



ELSEVIER

Journal of Chromatography A, 773 (1997) 169–178

JOURNAL OF
CHROMATOGRAPHY A

New sorbents for removal of heavy metal ions: diamine-glow-discharge treated polyhydroxyethylmethacrylate microspheres

Adil Denizli^{a,b,*}, Bekir Salih^b, Erhan Pişkin^a

^aChemical Engineering Department and Bioengineering Division, Beytepe, 06532 Ankara, Turkey

^bDepartment of Chemistry, Hacettepe University, Beytepe, 06532 Ankara, Turkey

Received 11 November 1996; revised 14 February 1997; accepted 18 February 1997

Abstract

Polyhydroxyethylmethacrylate (PHEMA) microspheres prepared by suspension polymerization, were treated with diamine-plasmas [i.e. ethylenediamine (EDA) and/or hexamethylenediamine (HMDA)] in a glow-discharge reactor in which the exposure time and glow-discharge power were changed between 5–30 min and 5–20 W, respectively. The microspheres were characterized by FTIR and elemental analysis. The maximum amounts of nitrogen deposited on the microspheres were 22.3 and 23.4 $\mu\text{mol/g}$ with the EDA- and HMDA-plasmas. Adsorption of Cu(II) and Pb(II) ions from aqueous solutions on these sorbents was investigated under different conditions. Adsorption equilibria were achieved in 1 h. Different adsorption capacities were obtained in the adsorption media containing different amounts of heavy metal ions and at different pH values. Adsorption capacity increased both with increase in exposure time and glow-discharge power. The maximum adsorption capacities achieved were 5.3 mg Cu(II)/g; 136.2 mg Pb(II)/g and 6.8 mg Cu(II)/g; 174.2 mg Pb(II)/g for the EDA- and HMDA-plasma treated PHEMA microspheres, respectively. © 1997 Elsevier Science B.V.

Keywords: Glow-discharge reactor; Sorbents; Heavy metals; Diamines; Polyhydroxyethylmethacrylate

1. Introduction

In recent years, heavy metals are among the most important contaminants in water sources and are becoming a severe public health problem. Heavy metals removal has been traditionally carried out by techniques such as membrane processes (e.g., dialysis, electrodialysis, reverse osmosis), neutralization-precipitation and ion-exchange, but usually with limited success. In recent years, adsorption has been shown to be an effective and economically feasible alternative method for removal of heavy metals [1–3]. Non-specific sorbents, such as acti-

vated carbon, metal oxides, silica and ion-exchange resins have been used [4–6]. Recently, specific sorbents have been proposed, consisting of a ligand (e.g., ion-exchange material or chelating agents) which interacts with the metal ions specifically, and a carrier matrix which may be an inorganic material (e.g., aluminium oxide or silica) or polymers (e.g., polystyrene or polymethylmethacrylate) [7,8]. Polymers have attracted the most attention as carrier matrices because they are easily produced in a wide variety of compositions, and modified into specific sorbents, by introducing a variety of ligands. Synthetic polymers have almost entirely displaced inorganic carriers, with few exceptions, in the separation of heavy metal ions [9,10].

*Corresponding author.

In this study, we prepared a new sorbent based on poly(hydroxyethylmethacrylate) (PHEMA) microspheres, which were functionalized by diamine-plasmas using a low temperature plasma technology (i.e. glow-discharge at room temperature) which has been widely utilized for surface modification of polymeric materials over the past decade [11–14]. In this communication, we present preparation and characterization of these microspheres and their adsorption capabilities for two selected heavy metal ions [i.e. Cu(II) and Pb(II) ions].

2. Experimental

2.1. Preparation of sorbent microspheres

The PHEMA microspheres were prepared by a suspension polymerization [15–18], which is briefly described here. The monomer, i.e. hydroxyethylmethacrylate (HEMA, Sigma) was purified by vacuum distillation under a nitrogen atmosphere. Ethylene glycol dimethacrylate (EGDMA, Merck) was used as the cross-linking agent. The polymerization initiator was 2,2'-azo-bis-isobutyronitrile (AIBN, BDH, UK). Polymerization was carried out in a dispersion medium consisting of a saturated aqueous solution of magnesium oxide (MgO, Sigma). The monomer phase containing HEMA, EGDMA and AIBN, was added to the dispersion medium within a laboratory type reactor (a two neck flask with a volume of 500 ml) provided with a blade type stirrer. In order to produce polymeric microspheres of about 200 μm in diameter and with a narrow size distribution, HEMA/EGDMA ratio, monomer/dispersion phase ratio, amounts of EGDMA, AIBN, and agitation speed were 1:3 (v/v), 1:10 (v/v), 0.33 (mol EGDMA/mol HEMA), 0.0015 (mol AIBN/mol HEMA) and 600 rpm, respectively. Polymerization was carried out at 70°C for 3 h and then at 90°C for 1 h. After cooling, the microspheres were separated from the polymerization medium by filtration, and the residuals (e.g., monomer, MgO, etc.) were removed by a cleaning procedure [16]. Briefly, microspheres were filled in a fixed-bed column, and washing solutions (a dilute HCl solution, and a water-ethanol mixture) were recirculated through the system which also includes an activated

carbon column, to be sure that the microspheres are clean. Purity of the microspheres was followed by observing the change in optical densities of samples taken from the liquid phase in the recirculation system, and also from the DSC thermograms of the microspheres obtained using a differential scanning calorimeter.

