In Situ Formation of Porous Molecularly Imprinted Polymer Membranes

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Received February 10, 2003; Revised Manuscript Received June 30, 2003

ABSTRACT: Molecularly imprinted polymer membranes for a model compound, atrazine, were prepared in situ from a monomer mixture containing methacrylic acid, tri(ethylene glycol) dimethacrylate, and atrazine using UV-initiated polymerization. To improve flexibility and mechanical stability of these membranes, oligourethane acrylate was added to the mixture of monomers. Polymeric additives were used to increase porosity of membranes and their permeability as well as to make them suited for filtration experiments. This process resulted in the formation of thin, flexible, and porous membranes containing atrazine-specific binding sites. The atrazine-imprinted membranes showed higher affinity to this herbicide than to structurally similar compounds (simazine, prometryn, and metribuzin). The binding capacity of MIP membranes was found to be significantly higher than that observed previously for MIP systems. The high affinity, specificity, and binding capacity of MIP membranes, together with their straightforward and easy preparation, provide a good basis for their application in separation and purification, e.g., in membrane chromatography.

Introduction

Over the past three decades, new molecular imprinting approaches for introducing affinity binding sites into synthetic polymers have been developed.[1,2] In this technique a highly cross-linked polymer is formed around a template molecule. The template is then removed by washing, leaving cavity in the polymer network with functional groups complementary to those of the template molecule. It has been shown that molecularly imprinted polymers (MIPs) can be developed for a variety of compounds;[1−3] their synthesis is a straightforward and inexpensive procedure. These polymers demonstrate very good thermal and mechanical stability and can be used in aggressive media.[4] Therefore, the molecular imprinting approach allows one to combine selectivity of natural receptors with stability and robustness of synthetic polymers.

MIPs have been widely used as a stationary phase for chromatographic separation,[5,6] as substitutes for antibodies in immunoassays,[7] as selective elements of electrochemical sensors,[8,9] and in solid-phase extraction (SPE).[10−12] Chromatographic and SPE applications traditionally utilize MIP particles prepared by grinding and sieving of synthesized polymer blocks or particles prepared by suspension polymerization. The first approach is time-consuming, may lead to the destruction of some binding sites in the polymer, and produces a relatively low yield of fraction with a narrow size distribution. In the second approach, the choice of monomers is limited to those which are not soluble in the dispersion phase. Additionally, the synthesized beads are not always uniform in their shape and size. Thus, again a sieving procedure is required which makes column packing time-consuming, expensive, and ineffective. It is also difficult to scale up the manufacturing of MIPs prepared using these approaches. Therefore, other less conventional approaches have been proposed to improve the quality of HPLC materials and facilitate the preparation procedure. Thus, Matsui et al.[13] described the preparation of porous MIP rods in situ inside of HPLC columns. This approach, however, suffers from quality control problems (not adequate mechanical strength and variations in porosity and surface area).[14−17]

Concurrent with these developments, membranes have become increasingly attractive alternatives to columns filled with particles for efficient affinity separations, including SPE.[18] Their preparation does not require grinding and their processing (e.g., packing in the membrane holder) and application is easy. The design of MIP membranes for chromatography and filtration is, however, difficult. The main problem is the high level of cross-linking, which is traditionally used in molecular imprinting. This results in formation of too fragile and brittle membranes and in a relatively low porosity, preventing their use in chromatography due to high backpressure and low fluxes. This problem was overcome by grafting of MIPs to the surface of commercial microfiltration membranes.[19−21] Although the membranes grafted with imprinted polymers possessed the required affinity and specificity, their capacity was limited, and it was difficult to adapt a grafting procedure to different template−monomer systems. The problem of MIP fragility was resolved by adding a flexible compound, i.e., oligourethane acrylate, to the polymer composition.[9] The casted membranes were flexible, but their porosity was still too low for chromatographic applications.

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10.1021/ma030105x CCC: $25.00

The present work is focused on solving the second problem: low through-membrane porosity in casted MIP membranes. The intention was to use polymeric additives to introduce additional pores in polymer systems and increase pore size. Atrazine was chosen as a model system for this study since this triazine herbicide has been widely used in developing MIP adsorbents, and the affinity and selectivity of these systems are well characterized.[22−25] The number of structurally similar compounds affiliated to the triazine herbicides implies broad possibilities for the control of specificity of the resulting polymer.

