Cobalt and zinc removal from aqueous solution by chemically treated bentonite

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Abstract Natural bentonite was treated by hydrochloric, nitric, and phosphoric acids followed by washing with sodium hydroxide in order to enhance its adsorption capacity. The sample that treated with hydrochloric acid followed by further treatment with NaOH showed the highest cation exchange capacity with a value of 51.20 meq/100 g. The zero-point of charge for this sample was found to be 4.50. Adsorption isotherms for both cobalt and zinc were fitted using Langmuir, Freundlich, and Redlich-Peterson and showed an adsorption capacity of 138.1 mg Co^{2+} and 202.6 mg Zn^{2+} per gram of treated sample.

Keywords Cobalt · Zinc · Heavy metals · Pollution · Adsorption · Bentonite · Treatment

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1 Introduction

Removal of heavy metals from aqueous solutions can be achieved by different technological methods. These methods include chemical precipitation, ion exchange, membrane filtration, electro-deposition, and flotation. Some of these methods have disadvantages and limitations. Precipitation, for example produces large amounts of sludge in solutions (Jandova et al. 2002) but membrane filtration, ion exchange, electro-deposition, and filtration are costly (Noble 1995; Sengupta 1997; Konishi et al. 1996; Bhattacharyya et al. 1998) Alternatively, adsorption can remove these metals efficiently at low cost (Al-Omari 2003; Ho and McKay 2000; Mavrov et al. 2003; Oren and Kaya 2006; Rashed 2001). Several solid materials can be employed as adsorbents. Activated carbon is considered an effective adsorbent because of its extensive porosity and large available surface area (Shawabkeh et al. 2002; Chen et al. 1997). However, the use of activated carbon as an adsorbent material for waste remediation in developing countries is a cost-challenging technique.

Several attempts have been made to substitute activated carbon by utilizing other adsorbents that have high sorption capacity with low cost. Accordingly, many researchers have tried to exploit naturally occurring materials for removal of heavy metals. Alvarez-Ayuso and Garcia-Sanchez (2003) utilized natural and Na-exchanged bentonite for removal of Cr^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, and Cd^{2+} from wastewaters of galvanic industries. Sheta et al. (2003) utilized natural zeolite and bentonite for studying the sorption characteristics of zinc and iron ions from solution. Al-Degs et al. (2000) employed diatomite and manganese oxide modified-diatomite for remediation of lead, copper, and cadmium ions from water. Khan et al. (1995) utilized bentonite for removal of Cr^{2+} and Ag^+ from aqueous

solution. Lin and Juang (2002) removed copper and zinc from aqueous solutions by sorption on surfactant-modified montmorillonate. Manning and Goldberg (1997) studied the stability of Arsenic at the clay mineral-water interface. Barbier et al. (2000) showed that Pb^{2+} and Cd^{2+} could be eliminated from aqueous solution efficiently by montmorillonate. However when most of these naturally occurring materials were used no further treatment followed.

Jordan has large reserves of bentonite, estimated at 200 million tons. On the other hand, Jordan has limited water resources and as a result there is a need to recycle wastewater for agricultural and outdoor. In our research bentonite was treated and tested as an adsorbent for removal of Co^{2+} and Zn^{2+} from aqueous solutions.

2 Experimental

Natural bentonite was collected from Tafila County, Jordan. The rocks were crushed, grinded, screened to different particle sizes, and stored in closed containers for further use. Treatment was made on the sample that passed 63 μm. Sample of 100 g was soaked with 500 ml of different oxidizing acid solutions (5 M) for 24 h at room temperature (22 ± 1°C). The acids used were HNO_3, H_3PO_4, and HCl. The soaked bentonite was washed several times with deionized water to remove the excess acid until the pH of the solution was 6. Part of each soaked solids was further treated with 500 ml portions of 5 M NaOH for 24 hours at room temperature (22 ± 1°C). All the treated bentonite samples were then filtered, dried at 105°C and stored for analysis.

Cation exchange capacity (CEC) was measured on all treated bentonite. The procedure was carried out by mixing 4.0 g of treated bentonite with 100 ml of 0.1 M CH_3CO-ONa, followed by washing with isopropyl alcohol and ammonium acetate solutions (100 ml, 0.1 M) to desorb the sodium back into the solution (Kahr and Madsen 1995). The concentration of the sodium ions was then analyzed using Shimadzu AA-6200 Atomic Absorption Spectrophotometer.

