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Solmaz Karabulut[a]; Abdülkerim Karabakan[a]; Adil Denizli[a]; Yuda Yürüm[b]
[a] Department of Chemistry, Hacettepe University, Ankara, Turkey [b] Department of Materials Science, Sabanci University, Izmit, Turkey

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CADMIUM (II) AND MERCURY (II) REMOVAL FROM AQUATIC SOLUTIONS WITH LOW-RANK TURKISH COAL

Solmaz Karabulut,[1] Abdülkerim Karabakan,[1]
Adil Denizli,[1],* and Yuda Yürüm[2]

[1]Department of Chemistry, Hacettepe University,
Beytepe, Ankara 06532, Turkey
[2]Department of Materials Science, Sabanci University,
Izmit, Turkey

ABSTRACT

Removal of heavy metal ions from aqueous solutions containing low-to-moderate levels of contamination using Turkish Beypazari low-rank coal was investigated. Carboxylic acid and phenolic hydroxyl functional groups on the coal surface were the adsorption sites for heavy metal ions via the ion-exchange mechanism. The equilibrium pH of the coal-solution mixture was the principal factor controlling the extent of removal of Cd(II) and Hg(II) from aqueous solutions. The optimum pH was 4.0, and the adsorption reached equilibrium in 30 minutes. The maximum adsorption capacities of the metal ions from their single solutions were 1.55 mg for Hg(II) and 1.42 mg for Cd(II) per g of coal. Based on a weight uptake by coal, Hg(II) was found to have a greater affinity for the adsorption sites than does Cd(II). The same behavior was observed during competitive adsorption, that is, adsorption from binary so-

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*Corresponding author. Fax: 90 312 2992163; E-mail: denizli@hacettepe.edu.tr

lutions. The adsorption phenomena followed a typical Langmuir isotherm. The maximum adsorption capacities (q_m) were calculated as 2.03 mg/g and 1.70 mg/g for Hg(II) and Cd(II), respectively. The K_d values were 8.2 mg/L for Cd(II) and 9.8 mg/L for Hg(II). The use of low-rank coal was considerably effective in removing Hg(II) and Cd(II) from aqueous solutions. High amounts of adsorbed metal ions could be desorbed (up to 90%) with 25 mmol/L EDTA. Low-rank Turkish coals are suitable for use in more than 10 cycles without experiencing significant loss of adsorption capacity.

Key Words: Turkish low-rank coal; Heavy metal ions; Adsorption; Metal removal

INTRODUCTION

Contamination of surface waters by heavy metal ions is becoming an increasingly serious condition. Ecological and health problems due to their toxic effects are evident at very low concentrations. Mercury and cadmium are the most toxic transition metals (1,2). Mercury has a very high tendency to bind proteins, and it mainly affects the renal and nervous systems (3). In humans, the initial symptoms include numbness of the lips and limbs. As the sickness progresses, permanent damage is done to the central nervous system, and the victim experiences visual constriction, loss of motor coordination, and in the final stages prior to death, loss of memory, speech, hearing, and taste. Several studies in both humans and experimental animals indicate a carcinogenic potential for cadmium (4).

Coal combustion, sewage wastewater, automobile emissions, mining activities, and the utilization of fossil fuels are just a few examples of the different ways that these toxic metals are released in the environment. The conventional techniques for the heavy metal removal are filtration, chemical precipitation, reverse osmosis, solvent extraction, and membrane techniques (5). The main limitation of these techniques is their low efficiency in the removing trace levels of metal ions. The adsorption is reported to be the best method for the removal of metal ions at a ppm level of concentration (6). Nonspecific sorbents, such as activated carbon, metal oxides, silica and ion exchange resins, have been used for heavy metal ion removal (7). Specific polymeric sorbents carrying chelating ligands that specifically interact with the metal ions have been considered for efficient removal (8–10). Although the adsorption capacities of low-rank coals are lower those of synthetic polymer-based ion exchange materials, the substantially lower cost of the bulk material shows great potential for the usage of low-rank coals as a means to displace heavy metal ions from wastewater.

