Preparation of Cibacron Blue F3GA-Attached Polyamide Hollow Fibers for Heavy Metal Removal

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ABSTRACT: Dye-affinity adsorption has been used increasingly for heavy metal removal. Synthetic hollow fibers have advantages as support matrices in comparison to conventional bead supports because they are not compressible and they eliminate internal diffusion limitations. The goal of this study was to investigate in detail the performance of hollow fibers composed of modified polyamide to which Cibacron Blue F3GA was attached for the removal of heavy metal ions. The Cibacron Blue F3GA loading was 1.2 mmol/g. The internal matrix was characterized by scanning electron microscopy. No significant changes in the hollow fiber cross-section or outer layer morphology were observed after dye modification. The effect of the initial concentration of heavy metal ions and medium pH on the adsorption efficiency were studied in a batch reactor. The adsorption capacity of the hollow fibers for the selected metal ions [i.e., Cu(II), Zn(II) and Ni(II)] were investigated in aqueous media with different amounts of these ions (10–400 ppm) and at different pH values (3.0–7.0). The maximum adsorptions of metal ions onto the Cibacron Blue F3GA-attached hollow fibers were 246.2 mg/g for Cu(II), 133.6 mg/g for Zn(II), and 332.7 mg/g for Ni(II). Furthermore, a Langmuir expression was calculated to extend the adsorption equilibrium. Nitric acid (0.1M) was chosen as the desorption solution. High desorption ratios (up to 97%) were observed in all cases. Consecutive adsorption/desorption operations showed the feasibility of repeated use of this novel sorbent system. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 3089–3098, 2002; DOI 10.1002/app.2338

Key words: hollow fibers; Cibacron Blue F3GA; sorbents

INTRODUCTION

Dye-affinity sorbents have been used increasingly for heavy metal removal.[1–3] Conventional chromatography with a packed column of gel beads as a support material is not easy to scale up because the pressure drop in packed columns is high, which leads to compaction of the bed under pressure and low flow rates.[4] Rigid porous particles

overcome the compressibility problem, but the particle size employed to prevent high operating pressures may lead to diffusional limitations that degrade performance. Packed-bed columns usually require long desorption times. In recent years, membrane chromatography has been introduced as an alternative to the traditional packed-bed column techniques.[5–7] The desirable properties of membranes are high porosity, large internal surface area, high chemical and mechanical stabilities, and the presence of functional groups for further derivatization.[7] The porosity and rigidity of the membrane structure provide high

flow-rates without special equipment. These membranes operate in convective mode, which results in reduced diffusion limitations and allows lower pressure drops and higher throughputs. Due to these advantages, microporous membranes are a very good alternative for heavy metal removal and have many advantages.[8–10] However, hollow fibers have advantages over flat membranes because a large surface area is available and also degraded membranes can be easily regenerated. Other potential advantages of hollow fibers are a short diffusion path, low pressure drop, and very short residence time for both adsorption and desorption.

The functionalization of hollow fibers has received increasing attention because of its applicability to many separation processes.[9,10] Recently, amidoxime-modified poly(acrylonitrile) fibers were used for uranium removal.[11] Iminodiacetate and glycidylmethacrylate-introduced polyethylene microfiltration hollow fibers were used for cobalt adsorption.[12] Phosphorylated polyethylene hollow fiber was prepared by radiation-induced cografting and used for metal separation.[13] A polypropylene hollow-fiber chromatographic system was used for trace-metal separation.[14] Poly-(acrylaminophosphonic-carboxyl-hydrazide)-type chelating fibers were used for the removal of heavy metal ions, including Cu(II), Cd(II), Co(II), Mn(II), Pb(II), Zn(II), Ni(II), and Cr(III).[15] Bis(2-ethylhexyl) phosphoric acid-impregnated polypropylene hollow fibers were used for selective preconcentration of Pb(II) ions.[16] Amidoxime, iminodiacetate, and phosphoric acid-functionalized polyethylene hollow fibers used for heavy metal collection have also been reported.[17]

In this work, a dye-affinity hollow fibers with polyamide as the support matrices were prepared. A dye-ligand, Cibacron Blue F3GA, was covalently attached to the polyamide hollow fibers and the adsorption–desorption behavior of heavy metal ions was investigated. System parameters, such as the adsorption conditions (i.e., initial concentration of heavy metal ions, medium pH), were varied to evaluate their effects on the performances of the dye-affinity hollow fibers.

