INTRODUCTION

Heavy metals are considered as one of the dangerous polluting elements on the Earth’s surface. They are quite widespread and the treatment for these elements is urgent. Therefore, efforts have been made to treat these polluted places taking into consideration the biological and physical aspects most relevant to the type of pollutants (Oyanader 2004).

Many techniques have been applied to treat polluted places, such as bioremediation, chemicals, and electro kinetic remediation. These techniques can be applied either in in-situ or ex-situ techniques.

The development of electro-kinetic technique to overcome the limits of several in-situ remediation techniques and also to be applied on fine grained soil. Electro kinetics is a modest technique, two electrodes are placed in the soil profile and passing a direct electric current between electrodes making one cathode and the other anode. The electric current passes through the soil profile and creates a path through which the ions can travel. This means that when the pH of the purging solution decreases, the removal efficiency increases. Using AOT as a soil-washing solution increased nickel dissolution and desorption from surface of the soil. Then, the AOT micelles containing nickel easily migrated to the cathode chamber by flow of the electro osmotic; thus, the removal efficiency increased (74.8%). In conclusion, the use of AOT is effective in enhancing nickel removal through the electro kinetic remediation. Bio remedies using banana peels is considered as a successful adsorbent material to avoid the reverse osmosis flow, this will give a new thought for the application these products as adsorption medium.

Keywords: electro-kinetic, nickel, soil, removal efficiency, AOT, BP.
Heavy metals may be present in the soil as interchangeable forms or soluble compounds such as ions. Generally, these metals are immobile due to their combination with various soil fractions and compartments like organic matters, carbonate, residual materials, hydroxide, and oxide (Srivastava et al. 2007).

Nickel in general is homogenously present in soil and typical contents of nickel in soil differ broadly based the parent rock with high levels in the topsoil linked with soil formation processes and anthropogenic pollution mainly ascribed to industrial and agricultural activities. The main concern about the effect of nickel spread in the soil is due to the role of the soil as the final sink for heavy metals and their transmission through the food chain to crops, vegetables and fruits grownup in polluted soils and thus it is consumed by humans or animals (Yahaya Iyaka, 2011). The maximum level of nickel contaminated in the soil of Iraqi according to soil quality standards set by World Health Organization (WHO) is 75 mg/kg.

The characteristics of surfactants including the adsorption into soil, the solubilizing ability, biological compatibility and toxicity are very important considerations. They can enhance desorption of the contaminants from soil, and enhance the biological treatment of organic matter by increasing the biological availability of contaminants. The removal of heavy metals from the soils includes the mechanisms of dissolution, ionic exchange and surfactant-associated complex. In addition to the traditional nonionic and ionic surfactants, vital surfactants, Gemini surfactants are also useful in soil remediation due to their good properties (Mao et al. 2015).

The aims of the current study were to investigate: (1) capability of using electro-kinetic method in removing nickel from contaminated soil, (2) effect of changing pH of the purging solutions (distilled water), (3) effect of using anionic surfactant (AOT, sodium dodecyl sulfo succinate) as enhanced condition in washing soil on the removal efficiency in electro-kinetic remediation (4) application of bio remides such as banana peels as a material of barrier coupled with electro-kinetic system, to prevent the flow of reverse osmosis during the treatment process.

**MATERIALS AND METHODS**

**Soil**

In this study, soil was used as a porous medium in all experiments. It was taken from a plant nursery in Baghdad. The soil samples were washed, then dried and sieved with sieve (2 mm) to obtain acceptable uniformity. This soil was artificially contaminated with nickel. Table 1 illustrates the soil properties.

**Nickel contaminant**

For each experiment, 700 grams of dry soil was taken. Then, 280 ml deionized water were mixed with 1.7342 grams nickel nitrate salt was added to obtain soil with 40% water content and 500 mg/kg nickel concentration in soil. The soil was mixed thoroughly and it was left for 24 hours after mixing to reach a state of stability and homogeneity.

