

Iono-molecular Separation with Composite Membranes

II. Preparation and characterization of polysulphone and composite nanoparticles

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This paper illustrates the possibility of producing iono-molecular separations using ionic colloidal ultrafiltration membrane of polysulphone synthetic solutions of cupric ions and nitro phenols through ultrafiltration assisted by polymeric nanoparticle composites based on polysulphone. In the present work, in order to reduce the operating pressure and increase the flow of water we are using the process of ultrafiltration through a polysulphone membrane in N-methylpyrrolidone 10% prepared by coagulation in isopropanol. The nanoparticles needed in colloidal ultrafiltration had been obtained through the immersion technique of precipitation of a solution of 5% PSf in N-methyl pyrrolidone containing 3% aniline in lower alcohols: methanol, ethanol, and isopropanol, followed by the oxidation of the remaining aniline in a solution of 10% hydrochloric acid and ammonium persulfate. The Nanoparticles of polysulphone (NP-PSf) and The three obtained variants of nanoparticles composites (NP-PSf-PANI) were morphologically (SEM) and (AFM), structurally and compositionally (FTIR) characterized and the results show that nanoparticles polysulphone have a much lower range than the composites. The Possibility of copper complexation by both nitrophenols, and by nanoparticle surface probably lead to the formation of more stable aggregates in the supply, which can sufficiently justify the increased retention. The Retentions of the chemical species in question use in all the tests made the same series: $R_{NP-PSf-PANI-M} > R_{NP-PSf-PANI-E} > R_{NP-PSf-PANI-P} > R_{NP-PSf}$

Keywords: nanoparticles, colloidal ultrafiltration, complex aqueous system, separation, membrane processes

Real systems are often very complex [1-3]. Thus, if we refer to a real aqueous system (fig. 1), it may contain a part from matrix (water):

- dissolved components: cations, anions, small molecular organic substances, soluble oligomers and polymers
- Dispersed chemical species: compounds with high molecular weight, insoluble polymers, micro-organisms
- nano species nanoparticles, nanowires, micellar aggregates

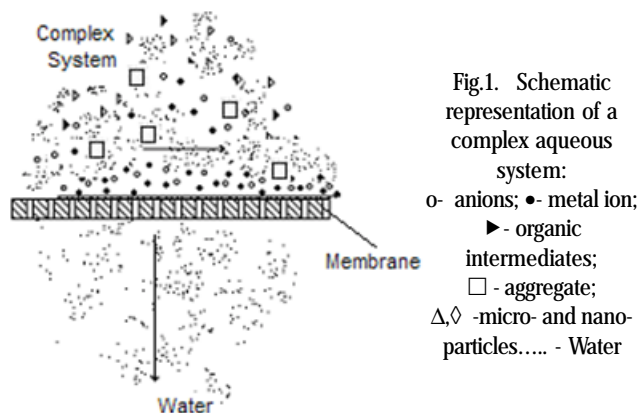


Fig.1. Schematic representation of a complex aqueous system:

- o- anions; •- metal ion;
- organic intermediates;
- - aggregate;
- Δ, ∇ - micro- and nano-particles; - Water

Exploiting the components of such a complex system is a very difficult problem and therefore a variety of conventional separation methods and techniques, for both the dispersed components (sedimentation, centrifugation, flotation, filtration, ...) [4-7], and for the dissolved ones

(extraction, ion exchange, chromatography, distillation ...) [8-11] was developed during the years.

The applicability of conventional separation methods often proved to be limited both in terms of selectivity and the technical and economic efficiency [12-15].

The interest for developing some poor sources of raw materials contributed to the explosive development of methods and techniques which have in common separation techniques of the membrane [16-20]. Therefore, membrane processes of separation of dispersed chemical species: microfiltration, ultrafiltration and nanofiltration, and dissolved chemical species: electro-dialysis and dialysis, reverse osmosis and hyper filtration, liquid membranes, pervaporation and membrane distillation [21-30] were also developed.

Starting with the development of artificial kidney and reverse osmosis for obtaining drinking water from seawater [31-33], membranes and membrane processes witnessed an explosive growth that also allowed an increase in both selectivity (retention) of membranes, and in flow permeates [34].

For this purpose more and more sophisticated and membrane materials [35] have been developed, the methods of preparation have been perfected [36] and the engineering process [37] has intensely developed.

However, membranes and membrane processes have failed to solve a number of practical problems such as: the high operating pressure (60-80 bar) in separating chemical species by reverse osmosis and the relatively small solvent flows (below 200L / m² H), which highly restricts the access

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of reverse osmosis both as a process of manufacturing drinking or ultrapure water, but also in obtaining valuable trace elements in dilute aqueous solutions [38].

