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POLYSULFONE MEMBRANES DOPED WITH POLYMER COLLOIDS FOR WATER DECONTAMINATION

Edina RUSEN[1], Alexandra MOCANU[2*], Adrian DINESCU[3], Gabriel MUSTĂȚEA[4], Aurel DIACON[5]

The aim of this study consists in the synthesis by soap-free emulsion polymerization and seeded polymerization of two different types of polymer colloids. The polymeric particles contain different amounts epoxy functional groups on the colloids surface. The polymer colloids have been used as support materials with high specific area for further functionalization with triethylenetetramine, for complexation of Cu^{2+} from aqueous samples. The active material for copper ions retention was encapsulated in PSF membranes and the performance of the membranes was determined by ICP-MS. The materials have been characterized by: SEM, FT-IR, ICP-MS.

Keywords: soap free emulsion polymerization, polysulfone membrane, SEM, ICP-MS, ion retentions

1. Introduction

Heavy metal contamination remains a stringent problem even for the XXI^st^ century, due to the intensive anthropogenic activit ies, extensive industry, mining and even hazardous events. The permanently increasing concentrations of heavy metals cause serious problems in terms of growth and development of flora and fauna of the polluted environments.

Although in some cases the deficiencies in copper, iron or zinc can cause health problems (e.g. anemia, osteoporosis, poor immune system, etc.), in large amounts they become toxic for human health (congenital malformations, vomiting, kidney or liver failure, and sometimes psychosis symptoms) [1].

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[1] Associate Professor, PhD, Dept. of Bioresources and Polymers Science, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania

[2] PhD, Dept. of Bioresources and Polymers Science, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: mocanu.alexandra53@yahoo.com

[3] PhD, National Institute for Research and Development in Microtechnologies (IMT-Bucharest), Romania

[4] PhD, National Institute of Research and Development for Food Bioresources − IBA Bucharest, Romania

[5] Lecturer, PhD, Dept. of Bioresources and Polymers Science, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania

For this reason, global health organizations, in collaboration with agriculture ministries of different countries, imposed severe regulations in order to maintain the amount of heavy metals accumulated in food and drinking water at acceptable levels [2, 3].

Research studies developed numerous methods for heavy metals removal such as chemical precipitation or adsorption [4], ion exchange [5, 6], electrochemical techniques [7], and membrane separation [8, 9]. Among these, membrane separation is widely used for wastewater treatment, due to the simplicity of manufacturing process, the thermal and chemical stability in acidic and alkaline media [10]. Polysulfone (PSF) is one of the most widely used membrane material in ultrafiltration and nanofiltration separation processes for water treatment, due to its good chemical and mechanical resistance, thermal stability and film forming capacity [10-13].

In the last decade, different additives or fillers have been used to improve the properties of polysulfone membranes designed for water treatment, including hydrophilicity, membrane flux, mechanical and anti-fouling properties, and efficiency retention of different inorganic or biological contaminating agents from wastewaters [12, 14, 15].

Polymer particles with well controlled dimensions (in the range of hundreds of nanometers) and self-organizing abilities have gained much interest as surface-active materials. Functionalized polymer nanoparticles have large specific surface area with much more center sites than bulk or irregular shape materials, fact which greatly improves the complexation or recognition process of different compounds, depending on the final application [16, 17].

Using soap-free emulsion polymerization techniques, polymer core-shell spheres with different functional groups can be adapted for various applications such as pH or temperature responsive materials [18], supports for drug release [19], optical devices for immunosensing and protein detection [20, 21], adsorbents for environmental protection [22].

Various studies proved that different structured materials based on polymer or hybrid colloids and compounds with free amino groups are good candidates for heavy metal complexation [23, 24].

In this study, our group obtained two different types of colloidal polymer particles by employing soap-free emulsion polymerization. The first system contains styrene (ST) with glycidyl methacrylate (GMA), while the second, ST with hydroxyethyl methacrylate (HEMA) seeded with GMA. Therefore, both types of polymer colloids contain epoxy rings on the surface, but in different quantity. The polymer colloids have been used as support materials with large specific area for further functionalization with triethylenetetramine (TETA), for complexation of Cu^{2+} from aqueous samples.

