Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Procion Blue MX-3G-Attached Microporous Poly(2-Hydroxyethyl Methacrylate) Membranes for Copper, Arsenic, Cadmium, and Mercury Adsorption

Adl Denzl[a]; Ridvan Say[b]; H. Nur Testerec[c]; M. Yakup Arica[d]
[a] DEPARTMENT OF CHEMISTRY, HACETTEPE UNIVERSITY, ANKARA, TURKEY [b] DEPARTMENT OF SCIENCE EDUCATION, HACETTEPE UNIVERSITY, ANKARA, TURKEY [c] DEPARTMENT OF CHEMISTRY, KIRIKKALE UNIVERSITY, KIRIKKALE, TURKEY [d] DEPARTMENT OF BIOLOGY, KIRIKKALE UNIVERSITY, KIRIKKALE, TURKEY

Online publication date: 16 August 1999

To cite this Article Denzl, Adl , Say, Ridvan , Testerec, H. Nur and Arica, M. Yakup(1999) 'Procion Blue MX-3G-Attached Microporous Poly(2-Hydroxyethyl Methacrylate) Membranes for Copper, Arsenic, Cadmium, and Mercury Adsorption', Separation Science and Technology, 34: 12, 2369 — 2381
To link to this Article: DOI: 10.1081/SS-100100778
URL: http://dx.doi.org/10.1081/SS-100100778

SEPARATION SCIENCE AND TECHNOLOGY, **34**(12), pp. 2369–2381, 1999

Procion Blue MX-3G-Attached Microporous Poly(2-Hydroxyethyl Methacrylate) Membranes for Copper, Arsenic, Cadmium, and Mercury Adsorption

ADİL DENİZLİ*
DEPARTMENT OF CHEMISTRY

RIDVAN SAY
DEPARTMENT OF SCIENCE EDUCATION

HACETTEPE UNIVERSITY
ANKARA, TURKEY

H. NUR TESTERECİ
DEPARTMENT OF CHEMISTRY

M. YAKUP ARICA
DEPARTMENT OF BIOLOGY

KIRIKKALE UNIVERSITY
KIRIKKALE, TURKEY

ABSTRACT

pHEMA membranes carrying 25.6 mmol Procion Blue MX-3G/m^2 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 maximum adsorption capacities of heavy metal ions onto Procion Blue MX-3G-attached membranes under noncompetitive conditions were 5.6 mmol/m^2 for Cu(II), 19.6 mmol/m^2 for As(III), 46.2 mmol/m^2 for Cd(II), and 119.6 mmol/m^2 for Hg(II). The competitive adsorption capacities of the heavy metal ions were 6.9 mmol/m^2 for Cu(II), 21.2 mmol/m^2 for As(III), 33.9 mmol/m^2 for Cd(II), and 52.5 mmol/m^2 for Hg(II). The same affinity order was observed under noncompetitive and competitive adsorption: Hg(II) > Cd(II) > As(III) > Cu(II). The adsorption of

* To whom correspondence should be addressed at P.K. 51, Samanpazari, 06242 Ankara, Turkey. Telephone and FAX: (90) 312 2352330. E-mail: denizli@eti.cc.hun.edu.tr

heavy metal ions increased with increasing pH and reached a plateau value at around pH 6.0. Adsorption of heavy metal ions from artificial wastewater was also studied. The adsorption capacities are 3.5 mmol/m^2 for Cu(II), 10.2 mmol/m^2 for As(III), 24.7 mmol/m^2 for Cd(II), and 37.3 mmol/m^2 for Hg(II). Desorption of heavy metal ions was performed using 0.1 M HNO_3. Procion Blue MX-3G-attached membranes are suitable for repeated use of more than 5 cycles without noticeable loss of capacity.

Key Words. Procion Blue MX-3G; pHEMA membranes; Heavy metal removal, copper(II), arsenic(III), cadmium(II), and mercury(II)

INTRODUCTION

Contamination of water sources (e.g., rivers, lakes) by heavy metal ions is important due to their toxic effects on living organisms even at very low concentrations (1). The necessity of removal of heavy metal ions in wastewater streams of hydrometallurgical and other metal industries, and subsequent possible reuse 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 in removal of heavy metal ions from aquatic media. Microporous affinity membranes can significantly reduce mass transfer limitations commonly encountered in column chromatography (5). As a conclusion, higher throughput, much lower operating pressure, and faster adsorption times are achieved in membrane systems (6). Membrane separation is also a promising technology from the energy-saving point of view for the selective separation of heavy metal ions (7).