EXPERIMENTAL

Materials

Commercially available polyamide hollow fiber was used as the basic matrix for heavy metal removal (Akzo; Wuppertal, Germany). Cibacron Blue F3GA was obtained from Polyscience (Warrington) and used without further purification. All other chemicals were reagent grade and were purchased from Merck AG (Darmstadt, Germany). All water used in the experiments was purified using a Barnstead (Dubuque, IA) ROpure LP® reverse osmosis unit with a high-flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpure® organic/colloid removal and ion-exchange packed-bed system. The resulting purified water (deionized water) had a specific conductivity of 18 MΩ cm^{-1}.

Methods

Dye Attachment to Polyamide Hollow Fibers

In the first step, polyamide hollow fibers were exposed to partial hydrolysis, and we avoided destroying mechanical integrity through the following procedure: The hollow fibers were magnetically stirred at 100 rpm with 3M HCl at a constant temperature of 30°C for 20 min. We then arrested the hydrolysis by washing with cold water (4°C). After hydrolysis, the polyamide hollow fibers were modified with Cibacron Blue F3GA. Cibacron Blue F3GA was covalently attached to the polyamide hollow fiber via the nucleophilic substitution reaction between the chloride of its triazine ring and the amide groups of the polyamide hollow fiber, with the elimination of NaCl under alkaline conditions. First, Cibacron Blue F3GA was dissolved in 10 mL of water (initial dye concentration = 4.0 mg/mL). This aqueous dye solution was transferred to the polyamide hollow fiber pieces (total length = 50 cm; total mass = 50 mg) in 90 mL distilled water, and then 4.0 g of NaOH were added. The medium was heated at 80°C in a sealed reactor and was stirred magnetically for 4 h. To remove the nonspecifically attached and/or diffused dye molecules in the pores, an extensive cleaning procedure was applied, which was as follows: The hollow fibers were first washed with deionized water and then were dispersed in methanol; the dispersion was sonicated for 2 h in an ultrasonic bath (200 watt; Bransonic 200). In the last stage, the hollow fibers were washed again with deionized water. Cibacron Blue F3GA-attached polyamide hollow fibers were stored at 4°C with 0.02% sodium azide to prohibit microbial contamination.

The release of the Cibacron Blue F3GA from the dye-attached hollow fibers was investigated at different pH values in the range of 3.0–7.0. These

media were the same that were used in the heavy metal adsorption experiments given later. Cibacron Blue F3GA release was also determined in the medium at a pH of 1.0 with $0.1M$ HNO_3, which was the medium used in the heavy metal desorption experiments. The medium with the Cibacron Blue F3GA-attached hollow fibers was incubated for 24 h at room temperature. Then, hollow fibers were removed from the medium, and the Cibacron Blue F3GA concentration in the supernatant was measured by spectrophotometry at 630 nm.

Characterization of Hollow Fibers

Elemental Analysis. The amounts of attached Cibacron Blue F3GA on the hollow fibers were obtained with an elemental analysis instrument (Leco, CHNS-932). The amount of Cibacron Blue F3GA attachment on the hollow fibers was calculated from these data by consideration of the sulfur stoichiometry.

Microscopic Observations. Microscopic observations and photographs of the the gold-coated hollow fibers were performed with a scanning electron microscope (SEM; Raster Electronen Microscopy, Leitz-AMR-1000, Germany).

Porosity Measurements. Pore volumes and average pore diameters greater than 20 Å were determined with a mercury porosimeter up to 2000 kg/cm^2 with a Carlo Erba model 200 (Italy). The surface area of the hollow fiber sample was measured with a surface-area apparatus (BET method).

Adsorption Studies

Adsorption of Cu(II), Zn(II), and Ni(II) from the single-metal-ion aqueous solutions was investigated in batch adsorption–equilibrium experiments. Effects of the initial concentrations of metal ions and pH of the medium on the adsorption capacity were studied. Aqueous metal ion solutions (20 mL) with different concentrations (10–400 ppm) were treated with the unmodified and Cibacron Blue F3GA-attached hollow fibers (total length = 50 cm; total mass = 50 mg) at different pH levels (3.0–7.0, adjusted with hydrochloric acid and sodium hydroxide). The flasks were magnetically stirred at an agitation speed of 600 rpm at room temperature. Copper nitrate, nickel nitrate, and zinc nitrate were used to prepare standard metal ion solutions. After the pre-

determined equilibrium time (2 h), the hollow fibers were separated from the adsorption medium, and the residual concentration of the heavy metal ions in the aqueous phase was measured with 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. Deuterium background correction was used. Pyrolitic-graphite-coated tubes were used for AAS measurements. All instrumental conditions were optimized for maximum sensitivity as described by the manufacturer. Each sample was read three times, and a mean value and relative standard deviation were computed. Calibrations were performed in the range of analysis, and a correlation coefficient for the calibration curve of .98 or greater was obtained. The instrument response was periodically checked with known metal standards. Adsorption values (mg/g) were calculated as the differences in initial and final heavy metal ion concentrations. To eliminate contamination, all glassware and plasticware were washed with RBS detergent (Pierce; Rockford, IL) and rinsed with deionized water.