The next step consisted in the encapsulation of copper adsorbing polymer particles in PSF membranes, and estimation of the retention capacity. Thus, the aim of this study was to develop a new approach in membrane manufacturing using functionalized colloidal particles, and to enhance the efficiency of doped PSF membranes for copper removal from wastewater.

2. Experimental

2.1. Materials

Styrene (ST) (Aldrich) has been purified through vacuum distillation. Glycidylmethacrylate (GMA) (Aldrich), hydroxyethyl methacrylate (HEMA) (Aldrich) has been passed through separation columns filled with Al_2O_3 to remove inhibitors. Potassium persulphate (KPS) (Merck) has been recrystallized from an ethanol/water mixture and then vacuum dried. Polysulfone (average Mn ~22,000) (PSF) (Aldrich), triethylenetetraamine (TETA) (Merck), 1-N-methyl-2-pyrrolidinone (NMP) (Aldrich), have been used with no previous purification.

2.2. Methods

a) Synthesis of ST-GMA and ST-HEMA colloidal particles

In a round bottom flask, 200 ml of distilled water, 13 ml of ST and 4 ml GMA, respectively HEMA, are introduced. The mixtures were purged with N_2 and stirred for 10 min at 80^0C, before adding 0.1 g of KPS dissolved in a small amount of distilled water. The mixtures were kept under continuous stirring for 8 h at 80^0C. In order to remove the unreacted monomer and initiator, the final dispersion has been dialyzed in distilled water for 7 days, using cellulose dialysis membranes (molecular weight cut-off: 12,000–14,000).

b) Synthesis of ST-HEMA colloidal particles seeded with GMA has been performed according to our previous study [25].

c) Synthesis of ST-GMA-TETA

In order to modify the polymer particles on the surface, the latex of ST-GMA was dried on hydrophilized glass plates by gravitational sedimentation at 70^0C for 1 h. The film was removed from the glass plates and grinded until a very thin powder was formed. 6 g of polymer powder have been added to 50 ml of TETA and left to react at 80^0C for 1 h. The modified particles ST-GMA-TETA were recovered by water precipitation, filtration and extraction, in order to remove the excess of TETA. The obtained white powder was dried at room temperature in vacuum, until a constant mass was obtained.

d) Synthesis of ST-HEMA-GMA-TETA

The functionalization with amine groups on the surface of the ST-HEMA-GMA particles was carried out at 75^0C for 12 h, by adding 1 ml TETA to 16 ml of latex. In order to remove the excess of TETA, the modified particles were precipitated in water, filtered, and extracted with acidified water for 24 h. The ST-HEMA-GMA-TETA particles were dried until constant mass.

