

Heavy Metal Removal from Aquatic Systems by Northern Anatolian Smectites

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Competitive adsorption of the heavy metal ions Cu(II), Cd(II) and Pb(II) from aqueous media onto northern Anatolian smectites with a mean particle diameter of 200 μm , was investigated. The adsorption rate and capacity of the smectite for the selected heavy metal ions, containing different amounts of these ions (5-900 mg/L) at values ranging from pH 1.0 to 7.0 were studied. Very high adsorption rates were observed at the beginning, and adsorption equilibria were then gradually achieved in about 30 minutes. The maximum adsorption of metal ions onto the smectite were found to be 41.46 mg Cd(II), 36.11 mg Pb(II) and 18.72 mg Cu(II) per gram of smectite. The order of affinity based on weight uptake by smectite was Cd(II)>Pb(II)>Cu(II). When the metal ions competed (in the case of adsorption from their mixture), the amounts of Cd(II), Pb(II) and Cu(II) ions adsorbed were 11.86 mg, 11.23 mg and 16.76 mg per gram of smectite, respectively. Desorption of the metal ions from smectite was studied in 0.5 M HNO₃ and very high desorption rates, greater than 95%, were achieved in all cases.

Introduction

Efforts to minimize production of hazardous waste and to remediate existing, accumulated waste has become one of the most important environmental challenges that the world faces today. According to recent surveys, the most common contaminants reported in groundwater are heavy metals. Therefore, inexpensive materials for removing and entrapping heavy metal wastes from contaminated water are required. Treatment of aqueous wastes containing soluble heavy metals requires concentration of the metals into a smaller volume followed by recovery or secure disposal. Different treatment techniques have been developed to remove either or both dissolved and suspended heavy metal ions from industrial waters and wastewaters. A number of traditional treatment techniques include precipitation-neutralization, ultra-filtration, reverse osmosis, electrodeposition, solvent extraction, foam flotation, cementation, filtration and evaporation. Adsorption on solid matrices is also reported to be a potential method for heavy metal removal^{1,2}. Nonspecific sorbents, such as activated carbon, metal oxides, and ion-exchange resins have been used. Specific sorbents consisting of a metal chelating ligand which interacts with the heavy metal ions specifically, and a carrier matrix which may be an inorganic material (e.g., activated carbon, alumina, silica or glass) or polymer microspheres (e.g., polystyrene or polymethacrylate) have also been reported^{3,4}.

Natural materials, such as clay minerals or low-rank coals, can also be utilized for the removal of heavy metal ions from polluted aqueous systems. Because of the substantially lower cost of the bulk material, clay minerals have great potential for utilization as a means of removing a range of metals from aqueous solutions⁵⁻⁷. Clay minerals have the property of sorbing anions and cations and retaining them in an exchangeable state; i.e., these ions are exchangeable for other anions and cations by treatment with such ions in a water solution. The exchange reaction is stoichiometric and thereby differs from simple sorption. This distinction, however, is sometimes difficult to make since nearly every ion exchange process is accompanied by sorption or desorption. The exchangeable ions are held around the outside of the silica-alumina clay mineral structural unit, and the exchange reaction generally does not affect the structure of the silica-alumina packet.

The submitted study is dedicated to the evaluation of the metal exchange capacity of northern Anatolian smectites for Pb, Cd and Cu.

Experimental

Adsorbent Characterization

The smectite used throughout the presented study was obtained from northern Anatolia, Turkey, and was crushed and sieved to obtain a particle size of 200 μm . The chemical composition and some physical properties of smectite are given in Table 1.

Table 1. Chemical/physical characteristics of smectite.

