

Polysulfone-C₆₀ and polysulfone-magnetic particles composite membranes for decontamination techniques

Aurelia Cristina Nechifor, Sergiu Sava, Stefan Ioan Voicu, Gheorghe Nechifor

Abstract — New polysulfone composite membranes (with fullerenes respectively functionalized magnetic particles) are presented in this paper with uses for pervaporation of volatile amino compounds and for removal of lead and mercury from aqueous solutions. The membranes were obtained by phase inversion technique and were characterized by Scanning Electron Microscopy, Fourier Transformed Infrared Spectroscopy and Thermal Analysis. The membranes exhibits good performances in the tested processes and showed that are suitable for these applications.

Keywords—composite membranes, decontamination techniques, fullerenes, magnetic nanoparticles, polysulfone.

I. INTRODUCTION

THE polysulfones constitute the most extensively studied class from the commonly used polymeric membrane materials: cellulose derivatives, polyamides, aromatic polymers with ether, ester, imide and imine groups [1, 2].

The physical and chemical characteristics of polysulfones allowed to apply all the membrane preparation methods, especially the phase inversion by immersion precipitation [3] which provides the possibility of (thermal and chemical) sterilization, the achievement of biocompatibility, and its functionalization by aromatic electrofilic substitution [4-9].

Fullerenes are polyhedral carbon cages, in which the sp² hybridized carbon is directly linked to other three carbon atoms in an arrangement of rings made up of five, respectively six atoms. From all synthesized fullerenes up to the present, the most studied one is C₆₀ due to the fact that it is one of the few known molecular structures being part of the I_h symmetry class [10, 11]. The applications of fullerenes

nowadays are of high scientific and technical interest [12], but they appeared sporadically in the membrane field.

The obtaining of the polysulfone - nanospecies composite membranes, in particular polysulfone - fullerene membranes, supposes the preparation of polymer homogenous solutions including the fullerenes [13]. The complete solubilization of the fullerenes within the polymeric solution is difficult, although it is much easier when compared to the inclusion of the carbon nanotubes. There is a wide range of solvents which may solubilize these species. The solvation of C₆₀ fullerenes requires the disruption of interfacial between the solvent molecules, interactions which may not be entirely compensated by the interactions between the solvent and fullerene due to its rigid geometry and its electric dipole moment value. The C₆₀ molecules are completely insoluble in protic or aprotic dipolar solvents, such as MeOH, MeCN, tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO). The solubility of fullerenes in alkanes is superior to that one in protic solvents, increasing from pentane to decane. The halides are excellent solvents for fullerenes (with best results for chloroform, tetrachloroethylene and 1,1,2,2 - tetrachlorethan). However, the aromatic amino-derivates such as aniline, N-methylaniline and N,N'- dimethyl aniline proved to be the best solvents [14-16].

The fullerene-based membrane materials using polyphenylenoxide as polymer have been recently obtained by Sterescu and Wesling [17, 18].

The manufacturing, characterization and modeling the properties of nanoparticles for biomedical, environmental and other applications have been possible due to the development and new researches in the domain of nanotechnologies. The nanoparticles with magnetic properties especially magnetite nanoparticles have been draw a lot of attention due to their use in previous domains. The coated particles have been attracted a lot of attention because of their importance in a fundamental understanding of properties and performance in their applications. The surfaces of these materials possess the completely different characteristics compared with the core element because of the composition gradient imposed by coating [19].

The obtaining of nano-functionalized membranes is one of the newer trends for amelioration of the membrane processes

Manuscript received April 8, 2011; Revised version received Month xx, 2011.

A.C. Nechifor is with the National Institute for Microtechnologies (IMT-Bucharest), 077190 Bucharest, Romania (corresponding author to provide phone: +40214023802; e-mail: nechiforus@yahoo.com).

S.I. Voicu, is with University Politehnica of Bucharest, 011061 Bucharest, Romania (e-mail: svoicu@gmail.com).

S. Sava is with University Politehnica of Bucharest, 011061 Bucharest, Romania (e-mail: sergiusava_cj@yahoo.com).

G. Nechifor is with the University Politehnica of Bucharest, 011061 Bucharest, Romania (e-mail: doru.nechifor@yahoo.com).

performances. In the last 20 years the membrane materials are continuously increasing with new polymer types, composite materials and nanosystems or ultra micro dispersed systems. Recognized selectivity of the magnetic nanoparticles based membranes is insufficient explored due to operating difficulties such as: phases mixing, contact surface, membrane phase recapture, membrane stability.