e) Synthesis of PSF membranes embedded with surface modified colloidal particles

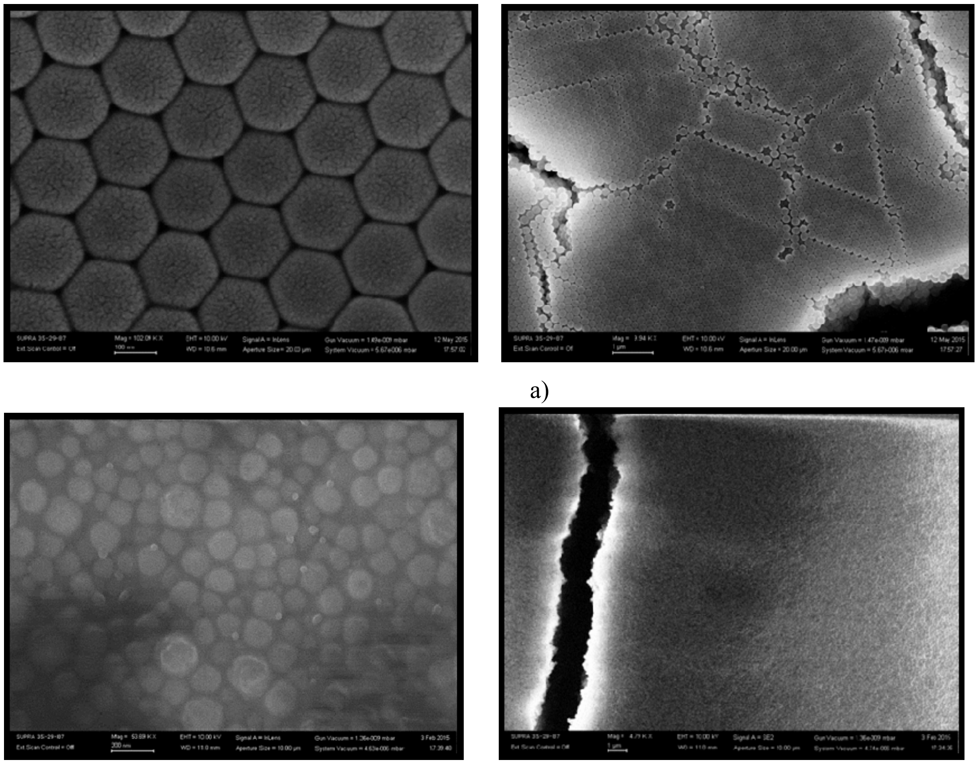
The polysulfone membranes were obtained by employing a wet phase separation procedure, as described by V. Kaiser et. al. [26], using NMP as polymer solvent and water as non-solvent. The 15% PSF solutions were casted on glass plates and immediately immersed in the deionized water coagulation bath. The same process was followed for the modified membranes embedded with 2% (wt.% by PSF content) polymer powder of ST-GMA-TETA, respectively ST-HEMA-GMA-TETA. The membranes were removed from the coagulation bath and kept for 12h in water at room temperature, in order to remove NMP. The porous materials were dried at room temperature for the next 12 h.

2.3. Characterization

The morphologies of polymer particles and PSF membranes have been investigated using FE-SEM (field emission-scanning electron microscope) - RAITH e_Line, at 10 kV acceleration voltage. The samples were sputtered with a thin layer of gold, prior to imaging. In order to prove the surface functionalization of the polymer particles, infrared absorption spectra have been recorded at room temperature with a Nicolet 6700 FTIR spectrometer in the range of 4000–400 cm^{-1}. The efficiency of the modified polymer membranes was quantified by the retention capacity of Cu^{2+} , evidenced with inductively coupled plasma-mass spectrometer (ICP-MS) NexIon 300q (Perkin-Elmer).

3. Results and discussions

The first step of this study consisted in the preliminary characterization of the initial polymer particles of ST-HEMA, respectively ST-GMA. In the case of ST-HEMA polymer particles (Fig. 1-a), it can be noticed the formation of an organized structure, specific to photonic crystal [27] with an average diameter of the polymer particles around 150 nm. In the second case, for ST-GMA particles, the diameter is ranging from 50 to 100 nm. This dimensional difference can be explained by the different solubility of the co-monomer in water (respectively HEMA and GMA). For ST-HEMA, the macroradicals precipitate at a higher chain length than for the ST-GMA copolymer, fact which is responsible for the dimensional variation between the two types of polymer particles [28].



a)

b)

Fig. 1: SEM images of ST-HEMA (a) and ST-GMA (b) polymer particles; the scale bars are 200 nm, respectively 1µm

Before the polymer particles surface functionalization with TETA, ST-HEMA, colloids have been seeded with GMA using soap-free emulsion polymerization. The particles have been characterized by SEM. In this case, the diameter of the particles is about 250-300 nm.