**Banana peels**

Bio remides using banana peels (BP) used in the electro kinetic system to prevent reverse osmosis. Inexpensive material (BP) which broadly exists in Iraq, was taken from the domestic wastes. The banana peels were used to prepare the adsorbent material in form of powder. Firstly, the banana peels were washed by distilled water 4–5 times to removal the impurities existent on its surface. Subsequently, they were left under sunlight for 7 days. After that, (BP) was dried in a furnace at 800°C for (10 hrs.) and dried again at

Table 1. Soil properties

| Property                                         | Value   |
|-------------------------------------------------|---------|
| Distribution of particle size (ASTM D 422)      | 76      |
| Sand (%)                                        | 13.6    |
| Silt (%)                                        | 10.4    |
| Clay (%)                                        |         |
| Atterberg limits (ASTM D 2487)                  | 25      |
| Liquid limit (%)                                | 20      |
| Plastic limit (%)                               | 5       |
| Plasticity index (%)                            |         |
| Specific gravity                                | 2.499   |
| Electric conductivity EC (µS/cm)                | 480     |
| Organic content (%)                             | 0.13    |
| Primary pH                                      | 7       |
| Porosity (n)                                    | 0.41    |
| Soil classification (USDA)                      | Sandy soil |
1000°C for 5 hrs. The resulting matter was cooled at temperature of the room and ground to powder. It was packed in 1.5 mm perforated plastic package of (4 cm by 8 cm by 8 cm high) and inserted in the system.

**sodium dioctyl sulfosuccinate (AOT)**

Sodium dioctyl sulfosuccinate (AOT) is an ion surfactant with a negative charge and Ionizer. This surfactant link to the particles has positive charge such as clay. It dissolves in water and actively in washing of soil. Its molecular formula is \((C_9H_{17}O_2)_{2}CH_2CHSO_3Na\), and molecular weight amounts to 444.57. AOT diffusions in de-ionized water with concentration \((10^{-1}M)\), were mixed by means of a magnetic stirrer (1000 rpm for 3–6 min) at constant temperature (Huiying Cao et al. 2019).

**Reactor Setup**

Figure 1 shows a schematic diagram for an electro-kinetic cell employed in the present study. The electro-kinetic cell made of glass rectangular, two electrodes chamber, two roller graphite electrodes (D: 6 cm, H: 8 cm) located at the ends of the system in electrodes chamber, power supply and a multi-meter. The reactor is a rectangular cube with the internal dimensions \((10 \text{ cm} \times 8 \text{ cm} \times 40 \text{ cm})\). The soil section length was 20 cm. BP was used as a barrier between the cathode compartment and the soil with a length (4 cm). Every electrode compartment has a length of 8 cm and consists of a graphite electrode, filter paper and control valve to control on the flow of solution out from system. Perforated plastic sheets are placed as a barrier to isolate the banana peels from the soil at one end and the cathode at the other end. The dimensions of each plastic sheet were \(10 \text{ cm} \times 8 \text{ cm}\); the sheets had holes \((D: 6 \text{ mm})\) with a distance of 1 cm between one hole and another. The LODESTAR LP3005D power supply was employed to provide the electrodes with a constant DC electric voltage in each test. The multi-meter was used to measure the electric current passing in the soil section during the experiment.

**Experimental process**

The contaminated soil sample was located in diaphanous electro kinetic cell as layers and it is homogenously pressed by a manual compressor. The sample was left in the system (24 hrs.) to reach a state of stability and homogeneity. Before that, the filter papers were located at the start and end of the soil section and the end of the banana peels chamber. The level of the purging solution in the electrode compartments was preserved constant to avoid creating of a hydraulic gradient through the soil sample. In all tests, the electro-kinetic cell was connected to the power supply with a constant DC voltage gradient \((1.5 \text{ VDC/cm})\) to prevent thermal generation.