In the second step, the PHEMA microspheres were treated with diamines, i.e. ethylenediamine (EDA, BDH, UK) and hexamethylene diamine (HMDA, BDH, UK) in a 60 cm long tubular vertical glow-discharge reactor having an internal diameter of 5.6 cm. A radio-frequency generator (13.56 MHz) was coupled to the reactor through external copper electrodes. One gram of PHEMA microspheres was placed on a tray in the reactor, which was sealed and pumped down to 0.013 Torr. The microspheres were exposed to the diamine plasmas for exposure times of 5–30 min and at different discharge powers in the range of 5–20 W. During the treatment, the reactor, which was mounted on a vortex mixer, was shaken vigorously to ensure that all of the microcarriers were exposed to the diamine plasma. After plasma treatment, the reactor was then brought up to atmospheric pressure, and the treated microspheres were kept in argon atmosphere until use.

2.2. Characterization of sorbent microspheres

In order to determine the swelling behavior, 1 g of dry microspheres were placed into distilled water and kept at a constant temperature of $25 \pm 0.5^\circ\text{C}$. Swollen microspheres were periodically removed and weighed by an electronic balance. The water content of the swollen microspheres was calculated using the following expression:

$$\text{Swelling ratio (\%)} = [(w_s - w_o)/w_o] \times 100 \quad (1)$$

where w_o and w_s are the weights of microspheres before and after swelling, respectively.

The optical micrographs of the dry (non-swollen) and swollen microspheres were taken under an optical microscope (Nikon, AlphabotYS, Japan) equipped with a dark-field phase-contrast attachment. The average size and standard deviation was determined from measurements of 100–300 microspheres on the optical micrographs.

The amounts of diamine deposited on the microspheres were evaluated as the amount of nitrogen, using a Leco, CHNS-932 (USA) elemental analyzer.

FTIR spectra of the the untreated and diamine-glow discharge-treated PHEMA microspheres were obtained using a FTIR spectrophotometer (FTIR 8000 Series, Shimadzu, Japan). The dry poly-(HEMA) microspheres (about 0.1 g) were thoroughly mixed with KBr (0.1 g, IR Grade, Merck, Germany), and pressed into a a tablet, and the spectrum recorded.

2.3. Adsorption studies

Adsorption of two selected heavy metal ions [Cu(II) and Pb(II) ions] from aqueous solutions was investigated in batch experiments. Aqueous solutions (20 ml) containing heavy metal ions in the range 1–500 ppm were treated with the untreated and diamine-treated PHEMA microspheres at different pH values in the range 2.0–7.8 (adjusted with universal buffer solutions) at room temperature, in flasks agitated magnetically at an agitation speed of 600 rpm. After the predetermined adsorption equilibrium time, the microspheres were separated from the medium by filtration, then the concentrations of the heavy metal ions in the aqueous phase were measured using a graphite furnace atomic absorption spectrophotometer (GBC 932 AA, Australia). The amount of adsorbed heavy metal ions was calculated by using the expression

$$Q = [(C_0 - C) \cdot V] / m \quad (2)$$

where Q is the amount of metal ions adsorbed onto unit mass of the microspheres (mg/g); C_0 and C are the concentrations of the metal ions in the medium before and after adsorption, respectively (mg/ml); V is the volume of the aqueous phase (ml); and m is the amount of the sorbent microspheres used (g).

3. Results and discussion

3.1. Properties of sorbent microspheres

Over the past decade there has been rapid exploration and commercialization of low temperature plasma

technology to improve the surface properties of polymeric materials without changing the bulk properties [19,20]. The plasma-discharge (in other terms “glow-discharge”) may be used to etch the surface (e.g., with argon plasma), to form individual reactive groups (e.g., amines from ammonia, hydroxyl from water, etc.), or to deposit a “polymer-like” coating (using organic vapors, polymerizable gases, etc.). This method has the advantage of changing surface properties without affecting bulk properties. Since the surface is a determinant issue in preparation of specific sorbents for separation processes, in this study we attempted to create amino-like groups on the PHEMA microspheres utilizing this technology. EDA and HMDA were selected as the nitrogen-carrying active monomers to introduce amino groups onto the microspheres in a glow-discharge system. Both the exposure time and glow discharge power were changed in order to alter the number of nitrogen-containing surface active groups.