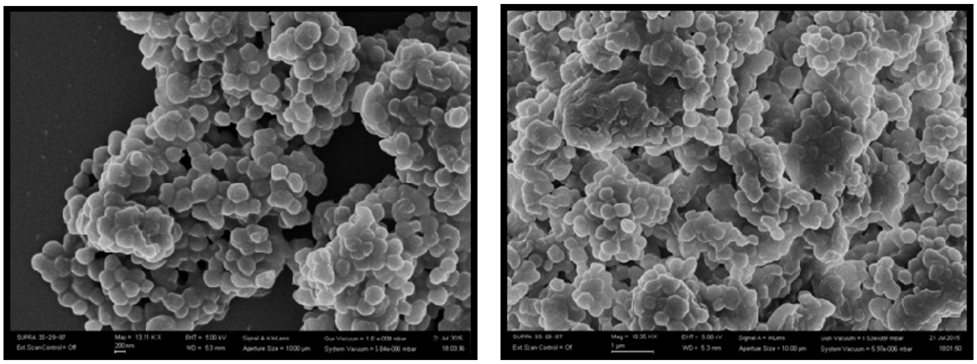
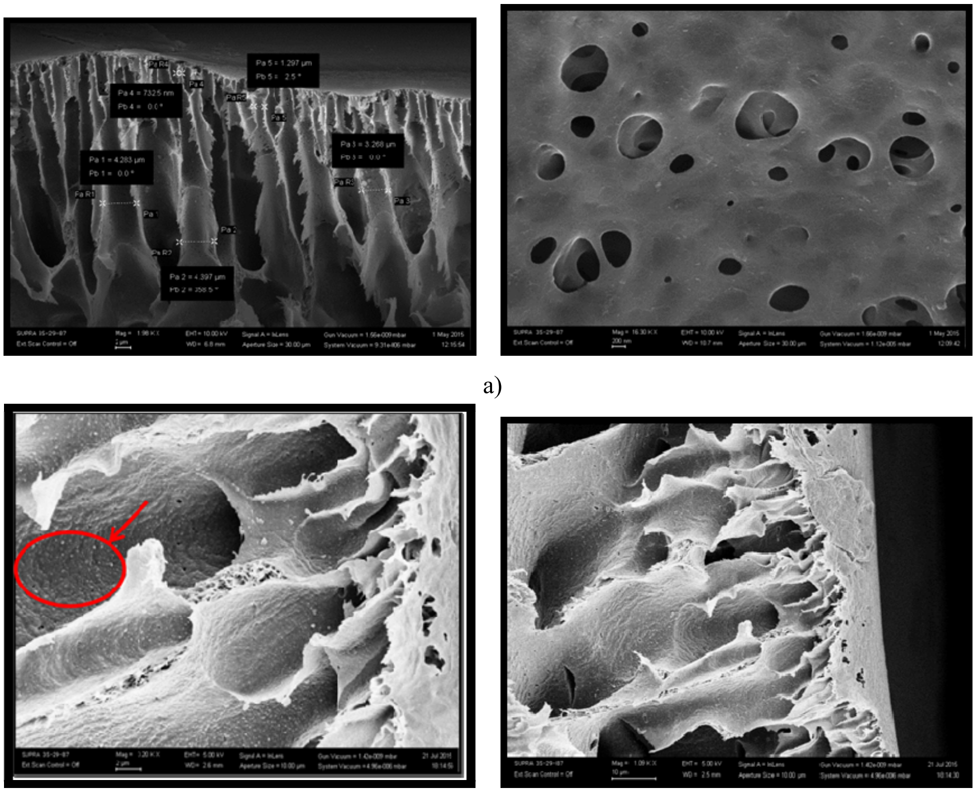


Fig. 2: SEM images of ST-HEMA-GMA; the scale bars are 200 nm, respectively 1µm

Obviously, the diameter after the seeded polymerization is higher, compared to ST-HEMA particles diameters. The complexation of metal cations is possible after the functionalization of the initial polymer particles with TETA. FT-IR analysis was used to render evident the modification of the functional groups from the surface of the polymer particles. The addition reaction, respectively the opening of the epoxy ring, was evidenced by the specific signals registered at 3500 cm^{-1}, specific for -OH groups, and by the signal intensity diminishing from 1144 cm^{-1}, which confirmed the epoxy ring consumption.

