Adsorption of copper and zinc by oil shale

Sameer Al-Asheh · Fawzi Banat

Abstract Oil shale is able to remove appreciable amounts of copper and zinc ions from aqueous solutions. It was noted that an increase in the adsorbent concentration with constant copper or zinc concentration resulted in greater metal removal from solution. An increase in the copper or zinc concentration with a constant sorbent concentration resulted in higher metal loading per unit weight of sorbent. For both metals, copper and zinc, equilibrium was attained after 24-h contact time. Increase in the initial pH or temperature of the metal solution resulted in an increase in the metal uptake per unit weight of the sorbent. Freundlich isotherm model was found to be applicable for the experimental data of Cu^{2+} and Zn^{2+}. The results showed that oil shale could be used for the adsorption of the Cu^{2+} and Zn^{2+} with higher affinity toward Zn^{2+} ions. Addition of sodium salt to the metal solution influenced copper removal positively, but inhibited zinc removal.

Keywords Adsorption · Copper · Oil shale · Zinc

Introduction

Pollution of water with toxic heavy metals is considered dangerous because of the potential toxic effects on aquatic life as well as to animal and plant life and humans. Industrial waste containing heavy metals is one of the major sources of water pollution. Metal processing, finishing, and plating industries are obvious sources of metal wastes (Dean and others 1977). Thus, it is recognized that finding methods for removal of heavy metals from these wastes is of great importance. These metals must be decreased to a level accepted by environmental regulations for different types of waters.

Copper and zinc are among the most toxic metals affecting the environment. Many studies have shown that these metals are toxic even at very low concentrations. However, these metals have many applications in the industry. For example, copper is known as an excellent conductor of electricity, widely used in the electrical industry in all gauges of wires for circuitry. Copper is also utilized in analytical reagents, in paints for ship keels and in electroplating. Copper acts as an irritant to the skin causing itching and dermatitis, and may cause keratinization of the hands and soles of the feet (Sitting 1981).

There are several methods to remove heavy metals from aqueous solutions, such as precipitation, ion exchange, evaporation, reverse osmosis, electrolysis and others. Adsorption and ion exchange are the most well known. The use of adsorbents, e.g. activated carbon and ion exchange resins, to remove trace metals from aqueous systems has been widely investigated (Huang and Ostovic 1978; Sengupta and Paul 1985; Maliou and others 1992). High capital and regeneration costs of activated carbon and ion exchange resins (Singh and others 1993), however, have encouraged researchers to look for other types of adsorbents that are less expensive. Carbonaceous materials developed from waste slurry generated in fertilizer plants were used for the removal of Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} from their aqueous solutions (Srivastava and others 1989). Tan and others (1985) considered the uptake of metal ions by chemically treated human hair. Jha and others (1989) investigated the use of chitosan. Rice-husk ash was found to be a good adsorbent for Hg^{2+} in aqueous solutions (Tiwari and others 1995). For the last 20 years, considerable research has involved materials of biological origin and many forms of biomass have been shown to be effective for the removal of heavy metals (Volesky and others 1987; Crist and others 1990; Avery and Tobin 1993). These materials are known as biosorbents. The uptake of metals by these materials is generally attributed to their constituents of proteins, carbohydrates and lignin, which contain functional groups, such as carboxyl, hydroxyl and amine groups that are primarily responsible for metal sorption (Kuyucak and Volesky 1988). Recently, researchers have also looked for sorbents from agricultural and forestry sources. For example, Lee and Low (1989) used moss for the removal of copper

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ions from solution. Al-Asheh and Duvnjak (1996) used canola meal as agricultural sorbent to remove various heavy metal ions from their aqueous solutions. Lee and others (1997) used crab shell for the removal of lead from aqueous solution.

Oil shale is a sedimentary rock containing solid and combustible organic matter (kerogen and bitumen) in a mineral matrix. It consists of sapropelic and humic types of organic matter. Most true oil shale contains 10 to 50% algal organic matters (sapropelic). Oil shale represent a significant source of fossil energy, however, its availability and its low cost make it a good candidate as an adsorbent for heavy metals.

This study was therefore undertaken to evaluate the possible use of locally available oil shale in the removal of Cu^{2+} and Zn^{2+} from aqueous solutions. The effect of different operating parameters, such as concentration of heavy metals, sorbent concentration, and initial pH on the uptake of heavy metals by this adsorbent was reviewed. Copper and nickel were selected as model components of toxic metals for this study.