Fig. 1 gives representative FTIR spectra for the untreated PHEMA, the EDA-treated PHEMA and the HMDA-treated PHEMA. The absorption peak observed at 1600 cm^{-1} may be considered as an indication of the presence of a N–H scissor band. The band observed at $3300\text{--}3500 \text{ cm}^{-1}$ represents the –OH functional group. After EDA- and HMDA-plasma treatment, the –OH band becomes sharp due to N–H stretching. This shows amine deposition on the polymeric structure. The CH_2/CH_3 ratios are 0.46, 0.62 and 0.92 for untreated, EDA- and HMDA-plasma treated microspheres, respectively. The increase in this ratio resulted from the increase of amounts of CH_2 due to the diamine (i.e. EDA and HMDA) deposition. This ratio was higher with HMDA-treatment.

The amounts of diamines deposited onto the microspheres in the glow-discharge treatment were evaluated from the elemental analysis data, presented in Table 1 as mmol of nitrogen per gram of the microspheres. As seen here, the number of nitrogen-carrying groups increased both with the exposure time and discharge power in the studied range. The maximum amounts of nitrogen deposition were 22.3 and 23.4 μmol nitrogen/g polymer for EDA-plasma and for HMDA-plasma treatments, respectively.

In order to exhibit the swelling behavior, swelling ratios of the untreated and glow-discharge-treated

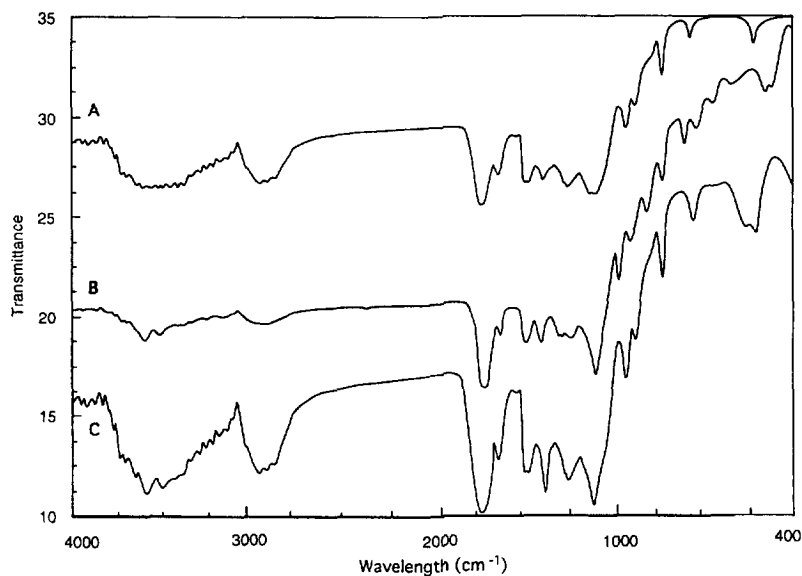


Fig. 1. FTIR spectra: (A) Untreated PHEMA; (B) EDA-treated PHEMA; (C) HMDA-treated PHEMA.

PHEMA microspheres were obtained at 25°C using Eq. (1) given above. The swelling ratio of the untreated PHEMA was about 55%, which was not high but was expected because we used a relatively high amount of cross-linker (EGDMA) in the basic polymerization recipe. It should be noted also that the swelling ratio of the microspheres did not change after the glow-discharge treatment.

3.2. Adsorption rates

Fig. 2A and Fig. 2B illustrate adsorption rates of heavy metal ions on diamine-glow-discharge-treated

PHEMA microspheres. These batch experiments were carried out using single (not mixed) solutions of the interested ions. Both glow-discharge and adsorption conditions are given in the figure legend. As seen from here, the non-specific adsorption (i.e. adsorption of heavy metal ions on the untreated PHEMA microspheres) was low, about 0.30 mg Cu(II)/g and 0.95 mg Pb(II)/g. There are no chelating groups on the untreated PHEMA microspheres, therefore this adsorption may be due to diffusion of heavy metal ions into the swollen matrix and weak interactions between metal ions and hydroxyl groups on the surface of the microspheres. While high

Table 1
Nitrogen deposition on the microsphere surfaces by glow-discharge treatment

Glow-discharge conditions		Nitrogen deposition	
Time (min)	Power (Watt)	With EDA-plasma ($\mu\text{mol/g}$)	With HMDA-plasma ($\mu\text{mol/g}$)
30	5	13.4	14.7
30	10	15.2	16.8
30	15	18.6	19.5
30	20	22.3	23.4
20	20	20.1	21.0
10	20	17.3	18.2
5	20	15.6	16.4

