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Cibacron Blue F3GA-incorporated macroporous poly(2-hydroxyethyl methacrylate) affinity membranes for heavy metal removal

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Abstract

Macroporous poly(2-hydroxyethyl methacrylate), poly(HEMA), membranes were prepared by UV-initiated photopolymerization of HEMA in the presence of an initiator (azobisisobutyronitrile, AIBN). An affinity dye, i.e., Cibacron Blue F3GA was then incorporated covalently. These affinity membranes with a swelling ratio of 58%, and carrying 10.67 mmol Cibacron Blue F3GA/m² membrane were used in the adsorption/desorption of some selected heavy metal ions [i.e., As(III), Cd(II) and Pb(II)] from aqueous media. Very high adsorption rates were observed and adsorption equilibria were reached in about 30 min. The maximum adsorptions of heavy metal ions onto the dye-incorporated affinity membranes from their single solutions were 12.6 mmol/m² for As(III), 61.0 mol/m² for Cd(II) and 79.0 mol/m² for Pb(II). However, when the heavy metal ions competed (in the case of the adsorption from their mixture) the amounts of adsorption for As(III), Cd(II) and Pb(II) were quite close. Desorption of heavy metal ions was carried out by using 0.1 M HNO₃ (pH 1.0). Up to 95% of the adsorbed heavy metal ions were desorbed in 60 min. Repeated adsorption/desorption cycles showed the feasibility of this novel affinity membrane for heavy metal removal.

Keywords: Affinity membranes; Adsorption; Cibacron Blue; Poly(2-hydroxyethyl methacrylate); Metals; Arsenic; Cadmium; Lead

1. Introduction

The presence of heavy metal ions in the environment is a major concern due to their toxicity to many life forms. Treatment of polluted waters containing into a smaller volume followed by recovery or secure disposal. Heavy metal ions can be removed by adsorption on solid carriers. Nonspecific sorbents, such as activated charcoal, metal oxides, silica and ion-exchange resins have been used [1–3]. Recently however, the use of specific sorbents has been

heavy metal ions requires concentration of the metals

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considered one of the most promising approaches [4–6]. Specific sorbents consist of a ligand (e.g., ion-exchange material or chelating agents) which interacts specifically with the metal ions and a carrier matrix which may be an inorganic material (e.g., aluminium oxide, silica or glass) or polymeric carriers [e.g., polystyrene, polyacrylamide, poly (maleic anhydride) or polymethylmethacrylate] [7–11].

As carrier matrices, polymers have attracted the most attention because they may be easily produced with a wide variety of compositions and modified into specific sorbents, by introducing a variety of ligands. Synthetic polymers both in membrane and bead forms have almost entirely displaced inorganic carriers, with few exceptions in the separation of heavy metal ions [12–15]. One of the most critical points in the use of porous sorbent systems is their pore structure. Optimization of pore structures of the carrier matrices is a very important issue to achieve both high adsorption rates and high adsorption capacities.

Supported liquid membranes have been also attracting attention as a potential method for heavy metal removal [16–19], which are basically three-phase membrane extraction processes. Two immiscible phases are separated by a membrane phase which is immiscible with the other two phases. Extraction of solute (e.g., metal ions) is achieved by the mass transfer between two miscible phases through the membrane phase.

In this study, we propose using a membrane, not as a mass transfer control unit as in the case of supported liquid membranes, but as a carrier matrix of a membrane-based sorbent system which may be applied in several ways including as a spiral-type membrane module [20]. This affinity membrane system using swellable, macroporous poly(2-hydroxyethyl methacrylate), poly(HEMA) membranes was prepared by UV-initiated photopolymerization of HEMA in the presence of an initiator (azobisisobutyronitrile, AIBN). An affinity dye, i.e., Cibacron Blue F3GA was then incorporated covalently. Adsorption/desorption of some selected heavy metal ions [i.e., As(III), Cd(II) and Pb(II)] from aqueous media was studied. Here, we present preparation and characterization of these affinity membranes, and the potential for their use in heavy metal adsorption/ desorption.