The use of different technologies and solutions for improving the quality of environment represent a major trend in the research activities [20-25].

The polysulfone / fullerene composites laying at the basis of asymmetric membrane formation and the synthesis of polysulfone-chemically modified magnetic particles composite membranes are studied in this paper. The obtained membranes were used for the pervaporation of aniline from aniline: N-methylaniline mixture. The use of aniline and its derivatives in colorants and dyes industry present a major impact for environment and usually, the small amounts or traces of unreacted aniline are difficult to be removed applying conventional methods. The polysulfone – chemically modified magnetic particles were used for heavy metals retention.

II. EXPERIMENTAL

A. Preparation of polysulfone solution in *N, N'*-dimethylformamide

The required amount of polymer (polysulfone - PSf offered by BASF, Ultrason S3010 sort) is introduced under magnetic stirring in a flask filled with *N, N'*-dimethyl formamide (DMF) as solvent until the desired concentration (15% PSf in DMF) is achieved. Using the reprecipitated and dried polymer, the preparation of the desired polymeric solution takes place within maximum 24 hours. Before use, the solution is deaerated by standing in the vacuum drier for 30 minutes.

B. Preparation of the polysulfone solution in chloroform

Similar to the preparation of the solution in DMF, a polysulfone solution in chloroform was prepared (10% polysulfone in chloroform). The dissolution is faster, only 12 hours being necessary to obtain the solution.

C. Dispersion of the fullerenes in the polymer solution

After the formation of the polymer solution, the fullerenes (98% pure C_{60}) are added in a proportion of 5% related to the polymer. The fullerene solution in the solubilized polymer is kept in ultrasoning for 48 hours for homogenization purposes.

D. Membrane formation

A determined quantity of polymer solution, 5mL, is deposited on a spectral glass support, and it is extended to a standard thickness of 250 μ m. The polymer film placed on glass is immersed in a coagulation bath containing an aqueous solution of isopropanol (50%) (in the case of the polymer solution in DMF). After coagulation, the membrane is washed using distilled water and methanol in order to remove the traces of solvent and coagulant. In the case of the membranes obtained from chloroform, the coagulation is performed with

methanol, using the same procedure of subsequent washing.

E. Preparation of composite membrane polysulfone-chemically modified magnetic particles

Magnetic nanoparticles are obtained by a variant of Massart method, which consists in ferric ions co-precipitation into a potassium hydroxide solution. The ferric salts (sulfates) are alum and Mohr salt with ammonium ions which moderate the precipitation process. The reactions are presented in Fig. 1.

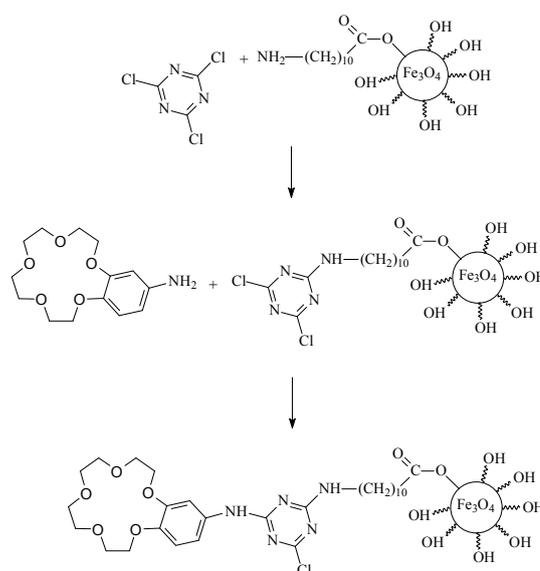


Fig. 1: Schematic representation of modified magnetic nanoparticles synthesis

250cm³ of Mohr salt solution 0,1M and 250cm³ of ferri-ammonium sulfuricum (ferri alum) are mixed under stirring into a recipient. 1,5L of potassium hydroxide 1M are added in three portions. After 4 hours, the black suspension is separated in magnetic field. The entire quantity of suspension is dialyzed until pH \approx 9 value is achieved. The magnetic particles are washed with methanol, ethanol and then with acetone. After magnetic separation the particles are covered and engraftment.

