Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

DYE AFFINITY POLY(2-HYDROXYETHYL METHACRYLATE) MEMBRANES FOR REMOVAL OF HEAVY METAL IONS

Adil Denizli[a]; Ridvan Say[b]; M. Yakup Arica[c]
[a] Department of Chemistry, Hacettepe University, Ankara, Turkey [b] Department of Science Education, Hacettepe University, Ankara, Turkey [c] Department of Biology, Kirikkale University, Kirikkale, Turkey

To cite this Article Denizli, Adil , Say, Ridvan and Arica, M. Yakup(2000) 'DYE AFFINITY POLY(2-HYDROXYETHYL METHACRYLATE) MEMBRANES FOR REMOVAL OF HEAVY METAL IONS', Journal of Macromolecular Science, Part A, 37: 4, 343 — 356

To link to this Article: DOI: 10.1081/MA-100101097

URL: http://dx.doi.org/10.1081/MA-100101097

J.M.S.—PURE APPL. CHEM., A37(4), pp. 343–356 (2000)

DYE AFFINITY POLY(2-HYDROXYETHYL METHACRYLATE) MEMBRANES FOR REMOVAL OF HEAVY METAL IONS

Adil Denizli*

Department of Chemistry
Hacettepe University
Ankara, Turkey

Ridvan Say

Department of Science Education
Hacettepe University
Ankara, Turkey

M. Yakup Arica

Department of Biology
Kirikkale University
Kirikkale, Turkey

Key Words: Procion Red HE-3B, Poly(HEMA) Membranes, Heavy Metal Removal, Copper(II), Arsenic(III), Cadmium(II), Mercury(II)

ABSTRACT

The dichlorotriazinyl dye-ligand Procion Red HE-3B-anchored poly(EGDMA-HEMA) membranes were used for removal of heavy metal ions (i.e., copper, arsenic, cadmium and mercury) from aqueous media containing different amounts of these ions (0.1-4.5 mmol/L) and at different pH values (2.0-8.0). The HE-3B-anchored membranes from their single solutions were 6.4

---

*Author to whom correspondence should be addressed. E-mail: denizli@eti.cc.hun.edu.tr

mmol/m^2 for Cu(II), 30.1 mmol/m^2 for As(III), 76.3 mmol/m^2 for Cd(II) and 130.3 mmol/m^2 for Hg(II). When the heavy metal ions competed (in the case of the adsorption from their mixture) the adsorption capacities were 7.8 mmol/m^2 for Cu(II), 24.5 mmol/m^2 for As(III), 27.6 mmol/m^2 for Cd(II) and 42.3 mmol/m^2 for Hg(II). The same affinity order was observed under non-competitive and competitive adsorption which was as follows: Hg(II) > Cd(II) > As(III) > Cu(II). The adsorption of heavy metal ions increased with increasing pH and reached a plateau value at around pH 5.0. Heavy metal ion adsorption from artificial wastewater was also studied. The adsorption capacities are 4.1 mmol/m^2 for Cu(II), 12.5 mmol/m^2 for As(III), 16.7 mmol/m^2 for Cd(II) and 21.3 mmol/m^2 for Hg(II). Desorption of heavy metal ions was achieved using 0.1 M HNO^3. The Procion Red HE-3B-anchored membranes are suitable for repeated use for more than 5 cycles without noticeable loss of capacity.

INTRODUCTION

Pollution of water sources (e.g. rivers, lakes and underground-water) by heavy metal ions is important due to their toxic effects on human physiology and other biological-ecological systems even at very low concentrations [1]. The necessity of removal of heavy metal ions in waste water streams of hydrometallurgical and other metal industries, and subsequent possible re-use of these valuable metal ions, has led to an increasing interest in selective sorbents [2-4]. Membrane separation has attracted increasing attention for its potential capability in the field of separation, and it has been shown to be an effective technique (minimizes mass transfer limitations and diffusion times) in removal of heavy metal ions from aquatic media. Membrane separation is also a promising technology from the energy-saving point of view for the selective separation of heavy metal ions [5].