Lignites and the lower-rank coals, such as brown and subbituminous coals, are highly oxygenated (20–30% (wt) dry ash free basis), with many carboxyl and phenolic hydroxyl groups. However, the high oxygen content of low-rank coals allow the unique capability for lignite to remove cations from solution via ion exchange with carboxylic acid and phenolic hydroxyl functional groups on the surface of the coals. Victorian brown coals, with cation exchange capacities that are dependent on the solution pH, can remove high concentrations of metals from aqueous solutions (11). The adsorption selectivities of lignites for first-order transition metal groups follow that of an Irving-Williams order, indicating that the group involved in the metal adsorption contains either a nitrogen or oxygen atom and is most likely a carboxylic site. The distribution of carboxyl groups in raw and heat-treated brown coals was recently estimated (12) and the total amount of carboxyl groups of heat treated coals was found to decrease by thermal decomposition.

Our aim for this study is to utilize a new and cheap adsorbent for the removal of heavy metals from large volumes of wastewater and other aqueous systems containing low-to-moderate levels of contamination in the Mediterranean and Marmara Seas. However, the unique aspect of the proposed system lies in the complete utilization of low-rank coals in the removal of heavy metals.

EXPERIMENTAL

Instrumentation

A Unicam 939 atomic absorption spectrophotometer (AAS) equipped with a Unicam Grafit Furnace-90 atomizer and a FS-90 autosampler was used for the determination of heavy metal ions. When the concentration of the supernatant Hg(II) was measured, AAS connected to a cold vapor unit (Hydride Generator, GBC HG 3000) was used. Deuterium background correction was done. Pyrolitic graphite-coated tubes were used for AAS measurements. For each metal solution, the mean of 10 AAS measurements was recorded. To eliminate contamination, all glassware and plasticware were cleaned with rinse-buffered saline detergent (Pierce, Rockford, Ill, USA) and rinsed with deionized water.

Coal Sample

The low-rank coal used throughout the experiments was obtained from Beypazari, Turkey. The composition of Beypazari lignite was determined from an elemental-analysis device (Leco, CHNS-932, USA). The lignite sample was ground under a nitrogen atmosphere to –65 mesh ASTM and stored under nitrogen. Pore volumes and average pore diameters greater than 20 Å were determined by mercury porosimeter up to 2000 kg/cm^2 with a Carlo Erba model 200. The surface area of the coal sample was measured with a surface area apparatus (Brunauer, Emmett, and Teller (BET) method).

Adsorption Studies

All water used in the experiments was purified by a Barnstead (Dubuque, Ia) ROpure LP® reverse osmosis unit with a high-flow cellulose acetate membrane (Barnstead D2731) and the organic and colloid compound were removed with a Barnstead D3804 NANOpure,® and ion-exchange packed-bed system. The resulting purified water (deionized water) has a specific conductivity of 18 megaohm/cm.

The effect of pH on the adsorption capacity of coal was investigated through the use of analytical grade nitrate solutions of 100 ppm Hg(II) and 100 ppm Cd(II) at pH 2.0–6.0. The suspensions were brought to the desired pH through the addition of sodium hydroxide (NaOH) and nitric acid (HNO_3). The pH was maintained in a range of ± 0.1 units until equilibrium was attained. In all experiments, coal concentration was kept constant at 1 g/100 mL of Hg(II) and Cd(II) solutions at room temperature and were magnetically stirred continuously. After 1 hour, the aqueous phase was separated from coal by centrifugation, and the concentrations of metal ion in the aqueous phase were determined by an atomic absorption spectrophotometer. All instrumental conditions were optimized for maximum sensitivity as described by the manufacturer. Each sample was subjected to AAS 10 times, and a mean value and relative standard deviation was computed from the readings. Calibrations were performed in the range of analysis, and a correlation coefficient for the calibration curve of 0.98 or greater was obtained. The instrument response was periodically checked with known metal standards.

Adsorption capacities and adsorption rates of metal ions from aqueous solutions were also studied in batch systems. The effect of initial metal ion concentration on the adsorption capacity of Beypazari coal, at the optimum pH, was determined through the use of of 10–100 ppm solutions of Hg(II) and Cd(II). One gram of coal (dry weight) was added to 100 mL of each aqueous solution of Hg(II) or Cd(II) at room temperature, and the coal solutions were stirred continuously. After 1 hour, the aqueous phase was separated from coal by centrifugation, and the concentrations of the metal ions in the aqueous phases were determined.