Experimental Section

Materials. Methacrylic acid and tri(ethylene glycol) dimethacrylate were purchased from Fluka (Gillingham-Dorset, UK). Chloroform, dimethylformamide, methyl ethyl ketone, toluene, ethyl acetate, and poly(ethelene glycol) (average molecular weight 1500, 3000, and 20 000) were obtained from Sigma (St. Louis, MO). 1,1′-Azobis(cycloxexane carbonitrile) was obtained from Aldrich (Milwaukee, WI). Oligourethane acrylate was synthesized as described previously[26] and supplied by the Pilot Plant of the Institute of Macromolecular Chemistry (Kiev, Ukraine). Atrazine, simazine, prometryn, and metribuzine (crystals of 99% purity) were purchased from Serva (Heidelberg, Germany). Atrazine crystals dissolved in distilled water were used as a stock atrazine solution for further experiments. The other chemicals were of analytical grade and were used as received without additional purification.

Molecularly Imprinted Polymer Membranes. MIP membranes were prepared using atrazine as a template, methacrylic acid as a functional monomer, and tri(ethylene glycol) dimethacrylate as a cross-linker. The molar ratio of the functional monomer to the template (5:1) was optimized earlier.[9] To obtain thin, flexible, and mechanically stable membranes, oligourethane acrylate (average molecular weight 2600) was added to the monomer mixture.[9,26] A typical preparation of the molecularly imprinted polymer membrane was carried out as follows. Atrazine (20 mg) was mixed with 40 mg of methacrylic acid, 306 mg of tri(ethylene glycol) dimethacrylate, 54 mg of oligourethane acrylate, 20 mg of 1,1′-azobis(cycloxexane carbonitrile), and 50% (w/w) of the organic solvent (with respect to weight of the monomers). Poly(ethylene glycol) was added to the monomer composition in the concentration 5−20% (w/w). Then a 60 μm gap between two glass slides was filled with the monomer mixture. To complete the polymerization, the slides with the mixture were exposed to UV light ($\lambda = 365$ nm, intensity 20 W m^{-2}) for 1 h. That was followed by the 8 h extraction procedure by methanol in a Soxhlet apparatus to remove nonpolymerized compounds and the template. To remove poly(ethylene glycol), the membranes were washed with water for 8 h. The membranes for the control experiments were prepared using the same procedure but in the absence of atrazine.

Characterization of MIP Membranes Performance. The membrane recognition properties were evaluated with respect to their ability to adsorb herbicides from the aqueous solution using a two-compartment separation cell (Security Guard HPLC cartridge system, Phenomenex, UK) divided in two parts by the membrane under investigation. The concentration of the substrate in the receiving phase was quantified either after extraction with 10 mL of chloroform using gas chromatography (column HP5MS, Hewlett-Packard GC system HP 6890 with mass-selective detector HP 5973) or directly in the sample using Hill reaction based on inhibition of chloroplast photosynthetic reaction by triazine herbicides.[27]

Determinations of the Pore Volume, Specific Surface Area, and Average Pore Radius in the MIP Membranes. Specific surface calculation of membranes was carried out by the Brunauer−Emmett−Teller (BET) method.[28] The BET equation was used in the following form for interpretation of the experimental data:

$$\frac{p/p_0}{a(1 - p/p_0)} = \frac{1}{Ca_{\mathrm{m}}} + \frac{C - 1}{Ca_{\mathrm{m}}}\frac{p}{p_0} \qquad (1)$$

where p/p_0 is the relative pressure of sorbate vapors; a the amount of sorbed substance, mmol/g; a_{m} the amount of substance in a continuous monomolecular layer, mmol/g; and C a constant.

The experimental data were presented as a dependence:

$$\frac{p/p_0}{a(1 - p/p_0)} = f\left(\frac{p}{p_0}\right) \qquad (2)$$

The X- and Y-intercepts allow one to obtain both the values C and a_{m}. The specific surface area was calculated using the following equation:

$$S_{\mathrm{sp}} = a_{\mathrm{m}} w N_{\mathrm{A}} \times 10^{-7}\ \mathrm{m}^2/\mathrm{g} \qquad (3)$$

where N_{A} is the Avogadro constant and w the area occupied with the single molecule of sorbate, and its value was found from the formula

$$w = 4 \times 0.866\left(\frac{M}{4\sqrt{2}\ dN_{\mathrm{A}}}\right)^{2/3} \qquad (4)$$

where M is the molecular weight of sorbate and d the sorbate density.

