The Influence of Changing the Polyaniline and Polysulphone Ratio on Composite PSF-PANI Membranes Performances

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The paper reports the performances of the polysulfone-polyaniline (PSf-PANI) porous composite membranes for various ratios PSf / PANI in membranes. Polysulfone-polyaniline porous composite membranes are obtained by phase inversion with chemical reaction. PANI is obtained in-situ by oxidative aniline polymerization. Composite membranes are morphologically studied by electron microscopy and characterized by thermal analysis and water solutions permeation at different pH and pressures. Polysulfone-polyaniline porous composite membranes UF processes performances to BSA separation are also reported.

Keywords: PSf-PANI membranes, phase inversion, hydrodynamic characteristics, rejection, BSA

The membrane techniques that use composite membranes are applied in various domains, replacing in many instances the technologies that use simple membranes [1, 2].

Polysulfone-polyaniline porous composite membranes (PSf-PANI) exhibit an interesting advantage because they use PSf as the base polymer (PSf has good mechanical and chemical properties, good stability in acid and basic aqueous solutions, good solubility in the usually solvents in the process of membrane production) and specially performances in bioanalysis and bioseparations [3, 4].

The paper presents the composite PSf-PANI membranes performances obtained by phase inversion, new immersion-precipitation technique with chemical reaction. The morphology and hydrodynamic characteristics are studied, as well as the capacity of separating albumin from bovine serum (BSA) – the reference protein.

Experimental part
Materials
- Polysulfone (PSf) – Aldrich
- Aniline – Merck
- N-methylpyrrolidone (NMP) – Merck
- Ammonium peroxodisulphate – Sigma-Aldrich
- Chlorhidric acid – Merck
- Polyvinylpyrrolidone K 30 – Fluka
- Polyethylene glycol 4000 - Scharlau
- BSA – Biochemika

Methods and proceedings
Polysulfone-polyaniline porous composite membranes are prepared by phase inversion, immersion-precipitation techniques in a stepwise procedure [5, 6], as follows:
- polysulfone solubilization in a solvent mixture;
- filtration of polymer solution to gels removal;
- air removal into a desicator;
- polymer film formation from polymer solution;
- coagulation of polymer film;
- chemical reaction.

Polysulfone-polyaniline porous composite membranes are obtained by polysulfone coagulation followed by oxidative polymerization of aniline from polymeric film.

A flowchart illustrating these steps in obtaining polysulfone-polyaniline porous composite membranes is presented in figure 1.

The polymeric base materials were PSf and PANI (obtained *in-situ*). Three solutions, with different concentration level of the PSf (10%PSf, 12%PSf, 14%PSf.) were used. The solvents were N-methyl pyrrolidone (NMP) and aniline. Viscosity correction agents used were polyvinylpyrrolidone (2% PVP K30) and polyethylenglycol (2% PEG 4000). The proportion between the base polymer PSf and aniline was the same in all three solutions (1:1).

For the polycondensation of the residual aniline in membrane pores, a solution of HCl 0,1M and ammonium peroxodisulphate 0.05M was used. The ammonium peroxodisulphate:aniline ratio was 1:1.

The paper presents the results of two experimental versions (denoted E1, E2) using the following non-solvent substances media:
- water in E1 version
- water with added aniline in E2 version, at saturation limit (1,9% solution) to prevent migration of the monomer in water and high aniline content in the membrane pores preformed and default in PANI composite membrane.

The non-solvent was selected to dissolve the PSf polymer [7].

In both versions, the three solutions with different concentration of the base polymer PSf were used. Six composite membranes with different characteristics were obtained.