Materials and methods

Adsorbent

Jordanian oil shale was used in this work. The shale utilized was in the form of solid rock. The oil shale was washed, ground and underwent screening analysis into different sizes before being used in the adsorption processes.

Batch sorption experiment

A certain amount of adsorbent was transferred into bottles containing 10 ml of Cu^{2+} or Zn^{2+} solution (in the form of $CuSO_4 \times 5H_2O$ or $ZnSO_4 \times H_2O$, respectively) to make the final sorbent concentration 4 mg/ml. Metal concentrations were in the range 10–100 ppm. A shaker (Kottermann, Germany) was used to agitate the mixture. Samples were taken at certain intervals for the purpose of studying the dynamics of the sorption process. Otherwise, equilibrium was allowed to occur and then the bottles were removed from the shaker for analysis. The sorbent was separated from the samples by centrifugation ($3,000 \times g$, 10 min) and the upper layer was analyzed for the metal under consideration using atomic absorption spectrophotometer (spectro AA10).

Neither precipitate nor metal ions adsorbed to the wall of the bottle with the tested metals under the experimental conditions. Each experiment was carried out in duplicate and the average results are presented in this work.

Results and discussion

Tests in this study showed that the oil shale was able to adsorb Cu^{2+} and Zn^{2+} from their aqueous solutions.

The results indicated that 97% of Cu^{2+} or Zn^{2+} was removed from their solutions when their initial concentrations were 100 and 60 ppm, respectively, and the sorbent concentration was 4 mg/ml.

The effect of adsorbent concentration on the sorption of copper and nickel was investigated. Different amounts of Cu^{2+} ions or Zn^{2+} ions were removed from their solutions by the sorbent depending on the sorbent concentration (Fig. 1). Figure 1 shows that the total metal removed from the solution was higher when the amount of adsorbent was increased. This trend is expected because, as the sorbent concentration increases, the number of sorbent particles surrounding the metal ions increases, or the ratio of sorbent particles to metal ions increases as these particles attach more metal ions to their surfaces.

To examine the effect of the initial metal concentration on uptake, which would give an indication of the sorption capacity of the shale, the sorbent was tested in Cu^{2+} or Zn^{2+} solutions with concentrations between 10 and 100 ppm. The results presented in Fig. 2A, B showed that an increase in the initial metal concentration resulted in an increase in the adsorption of Cu^{2+} or Zn^{2+}. This trend can be attributed to the progressive increase in electrostatic interactions, relative to covalent interactions, of the sites with lower affinity for Cu^{2+} or Zn^{2+} with an increase in the initial Cu^{2+} or Zn^{2+} concentrations (Van Cutsem and others 1984). Similar results for this increase in metal uptake with the increase in the initial metal concentration have been obtained using moss, *Hardwicia binata* bark and tea leaves for the sorption of Cu^{2+} (Al-Asheh and Duvnjak 1997), Hg^{2+} (Deshkar and others 1990) and Pb^{2+} (Singh and others 1993), respectively.

The results of Fig. 2 also show that the adsorption process is relatively rapid and equilibrium is almost attained after 24-h contact time, indicating that adsorption is pri-
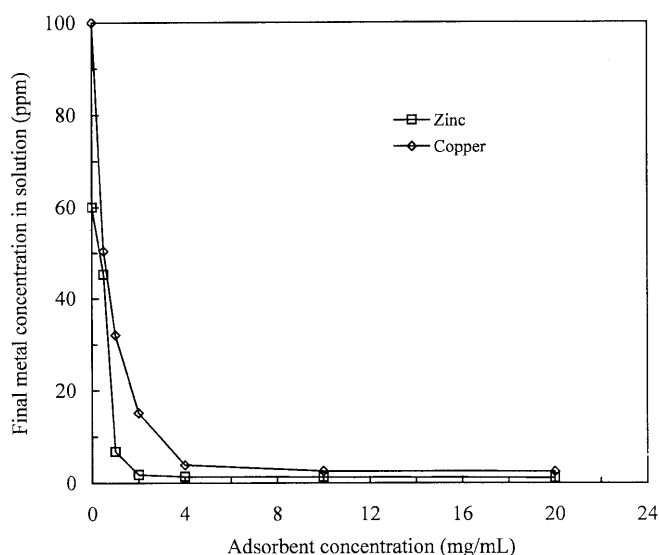