In the present study, we prepared Procion Red HE-3B anchored microporous poly(2-hydroxy ethyl methacrylate) [poly(HEMA)] membranes for removal of heavy metal ions. Swellable and micro-porous poly(HEMA) membrane sorbent was first prepared by photo-polymerization of HEMA. Procion Red HE-3B was then attached covalently as a dye-ligand for heavy metal adsorption. This specific sorbent system in the membrane form was studied in adsorption/desorption of some selected heavy metal ions, i.e., Cu(II), As(III), Cd(II) and Hg(II) from aqueous media.

EXPERIMENTAL

Procion Red HE-3B-Attached Poly(HEMA) Membranes

The poly(2-hydroxyethyl methacrylate) membrane was prepared as previously described [6]. The monomer, HEMA, was obtained from Fluka A.G. (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroquinone and stored at 4°C until use. 2 ml of HEMA containing 5 mg azobisisobutyronitrile (Fluka, Switzerland) as polymerization initiator was mixed with 3 ml of 0.1 M $SnCl^4$. The mixture was then poured into a round glass mold (9 cm in diameter) and exposed to ultraviolet radiation for 10 minutes under nitrogen atmosphere. The membrane obtained was washed several times with distilled water, and cut into circular pieces (1.0 cm in diameter) with a perforator.

Preparation and characterization of the poly(HEMA) membranes were reported in our previous papers [6, 7]. For the attachment of Procion Red HE-3B on the poly(HEMA) membrane surface, the following procedure was applied: 100 ml of solution containing 500 mg Procion Red HE-3B (BDH Ltd., UK) was poured into 50 ml of distilled water of the poly(HEMA) membrane pieces, and then 5.0 g of NaOH was added. These were then heated in a sealed reactor at 80°C for 4 hours at a stirring rate of 400 rpm. Any remaining chlorine atoms in the dye structure, after coupling, can be converted to amino groups by treating with 2 M NH_4Cl at pH 8.5 for 24 hours at room temperature. The Procion Red HE-3B-anchored poly(HEMA) membranes were removed, and washed with distilled water and methanol several times until all the physically adsorbed dye molecules were removed. The amount of Procion Red HE-3B molecules covalently attached to the poly(HEMA) membrane was calculated from the elemental analysis data of the dried samples obtained by using an elemental analysis device (Leco, CHNS-932, USA).

FTIR spectra of the Procion Red HE-3B, the plain and Procion Red HE-3B-anchored 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 a pellet, and the spectrum was then recorded. KBr was used for background elimination in the FTIR spectra.

Heavy Metal Adsorption/Desorption

Heavy metal ions adsorption from the single metal (nitrates were used) 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 capacity were studied. 20 ml of aqueous metal ion solutions with different concentrations (in the range of 0.1-4.5 mmol/L) were incubated with the untreated and/or Procion Red HE-3B-anchored membranes (0.01 m^2/L) at different pH (in the range of 2.0-8.0, adjusted with HCl and NaOH) at room temperature, in the flasks agitated magnetically at 600 rpm. The adsorption time was selected as 60 minutes in the preliminary experiments, which was assumed as the equilibrium adsorption time, because there was no significant change in the amount of adsorption after 60 minutes. The membranes were separated from the adsorption medium at the end of each adsorption experiment, and the concentration of the metal ions in the aqueous phase was measured by graphite furnace atomic absorption spectrophotometer (AAS, GBC 932 AA, Australia). Wavelengths are 193.7 nm for As(III), 228.8 nm for Cd(II), 253.7 nm for Hg(II) and 324.8 nm for Cu(II). Hg(II) concentration was determined by AAS connected with Hydrid Generator (GBC HG 3000). All instrumental conditions were optimized for maximum sensitivity as described by the manufacturer. For each sample, the mean of 10 AAS measurements was recorded. The amount of adsorbed heavy metal ions was calculated as:

$$Q = [\ (C_o - C_A)\ .\ V\ ]\ /\ A \qquad (1)$$

Where, Q is the amount of metal ions adsorbed onto unit surface area of the membrane ($mmol/m^2$); C_o and C_A are the concentrations of the metal ions in the initial solution and in the aqueous phase after adsorption, respectively (mmol/L); V is the volume of the aqueous phase (L); and A is the surface area of the membrane (m^2).