Polymer film was formed in a matter of seconds, at room temperature and humidity, using a *"doctor blade"* device type made from stainless steel, with 200 μm slot, to a smooth glass support. The coagulation time for each membrane was 3 min. The average time for the reaction to obtain each composite membrane was 3 h. Visually, the process was controlled by monitoring the colour from white, to violet and finally to blue. In the end, the composite
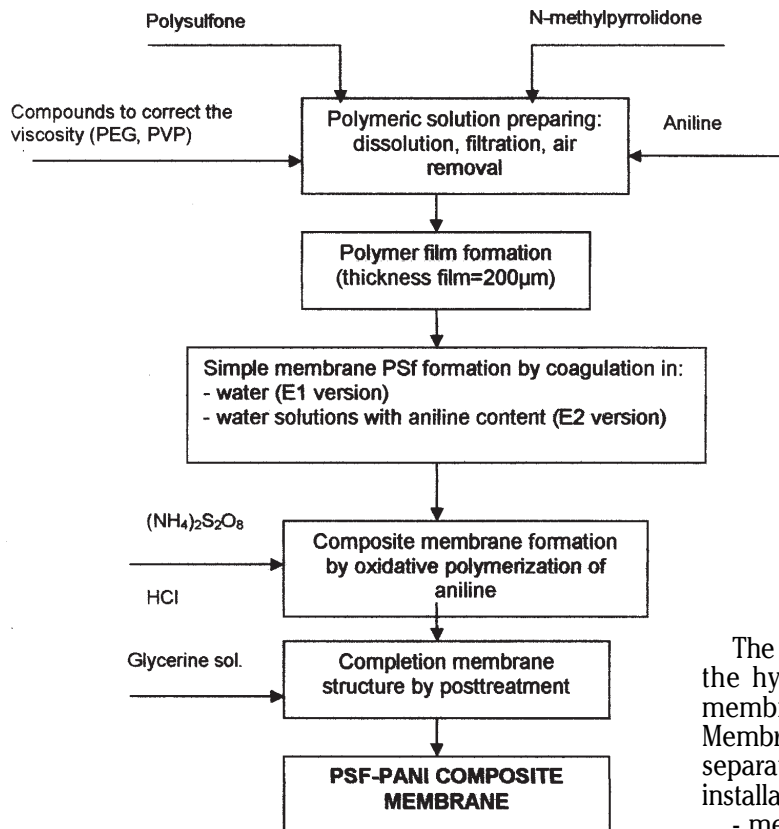
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Fig.1. Flowchart for obtaining composite PSf-PANI membranes

membranes were washed using fresh distilled water for eliminating the residual reaction compounds, followed by conditioning in glycerine solution 20%.

In these conditions, the following composite membranes were obtained:

- M1E1 – composite membrane PSf-PANI obtained from 10% PSf+PANI solution, coagulating in water (E1 version)

- M2E1 – composite membrane PSf-PANI obtained from 12% PSf+PANI solution, coagulating in water (E1 version)

- M3E1 – composite membrane PSf-PANI obtained from 14% PSf+PANI solution, coagulating in water (E1 version)

- M1E2 – composite membrane PSf-PANI obtained from 10% PSf+PANI solution, coagulating in water with aniline addition (E2 version)

- M2E2 – composite membrane PSf-PANI obtained from 12% PSf+PANI solution, coagulating in water with aniline addition (E2 version)

- M3E2 – composite membrane PSf-PANI obtained from 14% PSf+PANI solution, coagulating in water with aniline addition (E2 version)

The performances of the obtained composite membrane were determined by evaluating the hydrodynamic characteristics and the retention of reference compounds.

The hydrodynamic performances of the composite membranes obtained were determining by water solutions permeation at different pH (1, 3, 5, 7, 9, and 11) and pressures (2 bar, 4 bar, 5 bar and 6 bar). The flux is determined using the equation (1):

$$J = \frac{V}{S \cdot t} \qquad (\text{L/m}^2 . \text{h}) \qquad (1)$$

where:

J = the flux (L/m^2 . h);

V = the permeate volume (L);

S = the membrane effective area (m^2);

t = the time necessary for V liters of permeate to be collected (h).

The experimental setup that has been used to determine the hydrodynamic characteristics of the composite membranes was the KMS Laboratory Cell CF-1 (Koch-Membrane - Germany) ensuring a tangential flow mode in separated process. The functional characteristics of this installation were:

- membrane diameter: 76 mm;
- effective area: 28cm^2;
- feed tank volume: 0.5 L;
- liquid speed at tangential flow: 2m/s;
- pressure: 2-6 bar;
- maximum temperature: 70^{0}C

The separation performances of the obtained composite membranes were determined using two criteria:

- separating capacity of a reference protein (BSA), measured by evaluating the rejection rate (R); the rejection percentange is calculated using the equation (2):

$$R = \frac{C_{in} - C_p}{C_{in}} \cdot 100 \qquad (\%) \qquad (2)$$

where:

R = the rejection rate (%);

C_{in} = the concentration of the solute in the feed (mg/L);

C_p = the concentration of the solute in the permeate (mg/L).