2. Experimental

2.1. Preparation and characterization of poly(HEMA) membranes

The poly(2-hydroxyethyl methacrylate), poly-(HEMA), membrane was prepared as previously described [21]. The monomer, HEMA, was obtained from Fluka (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroquinone inhibitor and stored at 4°C until use. A 2-ml volume of HEMA containing 5 mg azobisisobutyronitrile (Fluka) as polymerization initiator was mixed with 3 ml of 0.1 M SnCl₄. The mixture was then poured into a round glass mould (9 cm in diameter) and exposed to ultraviolet radiation (12 W lamp, P.W. Allen, USA) for 10 min under nitrogen atmosphere. The membrane obtained was washed several times with distilled water and cut into square pieces (0.5 cm in length) with a perforator.

In order to incorporate the dye-ligand (i.e., Cibacron Blue F3GA) into the poly(HEMA) membrane, the following procedure was applied: 10 ml of the aqueous solution containing 300 mg Cibacron Blue F3GA (BDH, UK) was poured into 90 ml of the solution of the poly(HEMA) membrane pieces in distilled water, and then 4.0 g of NaOH was added. The medium was heated in a sealed reactor for 4 h at a stirring rate of 400 rpm, and at a constant temperature of 80°C. The Cibacron Blue F3GA-incorporated poly(HEMA) membranes were filtered and washed with distilled water and methanol several times until all of the physically absorbed (or adsorbed) dye molecules were removed. The amount of dye molecules covalently incorporated to the poly(HEMA) membrane was evaluated from the elemental analysis data of the dried samples obtained by using an elemental analysis device (Leco, CHNS-932, USA) [22].

In order to determine the swelling behaviour of poly(HEMA) membranes, initially dry membrane pieces (1 cm²) were placed into distilled water and kept at a constant temperature of $25\pm0.5^{\circ}$ C. Swollen membranes were periodically removed and weighed by an electronic balance (Shimadzu, Japan, EB. $280\pm1\times10^{-3}$ g). The water contents of the swollen membranes were calculated by using the following expression:

Swelling ratio% =
$$[(W_s - W_o)/W_o] \times 100$$
 (1)

where W_0 and W_s are the mass of membrane before and after swelling, respectively.

In order to observe the surface and bulk structures of the poly(HEMA) membranes, scanning electron micrographs of the gold coated samples were taken with a SEM (Model: raster electronen microscopy, Leitz-AMR-1000, Germany).

FTIR spectra of the dye (i.e., Cibacron Blue F3GA), and the plain and Cibacron Blue F3GA-incorporated poly(HEMA) membranes were obtained by using a FTIR spectrophotometer (FTIR 8000 Series, Shimadzu, Japan). The dry poly(HEMA) membrane (about 0.1 g) was thoroughly mixed with KBr (0.1 g, IR Grade, Merck, Germany) and pressed into tablet form and the spectrum was then recorded.

2.2. Heavy metal adsorption/desorption

Adsorption of As(III), Cd(II) and Pb(II) from the single metal ion (not together) aqueous solutions was investigated in batch adsorption-equilibrium experiments. Effects of the initial concentration of metal ions and pH of the medium on the adsorption rate and capacity were studied. 20-ml aliquots of aqueous metal ion solution of different concentrations (in the range of 0.024-4.45 mmol/l) were treated with the plain and Cibacron Blue F3GA-incorporated poly-(HEMA) membranes (the total external surface area of the dry membranes used in each batch: 0.01 m²/1), at different pH (in the range of 3.0-10.0, adjusted with universal buffer solution), at room temperature, in flasks agitated magnetically at an agitation speed of 600 rpm. After the predetermined adsorption time, the membranes were separated from the adsorption medium and the concentration of the metal ions in the aqueous phase was measured by using a graphite furnace atomic absorption spectrophotometer (GBC 932 AA, Australia). In order to prevent signal decreasing during the graphite furnace atomic absorption measumerents for As(III) analysis, 2000 ppm Ni(II) modifier was added to the sample solution (with a 1:1 ratio). The amount of adsorbed ions was obtained by using the following expression.

$$Q = [(C_0 - C) \cdot V]/A \tag{2}$$

where Q is the amount of metal ions adsorbed onto

unit surface area of the poly(HEMA) membrane (mg/m^2) ; C_o and C are the concentrations of the metal ions in the initial solution and in the aqueous phase after adsorption, respectively (mg/ml); V is the volume of the aqueous phase (ml); and A is the surface area of the poly(HEMA) membrane used (m^2) .