Competitive adsorption of heavy metal ions from their mixture was also investigated in a batch-wise manner. Nitrate salts were used for Cu(II), Cd(II) and Hg(II) ions source. As_2O_3 was used for As(III) source. A solution (20 ml) containing 0.5 mmol/L from each metal ions was treated with the Procion Red HE-3B-anchored membranes at a pH of 7.0 at room temperature, in the flasks stirred magnetically at 600 rpm. After adsorption equilibrium, the concentration of the metal ions in the remaining solution was measued by an atomic absorption spectrophotometer.

Adsorption of heavy metal ions from artificial wastewater was carried out in batch wise manner. A solution (20 ml) containing 0.5 mmol/L from each metal ions [i.e., Cu(II), As(III), Cd(II) and Hg(II)] was incubated with the Procion Red HE-3B-anchored membranes at a pH of 6.8 at room temperature, in the flasks stirred magnetically at 600 rpm. Artificial wastewater also contains Ni(II), Zn(II), Fe(II), Co(II), Sn(II) and Ag(I). Concentration of each metal ions in artificial waste water is 0.1 mmol/L. In order to adjust salinity, 700 ppm NaCl was added to the artificial wastewater. After adsorption, the concentration of the metal ions in the remaining solution was determined as described above.

In order to determine the reusability of the Procion Red HE-3B-anchored membranes, consecutive adsorption-desorption cycles were repeated five times by using the same membranes. Desorption of heavy metal ions was achieved by using 0.1 M HNO_3. The Procion Red HE-3B-anchored membranes carrying 6.5 mmol Cu(II)/m^2; 20.2 mmol As(III)/m^2; 23.1 mmol Cd(II)/m^2; 39.4 mmol Hg(II)/m^2 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 by using an atomic absorption spectrophotometer. The desorption ratio was calculated from the amount of metal ions initially loaded on the membranes and the final metal ions concentration in the desorption medium.

RESULTS AND DISCUSSION

Structure of Chelating Resin

The poly(HEMA) membranes used in the present study were prepared and characterized as in our earlier papers [6-8]. These membranes are hydrophilic, crosslinked structures which swell, but not dissolve in aqueous media depending on the degree of crosslinking density. The equilibrium swelling ratio is 58% (w/w).

Procion Red HE-3B was used as the dye-ligand, and covalently attached to the poly(HEMA) membranes. The chemical structure of Procion Red HE-3B is given in Figure 1. It should be noted that the possible active groups to react with heavy metal ions are SO_3H-, NH, N=N, triazine and OH groups. FTIR spectra of plain poly(HEMA), Procion Red HE-3B and poly(HEMA)-Procion Red HE-3B are given in Figure 2. FTIR spectra of both poly(HEMA) and poly(HEMA)-Procion Red HE-3B have the characteristic stretching vibration band of hydrogen bonded alcohol, O-H, around 3500 cm^{-1}. The FTIR spectra of Procion Red HE-3B-attached poly(HEMA) has some absorption bands different than those of poly(HEMA). These are at 3380 cm^{-1}, 1565 cm^{-1} and 1280 cm^{-1} characteristic N-H stretching, conjugated C=N and aromatic C-N vibration, respectively observed also in Procion Red HE-3B (Figure 1). Procion Red HE-3B-attached poly(HEMA) has a sharp shoulder absorption band at about 3500 cm^{-1} and inter-

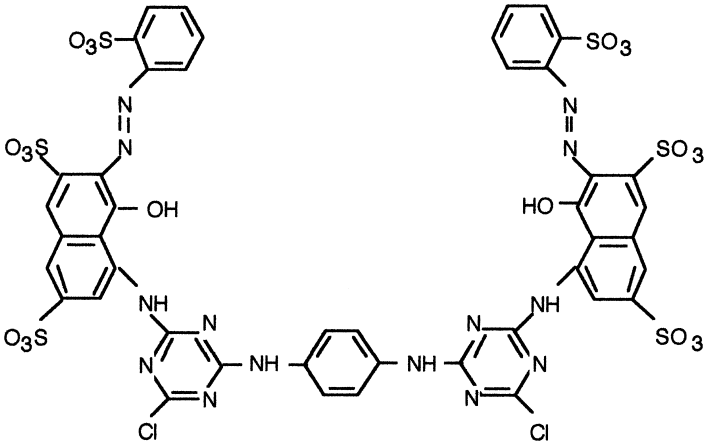

Figure 1. Chemical Structure of Procion Red HE-3B.