- retention (immobilization) capacity (I) of the reference protein BSA, upon the membrane surface and its microporous structure, by adsorption and ionic bounds formation between reactive functional groups of PANI and reactive functional groups of BSA ; the retention capacity is measured in weight units per surface unit of the membrane (mg/cm^2). The two equations [4] which are used to determine I are (3) and (4):

$$V_{in} \bullet C_{in} = V_p \bullet C_p + V_c \bullet C_c + m \qquad (3)$$

$$I = \frac{m}{S} \qquad (\text{mg/cm}^2) \qquad (4)$$

where:

V_{in} = the volume of the feed solution (L);

C_{in} = concentration of the solute in the feed (mg/L);

V_p = the volume of the permeate (L);

C_p = the concentration of the solute in the permeate (mg/L);

V_c = the volume of the concentrate (L);

C_c = the concentration of the solute in concentrate (mg/L);

I = retention (immobilization) capacity (mg/cm^2);

m = the total weight of the protein retention on composite membrane (mg);

S = effective area of the composite membrane (cm^2).

In the first experimental version a 1 g/L BSA solution dissolved in citric acid-sodium citrate buffer at pH = 4.9 was used. In the second experimental version a 1 g/L BSA solution dissolved in Tris-HCl buffer at pH = 7.4 was used [8].

The experimental setup that has been used in these experiments was the same KMS Laboratory Cell CF-1 (Koch-Membrane - Germany) ensuring a tangential flow mode in separated process. The experiments were conducted at 4 bar pressure.

In each of the two experimental versions the volume feed solution BSA was initially 0.5 L, with 0.25 L collected permeate and 0.25 L concentrate. The protein concentration in permeate and concentrate were determined by the Lowry method, on spectrophotometry UV-VIS [9, 10].

The calibration graph for the protein quantitative determination – reference BSA solution is shown in figure 2.

It was used the molecular absorption spectrometer Specord 205 (Analytic Jena, Germany) quartz containers 1 cm thickness. The absorbance was measured at λ = 751 nm. From the calibration graph the protein concentration in permeate and concentrate is inferred.
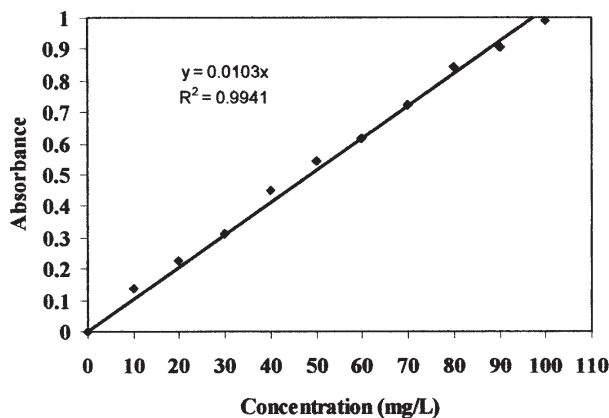

Fig.2.The calibration graph for the protein quantitative determination – reference BSA solution

The membranes were morphological and thermal investigated by Scanning Electron Microscopy (SEM) on FESEM Hitachi S 4500, and TGA/TDA Shimadzu Apparatus.

Results and discussions

The experiments realized along the described methodologies try to evaluate the influence of changing the PSf-PANI ratio upon the hydrodynamic and separation performances of the composite membrane, at different pH and pressures values.

The results obtained by testing the composite membranes, measuring the permeate flux solutions, at different pH and pressures values, in both experimental versions, are shown in figures 3 -5.The performed experiments for trans-membrane pressure influence and pH evaluation, for the obtained membranes by those two coagulation versions and three different polymer concentration solutions, reveals the following:

- the water flux increases with increased pressure, regardless of the type of the composite membrane prepared and the pH values which are tested;
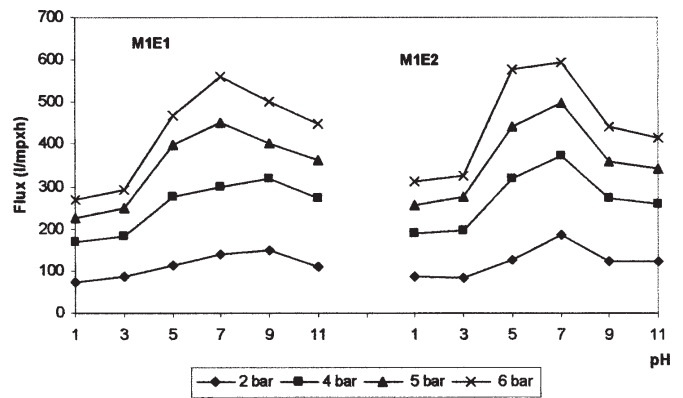