Competitive adsorption of As(III), Cd(II) and Pb(II) from their mixture was also investigated in batch-wise form. A solution (20 ml) containing different amounts of each metal ion was treated with the Cibacron Blue F3GA-incorporated poly(HEMA) membrane at a pH of 7.0, at room temperature in flasks agitated magnetically at 600 rpm. After adsorption, the concentration of the metal ions in the supernatant was obtained by an atomic absorption spectrophotometer.

Desorption of heavy metal ions was studied in 0.1 M HNO₃ solution at pH 1.0. The poly(HEMA) membrane loaded with metal ions was 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 by using an atomic absorption spectrophotometer. In order to prevent signal decreasing during the graphite furnace atomic absorption measumerents for As(III) analysis, 2000 ppm Ni(II) modifier was added to the sample solution (with a 1:1 ratio). The desorption ratio was calculated from the amount of metal ions adsorbed on the membrane and the final metal ion concentration in the desorption medium, by using the following equation.

Desorption ratio =
$$\frac{\text{Amount of metal ions desorbed to the elution medium}}{\text{Amount of metal ions adsorbed on the membrane}} \times 100$$
 (3)

In order to evaluate the reusability of the Cibacron Blue F3GA-incorporated poly(HEMA) membranes, adsorption/desorption cycles were repeated three times by using the same affinity membrane.

3. Results and discussion

3.1. Properties of poly(HEMA) membranes

Poly(HEMA) membranes prepared in this study are hydrophilic, cross-linked structures, i.e., hydrogels, therefore they do swell in aqueous media, but

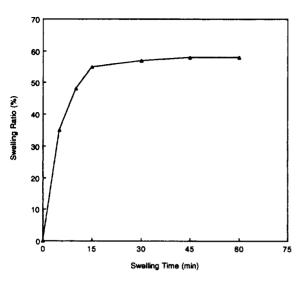
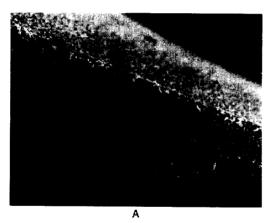


Fig. 1. Swelling of poly(HEMA) membrane as a function of time.



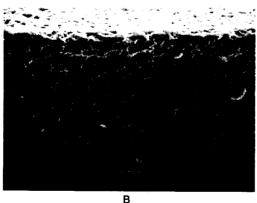


Fig. 2. SEM micrographs of poly(HEMA) membrane, (A) cross-section and (B) surface.

do not dissolve [23]. Fig. 1 shows swelling behaviour of a typical poly(HEMA) membrane prepared in this study. As seen here, swelling occurs rapidly and the equilibrium swelling is reached in about 20 min. Note that the equilibrium swelling value of the poly(HEMA) membrane used in heavy metal adsorption/desorption experiments performed here was about 58% in base weight.

The SEM micrographs given in Fig. 2A and Fig. 2B show the cross-section and surface structures of the poly(HEMA) membrane, respectively. As clearly seen here, the membrane exhibits an asymmetric and highly open pore structure which may lead to high internal surface area (implying high adsorption capacity) with low diffusional resistance in the matrix (implying high adsorption rate). Note that, achieving both high adsorption capacities and rates were the main concerns in the preparation of the affinity membranes for heavy metal removal in this study.

As mentioned before, Cibacron Blue F3GA was selected as the affinity ligand and incorporated within the poly(HEMA) membranes. Fig. 3 gives the chemical structure of this dye. Note that the possible active sites to react with heavy metal ions are -SO₃H, -NH and -NH₂ groups. Fig. 4 gives the FTIR spectra of the plain and dye-incorporated poly(HEMA) membranes and also of the dye. The bands observed at 1075 cm⁻¹, 1155 cm⁻¹, 1280 cm⁻¹ and 3380 cm⁻¹ represent symmetric stretching of S=O, asymmetric stretching of S=O and aromatic C-N vibration, respectively, as also pointed out on the chemical structure of the dye (Fig. 3). These bands may be considered as an indication of the presence of Cibacron Blue F3GA within the poly-(HEMA) membrane.