Competitive adsorption of Hg(II) and Cd(II) ions from a binary solution was investigated by a similar procedure followed for studying the ions independently. A 100-mL solution that contained 30 ppm of each metal ion was incubated with coal samples at room temperatures in the flasks stirred magnetically at 600 rpm. These studies were conducted at a constant pH of 4.0. After adsorption equilibrium was reached, the metal ion concentrations in the remaining solution were measured by AAS.

The amount of adsorbed metal ions (mg metal ion/g coal) was calculated from the decrease of metal ion concentrations in the medium by the determination of the adsorption volume and unit amount of the coal:

$$\text{Metal ions adsorbed} = \frac{(C_o - C) \times V}{m} \tag{1}$$

C_o and C are the metal ion concentrations in the aqueous phase before and after the incubation period, respectively (ppm); V is the volume of the aqueous phase (mL); and m is the amount of coal used (g).

To determine the reusability of the low-rank Turkish coals, adsorption/desorption cycles were repeated 10 times with the same sample. Desorption of metal ions was achieved through the use of 25 mM ethylenediaminetetraacetic acid (EDTA). The coals carrying 1.55 mg Hg(II)/g and 1.42 mg Cd(II)/g were placed in this desorption medium and stirred at 600 rpm for 60 minutes at room temperature. The final metal ion concentration in the aqueous phase was determined by an atomic absorption spectrophotometer. The desorption ratio was calculated from the amount of metal ions adsorbed on the coals and the final metal ion concentrations in the desorption medium by use of the following equation:

$$\text{Desorption ratio} = \frac{\text{amount of metal ions desorbed}}{\text{amount of metal ions adsorbed}} \times 100 \tag{2}$$

RESULTS AND DISCUSSION

Sorbent Properties

Figure 1 shows mercury porosimetry plot for Beypazari lignite. According to this graph, the pore size of Beypazari lignite varied between 100 Å and 400 Å. This indicated that the lignite contained mainly mesopores. The ionic diameters of the Hg(II) and Cd(II) ions were 2.2 Å and 1.94 Å, respectively. Specific surface area of the low-rank coal was 2.56 m^2/g by the BET method. The elemental analysis of Beypazari lignite is given in Table 1.

Adsorption of Heavy-Metal Ions

Effect of pH

The adsorption of heavy metal ions is strongly dependent on pH. In the absence of complexing agents, the hydrolysis and precipitation of the metal ions are

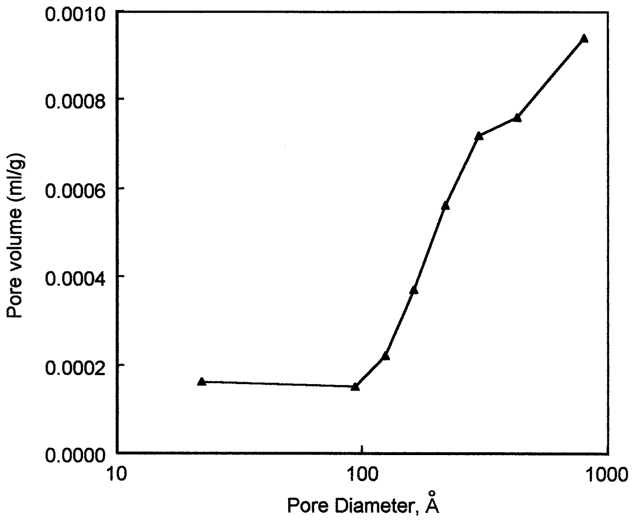

Figure 1. Pore size distribution of Beypazari lignite.

affected by the concentration and form of soluble metal species. The solubility of metal ions is governed by hydroxide or carbonate concentration. As discussed in detail by Reed, Arunachalam, and Thomas (13), hydrolysis of metal ions becomes significant at approximately pH 8.5 and pH 7.5 for Cd(II) and Hg(II), respectively. The theoretical and experimental precipitation curves indicate that precipitation begins above these pH values and also depends on the concentration of metal ions in the medium. Therefore, to establish the effect of pH on the adsorption of metal

Table 1. Elemental Analysis of Beypazari Lignite

	% (wt), daf
Carbon	61.2
Hydrogen	5.5
Sulfur (total)	5.3
Nitrogen	1.9
Oxygen (by difference)	26.1
Sulfur types	
Sulfate	0.9
Pyrite	0.3
Organic compounds	4.1