Fig.3. Water flux at different pH and pressures to composite membranes from 10%PSf solution in the experimental versions E1 and E2
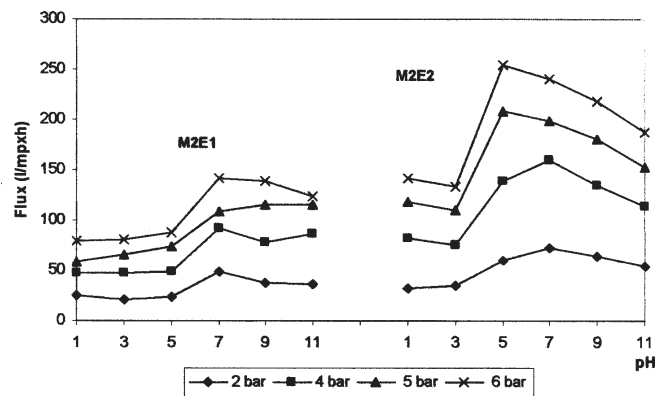

Fig.4. Water flux at different pH and pressures to composite membranes from 12%PSf solution in the experimental versions E1 and E2
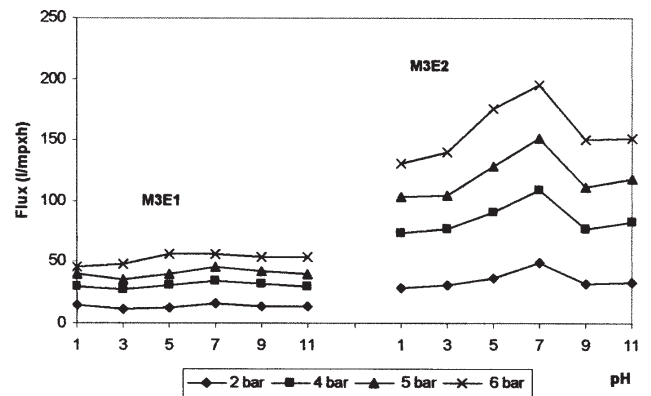

Fig.5. Water flux at different pH and pressures to composite membranes from 14%PSf solution in the experimental versions E1 and E2

- the maximal values of the water flux correspond to pH = 7, for each of composite membranes, at all pressures tested; at this pH value, doping state of PANI polymer composite gives a loose structure regardless of work pressure;

- increases of the PSf polymer concentration from the base solution used to prepare the composite membrane leads to improved hydrodynamic characteristics of the composite membrane (increase flux of the permeate); this phenomenon may be explained by a looser structure of the PANI-PSf composite membrane.

The effect was observed especially in the case of the composite membrane obtained from the highest concentration of the polymer solution (14% PSf), when

Table 1

THE RESULTS OBTAINED AT BSA PROCESSED BY ULTRAFILTRATION, USING
COMPOSITE MEMBRANE PREPARED IN VERSION E1

Type of membrane	Solution pH	Permeate flux (L/m²h)	BSA concentration (mg/l)		R (%)	I (mg/cm²)
			permeate	concentrate		
M1E1	4.9	140.1	246.4	1553.6	75.36	1.79
	7.4	189.4	187.6	1512.2	81.4	2.68
M2E1	4.9	40.2	151.8	1517.8	84.82	2.95
	7.4	76.2	78.2	1393.2	92.19	4.72

Tabel 2
THE RESULTS OBTAINED AT BSA PROCESSED BY ULTRAFILTRATION,
USING COMPOSITE MEMBRANE PREPARED IN VERSION E2

Type of membrane	Solution pH	Permeate flux (l/m²h)	BSA concentration (mg/L)		R (%)	I (mg/cm²)
			permeate	concentrate		
M1E2	4.9	151.2	181.6	1577.6	81.84	2.15
	7.4	196.3	78.4	1546.4	92.16	3.35
M2E2	4.9	74.6	83.8	1507.4	91.62	3.65
	7.4	114.8	14.2	1309.3	98.58	6.04

the difference between permeate flux determined in both experimental versions was the largest.

There is no effect of aniline addition in composite membranes prepared from 10%PSf solution; the permeate flux is similar in the two experimental versions. A possible explanation is that at lower PSf concentrations (10%), the membrane structure exhibits higher porosity. Increasing the PANI quantity does not lead to a significant increase of the permeate flux.