Elemental analysis of the plain and Cibacron Blue F3GA-incorporated poly(HEMA) membranes was performed and the incorporation of the Cibacron

Fig. 3. Chemical structure of Cibacron Blue F3GA.

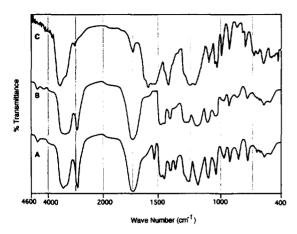


Fig. 4. FTIR spectra of (A) poly(HEMA), (B) Cibacron Blue F3GA, (C) Cibacron Blue F3GA-incorporated poly(HEMA) membrane.

Blue F3GA was found to be 10.67 mmol/m² from the stoichiometry.

The leakage of the dye was also studied. There was no leakage in any of the adsorption and desorption media which assured that the washing procedure was quite satisfactory for removal of physically adsorbed Cibacron Blue F3GA molecules from the poly(HEMA) membrane.

3.2. Adsorption/desorption studies

3.2.1. Adsorption rates

The adsorption rates of heavy metal ions [i.e., As(III), Cd(II) and Pb(II)] on the dye-incorporated poly(HEMA) membrane as a function of time were determined (Fig. 5). Note that these batch experiments were performed by using single (not together) solutions of the relevant ions. The initial concentrations of the ions within the aqueous phase were changed in the range of 0.024 to 4.45 mmol/l. As seen from this figure, very high adsorption rates are observed at the beginning of adsorption and then plateau values (i.e., show the adsorption equilibria) are gradually reached within 30 min for all metal ions. Adsorption of metal ions was very fast, especially when the metal ion concentration was high. This may be due to high driving force which is the metal ion concentration difference between the liquid (i.e., adsorption medium) and the solid (i.e., the membrane) phases, in the case of high metal ion concentration. Notice that Pb(II) and Cd(II) were adsorbed much faster than As(III) due to much higher affinity of the ligand (i.e., Cibacron Blue F3GA) molecules to these ions. The order of adsorption rate is as follows: Pb(II)>Cd(II)>As(III).

Experimental data on the adsorption kinetics of heavy metal ions by various sorbent systems in membrane and microsphere form have shown a wide range of adsorption rates. For example, Reed and Matsumoto [24,25] have considered 6 h as a short equilibrium time in their cadmium adsorption kinetic studies, in which they have used activated carbon as sorbent. Marchese et al. [26] have investigated separation of cobalt, nickel and copper ions with alamine liquid membranes and they reported that equilibrium was achieved in about 4-5 Shreedhara-Murthy and Ryan [27] have investigated mercury, copper, cadmium, lead and uranium adsorption on cellulose-dithiocarbamate resins and reported that the adsorption rates were very slow. Egawa [28] has studied uranium adsorption on polyacrylonitrile fibers containing amidoxime groups and reported 7 h equilibrium adsorption time. Teramoto et al. [29] reported that with a spiral-type supported liquid membrane model a steady state was reached in about 4 h. Note that in such an adsorption process, there are several parameters which determine the adsorption rate, such as 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, chelateformation rate and of course existance of other ions which may compete with the ions of interest for the active adsorption sites. All individual experimental studies published in the literature have been performed at different conditions. Therefore, it can be concluded that, it is almost impossible to compare the adsorption rates reported. However, the adsorption rates obtained with the affinity membranes produced by us seem to be very satisfactory.