preted as the N-H absorption. The bands at 1075 cm^{-1} and 1155 cm^{-1} represent symmetric stretching of S=O and asymmetric stretching of S=O, respectively, are due to Procion Red HE-3B bonded to poly(HEMA). These bands, however, do not appear, because plain poly(HEMA) also has some absorption bands in the same region. Thus, absorption bands of plain poly(HEMA) overlap with those of

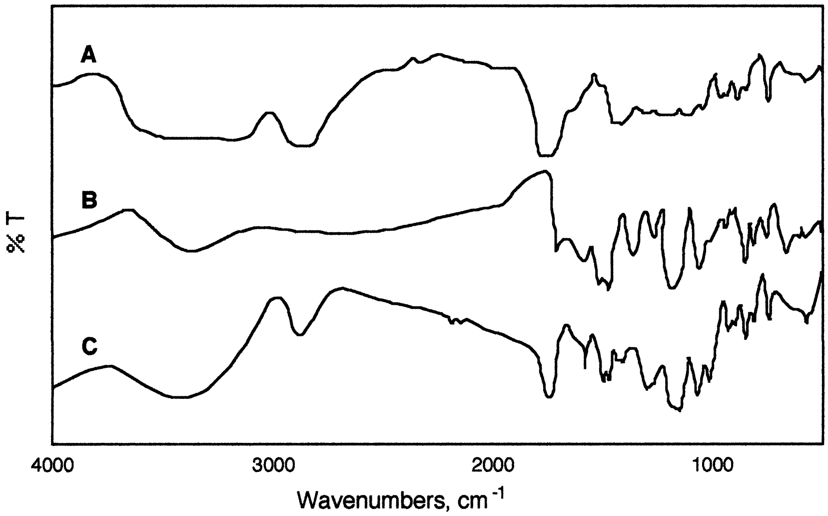

Figure 2. FTIR Spectra of (A) poly(HEMA); (B) Procion Red HE-3B; (C) Procion Red HE-3B-anchored poly(HEMA) membrane.

the Procion Red HE-3B at around these wavenumbers. For dye attached poly(HEMA) absorption band intensities in this region are higher than those of poly(HEMA), but the intensity increase is quite small because of the low concentration of Procion Red HE-3B on polymeric surface. On the other hand hydrogen bonded alcohol O-H stretching band intensity of plain poly(HEMA) is higher than that of poly(HEMA)-Procion Red HE-3B membrane. The reason for the loss of the -OH groups is as a result of the condensation reaction between -OH groups of poly(HEMA) and Cl atoms of Procion Red HE-3B.

Elemental analysis of the plain and Procion Red HE-3B-anchored poly(HEMA) membranes were performed, and the incorporation of the Procion Red HE-3B was found to be 17.5 mmol/m^2 from the nitrogen and sulphur stoichiometry.

Procion Red HE-3B leakage was also followed. There were no leakage in any of the adsorption and desorption media, which assured that the washing procedure used in the for removal of physically adsorbed Procion Red HE-3B molecules from the poly(HEMA) membrane was satisfactory.

Adsorption of Heavy Metal Ions

Effects of Initial Concentration of Metal Ions

Adsorption capacities of the heavy metal ions of the Procion Red HE-3B-anchored membranes are shown as a function of the initial concentration of metal ions within the aqueous phase in Figure 3. Note that these adsorption curves were obtained in the experiments where adsorptions from the single metal aqueous solutions were studied. It was observed that the amount of adsorption was significantly increased with increasing of the initial heavy metal concentration especially in the case Hg(II) and also for Cd(II). The maximum adsorption capacities of the Procion Red HE-3B-anchored membranes in the studied range are 6.4 mmol/m^2, 30.1 mmol/m^2, 76.3 mmol/m^2 and 130.3 mmol/m^2 for Cu(II), As(III), Cd(III) and Hg(II), respectively. The affinity order is Hg(II) > Cd(II) > As(III) > Cu(II).