In this communication we use Procion Blue MX-3G-attached microporous poly(2-hydroxyethyl methacrylate) [pHEMA] membranes for removal of heavy metal ions. Swellable and microporous pHEMA membrane sorbent was first prepared by photopolymerization of HEMA. Procion Blue MX-3G was then attached covalently as a dye-ligand for heavy metal adsorption. This specific sorbent system in the membrane form was studied in the adsorption/desorption of copper [Cu(II)], arsenic [As(III)], cadmium [Cd(II)], and mercury [Hg(II)] from aqueous media.

EXPERIMENTAL

Procion Blue MX-3G-Attached pHEMA Membranes

The poly(2-hydroxyethyl methacrylate) membrane was prepared as previously described (8). 2-Hydroxyethyl methacrylate (HEMA) was supplied from Fluka A.G. (Buchs, Switzerland), distilled under reduced pressure in the pres-

ence 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. pHEMA membrane was washed several times with distilled water and cut into circular pieces (1.0 cm in diameter) with a perforator.

For the attachment of Procion Blue MX-3G on the pHEMA membrane, the following procedure was applied: 100 mL of solution containing 500 mg Procion Blue MX-3G (BDH Ltd., UK) was poured into 50 mL of distilled water of the pHEMA 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.

Under these circumstances a chemical reaction took place between the group of the Procion Blue MX-3G containing chlorine and hydroxyl groups of the pHEMA, with the elimination of HCl, resulting in covalent attachment of Procion Blue MX-3G to the pHEMA (9). Any remaining chlorine atoms in the dye structure, after a coupling reaction, can be converted to hydroxyl groups by incubating the pHEMA membranes for 3 days at pH 8.5 at room temperature or to amino groups by treating with 2 M NH_4Cl at pH 8.5 for 4 hours at room temperature. The Procion Blue MX-3G-attached pHEMA membranes were then washed with distilled water and methanol several times until all the physically adsorbed dye molecules were removed. The amount of Procion Blue MX-3G molecules covalently attached to the pHEMA membrane was calculated from an elemental analysis data of the dried pHEMA membranes obtained by using an elemental analysis device (Leco, CHNS-932, USA).

FTIR spectra of the plain pHEMA and Procion Blue MX-3G-attached pHEMA membranes were obtained by using a FTIR spectrophotometer (FTIR 8000 Series, Shimadzu, Japan). The dry pHEMA membrane (about 0.1 g) was thoroughly mixed with KBr (0.1 g, IR Grade, Merck, Germany), and pressed into pellet form. The spectrum was then recorded.

Heavy Metal Adsorption/Desorption

Heavy metal ions adsorption from 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 0.1–4.5 mmol/L range) were incubated with the untreated and/or Procion Blue MX-3G-attached membranes (0.01 m^2/L) at different pH values (in the 2.0–8.0 range, adjusted with HCl and NaOH) at room temperature in flasks stirred magnetically at 600 rpm. The equilibrium

adsorption time was 60 minutes (determined in preliminary experiments because there was no significant change in the amount of adsorption after 60 minutes). The pHEMA membranes were removed from the adsorption medium at the end of the adsorption experiment and the concentrations of the Cu(II), As(III), and Cd(II) in the aqueous phase were measured by a graphite furnace atomic absorption spectrophotometer (AAS, GBC 932 AA, Australia). Hg(II) concentration was determined by an AAS connected with a Hydrid Generator (GBC HG 3000). All instrumental conditions were optimized for maximum sensitivity as described by the manufacturer. A mean of 10 AAS measurements was recorded for each sample. The amount of adsorbed heavy metal ions was calculated as

$$q = [(C_0 - C_A)V]/A \quad (1)$$

where q is the amount of metal ions adsorbed onto a unit surface area of the membrane (mmol/m^2); C_0 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 (mL); 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 batchwise manner. A solution (20 mL) containing 0.5 mmol/L from each metal ions was treated with the Procion Blue MX-3G-attached membranes at a pH of 7.0 at room temperature in flasks stirred magnetically at 600 rpm. After adsorption equilibrium, the concentration of the metal ions in the remaining solution was measured by an AAS.