The Zero Point of Charge (ZPC) for the bentonite was obtained by mixing a fixed mass of each treated sample with 0.1 M KNO_3 solution. The initial pH values were adjusted to a range from 2 to 12 by adding few drops of either HNO_3 or NaOH solution then left in an isothermal shaker (22 ± 1°C) for 24 h to equilibrate. The final pH values were measured and compared with the initial ones (Appel et al. 2003).

The surface functional groups of the treated samples were analyzed by Fourier Transform Infrared spectrophotometer (FT-IR) using Shimadzu FTIR-8400S. Sample of 3.0 mg was mixed thoroughly with 1.0 g of fine dried powder of KBr. The resulting mixture was hydraulically pressed at 10^4 kg/m² to obtain a thin, transparent disk. The thin disk was placed in an oven at 105°C for 4 h to prevent any interference of any existing water vapor or carbon dioxide molecules.

Adsorption isotherms for Co and Zn were conducted by mixing 0.1 g of the treated bentonite with 50 ml of different initial concentrations (25–200 mg/l) of each metal ion of interest. The solution was placed in an isothermal shaker (22 ± 1°C) for 24 h. The pH was adjusted to 6 by addition few drops of either HNO_3 or NaOH solutions. After equilibration the final concentration of each metal ion was measured using Schimadzu AA-6200 Atomic Absorption Spectrophotometer.

All chemicals were Aldrich reagent grade and all the glassware was Pyrex, washed several times with HNO_3, soap and deionized water to remove any adherent impurities on their surfaces.

3 Theory

The interaction between the solute and the surface of adsorbent can be expressed as a second order reversible reaction according to Chu and Hashim (2003)

$$S + X \underset{k_b}{\overset{k_f}{\longleftrightarrow}} S \cdot X$$
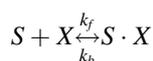
where S refers to the solute in solution, X is the active site of the adsorbent and $S \cdot X$ is the adsorbed solute on the surface. Several theoretical models were applied to predict the behavior of the experimental data. These models include Langmuir, Freundlich, and Redlich-Petersons.

Langmuir assumes that the solute fills a one-monolayer coverage on the adsorbent surface according (Langmuir 1916):

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$

where C_e (mg/l) and q_e (mg/g) refer to the equilibrium concentrations of adsorbate in liquid and solid phase respectively. q_m (mg/g) is the number of grams of adsorbate per gram of adsorbent in forming a complete monolayer on the surface, b (l/mg) is a constant related to the affinity of binding sites according:

$$b \propto e^{-\Delta H / RT}$$

Van Bemmelen (Freundlich) correlation is used to incorporate the effect of heterogeneous surface energies as (Freundlich 1906):

Table 1 Chemical composition of Jordanian bentonite

Component	wt.%
SiO_2	44.72
CaO	10.85
MgO	1.66
Fe_2O_3	4.20
Al_2O_3	17.11
TiO_2	0.57
Na_2O	2.83
K_2O	2.30

$$q_e = K_f C_e^{1/n}$$

where K_f (mg/l) is constant that is related to the enthalpy of adsorption according

$$K_f \propto RTnbe^{\Delta H/RT}$$

where n and R are constants and T is the temperature of the solution.

Unlikely Freundlich and Langmuir models, Redlich-Peterson's incorporated the features of both models to combine the heterogeneous surface for each monolayer, which can be described as (Chiou and Li 2002):

$$q_e = \frac{aC_e}{1 + bC_e^n}$$

where a, b, and n are constants.

4 Results and discussion

Bentonite is considered one of the most promising candidate materials that can be used as adsorbent for remediation of different metal ions and radioactive isotopes from wastewater. The chemical composition of this clay material contains 44.72% silica, 17.11% alumina, and 4.20% iron oxide, which represent the major part of the metal oxide (Table 1). The analysis of bentonite by XRD (Fig. 1) showed that it belongs to the smectite family, which is characterized by its expandable properties. It is rich in other minerals such as feldspar and mica, which are indicated by the peaks 17, 32, and 10°, respectively. Kaolinite shows symmetric peaks at 14 and 28°. Also some associate constituents such as quartz were found in the sample.