Van der Bruggen [39] at European Summer School in 2010 suggested a more pronounced implementation of nanotechnologies to increase the performance of membranes and membrane processes and a more active introduction of Nano science in membrane processes applications. Lately, as a result of this suggestion Research Group for Materials, Membranes and membrane processes of the Polytechnic University of Bucharest-oriented its research in separating the compounds dissolved in dilute aqueous solutions by creating advanced membrane materials based on nano species (nanoparticles, carbon nanotubes, fullerenes) and also by improving the engineering process through the segregation of the separation system or through aggregation of the dissolved chemical species (fig. 2) [40-49].

Thus, as presented in figure 2 there were performed aggregations of organic chemical species separately with surfactants [50], or complex nanoparticles were introduced in the separation system containing cupric ions [51].

This paper illustrates the possibility of producing it-molecular separations using colloidal ultrafiltration with polysulfone membrane of synthetic solutions of cupric ions and nitrophenols aided by polymeric nanoparticles composites based on polysulfone.

Experimental part

Materials and methods

Materials and membranes

Aniline, N-methylpyrrolidone, methanol, ethanol, isopropanol, hydrochloric acid, ammonium persulfate, copper sulphate p.a. and nitrophenols originated from Sigma-Aldrich. The pure water used for preparing synthetic solutions of copper sulphate and nitrophenols (10^{-7} - 10^{-4} Mmol / L) was obtained through Millipore system.

The membranes used in ultrafiltration were prepared from polysulfone solution (Udel) 10% in N-methylpyrrolidone (NMP, Merck) by coagulation with 1: 1 isopropanol-water [52-55].

Nanoparticles preparation

The composite nanoparticles of polysulfone (PSF) - polyaniline (PANI) were made from 5% solution Udel polysulfone (PSF), dissolved in N-methyl pyrrolidone (NMP) containing 3% aniline (A).

100 mL of PSF-NMP-A were dispersed by means of a capillary with an orifice of 0.500 mm in a conical flask (flask) of 2000 mL in which there are consecutively 1000 mL of methanol, ethanol, and then iso-propanol.

The nanoparticles obtained were transferred to 200 mL solution of 10% hydrochloric acid and 5% ammonium persulfate.

Ultrafiltration processes

CELFA System ultrafiltration plant has a supply container of 500 mL with an adjustable working pressure of 2-7 atm, recycling system that ensures a turbulent flow regime and the working surface of a 10 cm² membrane. After ultrafiltration the permeate flow is determined (J) and also the retention of the species of interest (R) using the solutions' absorbance and concentration [35]:

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

where:

c_f is the final concentration of the solute (copper or phenol),

c_o - initial concentration of solute (copper or phenol)

$$R(\%) = (A_o - A_{sample}) / A_o \quad (2)$$

where:

A_o - initial sample solutions absorbance

A_{sample} - current sample absorbance

Analytical methods

The determination of phenol is accomplished through the spectrophotometric method Spectrometer CAMSPEC [56, 57] and the measurement of copper is done by atomic absorption (Perkin Elmer Spectrometer).

FTIR analysis was performed on a Nicolet 6700 FT-IR analyzer which records from 400-4000 cm⁻¹. Infrared spectra were carried out using attenuated total reflection (ATR).

Morphological analysis of samples was performed by scanning electron microscopy (SEM). It used a higher solution microscope, Quanta 3D EGF model with dual beam and equipped with X-ray (EDX) Apollo X energy dispersive detector.

Atomic force microscopy (AFM) experiments were made using working mode called intermittent contact using a Nanosurf® AG Switzerland (EasyScan model 2) apparatus.

Results and discussions

To separate cupric ions or nitrophenols in aqueous solutions we can use reverse osmosis [54, 55] with polymeric membranes at pressures above 50 atm. Although water flows and the retention of the targeted substances are acceptable, the process needs expensive selective membranes and a high working pressure. This makes the process inefficient both technically and economically.

To reduce the operating pressure and increase the water flow, in the present work, it is used the ultrafiltration process through a membrane of polysulfone in N-methylpyrrolidone 10% obtained by coagulation in isopropanol. Asymmetric membrane structure (fig. 3) provide important and pure water flows continuously increasing the pressure [24,31,35] (fig. 4).