The total volume of pores in the membrane samples was calculated using the methanol absorption isotherms:

$$W_0 = aV \qquad (5)$$

where a is the maximum amount (mol) of sorbate absorbed with 1 g of sorbent and V is the volume of 1 mol of the sorbate.

The average pore radius for the membrane samples was found using the account obtained values of W_0 and S from the following expression:

$$r_{\mathrm{av}} = (2W_0/S) \times 10^4 \qquad (6)$$

Morphological Analysis. Electron micrographs were taken with a JEOL JSM 6310 scanning electron microscope (SEM). Samples of membranes were freeze-dried overnight before being examined by electron microscopy. After drying, these specimens were sputtered with palladium to avoid electrostatic charges and to improve image resolution. For the best representation, scanning of the whole samples was done before the micrographs were taken.

Results and Discussion

Most studies with imprinted polymers have been carried out using polymer particles either in batch or chromatographic mode. Only recently have free-standing membranes of MIPs been prepared and used for selective separation of structurally similar compounds and in chemical sensors.[29−32] As widely recognized, the specific structure of the imprinted cavity is preserved in the polymer network by the high degree of the polymer cross-linking.[1] However, highly cross-linked materials tend to yield very brittle and mechanically unstable films. To improve mechanical properties of MIP membranes, we used mixtures of methacrylates and oligourethane acrylate, which were expected to yield films with high mechanical stability and flexibility required for membrane preparation.[33]

The content of the cross-linker in the monomer composition designed for atrazine recognition was optimized earlier.[9] The optimal ratio between tri(ethylene

Table 1. Dependence of Water Flux through the MIP Membranes on the Nature of the Porogen Added to the Monomer Composition[a]

pore-forming component	pore vol, cm^3/g	specific surf. area, m^2/g	av pore radius, nm	water flux,[b] L/(m^2 h)
50% chloroform	0.022	9.5	4.62	0
50% ethyl acetate	0.024	9.7	4.96	0
50% methyl ethyl ketone	0.022	11.7	3.77	0
50% DMF	0.027	12.7	4.26	3045
5% PEG (M_w 20 000); 50% DMF	0.029	11.7	5.00	3057
10% PEG (M_w 20 000), 50% DMF	0.029	12.8	4.52	5992
15% PEG (M_w 20 000); 50% DMF	0.023	9.3	5.00	10791
20% PEG (M_w 20 000); 50% DMF	0.026	11.1	4.60	9996
15% PEG (M_w 20 000), 50% DMF (blank)	0.028	12.7	4.40	10000

[a] All the membranes were synthesized using methacrylic acid as a functional monomer, tri(ethylene glycol) dimethacrylate as a cross-linker, and oligourethane acrylate. [b] Measured at 40.7 MPa.

glycol) dimethacrylate and oligourethane acrylate in the monomer mixture was found to be 85:15 (w/w). Although the porosity of polymers synthesized under these conditions is reasonably high ($\sim$0.02 cm^3/g), the water fluxes through them were negligible. This can be explained by the absence of large through-membrane pores in the membrane structure, necessary for rapid mass transfer through the polymer. Polymer porosity can be increased by adding porogen, e.g., porogenic solvent or linear polymer, varying concentration of the free radical initiator, and/or changing polymerization temperature.[16,34−36]

To obtain membranes with high fluxes, organic solvents of different polarity (methyl ethyl ketone, ethyl acetate, chloroform, toluene, and dimethylformamide) were used as porogens. It was shown here (see Table 1) that addition of dimethylformamide resulted in formation of membranes with the water flux 3045 L/(m^2 h) (at 40.7 MPa), while addition of all the other solvents resulted in formation of the membranes that were not permeable for water. Dimethylformamide, which is a “poor” solvent for this type of polymer composition, facilitates formation of large pores because of an earlier onset of phase separation.[36] The increase in the concentration of dimethylformamide in the monomer mixture did not result in a significant increase in a water flux through the imprinted membranes. Therefore, a linear polymer, poly(ethylene glycol) (PEG), was added to the monomer composition for the further increase in the size and number of through-membrane pores.