Desorption of metal ions was performed in $0.1M$ HNO_3. The hollow-fibers-loaded metal ions were placed in this desorption medium and stirred at 600 rpm for 30 min at room temperature. The final metal ion concentration in the aqueous phase was determined with an AAS. The desorption ratio was calculated from the amount of metal ions adsorbed on the hollow fibers and the final metal ion concentration in the desorption medium with the following equation:

Desorption ratio

$$= \frac{\text{Amount of metal ions desorbed to the elution medium}}{\text{Amount of metal ions adsorbed on the hollow fibers}} \times 100 \quad (1)$$

To test the reusability of the Cibacron Blue F3GA-attached hollow fibers, adsorption–desorption cycles were repeated five times with the same hollow fiber pieces.

RESULTS AND DISCUSSION

Modified Polyamide Hollow Fibers

The SEM micrographs given in Figure 1 show the surface structure and the cross-section of the
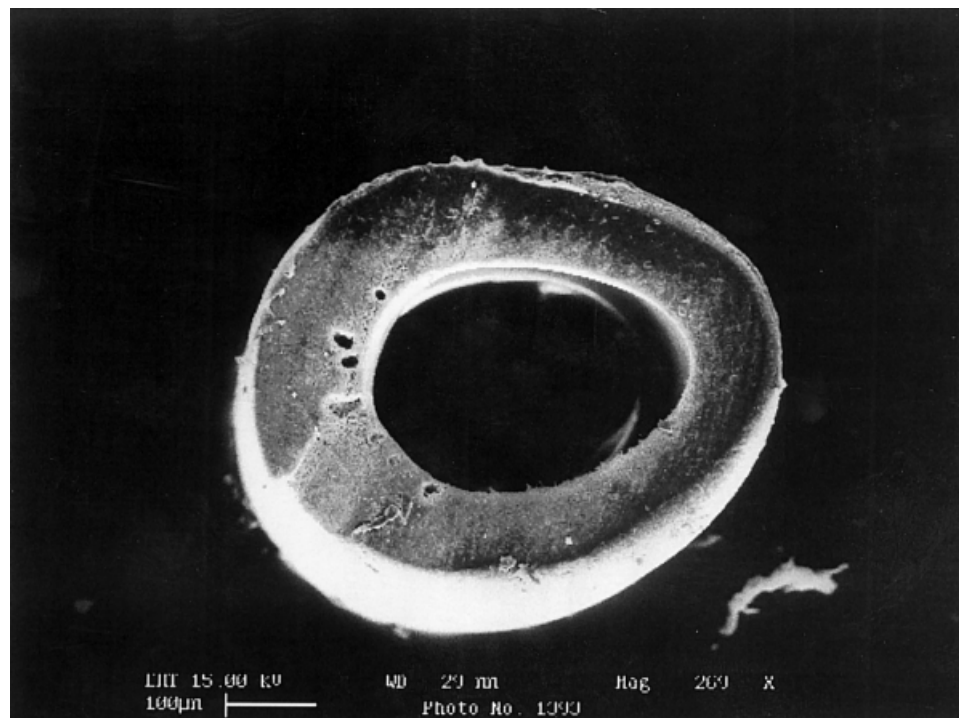
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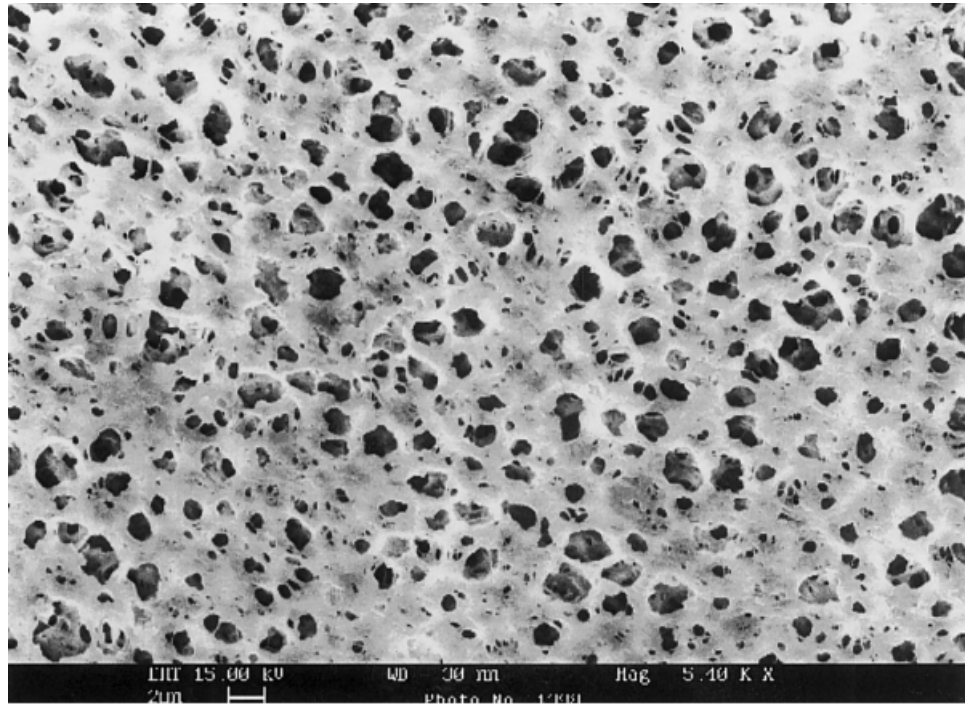
(a)