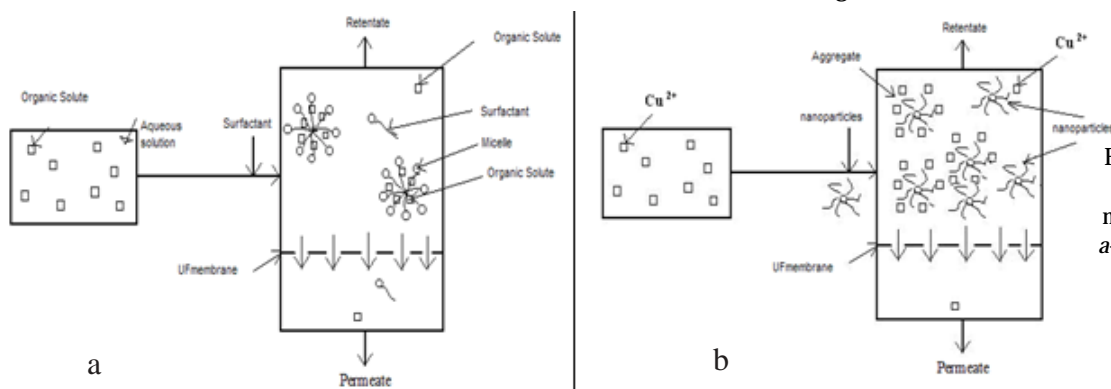


Fig. 2. Systems for the amplification of membrane processes: a- by adding surfactants and b- by adding the nanoparticles.

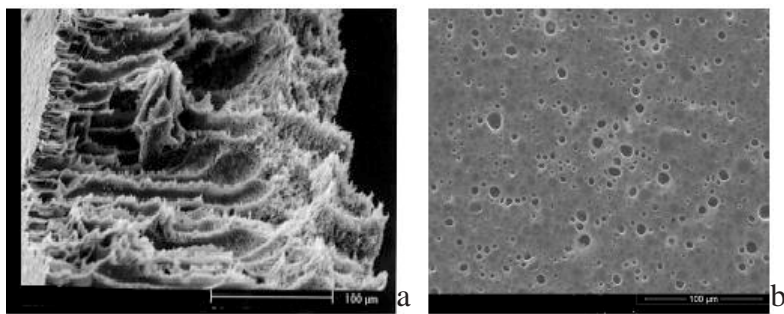
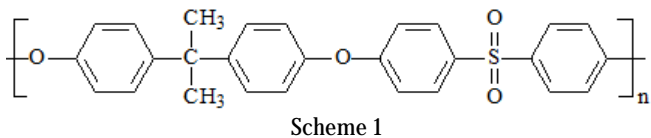


Fig. 3. The morphology of the membrane 10% PSf / NMP / iso-propanol (to section b-backside)

Pure water flows obtained from polysulfone ultrafiltration membrane are considered superior by at least an order of magnitude compared to the flows produced by reverse osmosis membranes [35,54,55].

Withholding cupric ions or nitrophenols by ultrafiltration membranes 10% PSf / NMP / iso-propanol is highly unlikely because of its structure (scheme 1) and therefore is studying the effect of introducing nanoparticles composite polysulfone-polyaniline (NP-PSf / PANI) in system power, which involves colloidal ultrafiltration is being studied. Thus, cupric ions or Nitrophenols of dilute aqueous solutions of nanoparticles are detained composite NP-PSf-PANI, after which the nanoparticles are retained by ultrafiltration membranes 10% PSf / NMP / iso-propanol.

Necessary nanoparticles were obtained by ultrafiltration of colloidal immersion precipitation technique (fig. 5) of a



5% solution in N-methyl pyrrolidone PSf containing 3% aniline in lower alcohols: methanol, ethanol and isopropanol [52-55], followed by oxidation of residual aniline with 10% hydrochloric acid solution and ammonium persulfate (scheme 2).

The ternary diagram polymer solvent-non-solvent (fig. 5) lane 1 shows that the polymer solvent is replaced slowly by a similar amount of non-solvent in the composition of the polymer solution to phase inversion, and the lane 2 indicates that the solvent is replaced relatively quickly by the non-solvent, at the same time as the concentration of the polymer system. Theoretically one way leads to microporous systems or gels, and the other to macroporous polymeric systems [24,35,55].

Phase inversion path for a polymer-solvent system can be controlled by choosing the appropriate solvent. In the present experiments the non solvents were the lower aliphatic alcohols, which have an interaction with the polysulfone decreasing in the series methanol > ethanol > iso-propanol

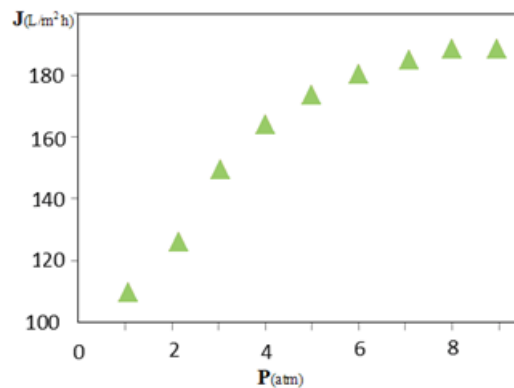
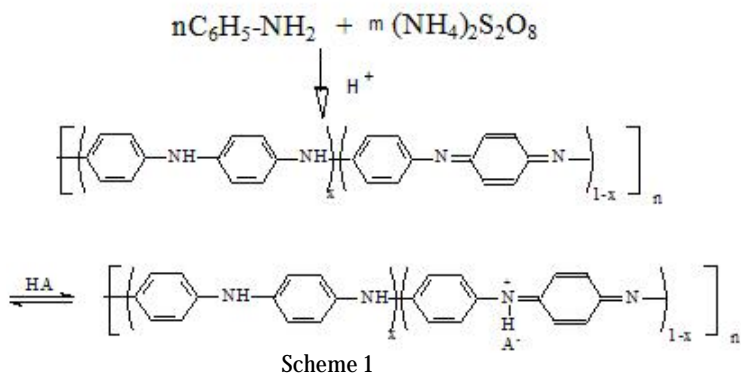