As mentioned before, unit surface area of the sorbent carries 17.5 mmol Procion Red HE-3B which was found by elemental analysis. From the stoichiometry, it seems that one immobilized Procion Red HE-3B molecule interact from one to eight metal ions depending on the type of metal. Note that the S, N and O atoms of Procion Red HE-3B are available for interaction with heavy metal ions. The number of the available active sites does not match with the number of heavy metal ions adsorbed. The heavy metal ions adsorption on the

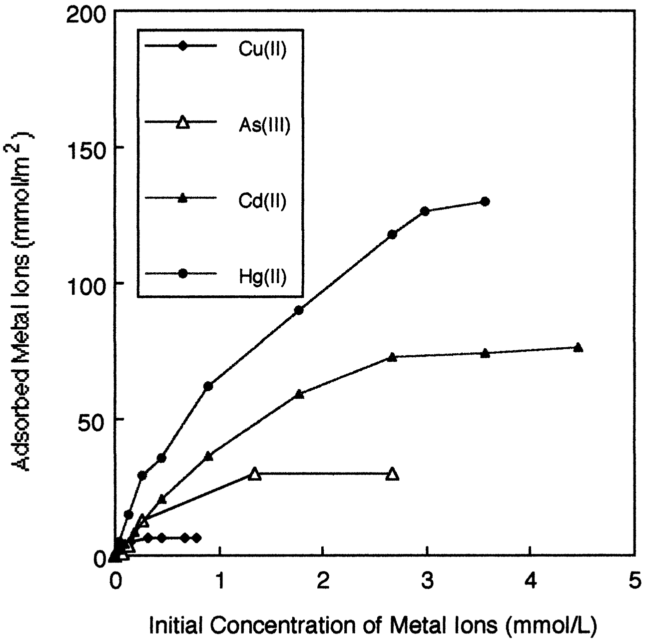

Figure 3. Heavy metal ions adsorption capacity of the Procion Red HE-3B-anchored poly(HEMA) membranes. Temperature: 20°C and pH: 7.0 and total membrane surface area in each batch: 0.01 m^2/L.

plain membranes (carrying no Procion Red HE-3B) is relatively low, about 0.54 mmol/m^2 for Cu(II), 0.33 mmol/m^2 for As(III), 1.07 mmol/m^2 for Cd(II) and 3.26 mmol/m^2 for Hg(II). Note that these membranes are highly swellable and also microporous, which therefore, may absorb (or entrap) heavy metal ions within the matrix of the swollen membrane. In addition, the hydroxyl and carbonyl groups may interact with heavy metal ions (similar to solvatation with water), which may cause these non-specific-adsorption. It seems that the adsorbed heavy metal ions are interacting with the heavy metal ions coming to the same adsorption site during the adsorption process, as a result, the adsorption is not monolayer, but rather multilayer (non-Langmuir type).

For comparison of adsorption capacities of the Procion Red HE-3B-anchored membranes, we calculated distribution coefficients (K_d) of metal ions between the sorbent phase and the adsorption medium at equilibrium, by using the following expression.

$$K_d = \frac{\text{Adsorbed Metal Ion (mmol) / Unit Surface Area of Membrane (m}^2\text{)}}{\text{Amount of Metal Ion in Solution (mmol) / Volume of solution (ml)}} \tag{2}$$

Note that the distribution coefficient defined as the ratio of the amount of metal ion adsorbed by unit surface area of the polymeric membrane to the amount of metal ion retained in 1 ml of the solution. Table 1 gives the K_d values. As seen here, much higher K_d value (indicating preferential adsorption) was obtained for Hg(II) ions than for Cd(II), As(III) and Cu(II) ions.