For evaluating the BSA separation capacity and immobilization capacity, only the composite membrane obtained via the two experimental versions E1 and E2 (using 10% PSf and 12% PSf solutions) were tested. This is because, as mentioned earlier, only these materials enable fluxes that can lead to faster permeation processes through the membranes.

The permeate flux, the BSA concentration in permeate and concentrate, the percent of rejection (R) and the immobilization capacity (I) of the composite membranes obtained in experimental versions E1 and E2 are given in table 1, and 2, respectively.

The performed experiments for BSA retention, for the obtained membranes by those two coagulation versions and two different polymer concentration solutions, can be discussed as following:

-the rejection values (R) and the immobilization capacity values (I) determined for the four composite membranes tested are higher at $pH = 7.4$ as compared to the same parameters determined at $pH = 4.9$. The explanation is that the $pH = 4.9$ value is very near the iso-electrical pH level of the BSA. In these conditions, the BSA protein does not exhibit electrical charge and does not interact with the
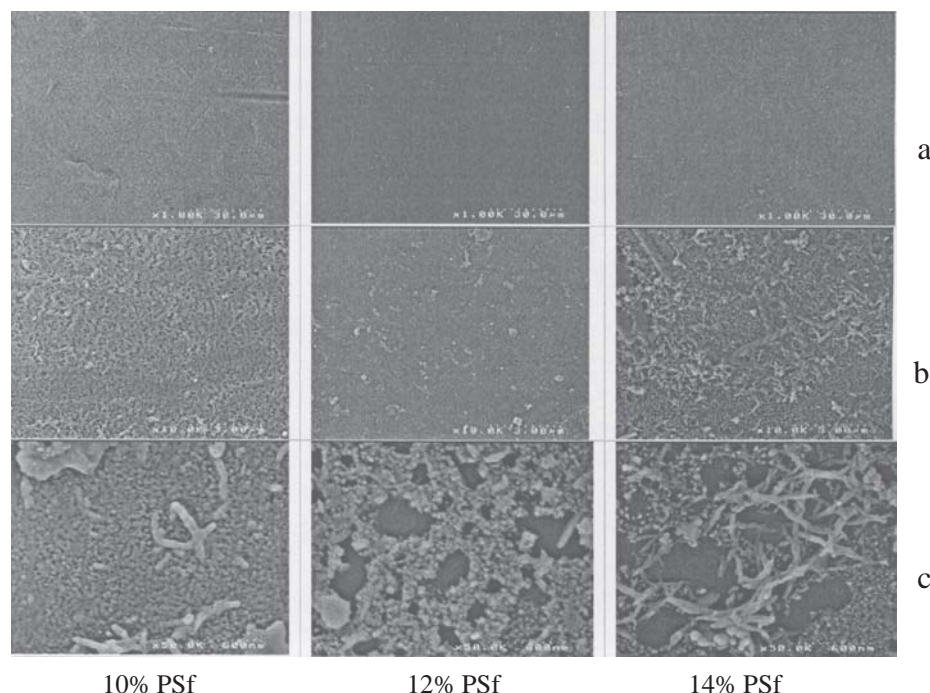
Fig.6. Scanning Electron Microscopy (SEM) on three types of membranes: 10% PSf, 12% PSf and 14% PSf for three magnification (*a*: x1000 *b*:x10000; *c*: 50000)
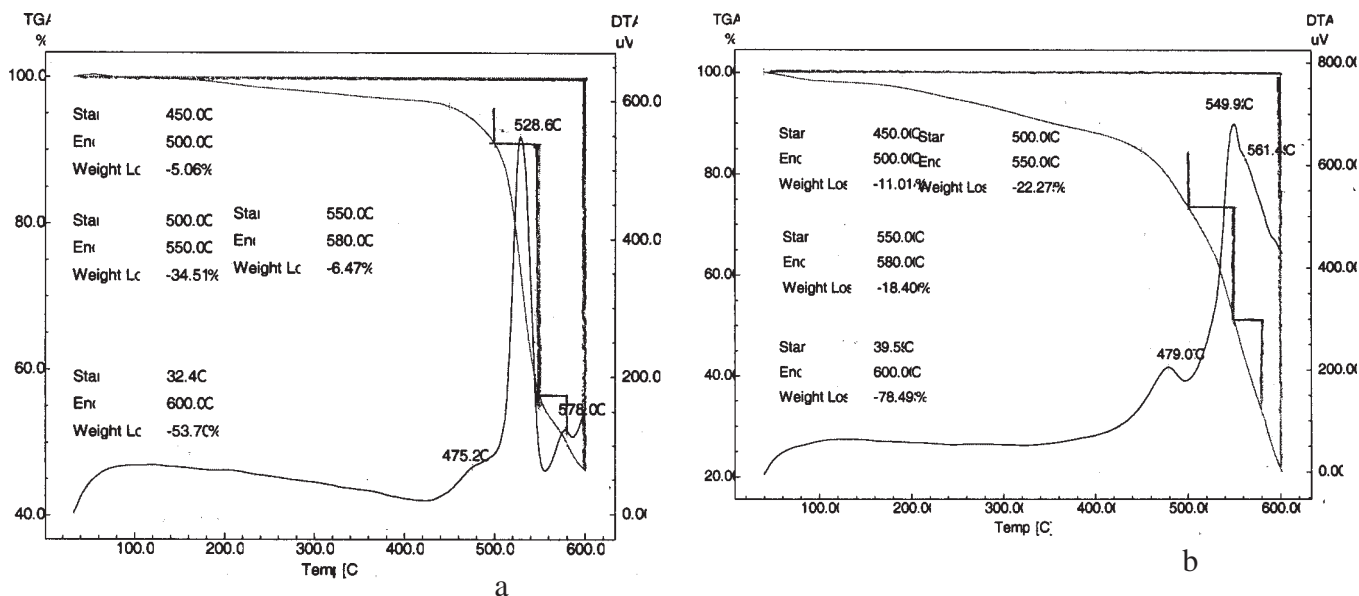
10% PSf   12% PSf   14% PSf