Fig. 4. Addition flow of pure water working pressure membrane 10% PSf / NMP / iso-propanol

Nanoparticles of polysulfone (NP-PSf) and the three variants of composite nanoparticles (NP-PSf-PANI) were characterized morphologically (SEM) si (AFM) [24,31,35], structurally and compositionally (FTIR) [24,25,35], and the results (table 1) show that nanoparticles have a much lower structure/than the composites

The nanoparticles have a spherical shape with diameters between 50 and 500 nm (table 1-SEM). The smallest nanoparticles are made of polysulfone, and the diameter of the composite decreases in the following order:



The spectral characteristics obtained by infrared spectrometry polysulfone-polyaniline nanoparticles are highlighted in figure 5 and table 2. All FTIR bands led to the identification of polysulfone with a probability of 98.5%. The presence of polyaniline in the composite nanoparticles is suggested by a large band specific to hydrogen bonds and less to nitrogen-aryl bonds, which are blurred by the large number of oxygen-aryl absorption bands that are present in the main polysulfone.

The amounts of residual aniline in polysulfone particles lead directly to a similar amount of polyaniline composite nanoparticles (FTIR -table 1).

The structure suggested by AFM (fig. 6 and table 1) is moderate in the composition of polysulfone, but it amplifies in the series of composite nanoparticles as follows: NP-PSf-PANI-M > NP-PSf-PANI-E > NP-PSf-PANI-P. The amount of polyaniline resulted in the composition of composite nanoparticles decreases in the same order [35], depending on the solvent in the coagulation bath: methanol > ethanol > iso-propanol. This shows that in case of a rapid coagulation of the polymer, polysulfone the residual amount of aniline in a nanoparticle is higher.

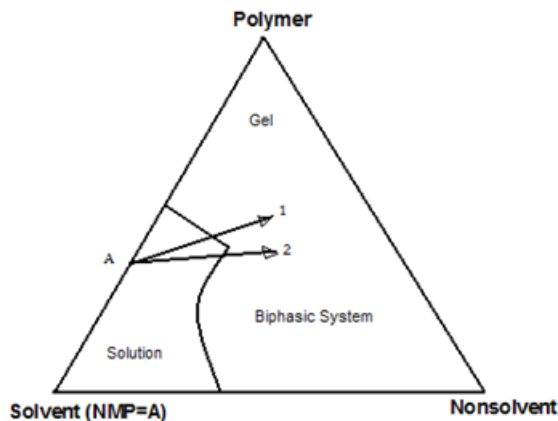


Fig. 5. Polymeric nanoparticles schematic course of formation by phase inversion from the initial composition of (1-slow, fast process 2)

Table 1
CHARACTERISTICS OF NANOPARTICLES IN POLYSULFONE (NP-PSf) AND COMPOSITE POLYSULFONE-POLYANILINE (NP-PSf-PANI)

Nanoparticle	SEM	AFM	FTIR
NP PSf			
NP PSf-PANI-M			
NP PSf-PANI-E			
NP PSf-PANI-P			

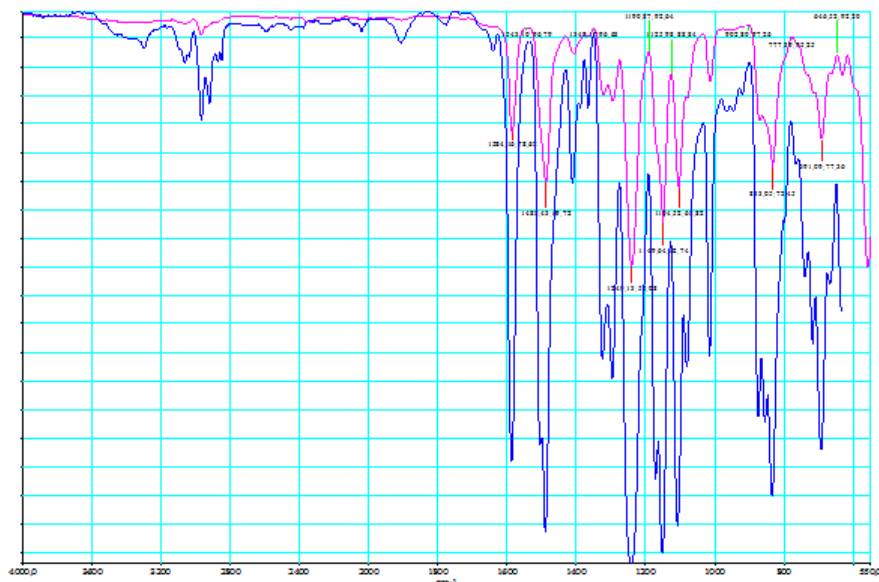
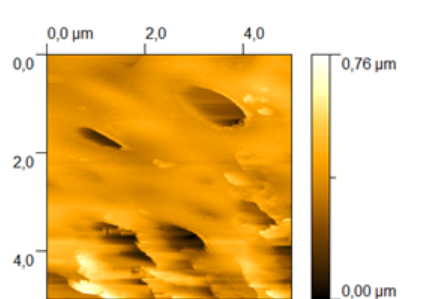