Adsorption of heavy metal ions from artificial wastewater was carried out in a batchwise manner. A solution (20 mL) containing 0.5 mmol/L from each metal ions [i.e., Cu(III), As(III), Cd(II), and Hg(II)] was incubated with the Procion Blue MX-3G-attached membranes at a pH of 7.0 at room temperature in flasks stirred magnetically at 600 rpm. The artificial wastewater also contained Ni(II), Zn(II), Fe(II), Co(II), Sn(II), and Ag(I). The concentration of each metal ions in artificial wasterwater was 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 Blue MX-3G-attached membranes, repeated adsorption–desorption cycles were done five times by using the same pHEMA membranes. Desorption of heavy metal ions was performed using 0.1 M HNO_3. Procion Blue MX-3G-attached membranes carrying 5.6 mmol Cu(II)/m^2, 15.5 mmol As(III)/m^2, 31.6 mmol Cd(II)/m^2, and 47.1 mmol Hg(II)/m^2 were placed in this desorption medium and stirred at 600 rpm for 30 minutes at room temperature. The final metal ion concentration in

the aqueous phase was determined by using an AAS. 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

pHEMA is a hydrophilic polymer. Due to its synthetic structure it is very inert toward microbial degradation and resistant to many chemicals. Its porosity can be arranged by changing the concentration of ions and pore-forming agent in the polymerization medium. The pHEMA membrane is a crosslinked structure which swells and whose amount of solvation in aqueous media depends on the cross-linking ratio. The equilibrium swelling ratio of pHEMA used in this study is 58% (w/w). Preparation and characterization details of pHEMA membranes were given in our earlier papers (10–12).

The SEM photograph given in Fig. 1 shows the surface structure of the pHEMA membrane. As seen here, the pHEMA membrane is highly porous, which may lead to a high internal surface area for diffusion–adsorption of heavy metal ions.

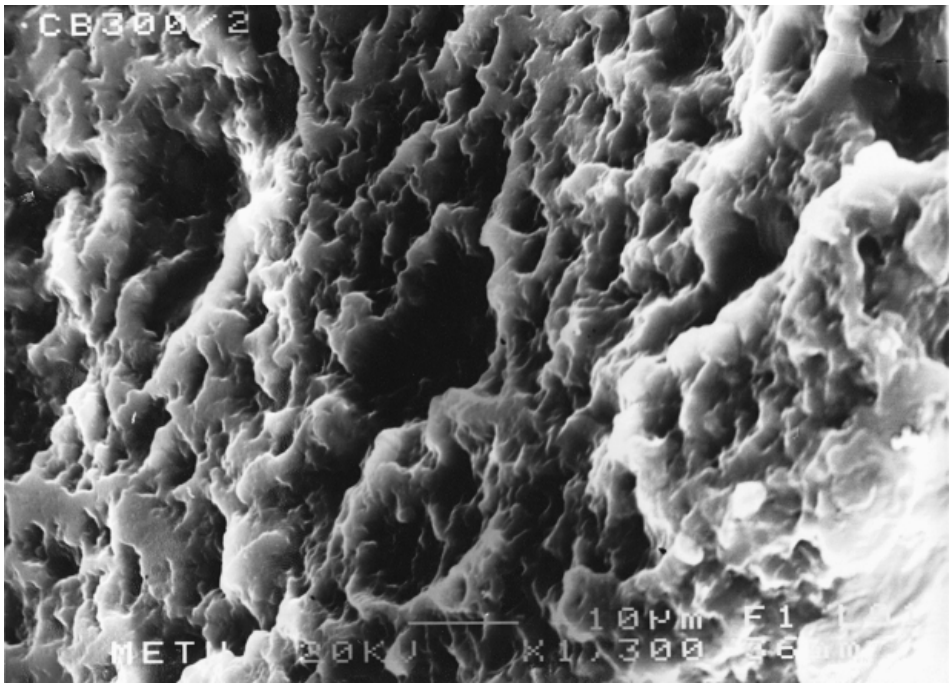

FIG. 1 SEM photograph of pHEMA membrane.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

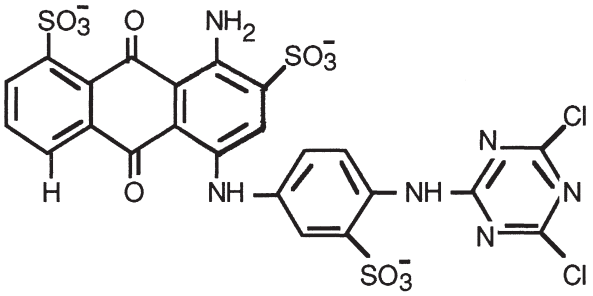

FIG. 2 Chemical structure of Procion Blue MX-3G.