Constituents	% w/w	Physical parameter Values	
SiO ₂	62.24	Mean particle diameter	200 μm
Al ₂ O ₃	15.94	pH	7.10
TiO ₂	0.19		
Fe ₂ O ₂	0.83		
Na ₂ O	0.77		
K ₂ O	0.76		
CaO	1.56		
MgO	3.23		
Loss on ignition	12.49		

Adsorption/Desorption/Reuse

Adsorption of heavy metal ions Cd(II), Cu(II) and Pb(II) from aqueous solutions was studied in batch systems. Adsorption rate and capacities were investigated. Nitrates of the respective metal ions were used. Aqueous solutions (25 mL) containing different amounts of heavy metal ions (5-900 mg/L) were treated with 100 mg of the smectite sample at different pH values (in the range of 1.0-7.0, which was adjusted with HNO₃ or NaOH at the beginning of the experiment and not controlled afterwards) at room temperature, in flasks agitated magnetically at 600 rpm. After the desired stirring periods (up to 60 min), the aqueous phases were separated from the smectite by filtration and the concentrations of the metal ions in these phases were measured by atomic absorption spectrophotometer. A Unicam 939 atomic absorption spectrophotometer equipped with a Unicam GF-90 atomizer and FS-90 autosampler was used. Deuterium background correction and pyrolytic graphite-coated tubes were used throughout the measurements.

The amount of the metal ions adsorbed per unit mass of smectite (mg metal ions/g smectite) were evaluated by the following expression:

$$\text{Metal ions adsorbed} = [(C_0 - C) \times V] / [m \times 1000] \quad (1)$$

Here, C_0 and C are the concentrations of the metal ions in the aqueous phase before and after the incubation period, respectively (mg/L); V is the volume of the aqueous phase (mL); and m is the amount of the smectite used (g).

Competitive heavy metal adsorption from aqueous solutions containing Cd(II), Cu(II) and Pb(II) were investigated by a procedure similar to that described above.

Desorption of heavy metal ions was achieved by using 25 mL of the eluent, i.e., 0.5 M HNO₃. The clay mineral, smectite, was loaded with the heavy metal ions under the following conditions: initial concentration of the heavy metal ions, 100 mg/L; amount of smectite, 100 mg; volume of the adsorption medium, 25 mL; pH, 5.0; temperature, 20°C; and adsorption time, 30 minutes. Then the system was placed in the desorption medium and stirred at 600 rpm for up to 60 minutes. The concentrations of the metal ions in the aqueous phase were as stated above. The desorption rate was calculated from the following expression:

$$\text{Desorption rate} = \frac{\text{Amount of metal ions desorbed to the elution medium}}{\text{Amount of metal ions adsorbed on smectite}} \times 100 \quad (2)$$

In order to achieve the reusability of the smectite, the adsorption-desorption cycle was repeated 3 times by using the same sorbent. Adsorption conditions were as follows:

initial concentration of the heavy metal ions, 100 mg/L from the adsorption of single metal ion solutions and 100 mg/L from the adsorption of ternary metal ion solutions (equal amounts of the metal ions were used); amount of smectite, 100 mg; volume of the adsorption medium, 25 mL; temperature, 20°C; and adsorption time, 60 minutes. The smectite was stirred in 25 mL of 0.5 M HNO₃ for up to 60 minutes and reloaded.

Results and Discussion

Adsorption Studies

Adsorption Rate

Figure 1 exemplifies adsorption rates of heavy metal ions by smectite as a function of time. The figure shows the changes in the amounts of the metal ions adsorbed over time, which were calculated by using the expression given in equation (1). Note that these batch experiments were performed by using single (not multiple) solutions of the ions of interest. Adsorption conditions are given in the figure legend. It should be noted that there was no precipitation in these groups of experiments under the concentration and pH conditions studied. Figure 1 shows that high adsorption rates were observed at the beginning, and then plateau values (i.e., adsorption equilibrium) are gradually reached within 30 minutes.