3.3. Adsorption capacites

3.3.1. Effects of initial concentration of metal ions

The heavy metal ion adsorption capacities of the Cibacron Blue F3GA-incorporated poly(HEMA) membrane as a function of the initial concentration of metal ions within the aqueous phase are given in

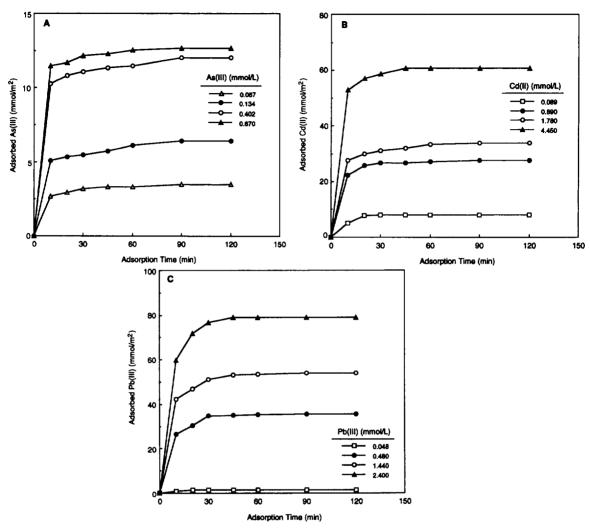


Fig. 5. Adsorption rates of heavy metal ions on the Cibacron Blue F3GA-incorporated poly(HEMA) membrane: (A) for As(III), (B) for Cd(II), and (C) for Pb(II). Temperature: 20°C; pH:7.0 and total membrane surface area in each batch, 0.01 m²/1.

Fig. 6. This figure was prepared by using the plateau values shown in Fig. 5. Note that adsorption capacities for As(III) ions were much lower than the others, therefore an enlarged graph for these ions is also given on the figure.

The amount of metal ions adsorbed per unit surface area of the polymer (i.e., the adsorption capacity) increased first with the initial concentration of metal ions then reached a plateau value which represents saturation of the active points (which are available for specific metal ions) on the membranes. These plateau values are 0.40, 3.56 and 1.92 mmol/l

for As(III), Cd(II) and Pb(II), respectively. The maximum adsorption capacities of the dye-incorporated poly(HEMA) membranes are 12.6, 61.0 and 79.0 mmol/m² of the membrane for As(III), Cd(II) and Pb(II), respectively, at pH 7.0. The order of affinity is as follows: Pb(II)>Cd(II)>As(III).

It should be noted that the non-specific adsorption values (adsorptions on the plain poly(HEMA) membrane) of heavy metal ions are relatively low, about 0.33, 1.07 and 1.21 mmol per m² of membrane for As(III), Cd(II) and Pb(II), respectively. Note that these membranes are highly swellable and also

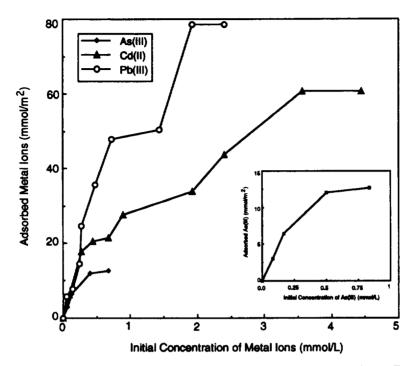


Fig. 6. Heavy metal ions adsorption capacity of the Cibacron Blue F3GA-incorporated poly(HEMA) membranes. Temperature: 20° C; pH:7.0 and total membrane surface area in each batch, 0.01 m²/1.

porous and therefore may absorb (or entrap) heavy metal ions within their matrix. In addition, the hydroxyl groups coming from the HEMA can interact with heavy metal ions (similar to solvatation with water), which may lead to high adsorption capacities.