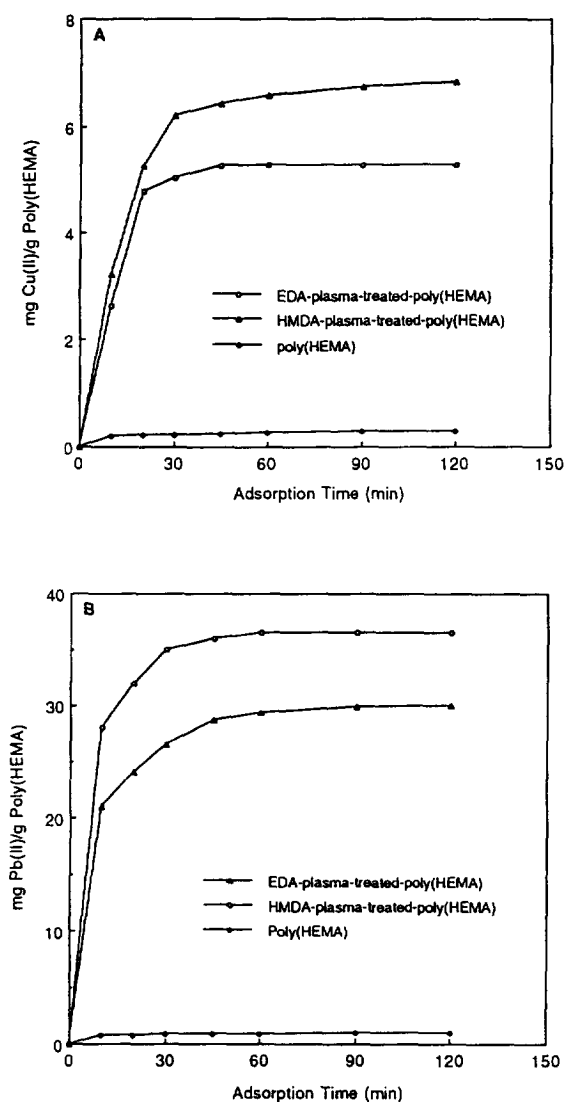


Fig. 2. Adsorption rates of metal ions on polymeric microspheres: (A) Cu(II); (B) Pb(II). Glow-discharge conditions: exposure time 30 min; discharge power: 20 W. Adsorption conditions: initial concentration of metal ions: 50 ppm; pH: 6.8; temperature: 20°C.

adsorption rates are observed with the glow-discharge treated PHEMA microspheres at the beginning of adsorption, plateau values (showing adsorption equilibrium) are gradually reached within 30–45 min. The adsorption rate of heavy metal ions onto the HMDA-treated PHEMA microspheres was higher than for the EDA-treated PHEMA microspheres. This may be due to higher amounts of nitrogen-

carrying active groups available for interaction with heavy metal ions in the case of the HMDA-glow-discharge treatment (see Table 1).

Several authors have presented a wide range of adsorption rates for the adsorption kinetics of heavy metal ions. For example, recently, Reed and Matsumoto have considered 6 h as a short equilibrium time in their cadmium adsorption kinetic studies, in which they have used activated carbon as sorbent [6]. Konishi et al. have investigated the recovery of zinc, cadmium and lanthanum by biopolymer gel particles of alginic acid. In their recent paper, they reported very high adsorption/desorption rates for lanthanum by alginic acid, with equilibrium achieved in about 60–90 min [21]. Shreedhara-Murthy and Ryan have investigated mercury, copper, cadmium, lead and uranium adsorption on cellulose–dithiocarbamate resins and reported that the adsorption rates were very slow [22]. Egawa studied uranium adsorption on polyacrylonitrile fibers containing amidoxime groups and reported a 7 h equilibrium adsorption time [23]. More recently, we have achieved very fast adsorption rates (15–60 min equilibrium time) for heavy metal ions with our microspheres carrying specific dye-ligands [24,25]. Note that in such an adsorption process, there are several parameters which determine the adsorption rate, such as agitation (or flow) rate in the aqueous phase, 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, chelate-formation rate, and of course the existence 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 under different conditions. Even though it is neither easy nor very correct to compare adsorption rate, from the data that we presented in this communication, we may conclude that the new sorbent is a very promising one.

3.3. Adsorption capacities: effects of pH

Metal ion-adsorption both on non-specific and specific sorbents is pH dependent [6,21–23,26]. In the absence of metal chelating 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. Hydrolysis of Cu(II) and Pb(II) ions becomes significant at approximately pH 6.5 and 8.0, respectively. The theoretical and experimental precipitation curves indicate that precipitation begins above these pH values, which also depends on the concentration of heavy metal ions in the medium. Therefore, in our study, in order to establish the effect of pH on the adsorption of heavy metal ions onto the diamine-plasma treated PHEMA microspheres, we repeated the batch equilibrium studies at different pH in the range of 2.0–7.8. Fig. 3A and Fig. 3B show the specific adsorption of heavy metal ions onto these glow-discharge treated PHEMA microspheres.

Adsorption around pH 2.0 was very low, maybe due to protonation of the amino-like groups created during glow-discharge treatment of the polymeric beads. Adsorption of heavy metal ions first increased with increasing pH and reached almost a plateau value. These plateau values for Cu(II) ions were around pH 4.5 and 6.0 for the EDA-plasma and for the HMDA-plasma treatments, respectively. While for Pb(II) ions, the plateau values were pH 4.0 and 3.5 for the EDA-plasma and for the HMDA-plasma treatments, respectively. Notice that adsorption capacities of the HMDA-treated microspheres were higher than EDA-plasma-treated microspheres for both ions at all pH values studied.