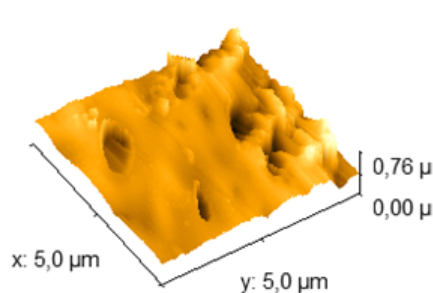
Fig. 6. FTIR characteristics of nanoparticles in polysulfone and polysulfone-polyaniline

Table 2
FTIR SPECTRA OBTAINED CHARACTERISTICS OF NANOPARTICLES

Wavenumber (cm ⁻¹)					Assignment
Polysulfone	NP-PSF	NP-PSF-PANI-M	NP-PSF-PANI-E	NP-PSF-PANI-P	
-		3100	3100	3100	Vibration specific hydrogen bonds =O...H si =N...H
		3600	3600	3600	
2980	2980	2980	2980	2980	Symmetrical and asymmetrical stretching vibration involving the whole methyl group
2880	2880	2880	2880	2880	
1584	1583	1583	1583	1583	Stretching vibration of the C = C aromatic
1488	1487	1488	1488	1488	
1410	1409	1410	1410	1410	C-H bending vibration of the methyl group
1325	1324	1325	1325	1325	Doublet resulting from the asymmetric extent of the sulfonic group O = S = O
1298	1299	1298	1298	1298	
1240	1239	1240	1240	1240	Stretching vibration of C-O-C links the aryl ether
1149	1149	1149	1149	1149	Symmetric stretching vibration sulfonic group O = S = O
1104	1104	1104	1104	1104	Vibrations of the aromatic ring
1092	1060	1070	1056	1056	
1027	1026	1026	1027	1012	Symmetrical vibration O = S = A sulfonic group.



a) Polysulfone (representation 2D 5x5 μm)



b) Polysulfone (representation 3D 5x5 μm)

Fig. 7. AFM characteristics of nanoparticles in polysulfone in bi and tri-dimensional representation

The nanoparticles obtained have been tested in the ultrafiltration of colloidal solution containing cupric ions and nitrophenols (fig. 7 and 8).

Cupric ions and nitrophenols retention is significantly superior in the ultrafiltration of composite nanoparticles compared to polysulfone nano particles. The results are justified by the very weak interaction of cupric ions and nanoparticles with polysulfone nitrophenols, most likely with oxygen atoms from the structure (scheme 1). In the case of composite nanoparticles, the interaction with cupric ions and nitrogen atoms results in a strong increase in retention, especially for nanoparticles containing more polyaniline (NP-PSf-PANI-M). It is interesting to note that

the retention of cupric ions is strongly influenced by the pH of the solution supply, benefiting from its growth (fig. 8).

The Ultrafiltration of solutions containing both cupric ions and nitrophenols shows that retentions are higher by 5-15 percentage points for all types of nanoparticles (fig. 10).

The possibility of copper complexation by both nitrophenols, and by nanoparticle surface, probably lead, to the formation of more stable aggregates in the supply, which can sufficiently justify an increasing in retention.

The Retentions of the chemical species in question use in all the tests made the same series:

$$R_{NP-PSf-PANI-M} > R_{NP-PSf-PANI-E} > R_{NP-PSf-PANI-P} > R_{NP-PSf}$$

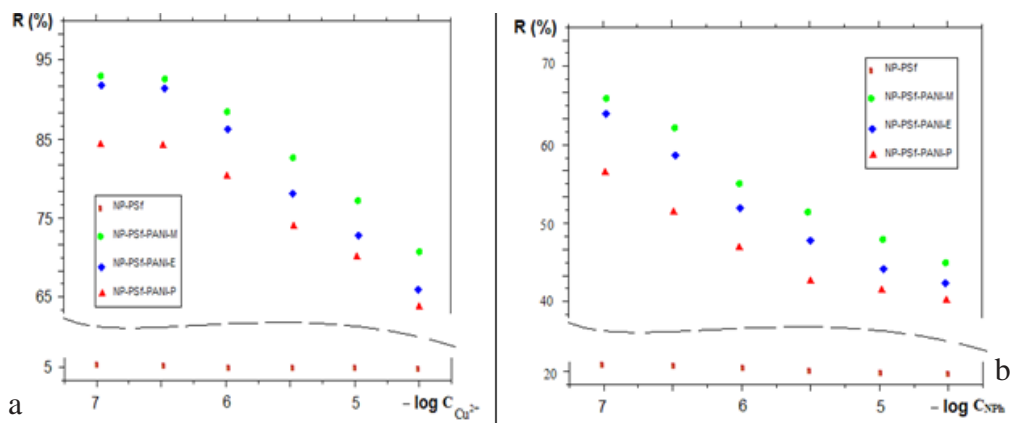


Fig. 8. The retention of the cupric ions (a) and nitrophenols (b) by ultrafiltration composite colloidal nanoparticles

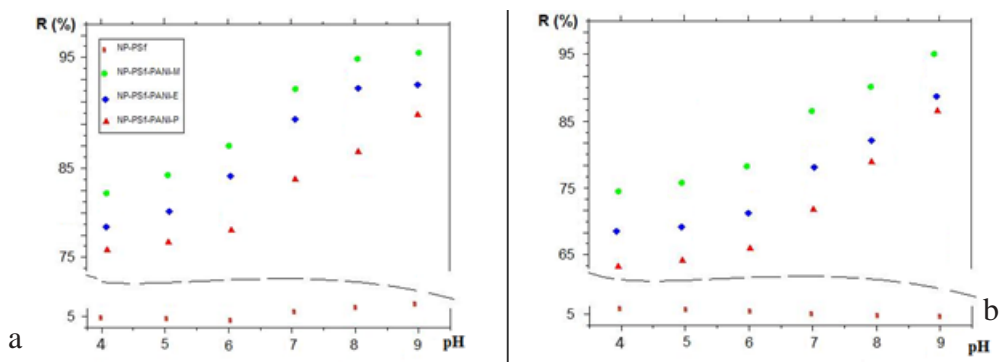


Fig. 9. Retention cupric ions (a) and nitrophenols (b) depending on the pH of the solution of colloidal nanoparticles by ultrafiltration food Composites

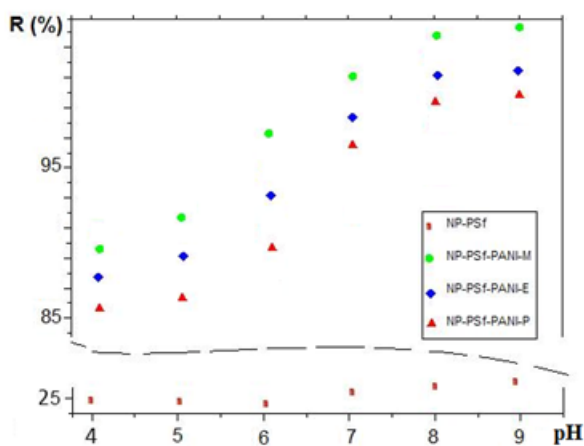


Fig. 10. Retention of cupric ions (a) and nitrophenols (b) mixed through colloidal ultrafiltration with nanoparticle composites

This observation is in good connection with both the chemical structure, and the morphology, especially in size and structure of nanoparticles.

Conclusions

The nanoparticles needed for colloidal ultrafiltration were obtained through the technique of immersing the precipitation of a solution of 5% PSf in N-methyl pyrrolidone containing 3% aniline into lower alcohols: methanol, ethanol, and isopropanol followed by oxidation of the remaining aniline into a solution of 10% hydrochloric acid and ammonium per sulfate. Cupric ions and nitro phenols retention is significantly superior compared to the composite ultrafiltration with nanoparticles in comparison to the polysulfone nano particle. The possibility of copper complexation by both nitrophenols, and by nanoparticle surface probably lead to the formation of more stable aggregates in the supply, which can sufficiently justify the increasing in retention.

