
Silt (%)	15.7
Clay (%)	11.3
Atterberg limits (ASTM D 2487)	
Liquid limit (%)	26
Plastic limit (%)	22
Plasticity index (%)	4
Specific gravity	2.289
Electric conductivity EC (µS/cm)	670
Organic content (%)	0.15
Primary pH	8
Porosity (n)	0.39
Soil classification (USDA)	Sandy soil

Chromium contaminant

The soil was mixed with $K_2Cr_2O_7$ solution, to obtain a concentration of chromium of about 300 mg/kg. The required quantity was dissolved in the tap water to obtain the required concentration of chromium. The sample was located in a fume hood with stirred daily until it was completely dry (3–4 days). After that, the soil was mixed with the tap water until the moisture content reached 30%. The sample was placed in the glass bowl with stirring. Finally, a sample was left for one day to reach a state of stability and homogeneity.

Garlic peels powder

Garlic peels were taken from the domestic waste. Then these peels were washed and rinsed with the tap water. After that, they were dried in an electric oven at 40° C and then stored in a dry container. The prepared peels were crushed and ground using a good-washed grinding tool to avert any probability of pollution. The ground materials were sifted to obtain the suitable particle size (Muthamilselvi et al. 2016). The finished garlic peel powder was packed into a perforated plastic bag (6 cm by 8 cm by 10 cm high) and placed in the reactor.

Electro-kinetic Reactor

Figure 1 illustrates a schematic diagram of an electro kinetic reactor utilized in this research. The reactor involves a cell of an electro-kinetic with two electrodes chambers, multi meter, and



Figure 1. Schematic diagram of electro-kinetic reactor

power supply. An electro-kinetic cell was made of Plexiglas and has the inside dimensions of [44 cm (L) x 8 cm (W) x 10 cm (H)]. Soil section length in this reactor was 20 cm. Garlic peels powder was utilized as barrier material in the reactor between a cathode compartment and the soil with length of 4 cm. Every electrode chamber contains the valve to adjust the flow out of the reactor, filter papers, and two graphite electrodes. Barriers of perforated plastic panels have been set up to separate the garlic peels powder chamber from the cathode at the end and the soil on the other end. Panels have dimensions of [10 cm (H) x 8 cm (W)] and holes [6 mm (D)]. The distance between the center of one hole and the center of another hole is one centimeter. Power supply was used for applying constant voltage to the electrodes. The multi-meter was utilized to monitor the voltages and measure the current passing across the soil section through the experiments.

Testing procedure

Various experiments were conducted to examine the effect of changing the pH value of purging solutions and voltages on the removal process percentage. Table 2 shows the operational conditions for the removal process. The purging solution used in all experiments was tap water. In the first experiment {EX-1}, EC of the tap water was 1480 µS/cm and pH was 4. The voltage value was 1.5 V/cm. The soil chromium concentration was (300 mg/kg) and the moisture content was 30%. In the second experiment {EX-2}, EC of the tap water was 1220 µS/cm and pH of 6 used in the electrodes chambers, other operational conditions are the same in the first experiment. In the third experiment {EX-3}, the pH of the tap water was 8 and EC= 970 μ S/cm, with the same other operational conditions in the previous two experiments. In the previous three experiments, the impact of changing the pH value of the purging solution on the removal percentage was studied. In the fourth experiment {EX-4}, the best conditions for the removal process were selected by changing the voltage value to 1 V/cm to study the impact of changing the voltage value on the removal percentage.

Nitric acid was added to the cathode chamber and sodium hydroxide to the anode chamber during experiments to maintain the required pH value of the purging solution at 4, 6, and 8.

After completing each experiment, the treated soil and garlic peels powder were extracted from the reactor. The treated soil was divided into five samples and both samples was weighed and stored for 24 hours in a glass container.

Table 2. Operational conditions

No.	Duration of remediation (days)	Initial concentration of chromium (mg/kg)	Voltage gradients V/cm	pH of purging solution	Goal of exp.
EX-1	5	300	1.5	4	Basis exp.
EX-2	5	300	1.5	6	Influence of pH
EX-3	5	300	1.5	8	Influence of pH
EX-4	5	300	1	4	Influence of voltage gradients

In order to determine the pH and electrical conductivity of each sample, 5 grams of each sample was placed in 12.5 ml of the deonized water. Then, the soil mix was left to settle for an hour after shaking for thirty minutes. Then, the EC and pH of the soil were measured. Table 2 displays the operational conditions of experiments in this study.

Analytical method

A microwave and nitric acid (65%) were used to the digest treated soil samples according to the U.S. EPA method 3051 (USEPA, 2007). The concentration of chromium was determined by an atomic absorption spectrophotometer.