In a tank of a colloidal mill (Retch) are introduced 50g magnetic nanoparticles and 5g amino acid in 150 cm³ of chloroform. After 24 hours of milling at 500 rotations per minute, the dark colored dispersion is washed with three portions of deionised water (150mL). The lighted colored dispersion is reintroduced in the ceramic tank of the mill with 3g cyanuric chloride and is mixed for 3 hours and after this the aminobenzo-18-crown ether and is mixed for another 3 hours. Finally, the brown dispersion is washed with three portions of deionised water. For polysulfone-modified magnetic synthesis, in a tank of colloidal mill are introduced 20g of modified magnetic nanoparticles in a polysulfone solution in chloroform (10%). After 4 hours of milling, portions of the solution are deposited onto a spectral glass and the polysulfone-modified magnetic nanoparticles composite membrane is obtained.

A composite matrix polysulfone-modified magnetic nanoparticles was synthesized in chloroform and a schematic representation of this composite matrix is shown in Fig.1.

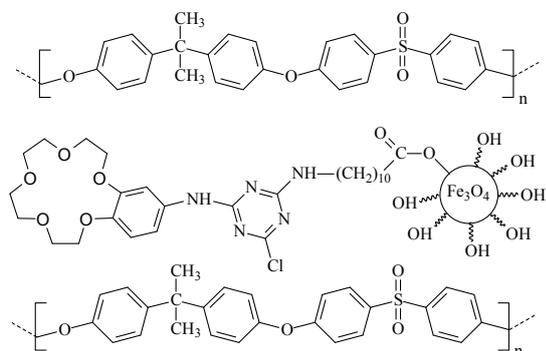


Fig. 1: Schematic representation of composite matrix

F. Membrane characterization

The synthesized materials were characterized by FT-IR spectroscopy (Bruker Vertex 70), DSC thermal analysis, TGA-DTA (TA Instruments 2950) and scanning electron microscopy (SEM) (Hitachi S 4500). The pervaporation tests were carried out into a standard laboratory apparatus. The volume of feed tank was 200 ml, the temperature of feed was controlled using a thermal circulating bath and the unit was operated with continuous circulation of feed. The tests were performed using a mixture of aniline : N-methylaniline in volume ratio 1:10. The disc membranes for tests had a standard diameter of 9 cm. The retention study of heavy metals onto magnetic particles from membrane was done in a permeation cell with two compartments separated by the membrane involved.

III. RESULTS AND DISCUSSIONS

The solutions obtained from polysulfone and fullerenes, for the synthesis of membranes by phase inversion, were prepared in dimethylformamide and chloroform, after prolonged homogenization in ultrasound field. In order to study the morphology and structure of the obtained membranes there were performed high resolution scanning electron microscopy, infrared spectroscopy and thermal analysis.

The carbon nanotubes are superior to the fullerene ones from the electric properties point of view. However, due to the fullerenes symmetry and their functionalization possibility, they are ideal candidates for sensing applications.

In the FT-IR spectra of the characterized membranes (Figure 3), both for the material obtained from chloroform (Figure 3a), and that obtained from dimethylformamide (Figure 3b), a 3-5 cm^{-1} shift of the polymer-specific absorption bands towards higher values is observed. This is most probably due to the electrostatic interactions taking place between the polymer and fullerenes.