Fig. 1
Effect of oil shale concentration on the removal of copper and zinc ions. Initial Cu^{2+} concentration: 100 ppm; initial Zn^{2+} concentration: 60 ppm
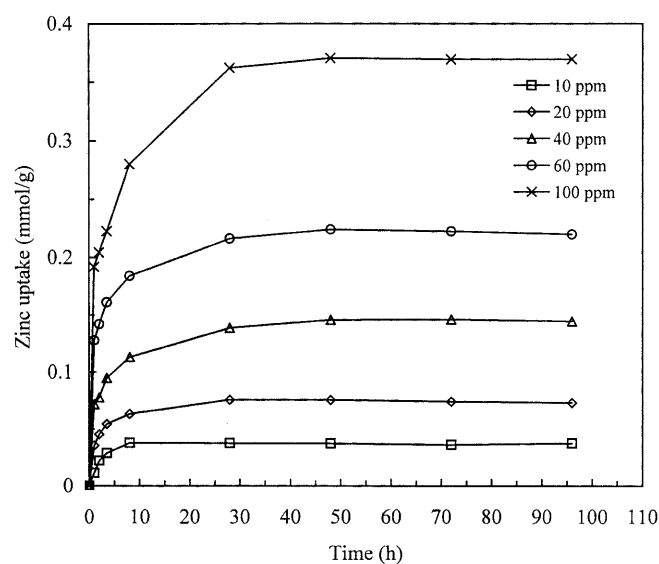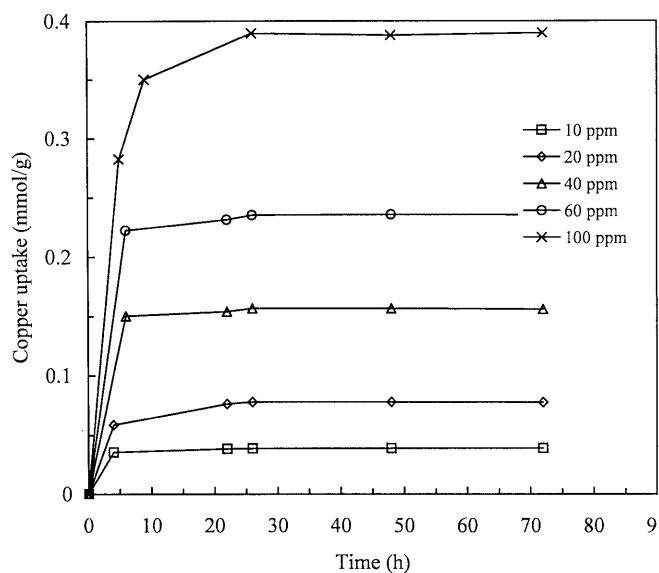
Fig. 2
A Effect of copper and **B** zinc concentrations on their uptakes by oil shale. Oil shale concentration: 4 mg/ml

Fig. 3
Relationship between equilibrium copper concentration and its uptake at various pH values using 4 mg/ml oil shale concentration. *Symbols* are experimental and *lines* are predicted data using the Freundlich model

marily occurring at the surface of the oil shale, i.e. physical adsorption. Plotting the results of Fig. 2 against the square root of the adsorption time (data not shown) demonstrates this conclusion. Straight lines represented most of these data, but these data did not intersect the origin. Therefore, intrapore diffusion could not be the controlling step, but it was involved in the adsorption process (Weber and Morris 1963).

The influence of initial pH of the solution on the uptake of Cu^{2+} by oil shale was also studied. Copper solutions at pH levels of 2, 4, 4.5 and 5 were prepared in concentrations between 10 and 100 ppm. Oil shale was added to these solutions to make the concentration 4 mg/ml, and adsorption was followed until equilibrium. The results (Fig. 3) showed that the increase in the initial pH of the
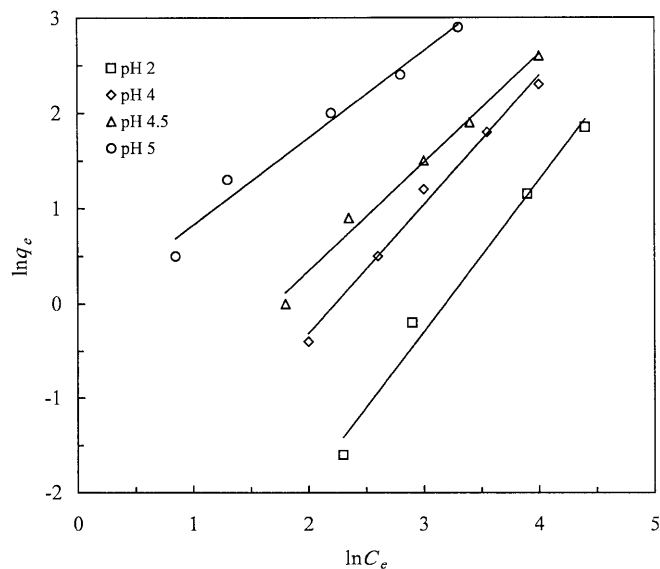
solution resulted in an increase of Cu^{2+} uptake by the oil shale.