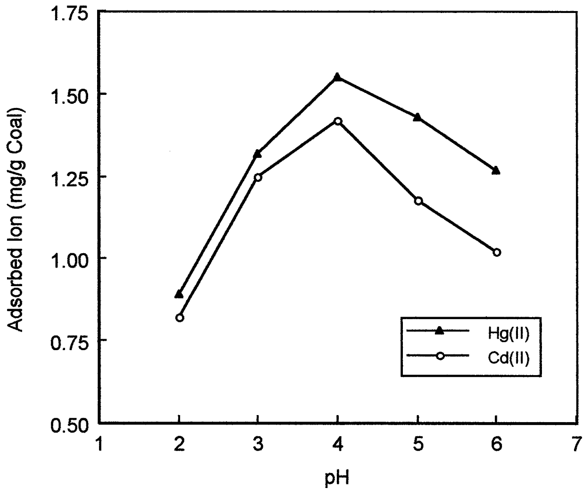

Figure 2. Effect of pH on adsorption of metal ions on low-rank Turkish coals. Initial concentration of metal ions was 30 ppm at 20°C.

ions onto the Beypazari coal, we repeated the batch equilibrium studies at pH 2.0–6.0.

Figure 2 shows the effect of pH on the adsorption capacity of Beypazari coal. As can be seen from the figure, adsorption of all heavy-metal ions first increased with pH and almost reached a peak value of approximately 4.0 for both Hg(II) and Cd(II). High adsorption at high pH values implies that metal ions interact with coal by chelating. The functional groups responsible from the exchange process contain either a nitrogen or an oxygen atom. Fourier Transform Infrared Spectroscopy studies of the raw and exchanged coals revealed that a significant amount of the heavy metal removal was due to the formation of exchanged metal carboxylates on the coal surface.

$$\text{Coal–COOH} = \text{Coal–COO}^- + \text{H}^+_{(aq)} \tag{3}$$

$$\text{M}^+_{(aq)} + n\,\text{Coal–COO}^- = (\text{Coal–COO})_n\,\text{M} \tag{4}$$

$$\text{Mn}^+_{(aq)} + n\,\text{OH}^- = \text{M(OH)}_n \tag{5}$$

In the coal-ion system at pH values less than 2.0, left-side term of Eq. (3) is the predominant form of the compounds. At the low pH, the ion exchange sites are mainly protonated and are less available for ion exchange. At the typical solution pH of 2.0–5.0, the carboxylic acid sites can be appreciably deprotonated; Eq. (4) proceeds such that the right-hand term becomes increasingly prominent, and metal ion removal is increased by increased pH. Within this pH range, the ion exchange process is the major mechanism for removal of metal ions from solution. For a pH value greater than 5.0, both ion exchange and metal hydroxide precipitation become significant in metal removal processes (Eq. 5). In addition, at pH > 4.0 the sorption capacity decreased with increasing pH because the coordination bonds between metal ions and phenolic hydroxyl functional groups and other ion exchangeable moieties on the coal surface are rather weak in the slightly acidic solution (i.e., pH 5.0 and 6.0). As a result, the adsorption of metal ions is negligible at low pH values and increases considerably at pH values of 3.0–4.0.

Adsorption Rate

Figure 3 shows the adsorption rates of Hg(II) and Cd(II) ions by coal as a function of adsorption time. These batch adsorption experiments were performed by use of single metal ion solutions. The amount of heavy metal ions adsorbed with time was calculated through Eq. (1). Adsorption conditions are given in the figure legend. The slopes of these curves reflect the adsorption rates. As seen, high adsorption rates were obtained. Ninety percent of the total soluble metal ions were removed from solutions within 20 minutes of contact time. This initial rapid metal adsorption has significant practical importance as it facilitates shorter adsorption columns, thus ensuring efficiency and economy.