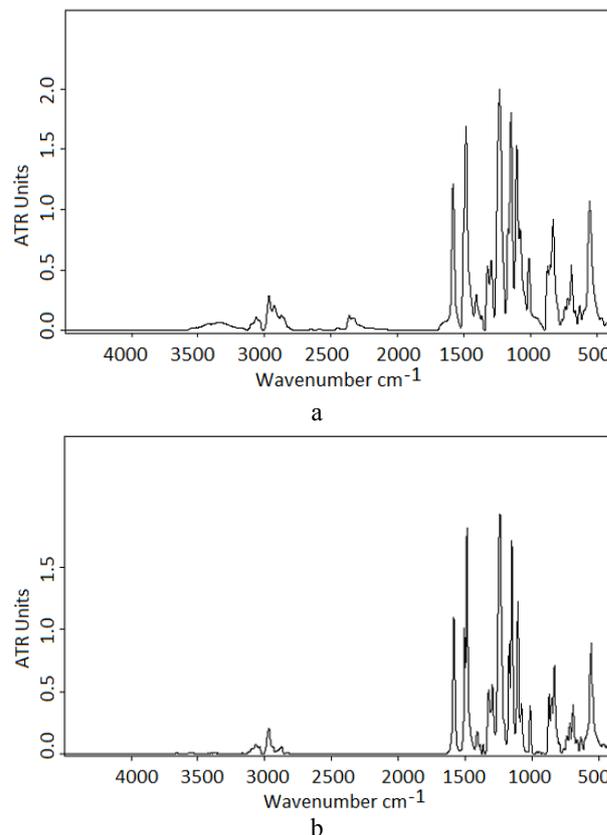


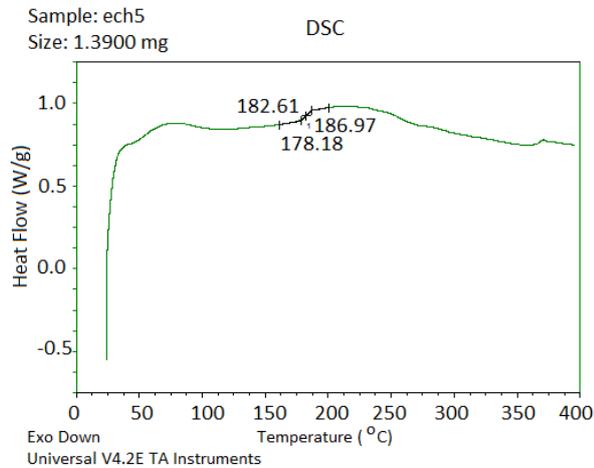
Figure 3. FT-IR spectrum of the PSf-C₆₀ composite membrane obtained from chloroform (a) and N, N'-dimethylformamide (b).

The specific absorption band for SO₂ group is shifted from 1325 cm^{-1} in the polysulfone membrane to 1321 cm^{-1} in polysulfone - C₆₀ fullerene composite membrane in chloroform, respectively to 1323 cm^{-1} in the polysulfone - C₆₀ fullerene composite membrane in N, N' dimethyl formamide. The specific absorption band for -CH₃ group is shifted from 1470 cm^{-1} for the polysulfone membrane to 1483 cm^{-1} for polysulfone - C₆₀ fullerene composite membrane in chloroform, respectively to 1487 cm^{-1} for the polysulfone - C₆₀ fullerene composite membrane in N, N' dimethylformamide. It could be observed that the specific absorption bands for electro-negatively charged groups are shifted towards lower values, while the specific absorption bands for other groups are shifted towards higher values.

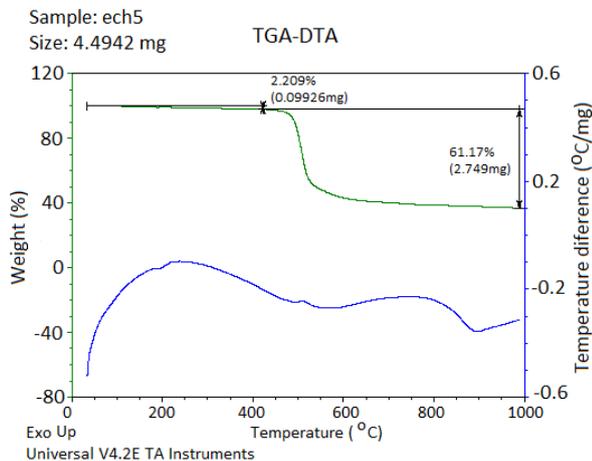
The thermal analysis was performed only on the PSf-C₆₀ composite membrane obtained in dimethylformamide (Figure 4).