Other researchers have also observed a pH trend in the biosorption process. For example, Ferro-Garcia and others (1988) investigated the uptake of Zn^{2+}, Cd^{2+} and Cu^{2+} by activated carbon obtained from agricultural by-products. This study obtained low metal uptake at low pH levels, whereas uptake was increased significantly at high pH levels (pH 5). The authors attributed their results to the change of the charge of the carbon surface with the change in pH. The electrostatic repulsion between cations and the positively charged surface of activated carbon took place at low pH values, whereas an increase in pH resulted in metal ions replacing hydrogen ions from the carbon and adsorption was increased. A similar explanation can be applied to the adsorption of Cu^{2+} by the oil shale, especially if an ion-exchange mechanism is involved in this sorption process.

The results of Fig. 3 were found to be well represented by the linearized Freundlich isotherm model:

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e$$

where q_e is the amount of the adsorbed metal ions per unit weight of sorbent (mmol/g) at the final equilibrium metal concentration, C_e (mmol/l), k is a Freundlich's constant related to the sorption capacity, and $1/n$ is the other Freundlich's constant related to the sorption intensity of a sorbent. The values of k and $1/n$ were evaluated from the intercept and the slope, respectively, of the linear plot of experimental data of $\ln q_e$ versus $\ln C_e$. These constants at various pH values are displayed in Table 1 for Cu^{2+}. The numerical values in Table 1 indicate that

Table 1
Freundlich's constants for the sorption of Cu^{2+} by oil shale

pH	k	1/n	R^2
2	0.0062	1.593	0.984
4	0.0486	1.354	0.990
4.5	0.1445	1.138	0.989
5.0	0.9136	0.914	0.975

sorption capacity of oil shale increases with an increase in pH values. Application of the Freundlich model to the equilibrium data of Cu^{2+} indicates the monolayer coverage of oil shale by the ions of Cu^{2+}, but this was to nondistinct or multiple sites of adsorption, unlike the Langmuir model that has distinct localized adsorption sites (Masel 1996).

To investigate the effect of temperature on the uptake of Cu^{2+} and Zn^{2+} by oil shale, the process was carried out using initial metal concentrations between 10 and 100 ppm at 25, 35 and 45 °C. The procedures were performed for 24 h to assure equilibrium. The results show (Fig. 4) that Cu^{2+} and Zn^{2+} uptake decreased with temperature, which indicates that the process is exothermic. The Freundlich isotherm model (Fig. 4) also represented these results. The Freundlich model gives a reasonable representation of these experimental data.

The particle size of oil shale would also influence the adsorption process significantly because adsorption is a surface phenomenon. Figure 5 shows that adsorption with smaller particles is higher than with larger particles. As the particle size decreases, the surface area per unit weight increases, and so does adsorption capacity of the adsorbent. The same trend is noted for Cu^{2+} and Zn^{2+} adsorption (Fig. 5A, B). The data of Fig. 5 were also well represented by the Freundlich isotherm model.

Soft and hard ions are among the complexing agents that interfere with the sorption of heavy metals by different types of adsorbents. Mozzarelli and Tubertini (1969) showed that K^+, Na^+, and Mg^{2+} did not interfere with the removal of many metal ions from their solutions using chitin. The results of Jha and others (1989) indicated that, in the presence of 100 ppm of Ca^{2+} ions and 5 ppm of Cd^{2+} ions, the initial rate of Cd^{2+} removal by chitosan decreased.