Many experiments were executed to investigate the effect of the difference in the pH values of purging solutions (distilled water) and the impact of using a anionic surfactant (AOT, sodium dioctyl sulfosuccinate) as enhanced condition on the removal process.

Table 2 shows the conditions of the experiments in the present study. In the first experiment (EX-1), the purging solution was distilled water with pH of 3 and an EC of 1325 µS/cm in both the cathode and anode chamber at voltage gradient of 30V, the nickel concentration in soil amounted to 500 mg/kg, whereas the moisture content equaled 40%. At (EX-2), distilled water with pH of 5 and an EC of 1160 µS/cm was used with the same
other conditions used in the first experiment. The purging solution at (EX-3) was distilled water at pH of 7 and other conditions in (EX-1) were kept. The three experiments were implemented to investigate the effect of the increased pH value on the removal process. At (EX-4), 10⁻¹M AOT solution was mixed with the soil (125 ml per 500g) manually in a polyethylene flask for at least (5 min) for homogeneity. Other conditions in the first experience remained the same.

In order to stabilize the pH values of the purging solution at 3, 5, and 7 in all tests, sodium hydroxide (NaOH) was added to the anode chamber, while nitric acid (HNO₃) was added to the cathode chamber. When the level of purging was decreased due to evaporation, this decrease was compensated by adding a purging solution in to the cathode and anode chamber.

After completing each experiment, (BP) and the treated soil were extracted from the cell. The treated soil was divided to five divisions and weighed every section and kept in a glass flask. For every division, five grams of dry soil were taken and mixed in (12.5 ml) of distilled water. Then, the mix was carefully shaken by hand for several minutes and left for one hour afterwards to precipitate the solids, then measure the pH and EC of the soil (Hansen et al. 2007).

Table 2. Experiments conditions

| EX NO. | Duration of remediation (days) | Initial concentration of nickel (mg/kg) | Types of purging solution | pH of purging solution | Objective of Exp. |
|--------|-------------------------------|----------------------------------------|---------------------------|------------------------|-------------------|
| EX-1   | 5                             | 500                                    | Distilled water           | 3                      | Baseline Exp.     |
| EX-2   | 5                             | 500                                    | Distilled water           | 5                      | Effect of pH      |
| EX-3   | 5                             | 500                                    | Distilled water           | 7                      | Effect of pH      |
| EX-4   | 5                             | 500                                    | Distilled water           | 3                      | Effect of enhanced surfactant (AOT) |

Digestion of the soil sample

Approximately (1 gr) of every division of the treated soil was located into digestion tube (250 ml), then (10 ml) nitric acid was added. The mix was heated in a hot sandy bath at 95 °C and for 40 minutes. After that, the temperature was increased to 150 °C. The mixture left boiling at least of 8 hours until a clear solution was achieved. 5 ml of nitric acid was added to the solution at least four times and digestion process completed after reducing the volume to about 1 ml. The inside walls of the tube were washed with distilled water. After the solution had cooled, 5 ml of (1% HNO₃) was added to it. The solution was filtered by filter papers (What man No. 42). The filtered solution is placed in a 25ml volume container with the addition of distilled water (Zeng, 2014). The nickel concentrations in the filtered solution were measured by an atomic absorption spectrophotometer (AAS).