From the DSC diagrams a change of the glass transition point (T_g) of polysulfone from 188 to 182.6°C is observed. Such small modification is due to the low content of fullerenes. Thus, out of the 5% initial concentration of fullerene related to the polymer, a percentage of only 2.2% fullerene remains in the formed membrane. This could be explained by the relatively big size of the membrane pores related to the

fullerene sizes, which results in their partial extraction during the coagulation process of the membrane formation.



a



b

Figure 4. Thermal analysis spectrums for the PSf-C₆₀ membrane obtained from dimethylformamide (a – DSC and b - TGA-DTA)

The scanning electron microscopy - SEM (Figure 5) of the polysulfone - fullerene composite membranes reveals a very compact structure for the membranes obtained from chloroform (Figures 3-1a and 3-1b). Such membranes could be potentially used in pervaporation or gas separation their absorption performances being amplified by fullerenes. For the membranes obtained from DMF (Figures 3-2a and 3-2b) a more relaxed structure, is observed. However, they have a higher compact degree than the polysulfone membranes. The second type of membranes could be used in filtration processes based on the adsorption property at the surface of fullerenes of the various organic chemical species or metallic ions. The performance of a separation process of a liquid mixture, similar to the separation of gases, requires operating pressures of over 40 atm.

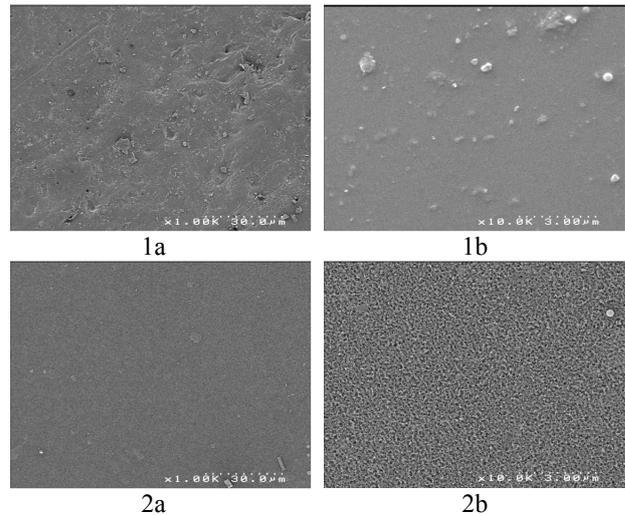


Figure 5. SEM surface images of the polysulfone - fullerene composite membranes obtained from chloroform (1a – x1000, 1b – x10000) and from N,N' – dimethyl formamide (2a – x1000, 2b – x10000).

The inconvenience of the use of high pressures in the separation of the volatile compound solutions was solved by applying the pervaporation. The vaporization of the desired component may be made in vacuum – vacuum pervaporation, or by entrainment using an inert gas – entrainment pervaporation. The pervaporation performances are amplified if the volatilized component has low vaporization heat (ethers, esters or hydrocarbons). Thus, the water-alcohol azeotrope is separated by water removal, and the halides – alcohol mixtures by alcohol vaporization. Lately, the economic aspects imposed the reorientation of the pervaporation towards the removal of the volatile compounds from the waste water.

The current tendency in the separation of gases and pervaporation underlines the use of composite membranes based on the high selectivity polymers.

For the aniline pervaporation tests, both types of obtained membranes were used, as well as a polysulfone membrane obtained from chloroform without fullerene. Best results were obtained for the polysulfone membrane with fullerenes obtained from chloroform. Such results are explained by the compact structure of the membrane and by the properties of the fullerenes. The results are presented in Figure 6.

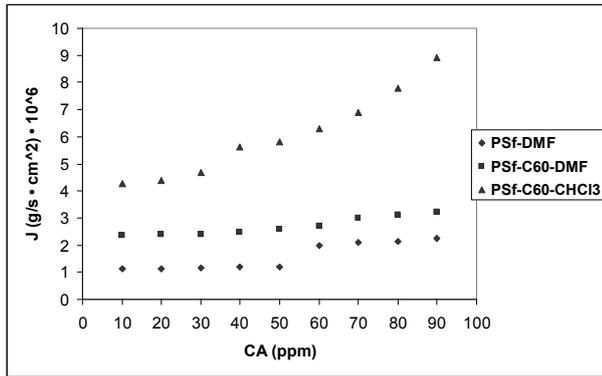


Figure 6. Aniline pervaporation flows for the selected membranes

The possibility of aniline removal from aniline aqueous solutions by pervaporation is highly dependent on the pH (Figure 7). The use of an alkaline pH increases considerably the efficiency of aniline pervaporation from the solution, whereas a pH below 6 makes the process practically inefficient, irrespective of the membrane type. It is absolutely reasonable to consider that the $\text{Ar-NH}_2 + \text{H}_3\text{O}^+ \rightleftharpoons \text{Ar-NH}_3^+ + \text{H}_2\text{O}$ balance should be shifted to the left, so that aniline may solubilize in the membrane and then diffuse to the vacuum compartment and be removed from the system.