Sorbents used in heavy metal removal are in particulate form in most of the cases. Reed and Matsumoto reported 90-120 mmol Cd(II)/m^2 with activated carbon having different porosities [9]. Egawa *et al.* have found 62.1 mmol uranium/m^2 removal by amidoxime containing acrylonitrile-diviniylbenzene copolymer beads [10]. Maeda and Egawa showed very low adsorption capacities which 1.5 mmol Pb(II)/m^2 and 1.6 mmol Cu(II)/m^2 by using methylmethacrylate-diviniylbenzene copolymer beads-aminomethyl-phosphonic acid macroreticular chelating polymeric resin-containing poly(styrene-divinyl-benzene) sorbents [11]. Denizli *et al.* used dye-affinity poly(HEMA) and polyvinylbutyral membranes for heavy metal adsorption [6,8,12]. The maximum amounts of adsorption capacities achieved were 22.2-61.0 mmol Cd(II)/m^2, 34.2-79.0 mmol Pb(II)/m^2 and 16.8 mmol Zn(II)/m^2. Comparing these data, it seems that the adsorption capacities achieved with the dye-attached membranes are satisfactory.

Effects of pH

Metal ion adsorption onto non-specific and specific sorbents is pH dependent [13-16]. In the absence of complexing agents, the hydrolysis and pre-

TABLE 1. Distribution Coefficients

Metal Ions	K_d
Cu(II)	14 942
As(III)	67 785
Cd(II)	85 873
Hg(II)	371 698

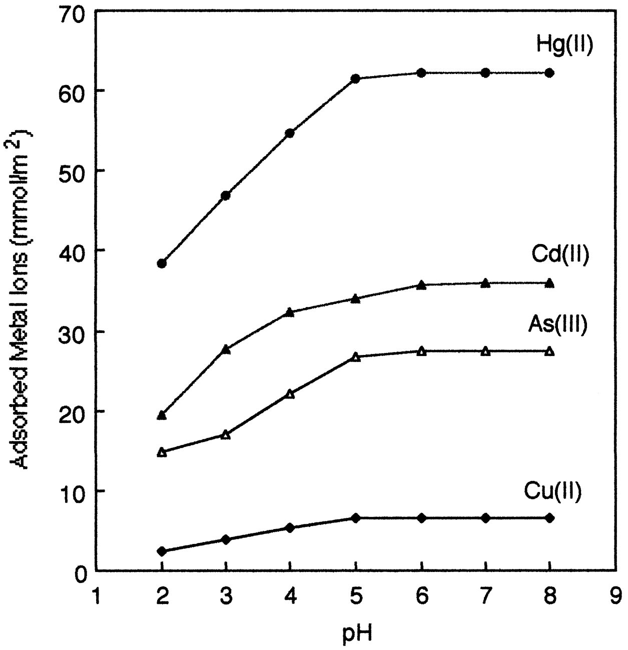

Figure 4. Effect of pH on adsorption of heavy metal ions on the Procion Red HE-3B-anchored poly(HEMA) membrane. Temperature: 20°C and total membrane surface area in each batch: 0.01 m^2/L; Initial concentration of metal ions: 0.78 mmol/L for Cu(II) and 0.5 mmol/L for As(III), Cd(II) and Hg(II).

cipitation 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 details by Reed and Matsumoto [17], hydrolysis of metal ions becomes significant at approximately pH 7.5-8.5 for studied metal ions. Therefore, in the present study, we changed the pH range between 2.0-8.0. The effect of pH on heavy metal adsorption is illustrated in Figure 4. It was observed that the adsorption capacities increased with increasing pH, reaching plateau values at around pH 5.0. Plateau values are 6.7 mmol/m^2 for Cu(II), 27.5 mmol/m^2 for As(III), 36.1 mmol/m^2 for Cd(II) and 62.3 mmol/m^2 for Hg(II). The difference in adsorption values can be explained by the different affinity of the heavy metal ions for the donor atoms in the dye-ligand Procion Red HE-3B.

Competitive Adsorption

Adsorption capacities of the Procion Red HE-3B-anchored membranes for metal ions under competitive conditions (adsorption from solutions con-

TABLE 2. Comparison of Adsorption of Heavy Metal Ions on the Procion Red HE-3B-Anchored Membranes: Concentration of Each Metal Ions: 0.5 mmol/L; pH: 7.0, T: 20°C.

