



Polypropylene prefilters with surface imprinted layer



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ABSTRACT

The paper focuses on preparation of dual purpose porous prefilter that can serve either as a filter or sorbent for removal of bisphenol A. To obtain such materials, a possibility to form imprinted layer of methyl methacrylate and ethylene glycol methacrylate copolymer was evaluated. The layer was grafted to plasma activated porous polypropylene filters. It was noted formation of some patches on the surface for lower grafting yield. The patches increased their size up to formation of continuous layer. It was noted that optimization of grafting parameters should be performed separately and the use of the same protocol as for bulk polymerization of molecularly imprinted polymers could not be applied. The dual purpose prefilters were able to catch bisphenol A during filtration and its concentration was reduced significantly while other phenol derivatives were not adsorbed. By the use of molecularly imprinted filters, the removal of bisphenol A was four time higher than that removal on non-imprinted membranes. The best sorption properties were obtained for materials grafted by monomers with 4:6 M ratio of methyl methacrylate to ethylene glycol dimethacrylate. The static sorption reached the value of 0.06 mmol g^{-1} and bisphenol A was rejected at 70% level in filtration of 0.2 mM BPA aqueous solution.

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1. Introduction

Endocrine disruptors (EDs) are the group of hormonally active agents that can affect the function of endocrine system, resulting in adverse health effects to human beings [1]. Bisphenol A (BPA), which belongs to the class of endocrine disruptors, even at extremely diluted concentration, can affect the development of organism mimicking action of female sex hormone. However, BPA is widely used as monomer in production of plastics (epoxy, phenolic, polysulfone and polyetherimide resins, polycarbonates, polyesters, polyacrylates and flame retardant materials), as an antioxidant or as an inhibitor in some polymer syntheses [2]. Hence, from the environmental conservation viewpoint and health security issue a search for materials that can be used for removal of BPA has attracted the attention. It seems that selective sorbents, prepared by molecularly imprinted techniques, can satisfy the request [2–4].

In the water treatment systems, the membranes are now integrated with such processes as flocculation or adsorption to improve separation efficiency and reduce treatment cost [5]. In such hybrid systems, membrane serves as filter that rejects complexes of specific sorbent with targeted endocrine disruptor giving ED-free water [6,7]. However, to simplify the system or to use it for specific targets, like juice of medical injection water, it could be

reasonable to combine filtration and sorption features and prepare one dual-purpose material. It is the main reason for growing interest in preparation of molecularly imprinted membranes (MIMs). Such materials can be prepared by means of the following methods [8–10]:

- polymerization of monomers in membrane pores in presence of template molecules,
- phase inversion when template molecule is dissolved in polymer/solvent solution,
- preparation of composites membranes when fine particles are suspended within membrane,
- grafting/coating of surface imprinting layer on membrane support.

The most versatile method seems to be the last one as it combines very popular ways of surface modification with formation of selective sorption sites for target molecules [11–13]. In this case, the sorption sites located on the surface are much more accessible for molecules than bulk imprints that dominate in (a–c) methods. Many strategies have been employed for surface imprinting. The aims of them were usually to enhance molecular recognition and to improve mass transfer [14]. Moreover, it seems that grafting being a simple and useful approach for tailoring the surface properties [15]. It has been used for preparation of imprinted layer,

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with the use of atomic transfer radical polymerization method [16], UV irradiation [17] or in assistance of cold plasma [18,19].

There are three reasons that raise plasma treatment to the most fascinating technique in polymer modification case. It is (a) fast, (b) effective, and (c) environmentally benign method [20]. Hence, the wide use of plasma for formation of surface layer is understandable. Plasma of non-polymerisable molecules generates radicals on the surface that can act as the starting points for monomer polymerization. However, when plasma activated surface is exposed to oxygen or air, more stable peroxides and hydroperoxides can be formed. They participated in graft polymerization initiated by UV irradiation or by heating of the system. Such method of plasma induced grafting has been exploited in our laboratory for last two decades and we decided to use it for grafting of molecularly imprinted layers. As the functional monomers to form the BPA imprinted layer methyl methacrylate and ethylene glycol dimethacrylate were selected. These monomers were used by us previously and were good candidates for formation of MIP particles suitable for removal of bisphenol A from aqueous solutions [7]. Hence, the possibility to obtain thin layer of molecularly imprinted polymer coat on microfilter pushed us to conduct this study. The goal of it was to see if experiences gained during preparation of MIP particle could be useful in preparation of molecularly imprinted membranes.