(b)

Figure 1 The representative SEM micrographs of polyamide hollow fibers: (a) inner surface, (b) outer surface, and (c) cross-sectional area.

(c)

**Figure 1** (*Continued from the previous page*)

polyamide hollow fibers. As shown in the inner, outer, and cross-sectional surface photographs, the hollow fibers had large pores (transport canals); the micropore dimensions were around 0.4 μm. The hollow fiber surface seemed rough and heterogeneous. These large pores reduced diffusional resistance and facilitated mass transfer because of a high inner surface area. This also provided higher heavy metal chelation and enhanced adsorption capacity. In contrast to the packed-bed columns, membrane chromatography brought the heavy metal ions into the proximity of the Cibacron Blue F3GA molecules in the large pores by convection, thus reducing the resistance to mass transfer. No significant changes of hollow fiber cross-section and outer layer morphology were observed after dye modification. The characteristic data of the commercialy available poly-

amide hollow fibers (obtained from the manufacturer) are summarized in Table I.

According to the mercury porosimetry data, the pore radii of the polyamide hollow fibers changed between 200 and 430 nm. This indicates that the hollow fibers contained mainly macropores. This pore diameter range was possibly available for diffusion of the heavy metal ions. Ionic diameters were 0.146 nm for Zn(II), 0.150 nm for Cu(II), and 0.144 nm for Ni(II). Based on these data, it was concluded that the polyamide hollow fibers had effective pore structures for liquid chromatographic separation of heavy metal ions. The specific surface area of the hollow fiber was found to be 16.0 m^2/g of polymer by the BET method after Cibacron Blue F3GA attachment. Therefore, these pores were not blocked by the dye molecules.

Table I Physical Properties of the Microporous Polyamide Hollow Fibers

| Type	Normal Pore Size (nm)	Maximum Pore Size (nm)	BET Surface Area (m^2/g)	Flux (mL/min bar cm)
P A 386 C	200 ± 5.0	430 ± 9.5	16.0	13
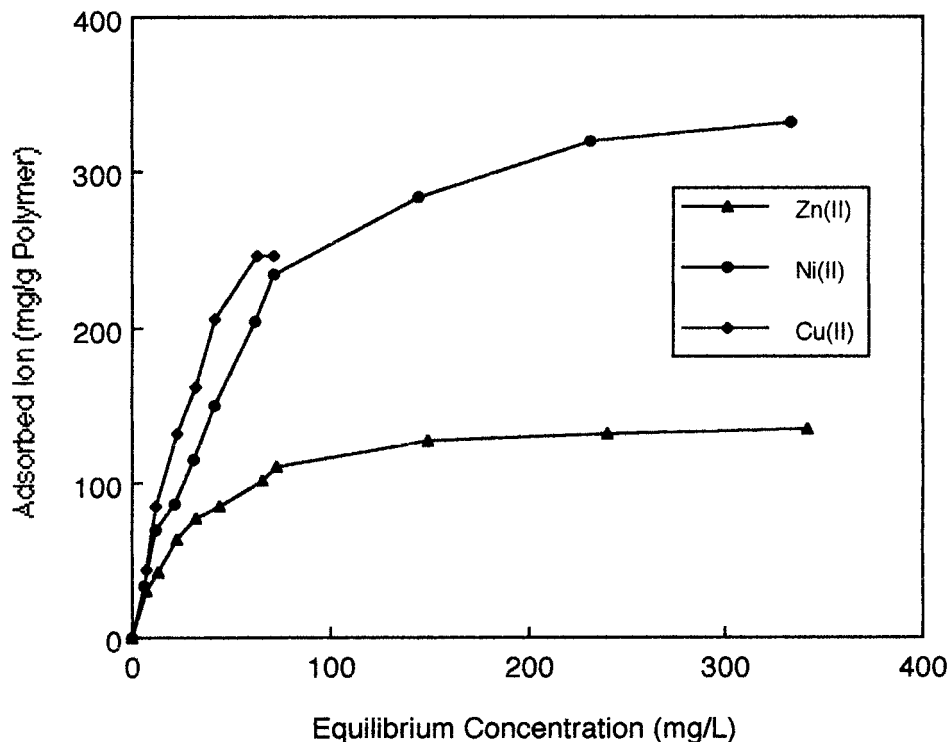
Figure 2   Adsorption capacity of Cibacron Blue F3GA-attached hollow fibers for metal ions. Cibacron Blue F3GA loading = 1.2 mmol/g; pH = 6.0; temperature = 20°C. Each datum is the average from five parallel studies.