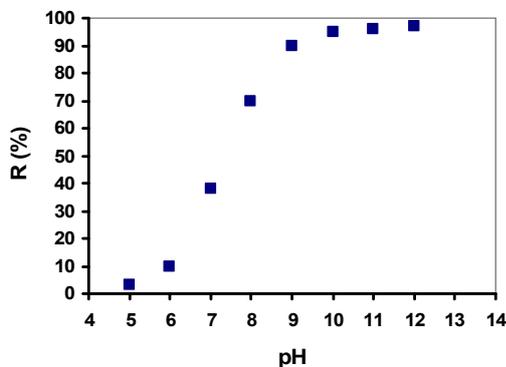


Figure 7. Removal of aniline retention versus pH for a 100 ppm aniline solution (R=retention)

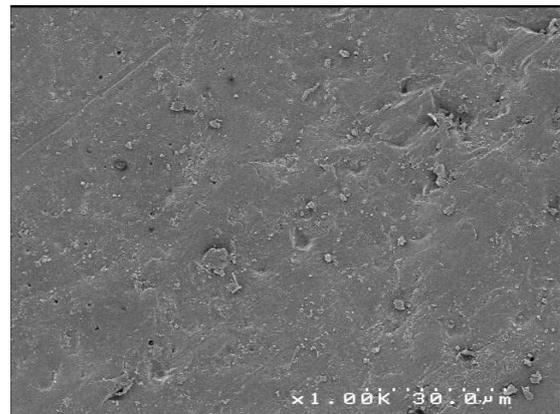
Practically, in its ionic form the aniline is actually insoluble in the membrane and its impermeability does not allow the development of the pervaporation process.

The development and implementation of new technologies for separation processes represents one of the great challenges of membranology. The pervaporation of the aromatic amine solutions presents particular importance, with specific applications in the pharmaceutical and dyes industry for the purification and separation of the residues resulted from the syntheses of aromatic intermediates.

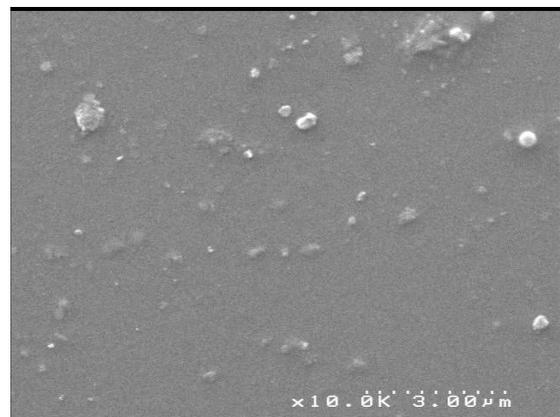
The membrane procedures are actually during an important evolution period, the technical issues being still doubled by economic considerations as well.

It should be known that the economic optimization of these procedures is complex as consequence of an increased number of parameters: operating pressure, crossing velocity, nature of the processed solution, conversion degree.

In the case of the composite membranes with magnetic particles, porous, asymmetric compact composite membranes were obtained by previous described method and were characterised by SEM Microscopy (fig. 8). Chemically modified magnetic nanoparticles with dimensions between 80-120 nm can be observed in membrane structure.



a



b

Figure 8. SEM images of surface composite membranes at x50000 (a) and x100000 (b)

Magnetic nanoparticles preparation by modified Massart method [2] starting from Mohr salt and alum lead to a system with molecular structure presented in Fig. 1. FT-IR spectroscopy (Fig. 4) indicates that nanoparticles are covered with a hydroxyl coating ($3000\text{-}3600\text{ cm}^{-1}$). The thermal analysis (fig. 5) indicates the dehydration (mass lost effect TG and endothermic effect DTA at 107°C). After the coating of magnetic nanoparticles in colloidal mill (for 4 hours) with chosen amino acid, covered nanoparticles are obtained. Their

characterization indicates the C-O (1560 cm^{-1}), C-H (2930 and 3000 cm^{-1}) bonds appearance.