Fig.7. Comparative thermal analysis of PSF membrane (a) and PSF/PANI composite membrane (b)

PANI reactive functional groups of the composite membranes;

-at $pH=7.4$ the PANI polymer has the best hydrodynamic characteristics, effect confirmed in the case of the two functional characteristics (R and I);

-the rejection percentage of the M2E1, M2E2 membranes type is higher than the rejection percentage of the M1E1, M1E2 membranes type corresponding to the higher polymer PSf and PANI concentrations from composite membrane; this is because from solution with higher concentration the obtained composite have lower cut-off values;

-increasing the PANI content in composite membrane leads to an increase of the immobilization capacity (I) ; the immobilization capacity (I) for composite membrane M2E2 is higher (28%) than composite membrane M2E1 and for composite membrane M1E2 is higher (25%) than composite membrane M1E1, at $pH=7.4$.

The scanning electron microscopy - SEM of the PSF-PANI composite membranes reveals a very compact structure for the membranes obtained from 12% PSf solution, figure 6a, b and c (potential uses being in ultraflitration and nanofiltration) and a more relaxed structure for the 14% PSf membrane (fig. 6a, b and c), but still more compact than the one of the entirely 10% PSf membranes, for membranes obtained on E2 version, figure 6a, b, c.

The membrane morphology is in complete accord with BSA retention, respectively the increasing of compact grade of membranes in order 10% PSf, 12% PSf (fig. 6).

The morphologic details at superior magnitude in figure 6 (**b**:x10000; **c**: 50000) are correlated with observations from hydrodynamic tests and BSA retention results.

The formation of polysulfone-polyaniline composite membranes was also demonstrated by thermal analysis (fig.7).

For polysulfone membrane obtained by coagulating in aniline solution has been highlighted the point of maximum loss chart, weight at 530°C specific degradation temperature for polysulfone. For polysulfone-polyaniline composite membrane obtained in-situ by oxidative aniline polymerization have emphasized two points in the diagram the maximum loss in weight at 480°C specific degradation temperature for polyaniline and at 530°C specific to degradation temperature for polysulfone.

Conclusions

The influence of an increased polyaniline / polysulphone ratio in the composite membrane structures led to the following experimental conclusions:

- improvement of the hydrodynamic performances of the composite membranes (increase of the permeate flux of the composite membrane obtained in experimental version E2 to the experimental version E1);

- concomitant increase in the separation capacity (R) and immobilization capacity (I) for the composite membrane with a higher PANI contents in relation to PSf;

- the membranes morphology obtained by Scanning Electron Microscopy is in complete accord with BSA retention and hydrodynamic tests and confirmed by thermal analysis.

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