In order to evaluate the feasibility of this mineral for wastewater remediation, several chemical treatments were made in order to enhance its removal capacity. These treatments involved mixing the bentonite with different acids and analyzed for their CEC values. It was found that the sample treated with hydrochloric acid followed by soaking with NaOH solutions showed the highest CEC of 51.20 meq/100 g (Fig. 2). The sample that was treated with phosphoric acid and followed by washing with water had the lowest CEC value. This could be attributed to the fact that hydrochloric acid is stronger than phosphoric acid ($pK_1 = 2.15$). Moreover, hydrochloric acid could attack the alkali and alkali earth oxides in the sample more severely than could phosphoric acid. This leads to opening more macro and micro pores in this material. Hence, more surfaces become available for adsorption and ion exchange. On the other hand, further treatment with sodium hydroxide could help building a new skeletal structure between silica and alumina leading to formation of new zeolite material. This was clearly appeared in the CEC values for these treated samples.

A FT-IR spectroscopic study for the treated bentonite is shown in Fig. 3. As can be seen there are absorption bands in the range of 3,400–3,650 cm^{-1}, 900–1,100 cm^{-1}, 500–
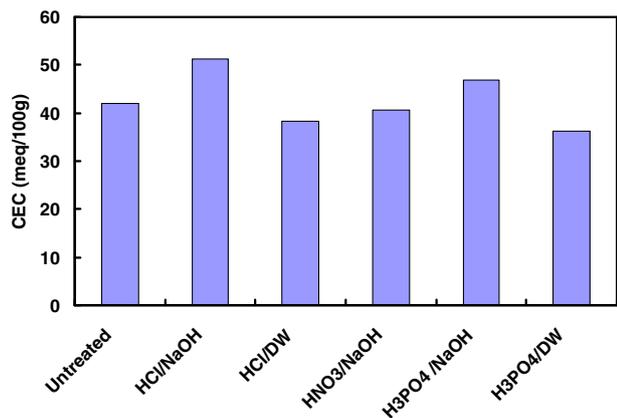
Fig. 1 X-Ray diffractogram of bentonite sample
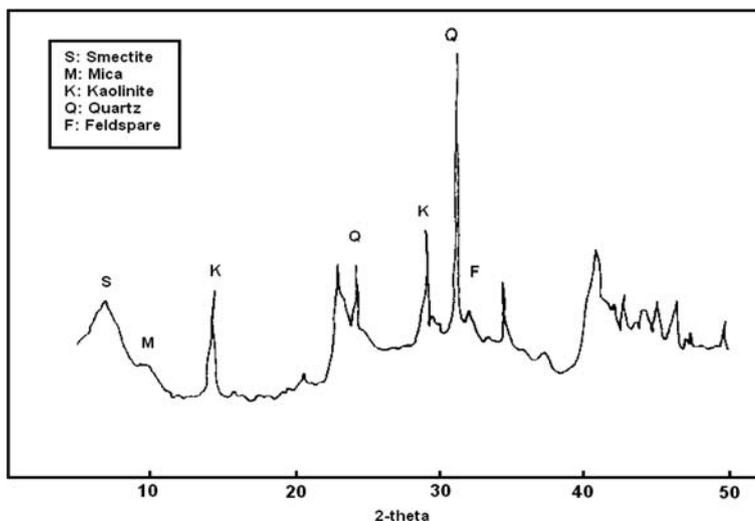
Fig. 2 Cation exchange capacity values for the treated bentonite

Fig. 4 Zero-point of charge value for the treated bentonite

600 cm^{-1} and a single band in the range of 1,600–1,700 cm^{-1}. The peaks at 3,416 and 3,620 cm^{-1} are due to lattice OH and bound water stretching vibrations. A strong and sharp band is detected at 1,031 cm^{-1} which is related to Si–OH stretching vibrations (Karahan et al. 2006). The weak absorption bands at 507 and 464 cm^{-1} can be attributed to the octahedral Si–O–Al bending vibrations, while the weak band at around 1,639 cm^{-1} may indicate a presence of carbonate bearing minerals in the sample left after treatment.

The Zero-point of charge for the treated bentonite was taken into consideration before determination of the removal capacity of bentonite. This ZPC determines the electrophoretic mobility where the net total particle charge is zero. This value was found to be 4.50 as shown in Fig. 4. As mentioned above this clay is composed of different minerals. These constituents contribute for 67% silica, 25.6% alumina, 6.2% iron oxide, and 0.85 % titanium

oxide after treatment in which silica incorporates the highest percentage among the other oxides. Silica has a pH_{ZPC} of 2.5 but alumina and iron oxides have an average pH_{ZPC} of 8.8 (Kosmulski 2002). Therefore, it is expected that the surface is negatively charged at pH higher than 4.5. The heterogeneous nature of the surface charge of bentonite results in the formation of ZPC continuum (Appel et al. 2003). For example, at pH 3, the bentonite possessing only silica that would have negatively charged surface, but the other metal oxides are positively charged. Silica surface is attracted towards positively charged pole but the opposite is true for the rest of the metal oxides. At pH values ranging from 4 to 7, the surface of bentonite exhibits amphoteric properties and acts as a buffer in this range. At pH values higher than 7, the addition of more hydroxyl groups from the basic solutions would break this buffer so that the surface no longer resist this change (Smiciklas