Two possible mechanisms of PEG-induced pore formation can be proposed. Similarly to the effect of “poor” solvents, PEG facilitates phase separation between the growing copolymer chains and a solvent, containing dissolved linear PEG, by increasing the level of their thermodynamical incompatibility. The pores are formed between the coalescent cross-linked polymer globules. Another likely mechanism involves formation of different microregions in the polymer structure. Because of the high molecular weight of PEG used in this system, the phase separation is not complete. Therefore, heterogeneous microphase nonequillibrium structures are formed that remain stable for an unlimited time, creating a semiinterpenetrating polymer network (semi-IPN) between the cross-linked copolymer and poly(ethylene glycol).[37,38] Incomplete phase separation in a fully formed IPN or semi-IPN leads to the appearance of interphase or transitive regions, which have more “defect” and porous structure as compared to the structure of pure individual components of IPN.[38−43] The semi-IPN represents a four-phase system consisting of microregions of the copolymer, microregions of the linear polymer (PEG), microregions of the copolymer enriched with the linear polymer, and microregions of the linear polymer enriched with the copolymer. Apparently, extraction of the linear polymer from the different regions of the polymerized membranes will result in formation of pores with wide size distribution.

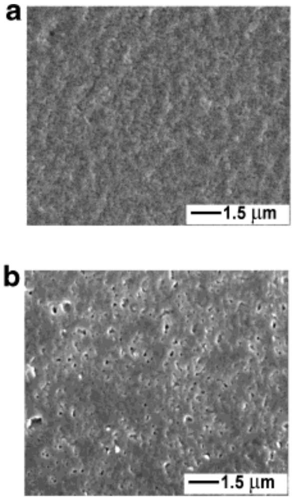

Figure 1. SEM microphotographs of the membranes synthesized with atrazine as a template, methacrylic acid as a functional monomer, tri(ethylene glycol) dimethacrylate as a cross-linker, and oligourethane acrylate; 50% DMF (a) and a mixture of 50% DMF and 15% PEG 20 000 (b) were used as porogens.

To analyze the influence of linear polymer on permeability and porosity of synthesized membranes, a set of polymers with varying molecular weight and concentration of PEG were prepared. Practically no increase in water flux was observed if low molecular weight PEGs (M_w 1500 and M_w 3000) were added to polymer composition (data not shown). The properties of synthesized membranes containing high molecular weight PEG (M_w 20 000) are summarized in Table 1. No correlation was found between water flux and surface area and membrane porosity measured by the BET method, which is not surprising since the major contribution to the surface area/porosity of macroporous polymers comes from pores smaller than 10 nm.

The effect of the porogen on the formation of large through-membrane pores can be clearly seen from SEM micrographs presented in Figure 1. As one can see, addition of high molecular weight PEG significantly increases water flux through the atrazine-imprinted membranes. The membranes synthesized with 50% (w/w) DMF containing 15% (w/w) poly(ethylene glycol) were characterized by the highest productivity and used in further experiments.

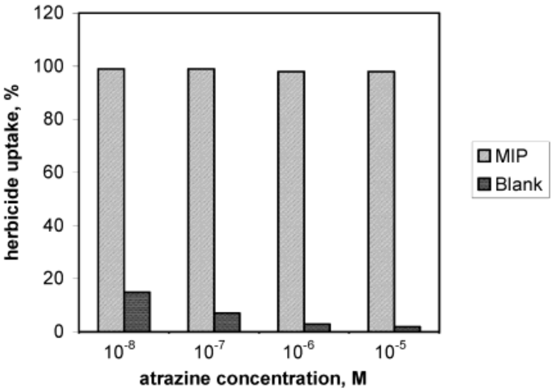

Figure 2. Dependence of MIP and blank membrane adsorption capability on the concentration of atrazine in the feed solution; DMF (50%) and PEG 20 000 (15%) were used as porogens (10 mL of 10^{-5} M atrazine solution was passed across the membranes). Note: The presented data are the average results of testing three different membranes with the same composition. The standard deviation was less than 5%.

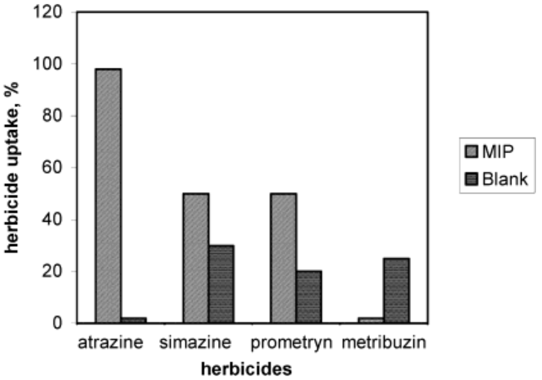

Figure 3. Selectivity of the atrazine-imprinted (MIP) and blank membranes to herbicides of the related chemical structure (10 mL of 10^{-5} M solutions of the herbicides was passed across the membranes). Note: The presented data are the average results of testing three different membranes with the same composition. The standard deviation was less than 5%.