The aim of this paper was to test if grafted layer of imprinted polymer on polypropylene matrix showed similar separation properties as polymer synthesized by bulk polymerization of monomers, and if the methodology for preparation of molecularly imprinted particles could be transferred to membrane grafting procedure.

2. Experimental

2.1. Materials

Porous polypropylene (PP) prefilter (Millipore AN2504700) with pore diameter of 2.5 μm were used as substrate. Prior to plasma treatment filters were rinsed with ethanol and dried at room temperature. All chemicals used in syntheses were purchased from Sigma Aldrich and applied without additional purification.

2.2. Plasma treatment

Dielectric barrier discharge plasma device (Dora Power Ltd., Poland) was used for prefilter modification. Plasma parameters were kept constant throughout whole study and they were: voltage 20 kV, current 5 mA, argon flow 30 L/h, modification time 60 s. Both sides of the filter were activated in plasma. After completing the plasma activation, the filters were kept 15 min in air to generate peroxide and/or hydroperoxide functionality on their surface.

2.3. Grafting procedure

After plasma modification the samples were immersed in 50% solution of monomers methyl methacrylate, MMA, and ethylene glycol dimethacrylate, EGDMA, in n-octane. To the solution 2 wt. % of AIBN was added as an additional initiator. The amount of BPA was set to 0, 2, 5 and 7 wt.% with respect to monomers. The filters were immersed in solution for 24 h, surface dried, placed in a laboratory dryer and kept at 60 °C from 30 min to 24 h. After modification, the non-polymerized components were extracted in Soxhlete with methanol for 24 h. In the case of absence of BPA in

the monomer mixture, the non-imprinted prefilters (NIM) were obtained.

2.4. Characterization of modified prefilters

2.4.1. Grafting yield

The grafting yield, GM [mg/cm²], was evaluated gravimetrically, and calculated according to the following equation:

$$GM = \frac{M_1 - M_2}{A} \quad (1)$$

where: M_1 and M_2 - weights of prefilter after and before modification, A - surface area of membrane ($A = 17.3 \text{ cm}^2$).

The accuracy of used analytical scale, Sartorius Genius ME215P, was 0.01 mg.

2.4.2. IR spectroscopy

To characterize the chemical compositions of prefilters, Perkin-Elmer System 2000 was used. For each sample, 64 scans with resolution of 4 cm^{-1} were collected.

2.4.3. Scanning electron microscopy

The morphology of prefilters surface was investigated by SEM microscope, Carl Zeiss EVO LS15, operated at 5.00 kV. Prior microscopy evaluation, the filter surface was sputter coated with gold.

2.4.4. Average pores size

The pores size (r) [μm] was calculated according to Eq. (2):

$$r = \sqrt{\frac{8Jd\eta}{p\varepsilon}} \quad (2)$$

where: J - water flux, d - thickness of prefilter, η - water viscosity, p - pressure, ε - porosity.

Porosity of the prefilters was determinate gravimetrically, according to the Eq. (3):

$$\varepsilon = \frac{M_w - M_d}{M_w} \quad (3)$$

where M_w , M_d - weights of wet and dry prefilter.

2.4.5. Pure water flux

Water permeability through prefilters was measured volumetrically in Amicon 8050 cell with transmembrane pressure of 0.001, 0.002 and 0.004 MPa. Before filtration prefilters were hydrophilized by immersion in 96% ethanol and fast transfer to pure water.

2.4.6. Static sorption

Sorption of BPA was studied in 0.2 mmol/L BPA aqueous solutions at 21 °C. Pieces of prefilter were shaken with 100 mL of solution for 24 h and concentration of BPA was determinate spectrophotometrically at 276 nm (UV-VIS, Jasco V-630). The static sorption (SS) [mmol g⁻¹], was calculated according to Eq. (4):

$$SS = \frac{(C_0 - C_1) \cdot V}{M_1 - M_2} \quad (4)$$

where C_0 , C_1 - concentration of BPA before and after sorption respectively, M_1 and M_2 - prefilter weights after and before modification, V - volume of BPA solution.

The sorption isotherms for the best sorbed MIM and its analogues without imprints were plotted and after this the imprinting factor (IF) and the maximum bisphenol A uptake (SS_{max}) and the distribution of binding sites was calc from Langmuir, Freundlich and Dubinin-Radushkevich isotherms were calculated.

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