The retentions of the chemical species in question use in all the tests made the same series:

$$R_{NP-PSf-PANI-M} > R_{NP-PSf-PANI-E} > R_{NP-PSf-PANI-P} > R_{NP-PSf}$$

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References

- FRANKENFELD, J.W., LI, N.N., John Wiley & Sons, Inc., New York, 1987
- MITTAL, K.L., SHOH, D.O., Surfactants in solution, Vol. 11, Springer Science+Business Media New York, 1991
- VAN DER BRUGGEN, B., DAEMS, B., WILMS, D., VANDECASTEELE, C., Separation and Purification Technology, **22-23**, 2001, p. 519
- TAN, B.H., TENG, T.T., OMAR, A.K.M., Wat. Res., **34**, no.2, 2000, p. 597
- POPESCU, G., ALBU, B., NUTA, D., RATA, D., ALDEA, E., DINESCU G., OLTEANU, M., Ultrafiltration of dyes in the presence of surfactants, Analele Universitatii din Bucuresti – Chimie, Anul XII (serie noua), vol. I-II, p. 49-54;
- HAMEED, B.H., RAHMAN, A.A., J. Hazard. Mater., **160**, 2008, p.576
- TERESA, A., REIS, M., ONDINA DE FREITAS, M.F., ISMAEL, M.R.C., CARVALHO, J.M.R., J. Membr. Sci., **305**, 2007, p.313
- LEE, S.Y., KIM, B.N., HAN, J.H., CHANG, S.T., CHOI, Y.W., KIM, Y. H., MIN, J., J. Hazard. Mat., **182**, 2010, p.936
- BALASUBRAMANIAN, A., VENKATESAN, S., Pol. J.Chem.Tech., **14**, 2012, p.46
- URTIAGA, A., GUTIERREZ, R., ORTIZ, I., Desalination, **245**, 2009, p.444
- LEE, A., ELAM, J.W., DARLING, S.B., Environmental Science Water Research & Technology, **2**, 2016, p. 17
- PETZOLD, G., SCHWARZ, S., Separation and Purification Technology, **31**, 2003, p. 318
- KOPECKY V., MIKULASEK P., Environment Protection Engineering, **31**, 2005, p. 187
- ARCHER, A.C., MENDES, A.M., BOAVENTURA, R.A.R., Environ. Sci. Technol., **33**, 1999, p. 2758