Cibacron Blue F3GA is a monochlorotriazine dye, and it contains three sulfonic acid groups and four basic primary and secondary amino groups. The chelation of metal ions to the dye molecules occurs mostly through oxygen and nitrogen atoms. The Cibacron Blue F3GA molecules were covalently attached to the hollow fibers. The Cibacron Blue F3GA-attached hollow fibers were extensively washed to ensure that there was no dye leakage from any of the dye-attached hollow fibers or in any media used at the adsorption and/or desorption stages. Visual observations (the color of the hollow fibers) ensured attachment of dye molecules. Unmodified and Cibacron Blue F3GA-attached hollow fibers were subjected to elemental analysis. The amount of Cibacron Blue F3GA attached to the hollow fibers was evaluated from these data, by consideration of the stoichiometry, which was found to be 1.2 mmol/g.

Adsorption Isotherms

Figure 2 shows the Cu(II), Zn(II), and Ni(II) adsorption curves of the Cibacron Blue F3GA-attached hollow fibers. The amount of metal ions adsorbed per unit mass of the polymer (i.e., adsorption capacity) increased first with the initial concentration of metal ions and then reached a plateau value, which represents saturation of the active adsorption sites (which were available for specific metal ions) on the hollow fibers. Adsorption of Zn(II) and Ni(II) ions reached saturation at higher bulk concentrations (i.e., at about 200 ppm), whereas Cu(II) adsorption reached saturation at a lower concentration (i.e., about 40 ppm). The binding capacities of the Cibacron Blue F3GA-attached hollow fibers were 246.2 mg/g (3.9 mmol/g) for Cu(II), 133.6 mg/g (2.0 mmol/g) for Zn(II), and 332.7 mg/g (5.7 mmol/g) for Ni(II). It appears that the Cibacron Blue F3GA-attached hollow fibers had the strongest affinity for Ni(II) ions. The affinity order of the metal ions was as follows:

$$Ni(II) > Cu(II) > Zn(II)$$
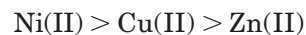
The nonspecific adsorptions of metal ions on the unmodified hollow fibers were very low, about 4.2 mg for Cu(II), 3.6 mg for Zn(II), and 8.7 mg for
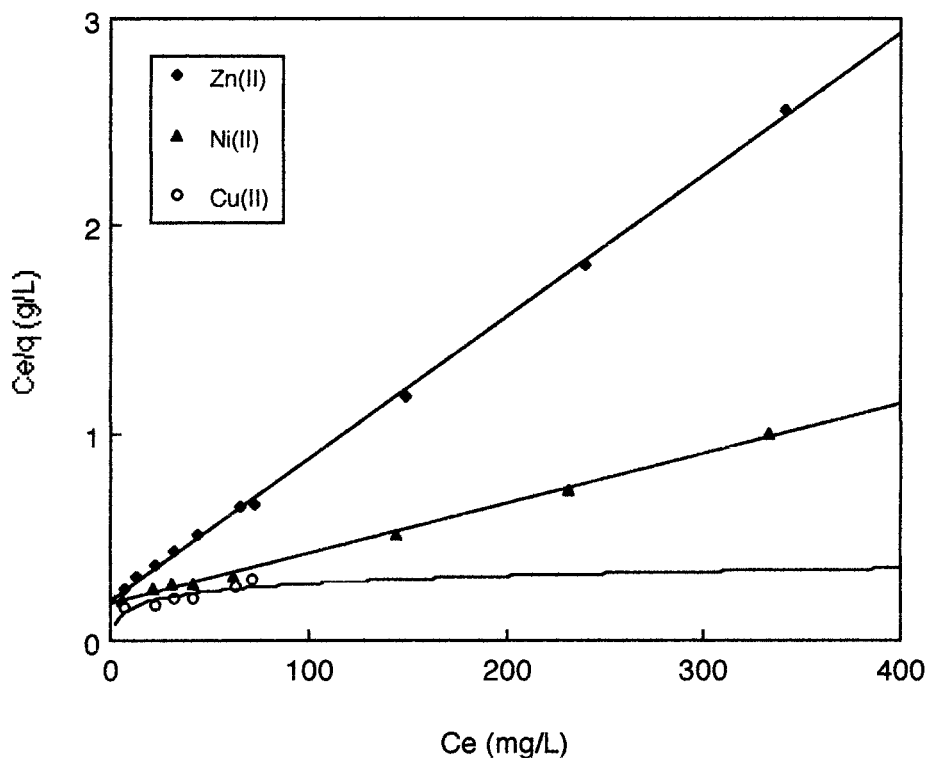
Figure 3   Linear representation of the Langmuir equation of heavy metal ions with dye-attached hollow fibers. Cibacron Blue F3GA Loading = 1.2 mmol/g; temperature = 20°C. Each datum is the average from five parallel studies.