3.4. Adsorption capacities: effects of glow-discharge exposure time

In order to study the effects of glow-discharge exposure time on adsorption, we treated the microspheres in the glow-discharge reactor with different exposure times between 5 and 30 min, in which the discharge power was 20 W. These microspheres were then used in the adsorption equilibrium studies in batch-wise systems. The Cu(II) and Pb(II) initial concentrations in the adsorption media were in the ranges 5–50 ppm and 1–500 ppm for Cu(II) and Pb(II), respectively. The pH, temperature and adsorption times were 6.8, 20°C and 2 h, respectively.

When we investigate the effects of the glow-discharge exposure time on adsorption capacities of the diamine-treated PHEMA microspheres for Cu(II) and Pb(II) ions, in all cases the amount of metal ions

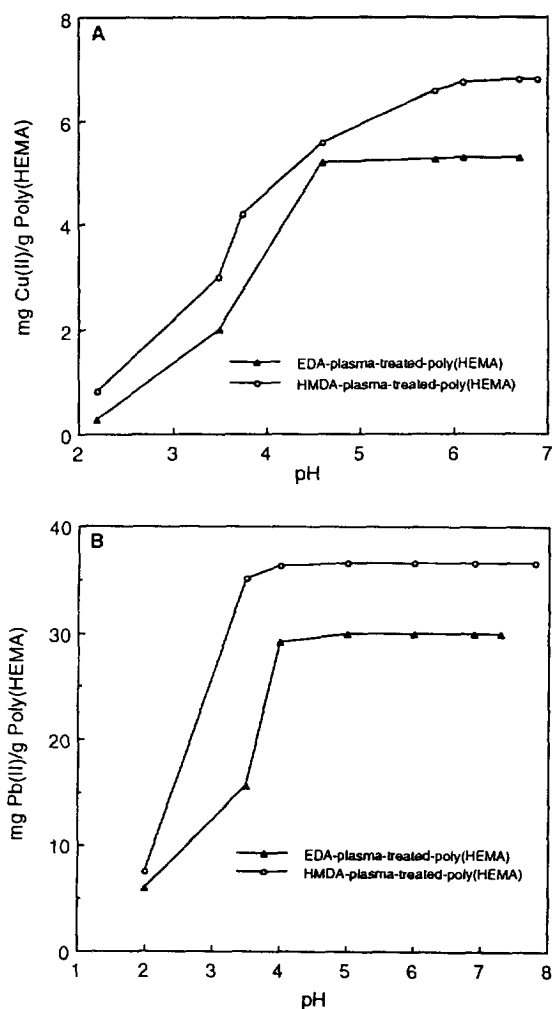


Fig. 3. Effects of pH on adsorption of heavy metal ions: (A) Cu(II); (B) Pb(II). Glow-discharge conditions: exposure time 30 min; discharge power: 20 W. Adsorption conditions: initial concentration of metal ions: 50 ppm; duration: 2 h; temperature: 20°C.

adsorbed per unit mass of the polymer (i.e. “the adsorption capacity”) first increased with the initial concentration of the respective ions and then reached a plateau, which represents saturation of the active groups on the microsphere surfaces available for metal ions.

Fig. 4A and Fig. 4B were prepared from the plateau values of the adsorption curves. Adsorption capacities of both the EDA- and HMDA-plasma treated microspheres for Cu(II) and Pb(II) ions