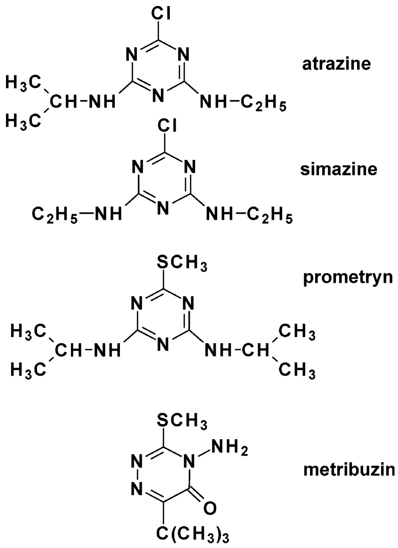

Figure 4. Chemical structures of triazine and triazinone herbicides.

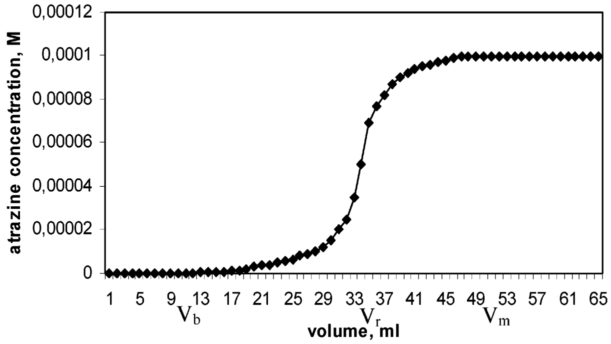

Figure 5. Breakthrough curve for the atrazine-imprinted membrane constructed on the basis of filtration experiments (10^{-4} M solution of atrazine was passed across the membrane). Note: The presented data are the average results of testing three different membranes with the same composition. The standard deviation was less than 5%.

The membranes' recognition properties were evaluated by measuring their capacity to adsorb atrazine from diluted aqueous solutions (10^{-8}–10^{-5} M). Atrazine solutions were filtered through the membranes at a rate 0.5 mL/min, and herbicide concentrations in both feed and permeate solutions were determined. In contrast to blank membranes, MIPs demonstrated high adsorption ability toward atrazine (Figure 2). One MIP membrane could be used repetitively for at least five times without loss of its binding efficiency.

The overall selectivity of the MIP membranes was evaluated in filtration experiments with atrazine analogues (simazine, prometryn, and metribuzine) (Figure 3). It was shown that atrazine-imprinted membranes had low nonspecific binding of compounds structurally similar to atrazine. The uptake of herbicides was dependent on their structures (Figure 4). Certain cross-reactivity with other triazine herbicides (simazine and prometryn) was observed, while the binding of triazinone metribuzine was negligible.

The adsorption capacity of the imprinted membranes was determined from a breakthrough curve measured in filtration experiments with diluted atrazine solution (10^{-4} M) (Figure 5). As one can see, the breakthrough curve for atrazine has a bilogarithmic shape, the inflection point of which is the retention volume V_r of atrazine. The V_r value measured in this experiment was 34 mL of 10^{-4} M solution. The breakthrough volume (V_b) representing the maximum sample volume, which can be applied to the membrane with 100% recovery, comprised 7 mL of 10^{-4} M solution for the membrane of 5 mm diameter. The adsorption capacity of the membrane was shown to be 12.5 mg/g of the polymer, which deviated approximately 25% from the theoretically expected one (calculated from the maximum theoretical number of imprinted binding sites). The binding capacity of the blank membrane was significantly lower (~0.625 mg/g of polymer). The binding capacity determined in this study for the MIP membranes has the highest value documented for imprinted polymers up to now. The high capacity of these new imprinted membranes can be explained in two ways. First, the polymer did not undergo grinding and mechanical deformation, and as a consequence the specific structure of imprinted binding sites is better preserved. The possibility that mechanical stress might be responsible for the partial destruction of binding sites has been indicated in our early work when polymer made in suspension demonstrated substantially higher affinity and selectivity than the polymer prepared by grinding of the bulk polymer.[44] The evidence that mechanical stress could be responsible for a destruction and/or