Ni(II) per gram of the polymer. The unmodified hollow fibers did not contain metal chelating groups. Preferred coordination structure and preferred coordinating ligand atoms may be used for this nonspecific adsorption. For example, metal ions may interact with nitrogen atoms as the ligand. Diffusion of metal ions into the pores of the hollow fibers may also contribute to this nonspecific adsorption.

An adsorption isotherm was used to characterize the interaction of the each heavy metal ions with the adsorbents. This provided a relationship between the concentration of heavy metal ions in the solution and the amount of heavy metal ions adsorbed onto the solid phase when the two phases were at equilibrium. The Langmuir adsorption model assumes that the molecules are adsorbed at a fixed number of well-defined sites, each of which can only hold one molecule. These sites are also assumed to be energetically equivalent and distant to each other so that there are no interactions between molecules adsorbed to adjacent sites.[18]

A semireciprocal plot of the experimental data for the adsorption of Cu(II), Zn(II), and Ni(II) ions

is presented in Figure 3. The corresponding semireciprocal transformations of the equilibrium data for heavy metal ions and Cibacron Blue F3GA-attached hollow fibers gave rise to a linear plot, indicating that the Langmuir model could be applied in this system, which was described by the equation:

$$dq/dt = k_1 C(q_m - q) - k_2 q \qquad (2)$$

where C is the concentration of heavy metal ions in solution (mg/L), q is the solid-phase concentration of the adsorbed heavy metal ions (mg/g), and q_m is the maximum adsorption capacity of the hollow fibers (mg/g). Equation (2) leads to

$$q^* = q_m C^*/(K_d + C^*) \qquad (3)$$

where K_d (k_2/k_1) is the desorption constant of the system.

The parameters q_m and K_d were determined by nonlinear regression with commercially available software and are shown in Table II. The standard deviation of the values determined by regression

Table II   Adsorption Parameters of Heavy Metals on Hollow Fibers

Metal Ion	$q_{m \text{ Measured}}$ (mg/g)	$q_{m \text{ Calculated}}$ (mg/g)	K_d (mg/mL)
Zn(II)	133.6 ± 3.8	136.6 ± 3.6	26.8 ± 1.20
Cu(II)	246.2 ± 4.8	248.4 ± 3.7	32.6 ± 1.32
Ni(II)	332.7 ± 5.9	370.0 ± 4.5	65.9 ± 1.44

Each datum is the average from five parallel studies.

analysis was comparatively low. When the Cibacron Blue F3GA-attached hollow fibers were used in the adsorption tests, the order of the q_m values for both cases was as follows:
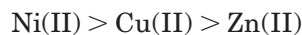
$$Ni(II) > Cu(II) > Zn(II)$$

The amount of Cibacron Blue F3GA loading on the surface of hollow fibers was 1.2 mmol/g. The binding ratios of the dye and heavy metal ions were found to be 5.0, 3.0, and 2.0 heavy metal ions per dye molecule for Ni(II), Cu(II), and Zn(II), respectively.

The measured adsorption capacities for Cibacron Blue F3GA-attached hollow fibers were lower according to the calculated adsorption capacities. This difference was due to the steric/geometric hindrances between the dye molecules and heavy metal ions on the surface of polyamide hollow fibers.

Effect of pH on Metal Binding

Metal ion adsorption on both nonspecific and specific sorbents is pH dependent. In the absence of metal chelating groups, the precipitation of the metal ions are affected by the concentration and form of soluble metal species. The solubility of metal ions is governed by hydroxide or carbonate concentration. Precipitation of metal ions becomes significant at approximately pH 7.0 for all metal ions. The theoretical and experimental precipitation curves indicate that precipitation begins above these pHs, which also depends on the concentration of metal ions in the medium. Therefore, in our study, to establish the effect of pH on the adsorption of metal ions onto the Cibacron Blue F3GA-attached hollow fibers, we repeated the batch equilibrium studies at different pH levels in the range of 3.0–7.0. In this group of experiments, the initial concentration of metal ions was 50 ppm for all ions. Figure 4 shows the pH effect.