RESULTS AND DISCUSSION

Effect of pH

Figure 2 shows the residual concentration of nickel in each section of the treated soil in the experiments (EX-1, EX-2 and EX-3). The concentration of nickel in the contaminated soil prior to the treatment process was 500 mg/kg. The nickel concentration after process was decreased and modified from (174–242) mg/kg close anode to (255–338) mg/kg close the cathode. With decreasing pH of the purging solution, the nickel concentrations were increased near the cathode, because most of the nickel has been absorbed from the soil and migrated towards the cathode. The maximum removal efficiency was 64.37% at pH of 3. The migration of nickel ions occurred from anode to cathode, and the quantity of the migrated nickel ions increased as the pH of the solution decreased, because the cation exchange capacity (CEC) of the soil also decreases along with the pH of the soil. Then, the tendency to adsorb nickel ions onto the soil particles also increases. Figure 3 shows the pH variation in the soil section from anode to cathode during the remediation process. The created hydrogen and hydroxyl ions migrated through the soil section in an opposite direction. The low pH of the soil indicates that the soil has a certain buffering capacity. In general, the soil pH values were low near the anode. The OH⁻ ions are restricted in the soil near the cathode.
while the H+ ions can continuously migrated. The increase in OH- has been known to cause precipitation of the metal contaminants, inhibit migrate of contaminants toward cathode electrode. The advance of the acid front base front is faster than the advance of base front because the OH- ions have lower ionic kinetics values than the H+ ions (Acar and Alshawabkeh, 1993).

Figure 4 shows the EC variance along the sample for the same experiments. The values of EC ranged from (2.65 to 3.33) µS/cm near the anode and from (1.1 to 1.9) µS/cm near the cathode. From Figure 5 it can be seen that when the experiments started, over time there was an increase in the current, and also the pH of purging solutions affected the current with a difference in the physiochemical properties, as in metals melting chemical dissolution/precipitation, etc. When the pH of purging solution began to decrease, the current reached preferable value because of the high solubility of metals and their transmigration (Hamed and Bhadra, 1997).

Because of the good adsorption capability of (BP), there is a lot of adsorbed nickel ions by (BP) due to the efficacy of salt ions in the soil with nickel ions. Finally, nickel ions adsorbed by (BP) were ranged of (24 to 42) mg/kg at (EX-3, EX-2 and EX-1) and 52 mg/kg at (EX-4).

**Effect of Surfactant Enhanced (AOT)**

At the EX-4, the soil sample was washed by using (10−1 M) AOT solution. The other conditions are the same as those used in the first experiment. It seems that the pH along the sample increased from (3.7) close the anode to (4.85) close the cathode after 5 days of treatment, as displayed in figure 6. Most of nickel disintegration and desorption from the soil happened after 5 days. Figure 7 shows a comparison of the concentration of nickel residue along the soil section without and with AOT.

**Removal Efficiency of Nickel**

The removal efficiency was calculated for each experiment according to the equation below:

\[
\text{Removal Efficiency } \% = \frac{\text{Initial conc} - \text{Residual conc}}{\text{Initial conc}} \times 100
\]

Figure 8 shows that the best removal efficiency was obtained in the fourth experiment (74.8%) when AOT was used as enhanced surfactant. Other removal efficiencies were (65.2%, 58.8% and 51.6%) at (EX-1, EX-2 and EX-3), respectively.
CONCLUSIONS

The present study showed that the electro kinetic remediation is successful in the removal of the metals (nickel) from the contaminated soil. Different experiments were conducted with varying degrees of results. The study showed that when the pH values of the purging solutions decrease, the removal efficiency increases. The nickel ion tendency for adsorption by soil particles decreases along with the pH value of the purging solution; the removal efficiency were (65.2%) at pH of 3, (58.8%) at pH of 5 and (51.6%) at pH of 7. It was also observed that the removal efficiency was greater than 65.2% when (AOT) was used as surfactant enhanced in the soil (74.8%). Therefore, the use of (AOT) in this study increased the removal efficiency. The banana peels (BP) is a good material to be used as a medium adsorbent to avoid reverse electro-osmosis flow, compared with other commercial adsorbent materials, and the adsorption technique by (BP) can be considered more beneficial, economic and environmentally friendly process.

Acknowledgment

The authors are grateful to Al-Mustansiriya University and the laboratories of the Environmental Engineering Department in the College of Engineering. We also send our regards to the editorial board in Journal of Ecological Engineering.

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