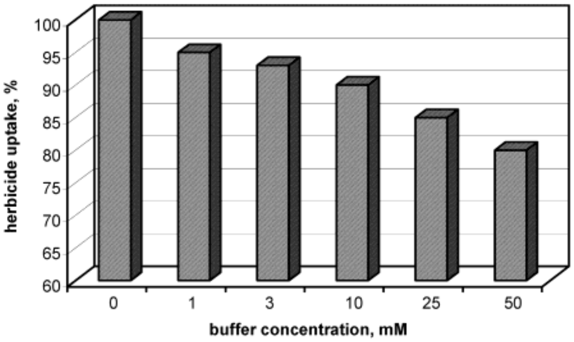

Figure 6. Dependence of the atrazine-imprinted membrane adsorption capability on the buffer concentration. Experiments were carried in sodium-acetate buffer pH 5. Note: The presented data are the average results of testing three different membranes with the same composition. The standard deviation was less than 5%.

deformation of specific binding sites was provided earlier for other affinity materials.[45,46] Second, it is possible that in contrast to polymer particles where internal areas are not accessible for mass exchange, porous membranes provide better accessibility of polymer binding sites for interaction with the template. The size of large transmembrane pores (according to SEM) is 70−200 nm, and they are connected to a large number of smaller pores with average diameter 4−5 nm. The binding sites available for binding are located at the polymer surface in both large and small pores. The atrazine adsorption is realized through the combination of pore diffusion and surface diffusion. The pore diffusion mechanism characterizes a transport in the stagnant liquid phase inside a porous stationary phase. In contrast, the surface diffusion mechanism describes mass transport along an adsorbing surface induced by a different loading of an adsorbed solute. For high-capacity porous membranes (including present case) the surface diffusion became a dominant mechanism, which provides an access for the analyte to all the binding sites on the polymer surface.[47] The presence of this mechanism in MIP membranes is evident from the breakthrough experiments when the sharpness of breakthrough curve is strongly dependent on feed concentration (data not shown).

Since presence of salts in drinking water can inhibit binding of atrazine to the surface of the imprinted membrane, influence of ionic strength of the feed solution was investigated. It has been shown that this factor did not significantly affect the adsorption capability of the membrane. However, the best sorption capabilities of the investigated membranes were achieved in the case of lower ionic strengths of the feed solution (0−10 mM) (Figure 6). The influence of pH of the feed solution was also investigated. It was shown that the more effective binding of atrazine was achieved under increasingly acidic conditions (pH 4−5) (Figure 7). With increasing mobile phase pH values the atrazine recovery decreases as a result of loss of hydrogen bond donor groups at the binding sites with the increase in the degree of ionization of the COOH groups.[48]

Conclusions

The novel thin, flexible, and porous molecularly imprinted membranes were prepared in situ using UV-initiated polymerization. Improvement of their mechanical and transport properties was achieved by adding the plasticizer, oligourethane acrylate, and a porogen,

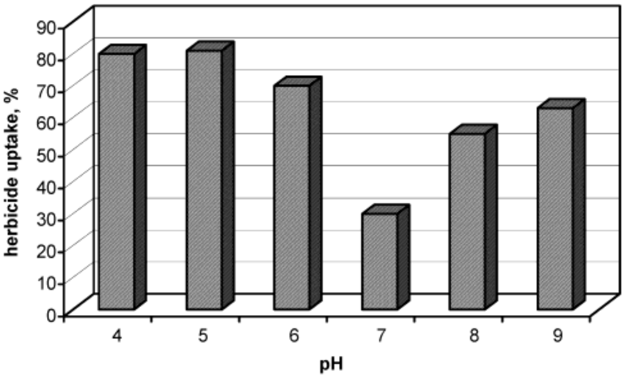

Figure 7. Dependence of the atrazine-imprinted membrane adsorption capability on pH of the mobile phase. The experiments were carried out in 50 mM buffer solutions pH 4.0−9.0. Note: The presented data are the average results of testing three different membranes with the same composition. The standard deviation was less than 5%.

poly(ethylene glycol), to the polymer composition. Imprinted membranes possessed enhanced affinity and binding capacity as compared to those of traditional MIP systems. High water fluxes and excellent robustness make them suited for membrane chromatography and filtration experiments.

Acknowledgment. Financial support from INTAS (Grant YSF-00-25) is gratefully acknowledged by T.S. S.P. acknowledges with gratitude the receipt of a Royal Society-Wolfson Research Merit Award.

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MA030105X