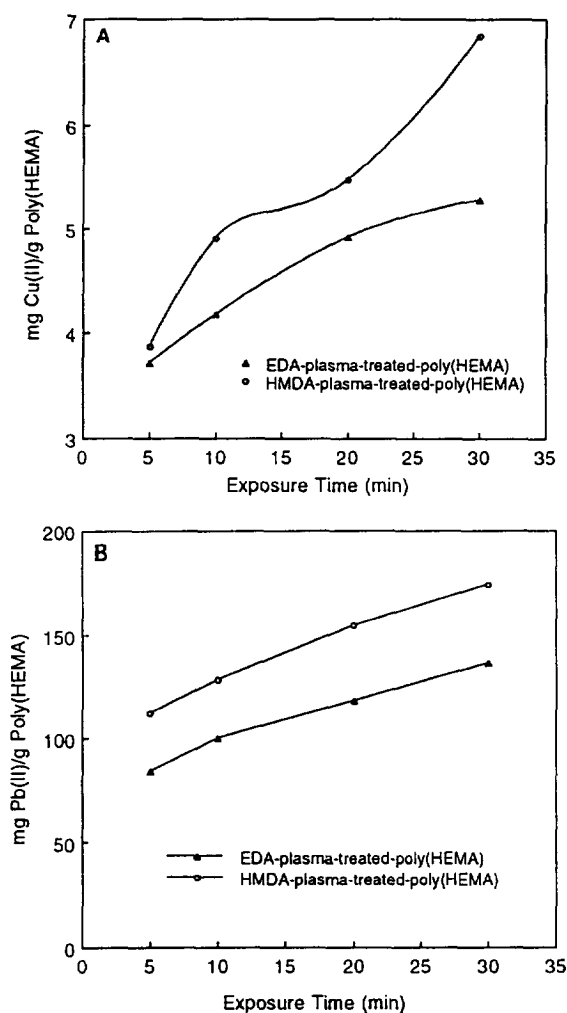


Fig. 4. Effects of glow-discharge exposure time on adsorption of: (A) Cu(II) ions; (B) Pb(II) ions. Glow-discharge power: 20 W. Adsorption conditions: initial concentration of metal ions: 50 ppm for Cu(II) ions and 500 ppm for Pb(II) ions; duration: 2 h; pH: 6.8; temperature: 20°C.

significantly increased with the glow-discharge exposure time. These effects can be attributed to the increase of the nitrogen-carrying groups on the microspheres by the increase in the plasma exposure time, as given in Table 1.

For comparison of adsorption capacities of the microspheres treated with both the EDA- and HMDA-plasmas at different exposure times, we calculated distribution coefficients (K_d) of metal ions between the sorbent phase and the adsorption medium at equilibrium, by using the following expression.

$$K_d = \frac{\text{Adsorbed metal ion (mg)/Amount of polymer (g)}}{\text{Amount of metal ion in solution (mg)/Volume of solution (ml)}} \quad (3)$$

Note that the distribution coefficient is defined as the ratio of the amount of metal ion adsorbed by 1 g of the polymeric sorbent to the amount of metal ion retained in 1 ml of the solution. Table 2 gives the K_d values. As seen here, in all cases much higher K_d values (indicating preferential adsorption) were obtained for Pb(II) ions than for Cu(II) ions.

3.5. Adsorption capacities: effects of glow-discharge power

In this group of experiments we treated the polymeric microspheres in the glow-discharge reactor with different glow-discharge powers in the range of 5–20 W, in which the exposure time was 30 min. These microspheres were then used in the adsorption equilibrium studies. The Cu(II) and Pb(II) initial concentrations in the adsorption media were in the ranges of 5–50 ppm and 1–500 ppm for Cu(II) and

Table 2
Effects of glow-discharge exposure time on K_d values

Exposure time (min)	K_d			
	EDA–Cu(II)	EDA–Pb(II)	HMDA–Cu(II)	HMDA–Pb(II)
5	91.40	212.66	95.97	313.60
10	105.69	268.38	130.15	379.68
20	130.50	336.69	150.96	505.16
30	143.48	413.04	207.90	616.67

Pb(II), respectively. The pH, temperature and adsorption time were 6.8, 20°C and 2 h, respectively.

If we look at the effects of discharge power on adsorption capacity of heavy metal ions as a function of initial concentration of heavy metal ions, in all cases the adsorption capacity increased first with the initial concentration of the respective ions and then reached plateau values similar to the effects of exposure time discussed before.

Heavy metal ions adsorption capacities of the EDA- and HMDA-treated PHEMA microspheres treated at different glow-discharge powers are given in Fig. 5A and Fig. 5B, respectively. Adsorption capacities of heavy metal ions increased with the increase in the discharge power, in both cases, which is due to the increase in the amount of active groups on the surface of PHEMA microspheres with discharge power, as given in Table 1.

For comparison of adsorption capacities of the microspheres treated with both the EDA- and HMDA-plasmas at different glow-discharge powers, we calculated distribution coefficients (K_d) using Eq. (3). Table 3 gives these K_d values. As seen here, in all cases much higher K_d values (preferential adsorption) were obtained for Pb(II) ions than for Cu(II) ions.

3.6. Adsorption capacities: comparison with related literature

A wide variety of sorbents with a wide range of adsorption capacities for heavy metal ions have been reported. Shreedhara-Murthy and Ryan found 4.8–27 mg Cu(II)/g removed by cellulose–dithiocarbamate resins [22]. Roozmond et al. showed 0.3–31.9 mg Cu(II)/g extracted with pyrazole-containing poly(styrene-divinylbenzene) sorbents [27]. Liu et al. achieved 93 mg Pb(II)/g and 16.5 mg Cu(II)/g adsorption capacities with N-hydroxymethyl thioamide resin [28]. Maeda et al. presented 107 mg Cu(II)/g and 88.7 mg Cu(II)/g with aminomethyl phosphonic acid containing methylmethacrylate/divinyl benzene copolymer beads [29]. Hudson and Matejka investigated the length of pendent groups (i.e. ethylenediamine, triethylenetetramine and pentaethylenhexamine) on Cu(II) ions-adsorption onto poly(styrene–divinyl benzene) copolymer beads and concluded that the type of pendent groups is im-