Fig. 3 FT-IR (Fourier Transform Infrared spectrophotometer) Spectra of the treated bentonite

et al. 2000). Thus, the ZPC of this mixture would be an average of the mobility of the charged particles in the system.

The adsorption isotherms for cobalt and zinc by HCl/NaOH-treated bentonite sample are shown in Figs. 5 and 6, respectively. The particle size of treated bentonite was less than 63 μm. For both isotherms the trend of the experimental data illustrate slightly favorable adsorption with monolayer capacity of 202.6 mg Zn^{2+} and 138.1 mg Co^{2+} per each gram of treated sample predicted by Langmuir model (Figs. 7 and 8). The high surface charge of the treated bentonite leads to either a proton exchange or surface reaction with the target metal ion. It can be noticed that a rapid increase in uptake of both Co^{2+} and Zn^{2+} occurred when the solution concentration was less than 50 and 1 mg/l, respectively. This increase in the metal uptake is accompanied by net release of H^+, or uptake of OH^-. In the first case the proton release comes from surface –OH groups as a result of ion exchange reactions or from the preferential adsorption of hydroxy complexes from solution. Although the surface of the treated bentonite is composed of different metal oxides, one of these metal oxides may facilitate precipitation of some ions by virtue of their opposite surface charge leading to hetrocoagulation of the surface (Corey 1981). Moreover, the solubility product of metal oxides, in general, is lowered at solid-solution interfaces as a result of low dielectric constant of the water at the interface (James and Healy 1972). Consequently, the hydrated surface of treated bentonite might act as a template for the formation of a surface coating of the hydroxide of the adsorbed ion. This would enhance the precipitation of these metal ions besides the adsorption on the treated bentonite surface at higher metal ion concentration. Kaya and Oren (2005) suggested that the
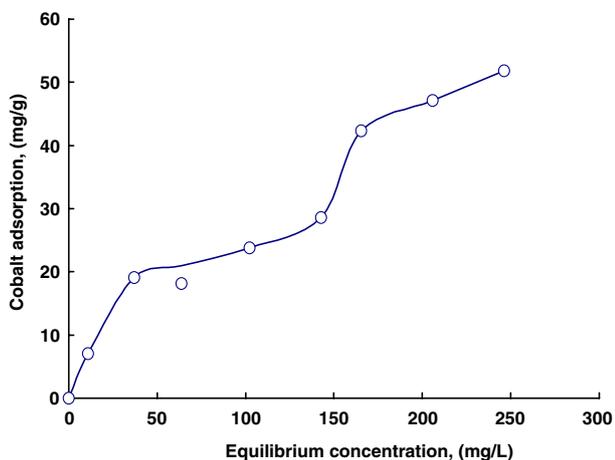

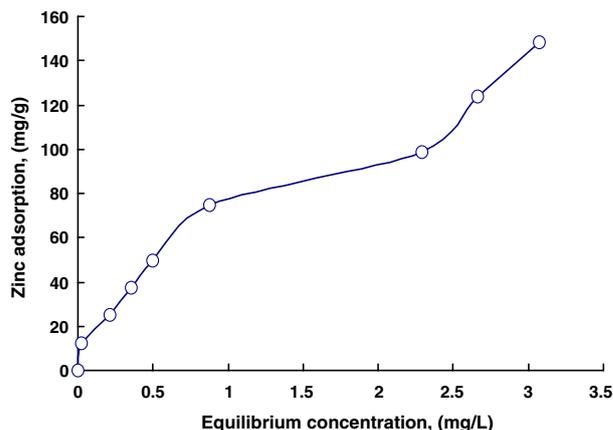**Fig. 6** Adsorption isotherm of zinc onto the surface of treated bentonite
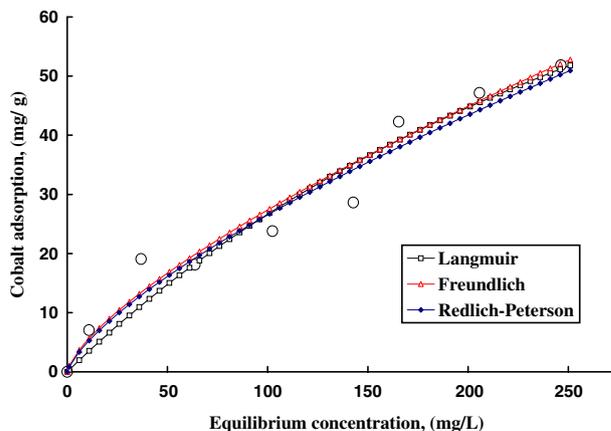
Fig. 7 Adsorption isotherm models for cobalt