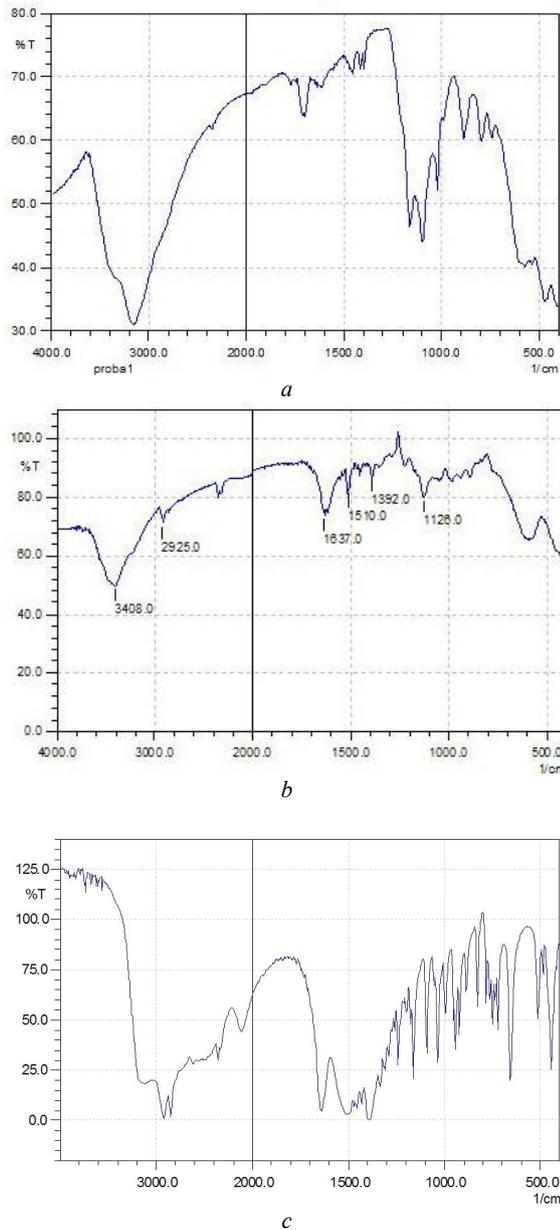


Figure 9. FT-IR spectra of magnetic nanoparticles (a), magnetic nanoparticles-cyanuric chloride (b) and magnetic nanoparticles-cyanuric chloride-crown ether (c)

The hydroxyl group number is reduced ($3000\text{-}3600\text{ cm}^{-1}$). The thermal analysis show a mass lost effect in several steps accordingly with desorption and dehydration of amino acid. Finally, complexant magnetic nanoparticles with amino crown ether are obtained.

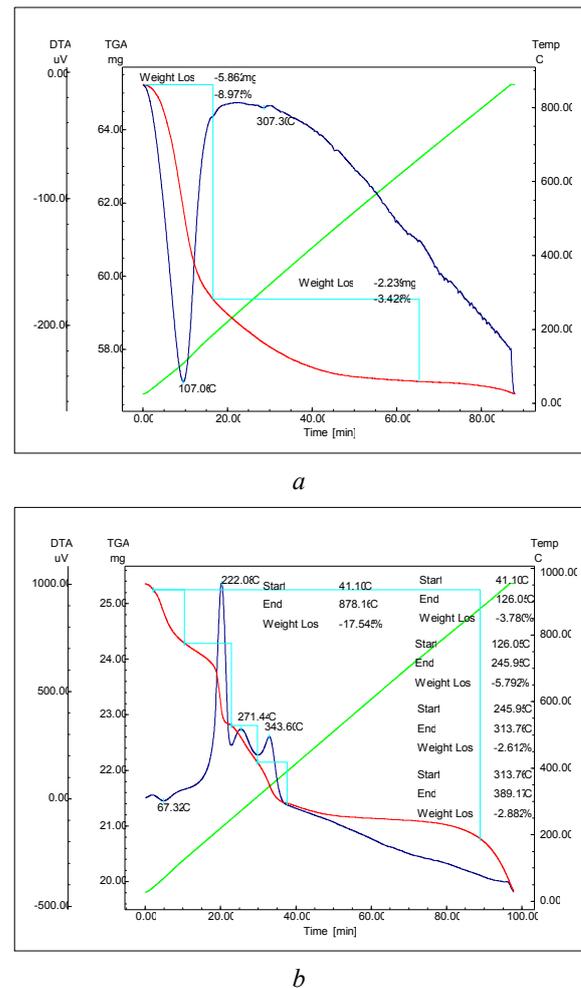


Figure 10. Thermal analysis for magnetic nanoparticles (a) and covered magnetic nanoparticles with crown ethers (b)