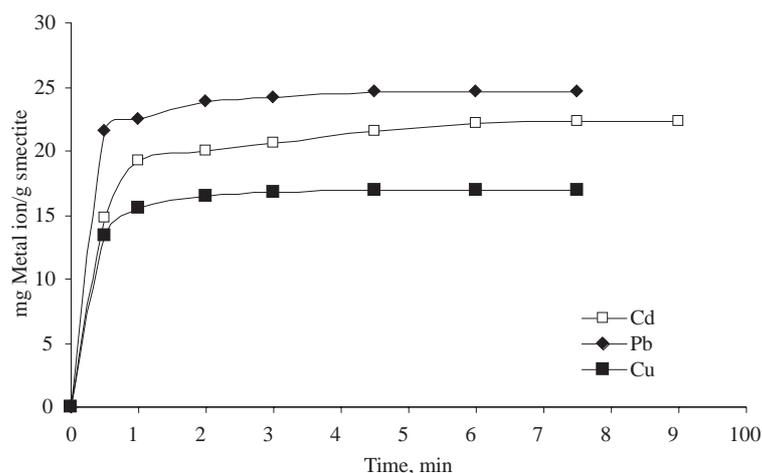


Figure 1. Adsorption rates of heavy metal ions by smectite. Adsorption conditions: initial concentration of metal ions, 100 mg/L; pH, 5.0; temperature, 20°C.

Various experimental data on the adsorption kinetics of heavy-metal ions by various sorbents have shown a wide range of adsorption rates^{2,8-10}. For example, Reed and Matsumoto considered 6 hours to be a short equilibrium time in their metal ions adsorption kinetics studies, in which have used activated carbon as sorbent². Konishi et al. have investigated the recovery of zinc, cadmium, and lanthanum by biopolymer gel particles of alginic acid. In their recent paper, they reported very high adsorption/desorption rates for lanthanum by alginic acid, in which equilibrium was achieved in about 60-90 minutes⁸. Murty and Ryan have investigated mercury, copper, cadmium, lead and uranium adsorption on cellulose-dithiocarbamate resins and reported that the adsorption rates were slow, but they were able to use a 30-minute equilibrium time reproducibly¹¹. Egawa has studied uranium adsorption on polyacrylonitrile fibers containing amidoxime group and reported 7 hour equilibrium adsorption time¹². Recently, our group was able to shorten the equilibrium times (5-90 minutes) for heavy metal adsorption by using dye-attached swellable poly(EGDMA-HEMA) microspheres¹³⁻¹⁵. Chakravarty et al. have studied copper removal from aqueous solutions by hematite and reported an equilibrium time of 75 minutes¹⁶.

Note that in such an adsorption process, there are several parameters which determine the adsorption rate: agitation rate in the aqueous phase, sorbent structural properties (e.g., size, porosity, surface area), amount of sorbent, metal ion properties (e.g., hydrated ionic radius), initial concentration of metal ions, pH, temperature, and, of course, the existence of other ions which may compete with the ions of interest for active adsorption sites. All individual experimental studies published in the literature have been performed under different conditions. Consequently, it is not possible to make a reasonable comparison of the adsorption rates reported.

Adsorption Capacity

In Figure 2, heavy metal ion adsorption capacities of smectite are presented as a function of the initial concentration of metal ions within the aqueous medium. This figure was prepared by using the plateau values of the adsorption rate curves. These batch experiments were performed by using single solutions of the ions of interest. Adsorption conditions are given in the figure legend. The hydrolysis and precipitation of the metal ions are affected by the concentration and form of soluble metal species. As discussed in detail by Reed and Matsumoto², the hydrolysis of metal ions becomes significant at approximately pH 8.5, pH 6.5

and pH 7.5 for Cd(II), Cu(II) and Pb(II) respectively. We have also estimated the theoretical precipitation concentrations of hydroxides of the respective metal ions at different pH values by using the K_{sp} values given in the literature. In consideration of this data, in order to eliminate the effects of precipitation we performed these group of experiments at pH, 4.0 for Cu(II), and 5.0 for Cd(II) and Pb(II). The amount of metal ions adsorbed per unit mass of smectite (i.e., adsorption capacity) increased with the initial concentration of the metal ions studied, as expected.