Procion Blue MX-3G is a dichlorotriazine dye-ligand (Fig. 2), and it contains three acidic sulfonate groups, four amino groups, and one triazine ring. The binding of heavy metal ions to the Procion Blue MX-3G molecules occurs especially through oxygen, sulfur, and nitrogen atoms. FTIR spectra of plain pHEMA and pHEMA-Procion Blue MX-3G are given in Fig. 3. FTIR spectra of both pHEMA and pHEMA-Procion Blue MX-3G have the characteristic stretching band of hydrogen-bonded alcohol, O—H, around 3500 cm^{-1}. The FTIR spectra of Procion Blue MX-3G-attached pHEMA has some absorption bands which differ from those of pHEMA. These are at 3380, 1570, and 1270 cm^{-1}, characteristic N—H stretching, conjugated C═N, and aromatic C—N vibration, respectively, and are also observed in Procion Blue MX-3G (Fig. 1). Procion Blue MX-3G-attached pHEMA has a sharp shoulder

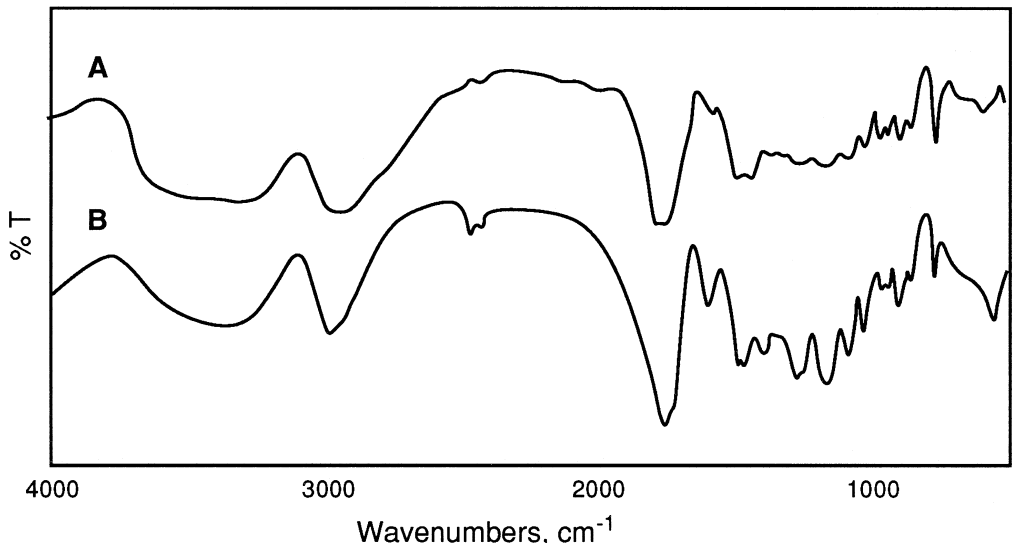

FIG. 3 FTIR spectra of (A) pHEMA and (B) Procion Blue MX-3G-attached pHEMA membrane.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

absorption band at about 3500 cm^{-1} which is interpreted as N—H absorption. The bands at 1075 and 1155 cm^{-1}, which represent symmetric and asymmetric stretching of S═O, respectively, are due to Procion Blue MX-3G attached to pHEMA. These bands, however, do not appear, because plain pHEMA also has some absorption bands in the same region. Thus, absorption bands of plain pHEMA overlap with those of the Procion Blue MX-3G at around these wavenumbers. For dye-attached pHEMA, absorption band intensities in this region are higher than those of pHEMA, but the intensity increase is quite small because of the low concentration of Procion Blue MX-3G on a polymeric surface. On the other hand, the hydrogen-bonded alcohol O—H stretching band intensity of plain pHEMA is higher than that of the pHEMA-Procion Blue MX-3G membrane. The reason for the loss of —OH groups is the result of the condensation reaction between -OH groups of pHEMA and —Cl atoms of Procion Blue MX-3G.

Elemental analyses of plain pHEMA and Procion Blue MX-3G-attached pHEMA membranes were performed, and the attachment of Procion Blue MX-3G was found to be 25.6 $mmol/m^2$ from nitrogen and sulfur stoichiometry.