A previous work reports the results for synthesis of new composite membranes polysulfone-carbon nanotubes for hemodialysis [1]. The composites were obtained in two ways: (a) by simple dissolving and dispersing the single-walled carbon nanotubes (SWNT) in a polysulfone solution in dimethylformamide in an ultrasonic bath followed by precipitation of the membrane in a phase inversion process in a bath of water and alcohol (i-propanol) and (b) by reaction between double-walled carbon nanotubes with amino groups modified surface (DWNT-NH₂) and formylated or chloromethylated polysulfone. At a maximum concentration of carbon nanotubes (5% in rapport with polymer) the maximum adsorption capacity of lead on membrane with single wall carbon nanotube is $49,2\text{mg}/\text{dm}^2$ and for membrane with double wall carbon nanotube (covalent interaction) is $56,2\text{mg}/\text{dm}^2$ of membrane.

The retention study of heavy metals onto magnetic particles from membrane was done in a permeation cell with two compartments separated by the membrane involved. The capacity of each cell of the permeation device is 200cc and the feeding and stripping solutions are circulated with a pump

having two ways. The volume of the feeding solution is 500cc and that of the stripping solution is 1000cc. The feeding solution contains Pb and Hg salts [$\text{Hg}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$, $10^{-6} - 10^{-9}\text{M}$ concentration] and the stripping solution is bi distilled water. The samples which are periodically collected are analyzed by atomic absorption spectroscopy using AnalyticJena instrument. The hemodialysis results are shown through the removal R% according to Eq. (1):

$$R (\%) = 100(c_i - c_f)/c_i \quad (1)$$

where R = the removal of the metal from the feeding solution (%), c_i = the initial metal concentration in the feeding solution, c_f = the current metal concentration of the feeding solution taken as sample. The results for Pb and Hg removal are presented in Table 1.

Table 1. Maximum adsorption of heavy metals in membranes

Magnetic nanoparticles concentration in membrane	Maximum adsorption capacity (mg $\text{Pb}^{2+}/\text{dm}^2$ of membrane)	Maximum adsorption capacity (mg $\text{Hg}^{2+}/\text{dm}^2$ of membrane)
10%	121.6	98.2
20%	194.8	139.4
30%	311.2	276.2
40%	453.8	387.7

IV. CONCLUSION

New C_{60} polysulfone - fullerene composite membranes were synthesized by phase inversion, chloroform, respectively N, N'- dimethylformamide being used as solvents. The C_{60} polysulfone - fullerene composite membrane presented excellent results in the pervaporation process of the aniline residual solutions resulted from syntheses in the pharmaceutical, respectively dyes industries.

For the aniline pervaporation tests, both types of obtained membranes were used, as well as a polysulfone membrane obtained from chloroform without fullerene. Best results were obtained for the polysulfone membrane with fullerenes obtained from chloroform. The obtained aniline pervaporation flow for polysulfone - C_{60} fullerene membrane was $9 \cdot 10^{-6} \text{ g/s}\cdot\text{cm}^2$, which is much higher than the bvalue of the polysulfone membrane ($2.3 \cdot 10^{-6} \text{ g/s}\cdot\text{cm}^2$).

The complexant magnetic nanoparticles having the structure magnetic nanoparticles-spacer-crown ether (Fe_3O_4 - ω amino acid-cyanuric chloride-amino benzo crown ether) were dispersed in chloroform and mixed with polysulfone. New polymeric composite membranes polysulfone-modified magnetic nanoparticles were obtained by solvent evaporation and the materials exhibit good results in the adsorption of Pb and Hg. This material can be used in decontamination processes for heavy metal removal from waste waters.

ACKNOWLEDGMENT

Ovidiu Cojocaru and Dr. Ruediger Bluhm from BASF are kindly acknowledged for providing the polysulfone material. Mr. Didier Cot from European Institute of Membranes in Montpellier is acknowledged for SEM images. Authors recognise financial support from the European Social Fund through project POSDRU/89/1.5/S/63700, 2010-2013, „Human Resource Development by Postdoctoral Research on Micro and Nanotechnologies”.

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