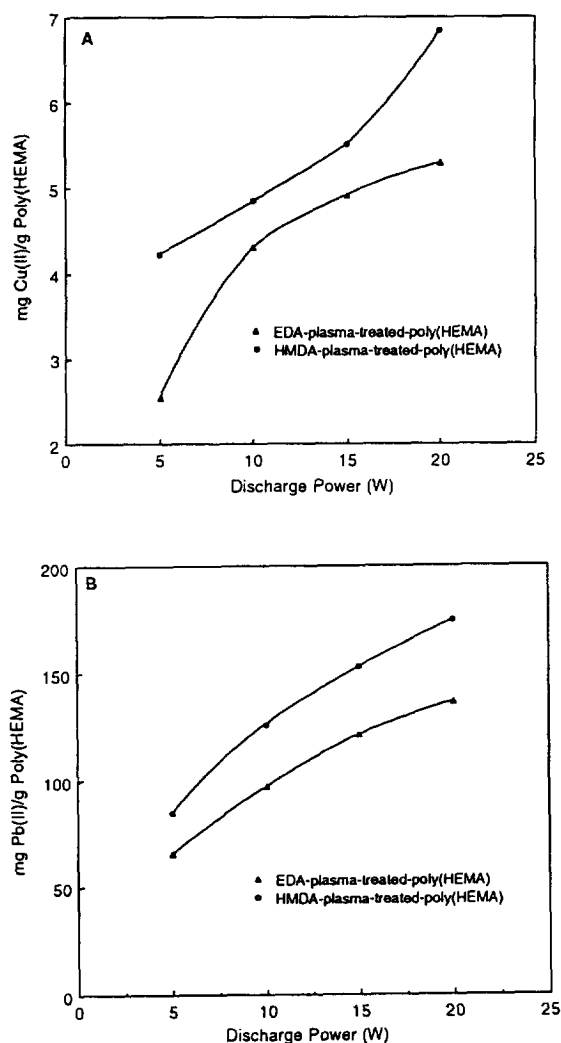


Fig. 5. Effects of glow-discharge power on adsorption of: (A) Cu(II) ions; (B) Pb(II) ions. Glow-discharge exposure time: 30 min. Adsorption conditions: initial concentration of metal ions: 50 ppm for Cu(II) ions and 500 ppm for Pb(II) ions; duration: 2 h; pH: 6.8; temperature: 20°C.

portant in the adsorption of heavy metal ions [30]. They reported adsorption capacities between 15.2–46.4 mg/g. Sağ and Kutsal have used *Zoogloea ramigera* microorganisms for heavy metal adsorption [31]. The maximum amounts of adsorption capacities achieved were 35 mg Cu(II) and 85 mg Pb(II)/g dry weight of microorganisms. Shambhu et al. immobilized polyamines (i.e. ethylenediamine, diethylenetriamine and triethylenetetramine) onto polystyrene

Table 3
Effects of glow-discharge power on K_d values

Exposure time (min)	K_d			
	EDA–Cu(II)	EDA–Pb(II)	HMDA–Cu(II)	HMDA–Pb(II)
5	58.45	194.80	107.29	395.65
10	109.88	377.08	125.27	720.00
15	130.51	613.43	152.30	1270.03
20	143.48	853.92	207.90	2690.50

and reached an adsorption value of 33 mg Cu(II)/g polymer [32]. Janus et al. used poly(vinyl amine) sorbent for copper adsorption and reported an adsorption capacity of 0.5 mg Cu(II)/g [33]. Khalfaoui et al. achieved an adsorption capacity of 0.04 mg Cu(II)/g on raw charcoal [34]. Denizli et al. used dye-immobilized P(EGDMA–HEMA) sorbents, in which the maximum adsorption capacities were 2.9 mg Cu(II)/g and 165 mg Pb(II)/g [24]. Marzal et al. immobilized ethylenediamine and hexamethylenediamine by glow-discharge method and obtained 5.3 mg Cu(II)/g for EDA and 6.8 mg Cu(II)/g for HMDA-plasma treatment [35]. Biçak et al. reported 155 mg Cu(II)/g by using sorbents based on *p*-dichloromethyl benzene [36]. From the data that we obtained in this study, we may conclude that the new sorbent presented in this communication is promising, especially for the adsorption of Pb(II) ions from aqueous media.

4. Conclusion

In this study, polyhydroxyethylmethacrylate (PHEMA) microspheres which were prepared by suspension polymerization, were treated with diamine-plasmas (i.e. ethylenediamine, EDA and/or hexamethylenediamine, HMDA) in a glow-discharge reactor for different exposure times and at different glow-discharge powers. By this very simple surface treatment method (i.e. glow-discharge), it was possible to incorporate nitrogen containing functional groups (most probably amino-like groups) on the PHEMA based microspheres. Note that this novel technique can be easily applied to any kind of polymeric microsphere to create the same surface groups (in other terms it is not a substrate dependent method).