Ions	Non-Competitive Adsorption ($mmol/m^2$)	Competitive Adsorption ($mmol/m^2$)
Cu(II)	6.5 ± 0.4	7.8 ± 0.6
As(III)	20.2 ± 1.1	24.5 ± 0.9
Cd(II)	23.1 ± 1.2	27.6 ± 0.8
Hg(III)	39.4 ± 1.5	42.3 ± 1.4

taining all heavy metal ions) for Cu(II), As(III), Cd(II) and Hg(II) are given in Table 2. It should be noted that the competitive adsorption capacities of the Procion Red HE-3B-anchored membranes for all metal ions were much higher than non-competitive conditions. The non-competitive adsorption capacities are 6.5 $mmol/m^2$ for Cu(II), 20.2 $mmol/m^2$ for As(III), 23.1 $mmol/m^2$ for Cd(II) and 39.4 $mmol/m^2$ for Hg(II) at 0.5 mmol/L initial concentration. But, the competitive adsorption capacities are higher than non-competitive adsorption capacities. They are 7.8 $mmol/m^2$ for Cu(II), 24.5 $mmol/m^2$ for As(III), 27.6 $mmol/m^2$ for Cd(II) and 42.3 $mmol/m^2$ for Hg(II). The Procion Red HE-3B-anchored membranes exhibits the following metal ion affinity sequence under competitive adsorption conditions: Hg(II) > Cd(II) > As(III) > Cu(II).

Adsorption from Artificial Wastewater

Adsorption capacities of the Procion Red-anchored membranes from artificial waste-water for Cu(II), As(III), Cd(II) and Hg(II) are shown in Table 3. It is worth noting that the adsorption capacities of the Procion Red HE-3B-anchored membranes from artificial wastewater for all metal ions were much lower than the competitive conditions and single solutions. The adsorption capacities are 4.1 $mmol/m^2$ for Cu(II), 12.5 $mmol/m^2$ for As(III), 16.7 $mmol/m^2$ for Cd(II) and 21.3 $mmol/m^2$ for Hg(II). The Procion Red HE-3B-anchored membranes exhibits the following metal ion affinity sequence: Hg(II) > Cd(II) > As(III) > Cu(II). In this case, Procion Red HE-3B-anchored membranes adsorbed other metal ions also. Therefore, adsorption of other metal ions reduces the adsorption capacities of Cu(II), As(III), Cd(II) and Hg(II) of membranes.

TABLE 3. Adsorption of Heavy Metal Ions from Artificial Wastewater on the Procion Red HE-3B-Anchored Membranes: Concentration of Each Metal Ions: 0.5 mmol/L, pH: 6.8, T: 20°C

Ions	Adsorbed Ion (mmol/m^2)
Cu(II)	4.1 ± 0.3
As(III)	12.5 ± 0.9
Cd(II)	16.7 ± 1.1
Hg(III)	21.3 ± 1.4

Regeneration of Membranes

To be useful in metal ion recycling prosesses, metal ions chelated should be easily desorbed under suitable conditions. Desorption experiments were performed with 0.1 M HNO$_3$ as the desorption agent. The Procion Red HE-3B-anchored membranes loaded the maximum amounts of the respective metal ions were placed within the desorption medium and the amount of metal ions desorbed in 30 minutes was measured. Table 4 shows the adsorption-desorption values of heavy metal ions by Procion Red HE-3B-anchored membranes after several cycles of consecutive adsorption and desorption. This table clearly shows

TABLE 4. Heavy Metal Ions Adsorption Capacity of Procion Red HE-3B-Anchored Poly(HEMA)membranes After Consecutive Adsorption and Desorption. Total Membrane Surface Area in Each Batch: 0.01 m^2/L. Initial Concentrations of Metal Ions 0.5 mmol/L

Cycle No	Cu(II)		As(III)		Cd(II)		Hg(II)	
	Adsorption (mmol/m^2)	Desorption (%)	Adsorption (mmol/m^2)	Desorption (%)	Adsorption (mmol/m^2)	Desorption (%)	Adsorption (mmol/m^2)	Desorption (%)
1	6.50	98.3	20.20	99.7	23.12	97.5	39.40	98.4
2	6.47	97.1	20.15	98.5	23.02	98.1	39.27	97.6
3	6.41	97.5	20.12	99.1	22.89	97.7	39.11	98.5
4	6.39	98.9	19.95	97.3	22.75	99.1	38.86	98.8
5	6.35	98.6	19.87	98.8	22.66	97.3	38.74	99.1

that the Procion Red HE-3B-anchored membranes can be used repeatedly without losing significantly their adsorption capacities for all metal ions studied here.