The adsorption capacities of the Cibacron Blue F3GA-attached hollow fibers were 85.1 mg (1.3 mmol), 149 mg (2.53 mmol), and 205 mg (3.2 mmol) per gram of the polymer for Cu(II), Zn(II), and Ni(II), respectively. It appears that the Cibacron Blue F3GA-attached hollow fibers had the strongest affinity for Ni(II) ions at low metal ion concentrations. The affinity order of metal ions was as follows:

$$Cu(II) > Ni(II) > Zn(II)$$

Cibacron Blue F3GA-attached hollow fibers exhibited a low affinity for heavy metal ions in acidic conditions (pH < 4.0), a somewhat higher affinity between pH 6.0 and 7.0. The difference in the adsorption behavior of Ni(II) and Cu(II) compared to Zn(II) can be explained by the different affinity of heavy metal ions for the donor atoms (i.e., oxygen and nitrogen) in the dye–ligand Cibacron Blue F3GA. A difference in coordination behavior was most probably also the case for the attached Cibacron Blue F3GA ligand resulting in a relatively high adsorption of metal ions at high pH under noncompetitive adsorption conditions.

Comparison with the Related Literature

In the literature, a wide variety of adsorbents with a wide range of adsorption capacities for heavy metal ions have been reported. Dev and Rao reported 51.5 mg of Cd(II)/g and 79 mg of Pb(II)/g adsorption capacities for polystyrene–vinylbenzene macroreticular resin functionalized with bis-(N,N'-salicylidene) 1,3-propanediamine.[19] Roozemond et al. showed an adsorption capacity of 40 mg of Cd(II)/g with pyrazole-containing poly(styrene-divinyl benzene) adsorbents.[20] Ibrahim et al. used thionein-immobilized pHEMA microspheres and removed 44.8 mg of Cd(II)/g from aqueous solution.[21] Denizli et al. prepared magnetic poly(methylmethacrylate) microspheres modified with ethylene diamine, and they reported 12.8 mg of Cu(II)/g.[22] Arpa et al. used dye-affinity microspheres for heavy metal removal, and they achieved 16.5 and 4.4 mg/g adsorption capacities for Pb(II) and Cd(II) ions, respectively.[23] Sarkar et al. used salicyl-aldoxime-modified silica gel for the recovery of Cu(II), Co(II), Ni(II), Zn(II), and Fe(III) ions, and they reported adsorption capacities in the range of 2.5–10.0 mg/g.[24] Denizli et al. prepared dithiocarbamate-modified polystyrene microbeads, and the adsorption capacities were 1.92 mg/g for Cd(II), 3.76
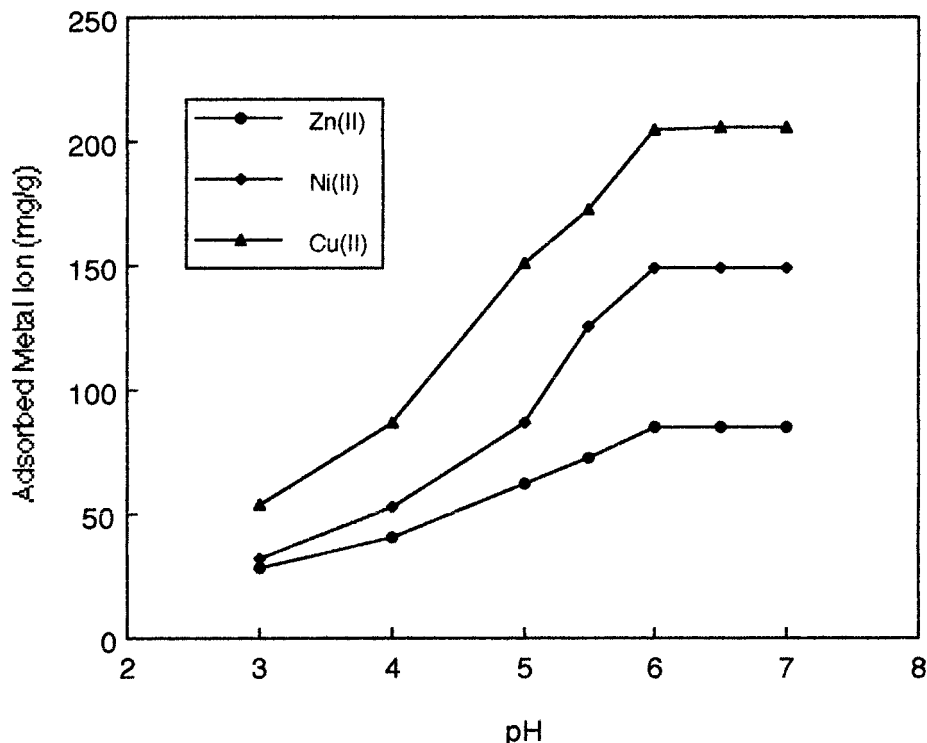
Figure 4 Effect of pH on adsorption of metal ions on Cibacron Blue F3GA-attached hollow fibers. Cibacron Blue F3GA loading = 1.2 mmol/g; initial concentration of metal ions = 50 ppm; temperature = 20°C. Each datum is the average from five parallel studies.