Fig. 5 Adsorption isotherm of cobalt onto the surface of treated bentonite
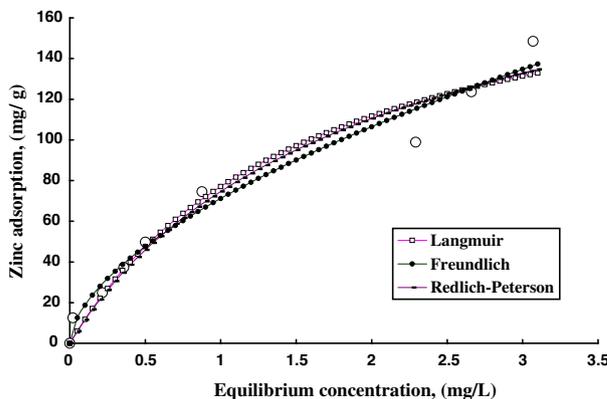

Fig. 8 Adsorption isotherm models for zinc

Table 2 Isotherm parameters for cobalt

Model	Constants	$\sum (error)^2$	R^2
Langmuir	$q_m = 138.17$	141	0.944
	$b = 2.39 \times 10^{-3}$		
Freundlich	$K_f = 1.02$	107	0.957
	$n = 1.40$		
Redlich-Peterson	$a = 2.00$	109	0.956
	$b = 1.43$		
	$n = 0.33$		

Table 3 Isotherm parameters for zinc

Model	Constants	$\sum (error)^2$	R^2
Langmuir	$q_m = 202.63$	767	0.964
	$b = 0.61$		
Freundlich	$K_f = 71.22$	541	0.974
	$n = 1.72$		
Redlich-Peterson	$a = 125.00$	736	0.965
	$b = 0.67$		
	$n = 0.90$		

interaction between zinc ions and bentonite layers can be described by the equilibrium:

$$mZn^{2+}_{solution} + 2M^{m+}_{bentonite} \rightarrow mZn^{2+}_{bentonite} + 2M^{m+}_{solution}$$
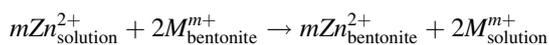
where m is the valence of the exchangeable cation, M, that exist in bentonite interlayer such as Na, K, Ca, and Mg. They showed that the adsorption of Zn^{2+} would much be enhanced by bentonite rich in sodium ions rather than that of natural bentonite as a result of having more expanded sheets between layers than the natural bentonite. This improvement by Na-enriched bentonite will be higher in the presence of Cl^- ions which supports the higher sorption capacity of the HCl/NaOH-treated bentonite among the treatment by other acids.

On the other hand, adsorption of some of the metal ions such as Co^{2+} may involve an increase in surface charge of the adsorbent as a result of desorption of other metal that incorporated in the surface structure (Murray 1975). The experimental data was fitted using different isotherm models and compared according to their correlation coefficient and sum of square errors (Tables 2 and 3). It is obvious that the three model best fits both experimental data adequately whereas Freundlich showed a regression coefficients of 0.957 and 0.974 for both cobalt and zinc isotherms, respectively. Also, the sums of the square errors were found to be the least for this model with values of 107 and 541 for Co and Zn isotherms, respectively.

5 Conclusion

Bentonite is considered as one of the naturally occurring materials that are illegible for removal of heavy metals from aqueous solutions. Treatment of this material with hydrochloric acid followed by washing with sodium hydroxide opened more macro and micro pores within the structure of original sample, which make it a suitable adsorbent for wastewater treatment. In order to further enhance the sorption capacity of this material it is recommended to study the effect of curing temperature during the treatment with sodium hydroxide. This may lead to enhancing the percentage of formation of zeolite in the treated sample.

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