CONCLUSION

Microporous poly(HEMA) membranes containing 17.5 mmol Procion Red HE-3B/m^2 were used for adsorption/desorption of Cu(II), As(III), Cd(III) and Hg(II) ion from aqueous solution under non-competitive and competitive conditions. Important results were given as follows: The maximum adsorption capacities of these affinity membranes from their single metal ions solutions were 6.4 mmol/m^2 for Cu(II), 30.1 mmol/m^2 for As(III), 76.3 mmol/m^2 for Cd(II) and 130.3 mmol/m^2 for Hg(II). When the heavy metal ions competed (in the case of the adsorption from their mixture) the amounts of adsorption were 7.8 mmol/m^2 for Cu(II), 24.5 mmol/m^2 for As(III), 27.6 mmol/m^2 for Cd(II) and 42.3 mmol/m^2 for Hg(II) at 0.5 mmol/L initial concentration. Procion Red HE-3B-anchored membranes exhibits the following metal ion affinity sequence under non-competitive and competitive conditions: Cu(II) < As(III) < Cd(II) < Hg(II). The adsorption capacities of the Procion Red HE-3B-anchored membranes from artificial wastewater for all metal ions were much lower than the competitive conditions. The adsorption capacities are 4.1 mmol/m^2 for Cu(II), 12.5 mmol/m^2 for As(III), 16.7 mmol/m^2 for Cd(II) and 21.3 mmol/m^2 for Hg(II). Consecutive adsorption and desorption cycles showed the feasibility of this Procion Red HE-3B-anchored membranes for heavy metal adsorption.

REFERENCES

[1] C. S. Luo and S. Huang, *Sep. Sci. and Technol., 28*, 1253 (1993).

[2] D. A. Harkins and G. K. Schweitzer, *Sep. Sci. and Technol., 26,* 345 (1991).

[3] A. Sugii, N. Ogawa, and H. Hashizume, *Talanta, 27*, 627 (1980).

[4] S. Hunt in, *Immobilization of Ions by Bio-Sorption*, H. Ecclos and S. Hunt, Eds., Ellis Horwood, Chichester, Chap. 1, 1986.

[5] J. Marchese, M. Campderros, and A. Acosta, *J. Chem. Tech. and Biotechnol., 64,* 293 (1995).

[6] A. Denizli, B. Salih, M. Y. Arica, K. Kesenci, V. Hasirci, and E. Piskin, *J. Chromatogr. A*, *758*, 217 (1997).

[7] M. Y. Arica, A. Denizli, B. Salih, E. Piskin, and V. Hasirci, *J. Membr. Sci.*, *129*, 65 (1997).

[8] A. Denizli, K. Kesenci, M. Y. Arica, B. Salih, V. Hasirci, and E. Piskin, *Talanta*, *46*, 551 (1998).

[9] B. E. Reed and N. R. Matsumoto, *Sep. Sci. and Techol*, *28*, 2179 (1993).

[10] H. Egawa, T. Nonaka, S. Abe, and M. Nakayama, *J. Appl. Polym. Sci.*, *45*, 837 (1992).

[11] H. Maeda and H. Egawa, *J. Appl. Polym. Sci.*, *33*, 1275 (1987).

[12] A. Denizli, D. Tanyolaç, B. Salih, E. Aydinlar, and E. Piskin, *J. Membr. Sci.*, *137*, 1 (1997).

[13] R. S. Shreedhara-Murthy and D. E. Ryan, *Analytica Chimica Acta*, *140*, 163 (1982).

[14] C. Kantipuly, S. Katragadda, A. Chow, and H. D. Gesser, *Talanta*, *37*, 491 (1990).

[15] A. Denizli, B. Salih, and E. Piskin, *React. and Funct. Polym.*, *29*, 11 (1996).

[16] Y. Konishi, S. Asai, Y. Midoh, and M. Oku, *Sep. Sci. and Techol.*, *28*, 1691 (1993).

[17] B. E. Reed and M. R. Matsumoto, *Carbon*, *29*, 1191 (1991).

Resubmit date June 23, 1999
Final revision received October 10, 1999