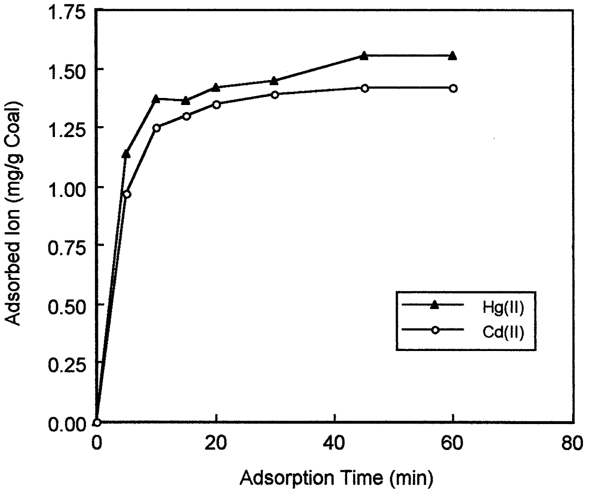

Figure 3. Adsorption rates of metal ions on the low-rank Turkish coals. Initial concentration of metal ions was 30 ppm in pH 4.0 medium at 20°C.

Data on the adsorption kinetics of metal ions for both inorganic and polymeric adsorbents have reported a wide range of equilibrium adsorption times. For example, Reed, Arunachalam, and Thomas et al. considered 6 hours a short equilibrium adsorption time in their cadmium and lead adsorption kinetic studies, in which granular activated carbon was the sorbent (13). Cox et al. studied mercury (II) adsorption on a carbonaceous sorbent prepared from flax shive, and they reported a 120 hour equilibrium time due to intraparticle diffusion (14). Suh and Kim used different inorganic and biological sorbents for removal of Pb(II) from aqueous solutions (15). They showed that their system required 6 hours to reach equilibrium. Sarkar, Datta, and Sarkar investigated the effect of shaking time on the adsorption of heavy metals on silica and reported that equilibrium adsorption time is 2 hours (16). Shreedhara-Murthy and Ryan investigated mercury, copper, cadmium, lead, and uranium adsorption on cellulose-dithiocarbamate resins and reported that the adsorption rates were very slow (17). Egawa, Nakayama, and Sugihara studied uranium adsorption on polyacrylonitrile fibers that contained amidoxime groups and reported a 7-hour equilibrium adsorption time (18). Marchese, Campderros, and Acosta investigated separation of cobalt, nickel, and copper ions with alamine liquid membranes, and they reported that equilibrium was achieved in approximately 4–5 hours (19). Teramoto et al. reported that a spiral-type supported liquid-membrane module reached steady state in approximately 4 hours (20). Denizli et al. used dye immobilized poly(HEMA) membrane for removal of Hg(II), As(III), Cd(II), and Pb(II), and they reported that adsorption equilibria was achieved in 1 hour (21). Several parameters determine the adsorption rate, such as stirring rate (or flow) in the aqueous phase, the physical nature of the sorbent (e.g., porosity, surface area), amount of sorbent, ion properties (e.g., atomic/ionic radius), initial concentration of metal species, steric effects, chelate-formation rate, and existence of other metal ions that may compete with the ion of interest for the active adsorption sites. Hence, comparisons between reported adsorption rates are difficult to make. However, the adsorption rates obtained with the low-rank Turkish coals seem to be very satisfactory.

Adsorption Isotherms

Heavy-metal ion adsorption isotherms of Beypazari low-rank coal are presented in Fig. 4 as a function of the initial metal-ion concentrations in the aqueous medium. Adsorption conditions are given in the figure legend. The amount of metal ions adsorbed per unit mass of coal (i.e., adsorption capacity) increased with the initial concentration of metal ions, as expected. To reach the plateau values, which represent saturation of the active coal-sample sites available for interaction with metal ions (to obtain the maximum adsorption metal-ion capacities), the initial concentrations were increased up to 40 ppm for both Hg(II) and Cd(II). The maximum adsorption capacities were 1.55 mg and 1.42 mg per gram of coal for

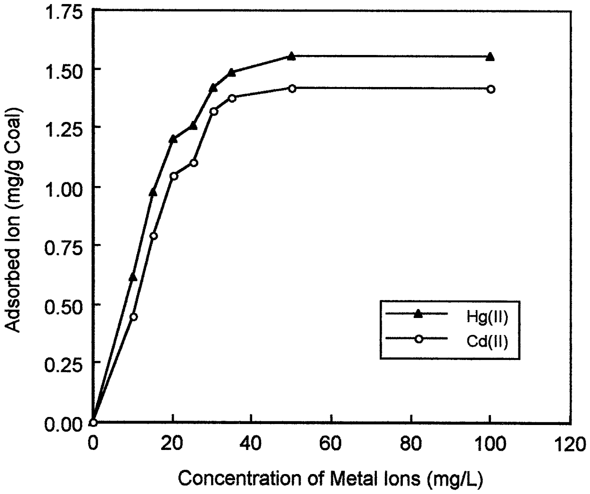

Figure 4. Metal ions adsorption capacity on the low-rank Turkish coals in pH 4.0 medium at 20°C.