The effect of Na^+ concentration on the removal of Cu^{2+} or Zn^{2+} from aqueous solutions using oil shale was also considered in this study. Sodium ions influence the Cu^{2+} removal positively regardless of the initial concentration of Na^+ under the experimental conditions (Fig. 6). Lower NaCl concentrations, up to 0.1 M, resulted in more Cu^{2+} removal than at higher Na^+ concentrations. However, the results showed (Fig. 6) that Na^+ has a negative influence on the removal of Zn^{2+} from solution. The amount of Zn^{2+} removal decreased with an increase in the initial Na^+ concentration. The latter is consistent with the results of Deshkar and others (1990), who reported a negative effect of soft and hard ions on the
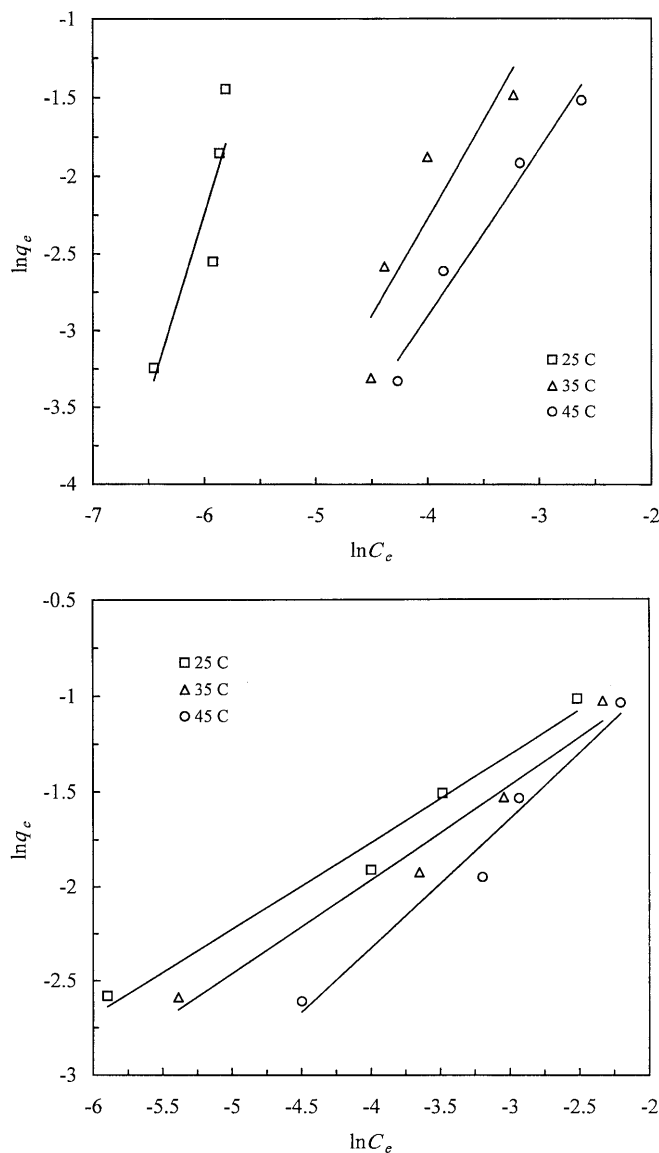

Fig. 4
Relationship between equilibrium A Cu^{2+} and B Zn^{2+} concentrations and their uptakes at various temperatures using 4 mg/ml of oil shale concentration. *Symbols* are experimental and *lines* are predicted data using the Freundlich model

sorption of Hg^{2+} by *Hardwickia binata* bark when their concentrations were raised from 40 to 200 ppm. However, there are also data that show an increase in Hg^{2+} sorption by activated carbon with an increase of Ca^{2+} concentration (Thiem and others 1976).

Conclusions

Oil shale can be used as a sorbent for Cu^{2+} and Zn^{2+} ions. The uptake of Cu^{2+} by oil shale was higher than that of Zn^{2+}. Up to 97% of the initial Cu^{2+} or Zn^{2+} concentrations were removed when their initial concen-