3.4. Effects of pH

Metal adsorption is usually pH dependent [2,9,15,28,30-32]. In the absence of complexing agents, the hydrolysis and 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. As discussed in detail by Reed and Matsumoto [19], hydrolysis of metal ions becomes significant at basic pHs. In our case, precipitation of Cd(II), As(III) and Pb(II) ions occur approximately at pH 8.5, pH 6.5 and pH 7.5, respectively, which also depends on the concentration of metal ions in the medium. Therefore, here, in order to establish the effect of pH on the adsorption of metal ions onto the Cibacron Blue

F3GA-incorporated poly(HEMA) membranes, we repeated the batch equilibrium studies at different pH in the range of 3.0-10.0 at low metal ion concentration. Fig. 7 shows the specific adsorption (i.e., adsorption by chelating with the Cibacron Blue F3GA molecules incorporated on the poly(HEMA) membrane) of metal ions. Adsorptions of Cd(II) and Pb(II) ions first increased with increasing pH, due to changes of the ionization states of the reactive groups on the dye molecules, and reached almost a plateau value around pH 6.0 for Cd(II) and 5.0 for Pb(II). The maximum adsorption of As(III) ions on the poly(HEMA) membrane was observed at pH 7.0. Significantly lower adsorption capacities were obtained below and above pH 7.0 for As(III) ions, which may be explained as follows: The standard solution that we have used for arsenic was prepared from As₂O₃ by dissolving in 12% NaOH {not by dissolving pure metal pieces in acidic solutions, which was the case for Cd(II) and Pb(II)}. Therefore this standard solution contains arsenic in the form of H₃AsO₃ in acid media but H₂AsO₃ in basic and

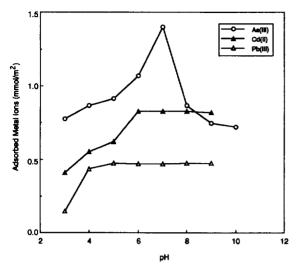


Fig. 7. Effect of pH on adsorption of heavy metal ions on the Cibacron Blue F3GA-incorporated poly(HEMA) membrane. Temperature: 20°C and total membrane surface area in each batch, 0.01 m²/l. Initial concentrations of metal ions: 1.34, 0.089 and 0.048 mmol/l for As(III), Cd(II) and Pb(II), respectively.

 ${\rm HAsO_3^{-2}}$ in strong basic media. ${\rm H_3AsO_3}$ form is the favorable form for chelating with the immobilized dye molecules on the membrane surface. Above pH 7 due to the existence of much less favorable forms, i.e., ${\rm H_2AsO_3^{-2}}$ and ${\rm HAsO_3^{-2}}$ adsorption decreased.

3.5. Competitive adsorption

We also investigated competitive adsorption of As(III), Cd(II) and Pb(II). The solutions containing different amounts of each metal ion were incubated with the Cibacron Blue F3GA-incorporated poly-(HEMA) membranes in batch fashion as described before. Fig. 8A,B shows that the amounts of adsorption for each heavy metal ion are as follows: 11.0 mmol/m² for As(III), 14.2 mmol/m² for Cd(II), and 9.6 mmol/m² for Pb(II) when their initial concentrations were low, and 36.0 mmol/m² for As(III), 42.0 mmol/m² for Cd(II) and 44.4 mmol/m² for Pb(II) when their concentrations were high. It is quite interesting to note that the adsorption capacity of the Cibacron Blue F3GA-attached poly-(HEMA) membranes for Pb(II) ions (in the case of adsorption from single metal ions solutions) was much higher than from other ions, especially from As(III), however, when they exist in the same

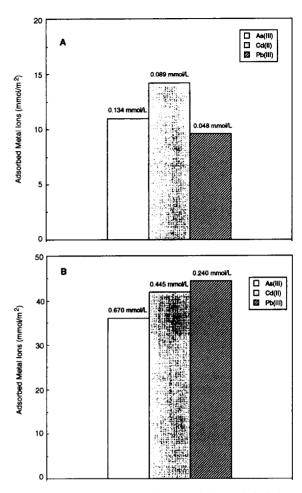


Fig. 8. Competitive adsorption of As(III), Cd(II) and Pb(II) ions on the Cibacron Blue F3GA-incorporated poly(HEMA) membranes at the different metal initial concentrations given at the top of each bar graph. Temperature: 20°C and total membrane surface area in each batch: 0.01 m²/l.

concentrations, they do compete for the same active points. It should also be noted that the extent of adsorption of each type of metal ion is strongly dependent upon their relative concentrations within the mixture. Therefore, it is almost impossible to generalize the order of adsorption or to define the extend of adsorption for each metal ion when they compete. It was also interesting to note that adsorption of As(III) was higher when it was adsorbed from the mixture than when it was adsorbed from its single solution, which may be explained as follows: in competitive adsorption, when one heavy metal ion

interacts with the immobilized dye molecule on the carrier surface, the steric conformation of the dye molecule changes which may be more favorable for the other metal ions to be adsorbed in the later part of the process.