Hg(II) and Cd(II), respectively. The Cd(II) had a lower order of affinity, based on a weight uptake by coal, than did Hg(II). The maximum adsorption capacities were 7.7 μmol Hg(II)/g coal and 12.6 μmol Cd(II)/g coal; therefore, the order of affinity, based on molar capacity, was Cd(II) > Hg(II).

The difference in adsorption behavior of Hg(II) compared to Cd(II) can be explained by the different affinity of heavy metal ions for the donor atoms (i.e., oxygen, sulfur, and nitrogen) in the coal structure. A difference in coordination behavior is most probably another cause for groups complexing on the coal sample. This complexation results in a relatively high adsorption of Hg(II) under noncompetitive adsorption conditions.

Semireciprocal plots of the experimental data for Hg(II) and Cd(II) adsorption are presented in Fig. 5. The corresponding semireciprocal transformations of the equilibrium data for metal ions gave rise to a linear plot, indicating that the Langmuir model could be applied in these systems and can be described by the equation:

$$Q = \frac{Q_m C^*}{(k_d + C^*)} \tag{6}$$

where C^* is the equilibrium concentration of adsorbate in solution; Q is the solid-phase concentration of the adsorbed molecules; Q_m is the maximum adsorption capacity of the adsorbent; and $k_d = k_2/k_1$ is the dissociation constant of the system.

The semireciprocal plot of $1/q$ vs. $1/C^*$ was employed to generate the intercept of $1/q_m$ and the slope of k_d/q_m. The maximum capacity (q_m) data for Hg(II) and Cd(II) adsorption were obtained from experimental data. The correlation coefficients (R^2) were 0.958 for Hg(II) and 0.989 for Cd(II), indicating that the Langmuir model can be applied in this sorbent system. The maximum adsorption capacities (q_m) were 2.03 mg/g and 1.70 mg/g for Hg(II) and Cd(II), respectively. The K_d values were 8.21 mg/L for Cd(II) and 9.81 mg/L for Hg(II).

In the literature, different nonspecific carriers with a wide range of adsorption capacities for metal ions have been reported. Lopez et al. investigated the applicability of blast furnace sludge, generated during the purification of blast furnace gases, as an adsorbent to remove metals from industrial effluents, and they reported lead adsorption capacity of up to 64 mg/g (22). Reed and Matsumoto found 15 mg Cd(II)/g adsorption capacity by commercially available, powdered, activated carbon (23). Khalfaoui, Meniai, and Borja used raw charcoal for removal of copper from industrial wastewater, and they showed it had an adsorption capacity of 0.04 mg/g (24). Filho, Gushikem, and Polito reported a 0.92 mg Zn(II)/g adsorption with 2-mercaptobenzothiazole-loaded natural clay (25). Orumwense used kaolinitic clay, Giru clay from Nigeria as an adsorbent for the removal of lead from water (26). The maximum amount of adsorption capacity achieved was 7.0 mg Pb(II)/g. Lafferty and Hobday used low-rank Victorian brown coal in which the maximum adsorption capacities were 14 mg Zn(II)/g and 16 mg Cu(II)/g (11). Budinova et al. prepared activated carbons by water vapor

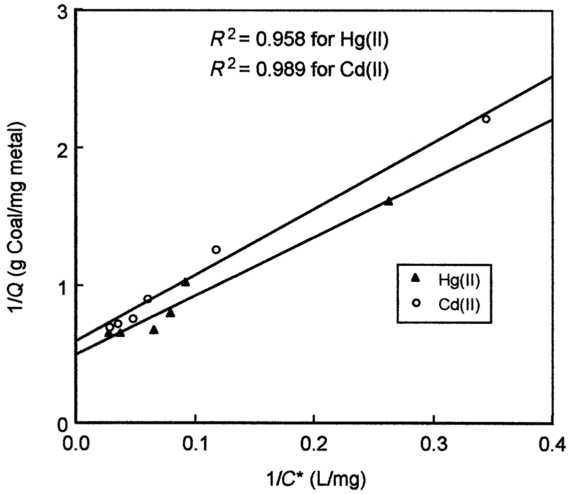

Figure 5. Linear representation of Langmuir equation of heavy metals with coals in pH 4.0 medium at 20°C.