In order to reach the plateau values which represent saturation, i.e., to obtain the maximum adsorption capacity of smectite for ions of interest, we increased the initial concentration of the metal ions up to 900 mg/L, 400 mg/L and 500 mg/L for Cd(II), Pb(II) and Cu(II) respectively. The maximum adsorption capacities found were as follows: 41.46 mg Cd(II)/g smectite; 36.11 mg Pb(II)/g smectite; and 18.72 mg Cu(II)/g smectite. The order of affinity based on a weight uptake by smectite is Cd(II)>Pb(II)>Cu(II). Note that the maximum adsorption capacities on molar basis are 0.37 mmol, 0.17 mmol and 0.29 mmol per gram of smectite for Cd(II), Pb(II) and Cu(II) respectively. Therefore the order of affinity is as follows: Cd(II)>Cu(II)>Pb(II).

It is well known that metal ion removal by both non-specific and specific sorbents is pH dependent^{2,8-10}. Therefore in this study, in order to establish the effect of pH on the adsorption of metal ions onto smectite, we repeated the batch equilibrium studies at different pH values in the range of 1.0 - 7.0. Figure 3 exemplifies the effect of pH on adsorption. Experimental conditions are given in the figure legend. As seen from the figure, retention of all heavy metal ions evaluated in this study first increased with pH, and then reached a plateau value around pH 4.0 for Cu(II) and pH 5.0 for Cd(II) and Pb(II). Fields and Schofield pointed out that in allophane, smectite and similar clays, the characteristic variable charge on the lattice with varying pH causes an increase of cation retention with increasing pH¹⁷. In their studies with hematite, Chakravarty et al.¹⁶ also observed a similar behaviour for the removal of Cu(II) ions from aqueous solutions.

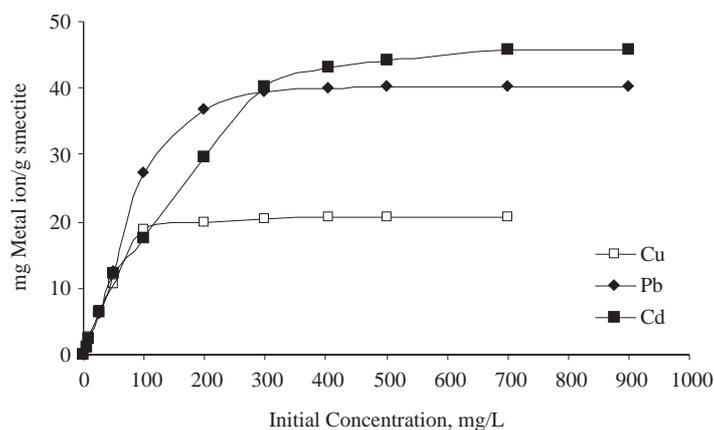


Figure 2. Adsorption capacity of smectite for heavy metal ions. Adsorption conditions, pH, 4.0 for Cu(II) and 5.0 for Pb(II) and Cd(II); adsorption time: 30 minutes; temperature: 20°C.

Competitive Adsorption

In this group of experiments, competitive adsorption of Cd(II), Pb(II) and Cu(II) ions from their ternary solutions was investigated. Solutions (25 mL) containing 100 mg/L of metal ions were treated with 100 mg of smectite for 30 minutes at pH 5.0 and at a temperature of 20°C.