3.6. Desorption and repeated use

Desorption of the adsorbed metal ions from the Cibacron Blue F3GA-incorporated poly(HEMA) membranes was also studied in a batch experimental

set-up. The poly(HEMA) membranes loaded with the maximum amounts of the respective metal ions were placed in the desorption medium containing 0.1 M HNO₃ at pH 1.0 and the amount of metal ions desorbed in 30 min was measured. The desorption ratio was then calculated by using the expression given in Eq. (2). Fig. 9 shows that recoveries (or desorption ratios) are very high (up to 85%) with the eluent system and conditions used for all heavy metal ions studied.

In order to study the reusability of the Cibacron

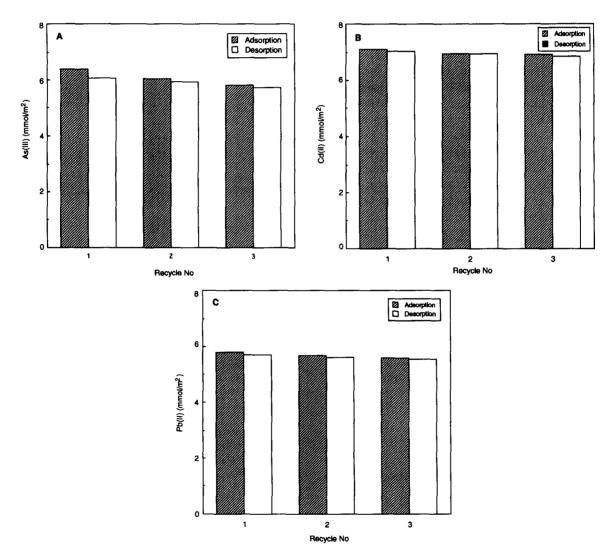


Fig. 9. Adsorption/desorption and repeated use of the Cibacron Blue F3GA-incorporated poly(HEMA) membranes: (A) for As(II), (B) for Cd(II), (C) for Pb(II). Total membrane surface area for each batch, 0.01 m²/l. Initial concentrations of metal ions: 0.134, 0.089 and 0.048 mmol/l for As(III), Cd(II) and Pb(II), respectively.

Blue F3GA-incorporated poly(HEMA) membranes, adsorption/desorption cycles were repeated three times using the same membrane. Fig. 9 shows that the affinity membranes can be used for resorption repeatedly without significantly losing their adsorption capacities for all metal ions studied here.

4. Conclusions

Swellable (with a swelling ratio of 58%) and macroporous poly(HEMA) affinity membranes were prepared by UV-initiated photo-polymerization of HEMA and AIBN (i.e., the initiator). An affinity dye, i.e., Cibacron Blue F3GA was then covalently incorporated into these membranes with a membrane phase concentration of 10.67 mmol/m² membrane. Adsorption/desorption of some selected heavy metal ions [i.e., As(III), Cd(II) and Pb(II)] from aqueous media on these membranes led to the following conclusions: very high adsorption rates were observed and adsorption equilibria were reached in about 60 min. Adsorption capacities of these affinity membranes from their single metal ion solutions were 12.6 mmol/m² for As(III), 61.0 mmol/m² for Cd(II) and 79.0 mmol/m² for Pb(II). However, when the heavy metal ions competed (in the case of the adsorption from their mixture) the amounts of adsorption for As(III), Cd(II) and Pb(II) were quite close and ranged from 11.0 to 44.4 mmol/m² depending on the initial concentrations of the respective ions. Adsorbed metal ions were successfully (up to 95%) desorbed by using 0.1 M HNO₃ (pH 1.0) as the eluant. Repeated adsorption/desorption cycles showed the feasibility of this novel affinity membrane for heavy metal removal.

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