pyrolysis of agricultural by-products such as apricot stones, coconut shells, and lignite coal (27). They reported 12.7 mg Cu(II)/g maximum adsorption capacity for lignite coal. Bassi, Prasher, and Simpson studied adsorption of several metal ions on commercially available chitosan, and they reported 0.95 mg Zn(II), 1.37 mg Cu(II), 0.94 mg Cd(II), and 1.02 mg Pb(II) per gram of biosorbent (28). Allen and Brown reported the adsorption of copper, cadmium, and zinc in single-component and multicomponent mixtures in aqueous solutions by lignite (29). They obtained 27.9 mg Cu(II)/g, 40.4 mg Cd(II)/g, and 24.5 mg Zn(II)/g adsorption capacities. The adsorption capacities that we achieved are comparable with the values reported in previous publications.

Competitive Adsorption

In this group of experiments, competitive adsorption of Hg(II) and Cd(II) from their binary solution was investigated. The initial metal ion concentrations were chosen as 30 ppm for each metal ion. One gram of coal (dry weight) was added to 100 mL of the binary solution at pH 4.0. The amount of metal ions adsorbed were 1.98 mg and 1.65 mg per g of coal for Hg(II) and Cd(II), respectively (Table 2). The observed affinity order in adsorption was found to be same under competitive conditions and noncompetitive conditions: Hg(II) > Cd(II). The coal showed more affinity for Hg(II) ions under a weight-base determination.

Desorption of Metal Ions

To be useful in metal ion recycling processes, complexed metal ions should be easily desorbed under suitable conditions. Desorption experiments were performed with 25 mmol/L EDTA as the desorption agent. The low-rank Turkish lignites loaded with the maximum amounts of the respective metal ions were placed within the desorption medium, and the amount of metal ions desorbed in 60 minutes was measured. Table 3 shows the adsorption-desorption data of heavy metal

Table 2. Competitive Adsorption of Hg(II) and Cd(II) on Lignite

Metal Ion	Noncompetitive Adsorption (mg/g)	Competitive Adsorption (mg/g)
Hg(II)	1.55	1.98
Cd(II)	1.42	1.65

Table 3. Adsorption-Desorption Cycles for Hg(II) and Cd(II)

	Hg(II)		Cd(II)	
Cycle No.	Adsorption (mg/g)	Desorption (%)	Adsorption (mg/g)	Desorption (%)
1	1.55	87.2	1.42	88.0
2	1.51	89.5	1.42	87.1
3	1.50	86.1	1.40	87.9
4.	1.48	88.4	1.37	86.6
5	1.49	84.3	1.35	88.3
6	1.45	86.2	1.30	85.3
7	1.41	87.2	1.26	86.4
8	1.40	83.8	1.24	87.8
9	1.38	85.6	1.21	86.2
10	1.35	88.5	1.19	87.3

ions after 10 cycles of the consecutive adsorption and desorption procedure. This table clearly shows that these microbeads can be used repeatedly without significantly losing their adsorption capacities for the metal ions studied.

CONCLUSION

Adsorption can be an effective process for the removal and recovery of heavy metal ions from aqueous solutions. The removal of heavy metal ions from polluted environmental aquatic systems is only the first step in any remediation process. One possible advantage of using low-rank coals as the ion exchange medium in the remediation process is that the calorific content of the coal and the mineral matter inherent in the lignite could be used in a volume reduction step to produce a stabilized solid waste. For the metals investigated, the optimum adsorption was achieved at pH 4.0, which is clearly compatible with most environmental systems. Although the adsorption capacities of low-rank coals obtained in this study, 1.55 mg for mercury and 1.42 mg for cadmium per gram of coal, are significantly lower in comparison to those of synthetic ion exchange resins, the substantially lower cost of the low-rank coal indicates great potential for the removal of heavy metal ions from aqueous systems.

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