Fig. 6
Effect of Na$^+$ concentration on the uptake of Cu^{2+} and Zn^{2+} using 4 mg/ml of oil shale concentration. Initial metal concentration: 100 ppm
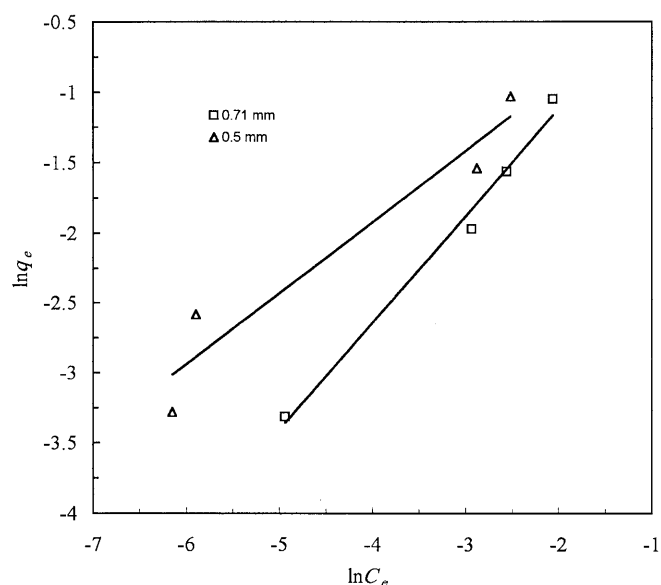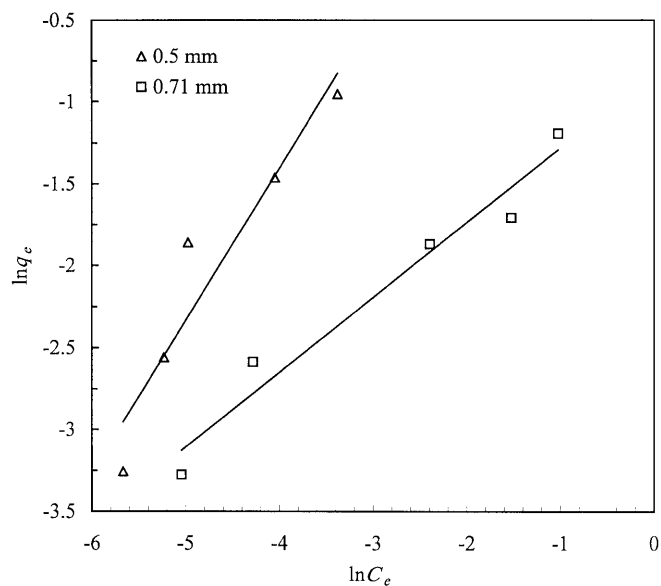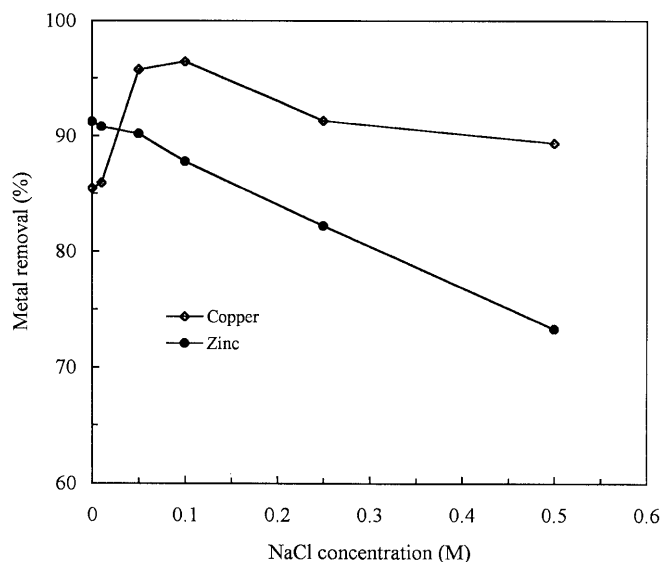

Fig. 5
Effect of particle size of oil shale on the uptake of A Cu^{2+} and B Zn^{2+} using 4 mg/ml of oil shale concentration. *Symbols* are experimental and *lines* are predicted data using the Freundlich model

trations were 100 and 60 ppm, respectively. An increase in the oil shale concentration in the suspension resulted in an increase of metal removal from the solution. An increase in the metal concentration or an increase in the initial pH of the metal solution, or a decrease in the temperature of the suspension, resulted in an increase of copper and zinc adsorption. The Freundlich isotherm model fits the copper and zinc experimental data reasonably well. Smaller particles of oil shale showed higher uptake of Cu^{2+} and Zn^{2+} than that of bigger particles. The addition of Na$^+$ to the sorbent-Cu^{2+} suspension resulted in more metal removal compared with that when Na$^+$ ions are added to the sorbent-Zn^{2+} suspension.

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