A relative facile, low-cost encapsulation procedure was employed, in order to render evident the complexation capacity of the functionalized polymer particles. Thus, the polymer particles were embedded into ultrafiltration polymer membranes for wastewaters decontamination of heavy metal ions. For this reason, polysulfone was chosen as a polymer matrix for the encapsulation of ST-GMA-TETA, respectively ST-HEMA-GMA-TETA particles. The next step consisted in the morphological characterization of the modified polysulfone membranes (Fig. 3).



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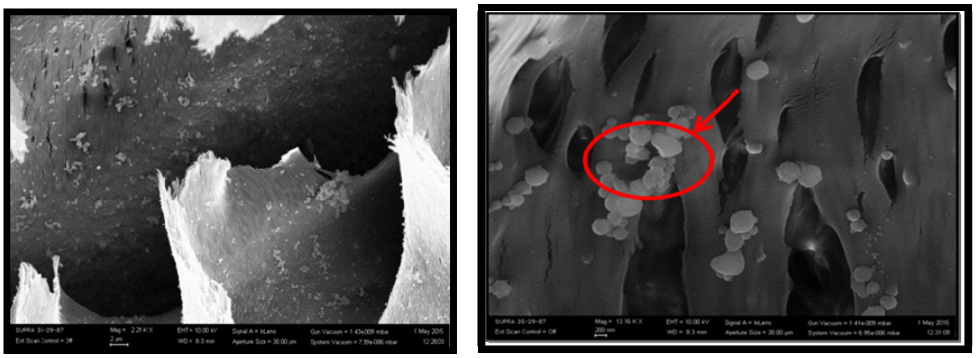
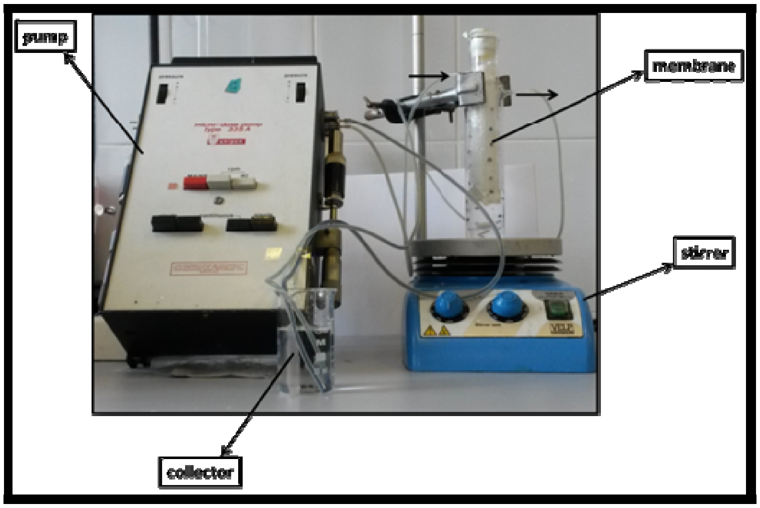


c)

Fig. 3: SEM images of a) PSF, b) PSF-ST-HEMA-GMA-TETA and c) PSF-ST-GMA-TETA membranes

The comparative presentation of the obtained membranes emphasizes the preservation of channels (4.3 µm), and pores dimensions (1µm). In the case of modified polysulfone membranes, the polymer particles are uniformly dispersed both inside the channels, and in the channels walls. The distribution of the particles in this way is particularly important, considering the water flow inside these channels, which increases the probability for complexation/adsorption of heavy metal cations. The polymer ST-GMA-TETA particles are only attached on the membrane's channels walls (Fig. 3 c – red circle), while the ST-HEMA-GMA-TETA particles are embedded in the channels (Fig. 3 b – red circle). This structural difference could influence the retention capacity of metal ions, leading to an increased contact surface between the polymer particles and water flow. In order to quantify the retention capacity of copper ions, the modified membranes were introduced into a recirculating system, similar to the design used in our previous study [29]. The jacketed reactor was connected to a pumping system with magnetic stirrer and collecting recipient presented in Scheme 1.