Influence of pH

Figure 2 indicates the residual concentration of chromium in the soil section after remediation process in (EX-1, EX-2, and EX-3). The initial chromium concentration in the contaminated soil prior to the remediation was 300 mg/kg. The concentration of chromium in the soil decreased after remediation, where it ranged between (101-147) mg/kg close to the anode and close to the cathode between (152-190) mg/kg. As the pH value of the purging solution decreased, the chromium concentrations increased near the cathode, as a result of most chromium being absorbed from the soil and migrated towards the cathode. The highest removal percentage was 66.3% at pH equal to 4. The movement of chromium ions during the experiment was from anode to cathode. The quantity of chromium ions transported increased as the pH value of the purging solution decreased, due to the decrease in the cation exchange capacity (CEC) of the soil along with the soil pH. Hence, the tendency of soil particles to adsorb chromium ions decreases. Figure 3 indicates the change in the pH value of the soil section from anode to cathode after the remediation. The formed hydrogen and hydroxyl ions also moved across the soil



Figure 2. Chromium concentrations (mg/kg) versus distance from the anode at different pH values of the purging solutions



Figure 3. Soil pH versus distance from the anode at different pH values of the purging solutions

section in opposite directions. The low pH of the soil indicates that the soil has a specific buffering capacity. Generally, the soil pH values were higher at the cathode and low at the anode. The OH⁻ ions are trapped in the soil near the cathode, while the H⁺ ions can move continuously. It is also known that an increase in the OH⁻ ions leads to an increase in the deposition of heavy metal pollutants; hence, it hinders the transport of pollutants towards the cathode. The acid front progresses higher than the base front progresses due to countering the flow of electro osmotic and the ions of H⁺ have higher ionic migration ability than the ions of OH⁻ (Acar and Alshawabkeh 1993). The experiments conducted in this study proved that the pH has an obvious influence on the migration of chromium in the soil.

Figure 4 indicates the change of EC values along the soil profile. The values of EC were ranged roughly from 2.3 to 3.5 mS/cm nearby the anode to roughly 0.9 to 1.9 mS/cm nearby the cathode. Figure 5 shows that over time there was an increase in the electric current, also the pH value of the purging solution had an effect on the current with a change in the chemical and physical properties, as in the case of melting and chemical precipitation of metals, etc. As the pH of the purging solution decreased, the current began to reach the preferred value due to the high solubility and transmigration of the metal (Hamed and Bhadra, 1997).

In this study, the garlic peels powder was utilized in coupled barrier to avert reverse osmosis flow, which has a counteracting impact on the magnitude and direction of the chromium transportation during the remediation. Garlic peels powder has been proven effective in the process of chromium adsorption from aqueous solution. As a result of the high adsorption capability of the garlic peels powder, a small amount of chromium ions was adsorbed by the garlic peels powder to the competition of salt ions in the soil with chromium ions. The quantity of chromium ions adsorbed by garlic peels powder was around between 18 to 25 mg/kg.



Figure 4. Soil EC versus distance from the anode at different pH values of the purging solutions



Figure 5. Current (mA) versus time (hrs) at different pH values of the purging solutions

Influence of voltage gradient

Figures 6 and 7 illustrate the relationship between the first and fourth experiment under the same conditions (pH of 4, initial chromium concentration of 300 mg/kg), but under different voltages applied, i.e. 1.5 and 1 V/cm, respectively. Figure 6 illustrates the change of residual chromium concentration in soil section after the remediation from the anode to the cathode, while Figure 7 illustrates the change in the soil pH value after the remediation from the anode to the cathode. From figure 6, it is observed that the quantity of migrated chromium ions from the anode to the cathode increases along with voltage gradient, which means an increase in the removal percentage. When a higher voltage was applied, a high current was generated, causing an increase in the level of electrolysis reactions at the cathode and the anode. The electrolysis reactions produce

 OH^{-} and H^{+} at a faster level than the soil allows for transportation (Reddy and Shirani 1997).

The soil pH values ranged from 5.5 at the anode to 7.2 at the cathode. The increase in the pH from anode to cathode was gradual and approximately slight, since the soil has a great buffering capacity (Reddy and Shirani 1997).

Removal percentage

The percentage of chromium removal was calculated for every experiment according to the formula below:

Removal Percentage % =
$$\frac{\text{Initial conc.} - \text{Residual conc.}}{\text{Initial conc.}} \times 100$$

Figure 8 indicates that the best percentage of chromium removal was in the first experiment (66.3%). Other percentages of chromium removal were (53.3%, 49.7%, and 61%) at (EX-2, EX-3, and EX-4), respectively.



Figure 6. Chromium concentrations (mg/kg) versus distance from the anode at different voltage gradient



Figure 7. Soil pH versus distance from anode at different voltage gradient



Figure 8. Removal percentage of chromium (%)

CONCLUSIONS

This paper demonstrated the success of electro-kinetic remediation in removing chromium from the contaminated soil. Different experiments were carried out under various operating conditions. These experiments demonstrated that when the pH of purging solutions increase, the removal percentage decreases. The removal percentages were 66.3% at pH of 4, 53.4% at pH of 6, and 49.7% at pH of 8. It has been observed that an increase in voltage leads to an increase in removal percentage, the removal percentage was 66.3% at 1.5 V/cm and 61% at 1 V/cm. Garlic peels powder was proven to be a good adsorbent to avert the reverse osmosis flow, compared to other commercial absorbents, and the adsorption technique can be considered successful when using garlic peels powder, as well as economical and environmentally friendly.

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