15. MAJEWSKA-NOWAK, K., KOWALSKA, I., KABSCH-KORBUTOWICZ, M., *Desalination*, **200**, 2006, p. 283
16. TANCZOS, S.K., MIRON, A.R., DINU, A., RADUCU, A., CRISTEA, A., NECHIFOR A.C., *Rev. Chim. (Bucharest)*, **65**, no. 7, 2014, p. 744
17. MAJEWSKA-NOWAK, K., *Environment Protection Engineering*, **31**, 2005, p. 229
18. PUASA, S.W., RUZITAH, M.S., SHARIFAH, A.S.A.K., An overview of Micellar - Enhanced Ultrafiltration in Wastewater Treatment Process, 2011 International Conference on Environment and Industrial Innovation IPCBEE, vol.12, **2011**, © (2011) IACSIT Press, Singapore;
19. MAJEWSKA-NOWAK, K., KOWALSKA, I., KABSCH-KORBUTOWICZ, M., *Desalination*, **184**, 2005, p. 415
20. MAJEWSKA-NOWAK, K., *Environment Protection Engineering*, **4**, 2009, p. 111
21. KIMA, C.K., KIMB, S.S., LIMC, J.C., KIMD, J.J., Removal of aromatic compounds in the aqueous solution via micellar enhanced ultrafiltration. Part 1. Behaviour of non-ionic surfactants, *J. Membr. Sci.*, **147**, 1998, p.13
22. MUNIR, A., Dead End Membrane Filtration, ENE 806, Laboratory Feasibility Studies in Environmental Engineering, Springer, **2006**
23. AHMAD, A.L., PUASA, S.W., ZULKALI, M.M.D., *Desalination*, **191**, 2006, p. 153
24. VOICU, S.I., ALDEA, F., RADUT, M., NECHIFOR, G U.P.B. Sci. Bull., Series B, Vol. **70**, no. 3, 2008, p. 39
25. JINHUIHUANG, LEIPENG, GUANGMING ZENG, XUE LI, YONG ZHAO, LIUXIA LIU, FEI LI, QI CHAI, Separation and Purification Technology, **125**, 201, p. 83
26. POZNIAK, R., POZNIAK, G., WILK, K.A., *Chem. Eng. Trans.*, **17**, 2009, p. 1693
27. MAJEWSKA-NOWAK, K., KOWALSKA, I., KABSCH-KORBUTOWICZ, M., *Desalination*, **198**, 2006, p. 157
28. BAEURLE, S.A., KROENER, J., *Journal of Mathematical Chemistry*, **36**, 2004, p. 409
29. MAJEWSKA-NOWAK, K., *Environment Protection Engineering*, **32**, 2006, p.78
30. SUN, O., YANG, L., *Water Research*, **7**, 2003, p. 315
31. BATRINESCU, G., CONSTANTIN, M.A., CUCIUREANU, A., NECHIFOR, G., *Polymer Engineering and Science*, **54**, no. 7, 2014, p. 1640, DOI: 10.1002/pen.23707
32. MARCUCCI, M., NOSENZO, G., CAPANELLI, G., CIABATTI, I., CORRIERI, D., GIARDELLI, G., *Desalination*, **138**, 2001, p. 75
33. NECHIFOR, G., LUCA, N., POPESCU, G., NECHIFOR, M., *Rev. Roum. Chim.*, **34**, no. 11-12, 1989, p. 2047
34. ZAGHBANI, N., HAFIANE, A., DHAHBI, M., *Desalination and Water Treatment*, **6**, 2009, p. 204
35. RIKABI, A.A.K.K., NECHIFOR, A.C., MOHAMMED, T. J., OPREA, O., MIRON, A.R., SEGARCEANU, M., VAIREANU, D.I., *Rev. Chim. (Bucharest)*, **67**, no. 9, 2016, p. 1489
36. KAMINSKI, W., KWAPINSKI, W., *Pol. J. Environ. Stud.*, **9**, 2000, p.37
37. NG, Y.S., JAYAKUMAR, N.S., HASHIM, M.A., *J. Hazard. Mat.*, **184**, 2010, p.255
38. BUSCA, G., BERARDINELLI, S., RESINI, C., ARRIGHI, L., *J. Hazard. Mat.* **160**, 2008, p.265
39. VAN DER BRUGGEN, B., European Membrane Society Summer School, Bucharest, 15-20 June, Romania, **2010**
40. NECHIFOR, G., ALBU, B.G., RATA, D., POPESCU, G., *Rev. Chim. (Bucharest)*, **47**, no. 3, 1996, p. 260
41. SERBAN, B., RUSE, E., MINCA, M., PASARE, J., NECHIFOR, G., *Rev. Chim. (Bucharest)*, **51**, no. 4, 2000, p. 249
42. NECHIFOR, A.C., RUSE, E., NECHIFOR, G., SERBAN, B., *Rev. Chim. (Bucharest)*, **53**, no. 1, 2002, p. 20
43. NECHIFOR, G., VOICU, S.I., NECHIFOR, A.C., GAREA, S., *Desalination*, **241**, no. 1-3, 2009, p. 342
44. RIKABI, A.A.K.K., CUCIUREANU, A., CHELU, M., MIRON, A.R., ORBECI, C., POPA, A.G., CRACIUN, M.E., *Rev. Chim. (Bucharest)*, **66**, no. 8, 2015, p. 1093
45. DIACONU I., GIRDEA R., CRISTEA C., NECHIFOR G., RUSE E., Totu E. E., *Rom Biotech Lett.*, **15**, no. 6, 2010, p. 5703
46. DIACONU I., ABOUL-ENEIN H.Y., AL-OMAR M.A., NECHIFOR G., RUSE E., BUNACIU A.A., TOTU. E.E., *Arab. J. Chem.*, **4**, no. 1, 2011, p. 99
47. DIACONU I., NECHIFOR G., NECHIFOR A.C., RUSE E., TOTU, E.E., *UPB.Sci.Bull. Series B*, **71**, no.4, 2009, p. 61
48. DIACONU, I., NECHIFOR, G., NECHIFOR, A.C., TOTU, E.E., RUSE, E., *Rev. Chim. (Bucharest)*, **60**, no. 12, 2009, p. 1243
49. VOICU, S.I., ALDEA, F., NECHIFOR, A.C., *Rev. Chim. (Bucharest)*, **61**, no. 9, 2010, p. 817
50. TANCZOS S.K., CHICAN, I., MIRON A. R., RADU, D. A., RADUCU, A., NECHIFOR, A. C., *Rev. Chim. (Bucharest)*, **65**, no. 6, 2014, p.636
51. COROBEA, C., DONESCU, D., RADITOIU, V., VOICU, S.I., NECHIFOR, G., *Rev. Chim. (Bucharest)*, **57**, no. 9, 2006, p. 981
52. VOICU, S.I., STANCIU, N.D., NECHIFOR, A.C., VAIREANU, D.I., NECHIFOR, G., *Romanian Journal of Information Science and Technology*, **12**, no.3, 2009, p. 410
53. POPESCU, G., NECHIFOR, G., ALBU, B., LUCA, N., *Rev. Roum. Chim*, **34**, no. 2, 1989, p. 577
54. RIKABI, A.A.K.K., BALABAN (CHELU), M., HARABOR, I., ALBU, P.C., SEGARCEANU, M., NECHIFOR, G., *Rev. Chim. (Bucharest)*, **67**, no. 9, 2016, p. 1658
55. CUCIUREANU, A., BATRINESCU, G., BADEA, N.N., RADU, D.A., NECHIFOR, G., *Mat. Plast.*, **47**, no. 4, 2010, p. 416
56. ZAHARIA, I., DIACONU, I., RUSE, E., NECHIFOR, G., *Rev. Chim. (Bucharest)*, **66**, no. 2, 2015, p. 169
- DIACONU, I., ZAHARIA, I., RUSE, E., NECHIFOR, G., *Dig. J. Nanomater. Bios.*, **7**, no. 3, 201

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