The membranes are fixed on a quartz cylinder placed in a perforated tube that enables the water flow through the reactor's jacket in a single direction.



Scheme 1: The experimental set-up [29]

The retention capacity has been estimated using ionic (ICP-MS) technique and the following equations [30]:

$$R = \frac{100 * n_t}{n_0} \quad (1)$$

where: R = retention ratio of the membrane

n_t = the quantity (mol) of metal ions M retained in the membrane

n_0 = the initial quantity (mol) of metal ions in the solution

The results are presented in Fig. 4.

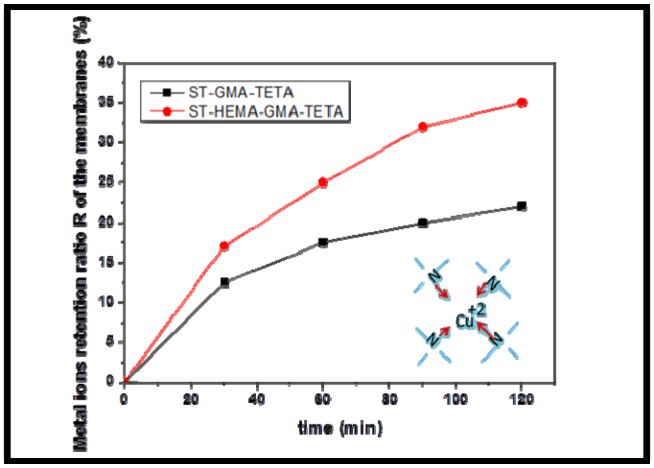
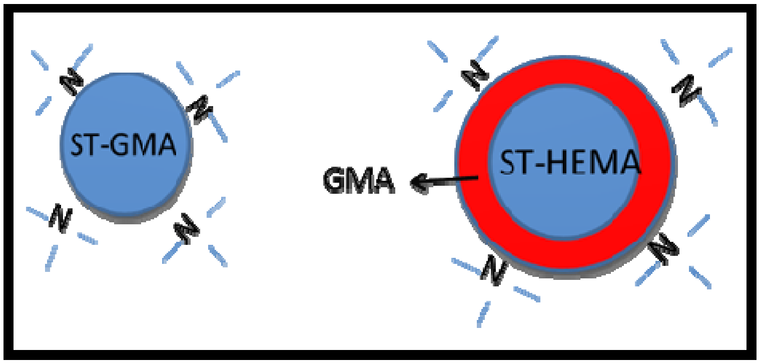


Fig. 4: Metal ions retention ratio of the studied membranes

The metal ions retention ratios for the two membranes determined by ICP-MS analysis are presented in Fig. 4. Thus, for ST-GMA-TETA, the capacity was evaluated at 22%, whereas for the membrane containing ST-HEMA-GMA-TETA colloids, the maximum was determined at 35.1 %. Therefore, although the contact area (specific surface) of the first particles is higher (smaller diameters), the retention capacity is lower. This behavior could be explained by the amount of TETA on the surface of the particles, indirectly by the density of epoxy rings on the particles. Obviously, in the case of the seeded polymerization, the polymer particles are covered by polyGMA, as presented in Scheme 2.



a) b)
Scheme 2: ST-GMA-TETA (a) and ST-HEMA-GMA-TETA (b) particles design

4. Conclusions

Two different types of colloidal polymer particles employing soap-free emulsion polymerization have been obtained. The first system contains ST and GMA, while the second one, ST and HEMA seeded with GMA. The morphology of both systems was investigated using SEM. The polymer colloids have been functionalized on the surface with TETA, for complexation of Cu^{2+} from aqueous samples. The next step was the encapsulation of copper adsorbing polymer particles in PSF membranes, followed by the estimation the retention capacity.

The retention ratio has been estimated 22% for the PSF membrane containing ST-GMA-TETA polymer particles, while for ST-HEMA-GMA-TETA, the value was about 35.1%, due to the higher density of the epoxy rings (seeded polymerization).

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