Procion Blue MX-3G leakage was also followed. No leakage was found in any of the adsorption and desorption media, which showed that the washing procedure used for removal of physically adsorbed Procion Blue MX-3G molecules from the pHEMA membrane was satisfactory.

Adsorption of Heavy Metal Ions

Adsorption Rate

Adsorption rates of heavy metal ions onto Procion Blue MX-3G-attached pHEMA membranes were determined. High adsorption rates were observed at the beginning of adsorption, and then saturation values (i.e., adsorption equilibrium) were gradually achieved within 20 minutes. Adsorption of heavy metal ions was rather fast, especially when the metal ion concentration was high. This may be due to a high driving force, which is the heavy metal ion concentration difference between the adsorption medium and the membrane phases in the case of a high metal ion concentration. It should be also noted that Hg(II) was adsorbed much faster than the other metal ions [i.e., Cd(II), As(III), and Cu(II)] due to much higher affinity of Procion Blue MX-3G molecules for Hg(II) ions. The order of adsorption rate found was Hg(II) > Cd(II) > As(III) > Cu(II).

Effects of Initial Concentration of Metal Ions

Adsorption capacities of Procion Blue MX-3G-attached membranes for heavy metal ions are shown in Fig. 4. Note that these adsorption curves were obtained

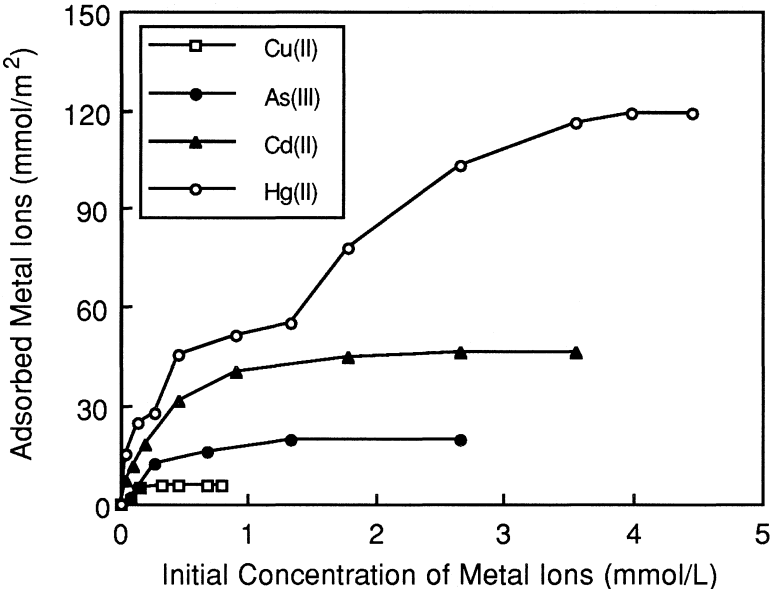

FIG. 4 Heavy metal ions adsorption capacity of the Procion Blue MX-3G-attached pHEMA membrane. *T*, 20°C; pH 7.0; and total membrane surface area in each batch, 0.01 m^2/L.

in experiments where adsorptions from single metal aqueous solutions were studied. It was observed that the amount of adsorption increased with an increase of the initial heavy metal concentration and then reached saturation. The maximum adsorption capacities of Procion Blue MX-3G-attached membranes in the range studied are 5.6, 19.6, 46.2, and 119.6 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).

The pHEMA membrane carries 25.6 mmol Procion Blue MX-3G/m^2. One immobilized Procion Blue MX-3G molecule interacts with from one to five metal ions depending on the type of metal. Note that the S, N, and O atoms of Procion Blue MX-3G are available for interaction with heavy metal ions. The number of available active groups does not match the number of heavy metal ions adsorbed. The adsorption of heavy metal ions on plain membranes (carrying no Procion Blue MX-3G) 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, so therefore they may absorb heavy metal ions within the pores of the swollen membrane. In addition, the hydroxyl and carbonyl groups of pHEMA may interact with heavy metal ions (similar to solvation with water), which may also cause nonspecific adsorption.