Adsorption of Cu(II) and Pb(II) ions from aqueous solutions on these sorbents was investigated under different conditions. As mentioned before, all individual experimental study related to the adsorption of heavy metal ions from aqueous media published in the literature, have been performed at different conditions, and therefore, it is neither easy nor correct to compare the adsorption rates and capacities reported by different groups. Almost 90% of the equilibrium adsorption values were achieved in less than 30 min, which can be considered as relatively fast adsorption rates. Adsorption capacities, which were dependent on the glow-discharge conditions (i.e. exposure time and discharge power) were also high in comparison with the existing adsorption data, especially for the Pb(II) ions. Therefore, we may conclude that the new sorbent presented in this communication is promising, especially for the adsorption of Pb(II) ions from aqueous media.

References

- [1] B.E. Reed, S.K. Nonavinakere, *Sep. Sci. Technol.* 27 (1992) 1985.
- [2] Z. Aksu, T. Kutsal, *Environ. Technol.* 11 (1990) 979.
- [3] A. Goto, A.S. Morooka, M. Fukamachi, K. Kusakabe, T. Kago, *Sep. Sci. Technol.* 28 (1993) 2229.
- [4] J.F. Pietrzyk, C.H. Chu, *Anal. Chem.* 49 (1977) 860.
- [5] K. Brajter, E. Dabek-Zlotorzynska, *Analyst* 113 (1988) 1571.
- [6] B.E. Reed, M.R. Matsumoto, *Sep. Sci. Technol.* 28 (1993) 2179.
- [7] K. Brajter, E. Dabek-Zlotorzynska, *Talanta* 37 (1990) 613.
- [8] C. Kantipuly, S. Katragadda, A. Chow, H.D. Gosser, *Talanta* 37 (1990) 491.
- [9] N. Kabay, H. Egawa, *Sep. Sci. Tech.* 28 (1993) 1985.
- [10] Y. Ito, T. Saegusa, *J. Macromol. Sci. Chem.* A13 (1979) 503.
- [11] H. Yasuda (Ed.), *Plasma Polymerization*, Academic Press Inc., Orlando, 1985.

- [12] H. Yasuda, J. Polym. Sci. Macromol. Rev. 16 (1981) 199.
- [13] E. Pişkin, J. Biomater. Sci. Polym. Ed. 4 (1992) 45.
- [14] R. D'Agostino (Ed.), Plasma Deposition, Treatment and Etching of Polymers, Academic Press Inc., New York, 1991.
- [15] A. Denizli, E. Pişkin, J. Chromatogr. B 666 (1995) 215.
- [16] A. Denizli, A.Y. Rad, E. Pişkin, J. Chromatogr. B 668 (1995) 13.
- [17] A. Denizli, E. Pişkin, J. Chromatogr. B 670 (1995) 157.
- [18] A. Denizli, E. Pişkin, V. Dixit, M. Arthur, G. Gitnick, Int. J. Artif. Organs 18 (1995) 90.
- [19] J.K. Hollahan, A.T. Bell (Eds.), Techniques and Applications of Plasma Chemistry, John Wiley and Sons, New York, 1974.
- [20] D.T. Clark, W.J. Feast (Eds.), Application of Plasmas to the Synthesis and Surface Modifications of Polymers, John Wiley and Sons, New York, 1978.
- [21] Y. Konishi, S.S. Asai, Y. Midoh, M. Oku, Sep. Sci. Technol. 28 (1993) 1691.
- [22] R.S. Shreedhara-Murthy, D.E. Ryan, Anal. Chim. Acta 140 (1982) 163.
- [23] H. Egawa, M. Nakayama, T. Nonaka, E. Sugihara, J. Appl. Polym. Sci. 33 (1987) 1993.
- [24] A. Denizli, B. Salih, E. Pişkin, React. Funct. Polym. 29 (1996) 11.
- [25] B. Salih, A. Denizli, E. Pişkin, Sep. Sci. Technol. 31 (1996) 715.
- [26] M.O. Çorapçioğlu, C.P. Huang, Carbon 25 (1987) 569.
- [27] D.A. Roozmond, Eur. Polym. J. 24 (1988) 367.
- [28] C.Y. Liu, H.T. Chang, C.C. Hu, Inorg. Chim. Acta 172 (1990) 151.
- [29] H. Maeda, H. Egawa, J. Appl. Polym. Sci. 33 (1987) 1275.
- [30] M.J. Hudson, Z. Matejka, Sep. Sci. Technol. 25 (1990) 1417.
- [31] Y. Sağ, T. Kutsal, Chem. Eng. J. 60 (1995) 181.
- [32] M.B. Shambhu, M.C. Theodorakis, G.A. Digenis, J. Polym. Sci., Polym. Chem. Ed. 15 (1977) 525.
- [33] L. Janus, J. Morcellet, M. Delporte, M. Morcellet, Eur. Polym. J. 28 (1992) 1185.
- [34] B. Khalfaoui, A.H. Meniai, R. Borja, J. Chem. Tech. Biotechnol. 64 (1995) 153.
- [35] P. Marzał, A. Seco, C. Gabaldon, J. Ferrer, J. Chem. Tech. Biotechnol. 66 (1996) 279.
- [36] N. Biçak, G. Koza, T. Atay, J. Appl. Polym. Sci. 61 (1996) 799.