mg/g for Cu(II), 6.17 mg/g for Pb(II), and 22.92 mg/g for Hg(II) ions.[25] When these data are compared, it seems that the adsorption capacities achieved with the Cibacron Blue F3GA-attached polyamide hollow fibers were very satisfactory.

Desorption and Repeated Use

Desorption of the adsorbed metal ions from the Cibacron Blue F3GA-attached hollow fibers was also studied in a batch experimental setup. The dye-attached hollow fibers carrying the maximum amounts of the respective metal ions were placed within the desorption medium containing $0.1M$ HNO$_3$, and the amount of metal ions desorbed in 2 h was measured. The desorption ratio was then calculated with the expression given in eq. (1). Desorption ratios were very high (up to 97%) with the desorption agent and conditions used for all metal ions.

To obtain the reusability of the Cibacron Blue F3GA-attached hollow fibers, the adsorption–desorption cycle was repeated five times with the same sorbent. As shown in Table III, the adsorp-

tion capacity of the sorbent for all metal ions did not significantly change during the repeated adsorption–desorption operations.

CONCLUSIONS

Heavy metal ions are known to be toxic, and especially cadmium, arsenic, mercury, chromium, copper, lead, nickel, selenium, silver, and zinc are released into the environment in quantities that pose a risk to living systems.[26] Removal of heavy metal ions from aquatic systems is carried out by classical methods of membrane techniques.[27] A chelating microporous polyamide hollow-fiber membrane containing Cibacron Blue F3GA was prepared and was applied to the removal of copper, zinc, and nickel ions from aqueous solutions. Cibacron Blue F3GA-carrying polyamide hollow-fiber membranes (1.2 mmol/g) showed great promise in the removal of heavy metal ions from aqueous media. Some results are summarized as follows: Adsorption of heavy metal ions on the

Table III   Heavy Metal Ions Adsorption Capacity of Cibacron Blue F3GA-Attached Hollow Fibers After Repeated Adsorption–Desorption Cycle

Cycle Number	Zn(II)		Cu(II)		Ni(II)	
	Adsorption (mg/g)	Desorption (%)	Adsorption (mg/g)	Desorption (%)	Adsorption (mg/g)	Desorption (%)
1	85.1 ± 2.4	95.5 ± 3.8	205.0 ± 9.6	96.6 ± 5.5	149.0 ± 7.2	95.5 ± 4.0
2	84.3 ± 2.6	97.2 ± 5.1	204.2 ± 8.8	98.4 ± 5.0	148.4 ± 6.5	97.2 ± 3.8
3	84.1 ± 2.3	96.8 ± 2.9	203.5 ± 7.9	97.2 ± 4.1	148.1 ± 5.7	95.7 ± 5.1
4	83.5 ± 2.2	97.9 ± 3.3	203.2 ± 9.2	95.4 ± 3.9	147.2 ± 7.5	96.4 ± 4.4
5	83.0 ± 2.7	98.5 ± 4.5	202.7 ± 9.0	98.3 ± 6.1	146.5 ± 6.6	95.8 ± 5.8

Each datum is the average from five parallel studies. Initial concentrations of metal ions = 50 ppm; pH = 6.0; temperature = 20°C.

unmodified polyamide hollow-fiber membranes was very low: 4.2 mg/g for Cu(II), 3.6 mg/g for Zn(II), and 8.7 mg/g for Ni(II) ions. The maximum adsorption capacities of the dye-modified membranes were 246.2 mg/g for Cu(II), 133.6 mg/g for Zn(II), and 332.7 mg/g for Ni(II) ions. The adsorption capacity increased with increasing pH, reaching plateau values at a pH of around 6.0. The order of affinity was Ni(II) > Cu(II) > Zn(II). Repeated adsorption and desorption cycles showed the feasibility of these dye-modified hollow fibers for heavy metal adsorption.

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