The sorbents used in heavy metal removal are generally in particulate form. Reed and Matsumoto reported 90–120 mmol Cd(II)/m^2 removal with activated carbon having different porosities (13). Egawa et al. found 62.1 mmol

uranium/m^2 removal by using amidoxime containing acrylonitrile–divinyl benzene copolymer beads (14). Maeda and Egawa showed very low adsorption capacities with 1.5 mmol Pb(II)/m^2 and 1.6 mmol Cu(II)/m^2 when using methyl methacrylate–divinylbenzene beads–aminomethyl phosphonic acid macroreticular chelating polymeric resin-containing poly(styrene–divinylbenzene) sorbents (15). Denizli et al. used dye-affinity polyvinylbutyral membranes for heavy metal adsorption (16, 17). The maximum adsorption capacities were 22.2–61.0 mmol/m^2 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 nonspecific and specific sorbents is pH dependent (18–21). In the absence of complexing agents, the hydrolysis and precipitation of 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. Reed and Matsumoto reported that hydrolysis of metal ions [e.g., Cu(II), As(III), Cd(II), Hg(II)] becomes significant at approximately pH 7.5–8.5 (22). Therefore, in the present study we changed the pH range to between 2.0 and 8.0. The effect of pH on heavy metal adsorption is shown in Fig. 5. It was observed that the adsorption capacities in-

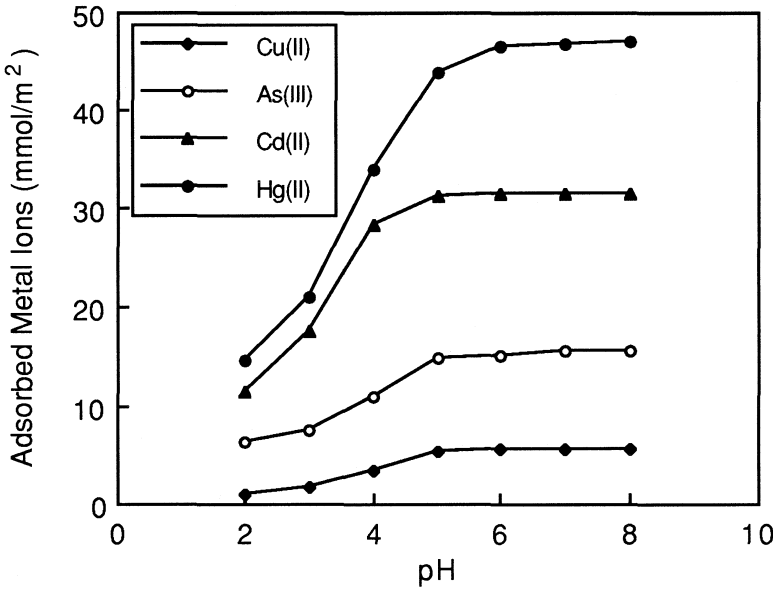

FIG. 5 Effect of pH on adsorption of heavy metal ions on the Procion Blue MX-3G-attached pHEMA membrane. Initial concentration of metal ions, 0.5 mmol/L; *T*, 20°C; and total membrane surface area in each batch, 0.01 m^2/L.

creased with increasing pH, reaching plateau values at around pH 5.0. Plateau values are 5.6 mmol/m^2 for Cu(II), 15.5 mmol/m^2 for As(III), 31.6 mmol/m^2 for Cd(II), and 47.1 mmol/m^2 for Hg(II). The difference in adsorption values can be explained by the different affinities of the heavy metal ions for the donor atoms (i.e., oxygen, nitrogen, and sulfur) in the dye-ligand Procion Blue MX-3G.

Competitive Adsorption

Adsorption capacities of Procion Blue MX-3G-attached pHEMA membranes for metal ions under competitive conditions (adsorption from solutions containing all heavy metal ions) for Cu(II), As(III), Cd(II), and Hg(II) are given in Table 1. It should be noted that the competitive adsorption capacities of Procion Blue MX-3G-attached pHEMA membranes for all metal ions were much higher than for noncompetitive conditions. The noncompetitive adsorption capacities are 5.6 mmol/m^2 for Cu(II), 15.5 mmol/m^2 for As(III), 31.6 mmol/m^2 for Cd(II), and 47.1 mmol/m^2 for Hg(II) at 0.5 mmol/L initial concentration. But the competitive adsorption capacities are higher than the non-competitive adsorption capacities: 6.9 mmol/m^2 for Cu(II), 21.2 mmol/m^2 for As(III), 33.9 mmol/m^2 for Cd(II), and 52.5 mmol/m^2 for Hg(II). Procion Blue MX-3G-attached pHEMA membranes show the following metal ion affinity order under competitive adsorption conditions: Hg(II) $>$ Cd(II) $>$ As(III) $>$ Cu(II).