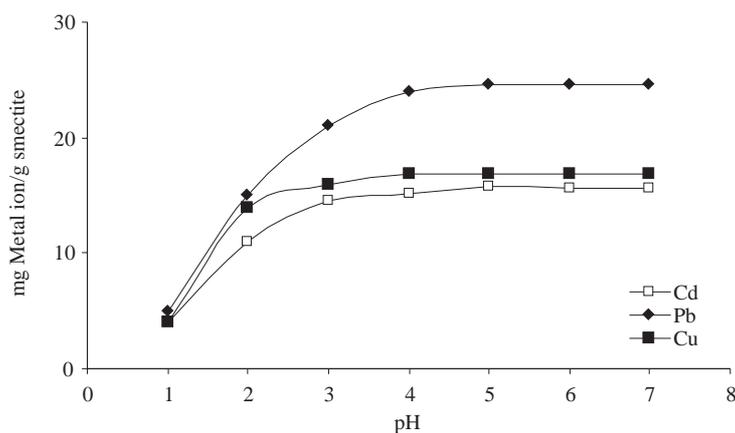


Figure 3. Adsorption capacities of smectite for metal ions at different pH. Adsorption conditions: initial concentration of the metal ions, 100 mg/L; adsorption time, 30 minutes; temperature: 20°C.

The amount of Cd(II), Pb(II) and Cu(II) ions adsorbed from their ternary solutions were as follows: 11.86 mg Cu(II)/g smectite; 11.23 mg Cd(II)/g smectite; 16.76 mg Pb(II)/g smectite. As can be seen from the results obtained, the amount of adsorbed Pb(II) ions was higher in terms of weight. When considered on a molar basis, however (0.187 mmol Cu(II)/g smectite; 0.099 mmol Cd(II)/g smectite; and 0.081 mmol Pb(II)/g smectite), it may be concluded that there is no indication of higher specificity of smectite for any of the metal ions studied. Therefore, it is almost impossible to generalize the order of adsorption or to define the extent of adsorption for each metal ion when they compete.

Desorption and Reuse

Desorption of the adsorbed metal ions from smectite was also studied in a batch experimental set-up. In the first group of experiments, the desorption rates of heavy metal ions from smectite loaded with 100 mg/L of the respective metal ions (loaded from their single metal ions solutions) were obtained. In the second group of experiments, the desorption rates of ions from smectite loaded with 100 mg/L of each of the metal ions, loaded from their ternary solutions, were studied. In order to achieve the reusability, of smectite, a adsorption/desorption cycle was repeated 3 times with the same sorbent. The data are presented in Table 2 and Table 3.

Table 2. Desorption of heavy metal ions from smectite. Adsorption conditions : initial concentration of metal ions, 100 mg/L from the adsorption of single metal ion solutions; amount of smectite, 100 mg; adsorption time, 30 minutes; pH, 5.0, Desorption conditions: desorption medium, 0.5 M HNO₃; desorption time, 60 minutes; temperature, 20°C.

Metal Ions	Metal Ions Adsorbed (mg/g smectite)			Desorption Rate (%)		
	First	Second	Third	First	Second	Third
Cu	16.51	12.81	13.21	96.5	96.7	96.3
Cd	15.77	15.18	13.35	96.7	96.8	95.6
Pb	24.58	22.86	21.23	98.5	98.9	96.9

Table 3. Desorption of heavy metal ions from smectite. Adsorption conditions: initial concentration of metal ions, 100 mg/L from the adsorption of ternary metal ion solutions, amount of smectite, 100 mg; adsorption time, 30 minutes; pH, 5.0b Desorption conditions: desorption medium, 0.5 M HNO₃; desorption time, 60 minutes; temperature, 20°C.

Metal Ions	Metal Ions Adsorbed (mg/g smectite)			Desorption Rate (%)		
	First	Second	Third	First	Second	Third
Cu	11.86	8.98	8.77	96.8	97.1	96.7
Cd	11.23	9.77	8.92	97.3	97.6	97.5
Pb	16.76	16.14	15.42	98.2	98.4	97.7

Because of the substantially lower cost, the material used has great potential for the removal of heavy metals from polluted aquatic systems. The adsorption rates and adsorption capacities obtained in this study are comparable to those reported for synthetic materials. The maximum adsorption capacities found were 41.46 mg Cd(II), 36.11 mg Pb(II) and 18.72 mg Cu(II) per gram of smectite. Competitive adsorption of these metal ions from their ternary solutions showed no significant indication of higher specificity of smectite for any of the metal ions studied. In the desorption and reuse studies, very high desorption rates, greater than 95%, were achieved.

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