Adsorption from Artificial Wastewater

Adsorption capacities of Procion Blue MX-3G-attached membranes from artificial wastewater for Cu(II), As(III), Cd(II), and Hg(II) are shown in Table 2. It is worth noting that the adsorption capacities of Procion Blue MX-3G-at-

TABLE 1
Comparison of Adsorption of Heavy Metal Ions on Procion Blue MX-3G-attached pHEMA Membranes[a]

Ions	Noncompetitive adsorption (mmol/m^2)	Competitive adsorption (mmol/m^2)
Cu(II)	5.6 ± 0.3	6.9 ± 0.4
As(III)	15.5 ± 0.6	21.2 ± 0.5
Cd(II)	31.6 ± 0.5	33.9 ± 0.7
Hg(III)	47.1 ± 0.5	52.5 ± 1.0

[a] Concentration of each metal ion: 0.5 mmol/L. pH: 7.0. *T*: 20°C. Total membrane surface area in each batch: 0.01 m^2/L.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

TABLE 2
Adsorption of Heavy Metal Ions from Artificial Wastewater on Procion Blue MX-3G-attached Membranes[a]

Ions	Adsorbed ion (mmol/m^2)
Cu(II)	3.5 ± 0.2
As(III)	10.2 ± 0.1
Cd(II)	24.7 ± 0.5
Hg(III)	37.3 ± 0.6

[a] Concentration of each metal ion: 0.5 mmol/L. pH: 7.0. *T*: 20°C. Total membrane surface area in each batch: 0.01 m^2/L.

tached membranes from artificial wastewater for all metal ions were much lower than for the competitive conditions and single solutions. The adsorption capacities are 3.5 mmol/m^2 for Cu(II), 10.2 mmol/m^2 for As(III), 24.7 mmol/m^2 for Cd(II), and 37.3 mmol/m^2 for Hg(II). Procion Blue MX-3G-attached membranes exhibit the following metal ion affinity sequence: Hg(II) > Cd(II) > As(III) > Cu(II). In this case, Procion Blue MX-3G-attached membranes also adsorbed other metal ions [i.e., Ni(II), Zn(II), Fe(II), Co(II), Sn(II), and Ag(I)]. The presence of other metal ions in the artificial wastewater decreases the adsorption capacities of pHEMA membranes for Cu(II), As(III), Cd(II), and Hg(II).

Regeneration of Membranes

To be useful in metal ion recycling prosesses, the metal ions chelated should be easily desorbed under suitable conditions. Desorption experiments were performed using 0.1 M HNO_3 as the desorption agent. Procion Blue MX-3G-attached pHEMA membranes loaded with the maximum amounts of the respective metal ions were placed in the desorption medium and the amount of metal ions desorbed in 30 minutes was measured. Table 3 shows the adsorption–desorption values of heavy metal ions by Procion Blue MX-3G-attached pHEMA membranes after several cycles of consecutive adsorption and desorption. This table clearly shows that Procion Blue MX-3G-attached pHEMA membranes can be used repeatedly without a significant loss of their adsorption capacities for all the metal ions studied here.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

TABLE 3
Heavy Metal Ions Adsorption Capacity of Procion Blue MX-3G-attached pHEMA Membranes after Repeated Adsorption–Desorption Cycle[a]

	Cu(II)		As(III)		Cd(II)		Hg(II)	
Cycle	Adsorption ($mmol/m^2$)	Desorption (%)	Adsorption ($mmol/m^2$)	Desorption (%)	Adsorption ($mmol/m^2$)	Desorption (%)	Adsorption ($mmol/m^2$)	Desorption (%)
1	5.60	96.7	15.50	95.6	31.58	95.5	47.10	97.1
2	5.44	96.2	15.39	97.4	31.47	97.2	46.87	93.3
3	5.27	98.1	15.11	98.3	31.44	95.7	46.72	90.6
4	5.20	95.5	14.88	96.4	31.29	96.4	46.59	94.5
5	5.03	94.9	14.76	99.0	31.14	95.8	46.44	95.8

[a] Initial concentrations of metal ions: 1 mmol/L. pH: 7.0. *T*: 20°C. Total membrane surface area in each batch: 0.01 m^2/L.

CONCLUSION

pHEMA membranes carrying 25.6 mmol Procion Blue MX-3G/m^2 were used for adsorption/desorption of Cu(II), As(III), Cd(III), and Hg(II) ions from aqueous solution under noncompetitive and competitive conditions. The important results were as follows. The maximum adsorption capacities of these pHEMA membranes from their single metal ions solutions were 5.6 mmol/m^2 for Cu(II), 19.6 mmol/m^2 for As(III), 46.2 mmol/m^2 for Cd(II), and 119.6 mmol/m^2 for Hg(II). Under competitive conditions the adsorption capacities were 6.9 mmol/m^2 for Cu(II), 21.2 mmol/m^2 for As(III), 33.9 mmol/m^2 for Cd(II), and 52.5 mmol/m^2 for Hg(II). Procion Blue MX-3G-attached pHEMA membranes show the following metal ion affinity order under noncompetitive and competitive conditions: Hg(II) > Cd(II) > As(III) > Cu(II). The adsorption capacities of Procion Blue MX-3G-attached membranes from artificial wastewater for all metal ions were much lower than for competitive conditions. The adsorption capacities found were 3.5 mmol/m^2 for Cu(II), 10.2 mmol/m^2 for As(III), 24.7 mmol/m^2 for Cd(II), and 37.3 mmol/m^2 for Hg(II). Repeated adsorption and desorption cycles showed the feasibility of using Procion Blue MX-3G-attached pHEMA membranes for heavy metal adsorption.

REFERENCES

1. C. S. Luo and S. Huang. *Sep. Sci. Technol.*, *28*, 1253 (1993).
2. D. A. Harkins and G. K. Schweitzer, *Ibid.*, *26*, 345 (1991).
3. A. Sugii, N. Ogawa, and H. Hashizume, *Talanta*, *27*, 627 (1980).
4. S. Hunt, in *Immobilisation of Ions by Bio-Sorption* (H. Ecclos and S. Hunt, Eds.), Ellis Horwood, Chichester, 1986, Chap. 1.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

5. S. Brandt, R. A. Golfe, S. B. Kessler, J. L. O'Connor, and S. E. Zale, *Biotechnology*, *6*, 779 (1988).
6. S. M. A. Bueno, C. Legallais, K. Haupt, and M. A. Vijayalakshmi, *J. Membr. Sci.*, *117*, 45 (1996).
7. J. Marchese, M. Campderros, and A. Acosta, *J. Chem. Tech. Biotechnol.*, *64*, 293 (1995).
8. M. Y. Arica and V. Hasirci, *Polym. Int.*, *32*, 177 (1993).
9. A. Denizli, M. Kocakulak, and E. Pişkin, *J. Macromol. Sci., Part A.*, *A35*, 137 (1998).
10. M. Y. Arica, H. N. Testereci, and A. Denizli, *J. Chromatogr. A*, *799*, 83 (1997).
11. A. Denizli, S. Şenel, and M. Y. Arica, *Colloids Surf. Sci., B*, *11*, 113 (1998).
12. A. Denizli, B. Salih, S. Şenel, and M. Y. Arica, *J. Appl. Polym. Sci.*, *68*, 657 (1998).
13. B. E. Reed and N. R. Matsumoto, *Sep. Sci. Technol.*, *28*, 2179 (1993).
14. H. Egawa, T. Nonaka, S. Abe, and M. Nakayama, *J. Appl. Polym. Sci.*, *45*, 837 (1992).
15. H. Maeda and H. Egawa, *Ibid.*, *33*, 1275 (1987).
16. A. Denizli, K. Kesenci, M. Y. Arica, B. Salih, V. Hasirci, and E. Pişkin, *Talanta*, *46*, 551 (1998).
17. A. Denizli, D. Tanyolaç, B. Salih, E. Aydinlar, A. Özdural, and E. Pişkin, *J. Membr. Sci.*, *137*, 1 (1998).
18. R. S. Shreedhara-Murthy and D. E. Ryan, *Anal. Chim. Acta*, *140*, 163 (1982).
19. C. Kantipuly, S. Katragadda, A. Chow, and H. D. Gesser, *Talanta*, *37*, 491 (1990).
20. A. Denizli, B. Salih, and E. Pişkin, *Reactive, Funct. Polym.*, *29*, 11 (1996).
21. Y. Konishi, S. Asai, Y. Midoh, and M. Oku, *Sep. Sci. Technol.*, *28*, 1691 (1993).
22. B. E. Reed and M. R. Matsumoto, *Carbon*, *29*, 1191 (1991).

Received by editor January 23, 1998
Revision received December 1998

PAGE 2382 IS BLANK

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Request Permission or Order Reprints Instantly!