

Iono-molecular Separation with Composite Membranes

III. Nitrophenols separation on polysulphone and composite nanoparticles ultrafiltration

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Building on the excellent results of extraction on a solid phase (polymer) this work combine adsorption nitrophenols (a, m, p-nitrophenols) on polymeric nanoparticles (NP-PSf) and composite (NP-PSf-PANI) with colloidal ultrafiltration. Colloidal ultrafiltration solutions of nitrophenols is done in an ultrafiltration plant, CELF System, with a capacity of 500 mL at 25°C, variable working pressure (1-10 atmospheres), turbulent flow regime (2-4 m/s) and usable filter polysulfone-membrane composites 10% in dimethylformamide coagulated with methanol polyaniline (PANI-PSf) 15 cm². Operational parameters of the process: concentration nitrophenols, nanoparticle concentration, pH of the feed solution were studied, trying to correlate the results of the colloidal ultrafiltration with the nature of the nanoparticles. Permeate flow is optimal at a pressure of 5 atm and nitrophenols retention depends on their nature. Good results have been obtained at pH = 3.1 for polysulfone nanoparticles (NP) and excellent retention at pH 1.3 or pH > 7, for composite nanoparticles (NP-PSf-PANI). Rejection o-nitrophenols is superior to the others two nitrophenols in all experiments.

Keywords: nanoparticles, colloidal ultrafiltration, nitrophenols, separation, membrane processes

Nitrophenols separation or removal from dilute aqueous solutions was the main target for environmental protection due to toxicity and possible accumulations, but also for the concentration and reevaluate of these compounds of high technological interest for: drugs, dyes, blasting explosives, pesticides, phenolic resins [1-4].

Nitrophenols containing aqueous effluent sources close to the limit of solubility are numerous: chemical and pharmaceutical, dyes and drugs, explosives, textile and leather industries [5-9].

This various toxic phenolic compounds, including Nitrophenols in watery effluent is caused by their relatively high solubility in water (table 1) [10-14].

No.	Compound	Solubility in water 20 °C (g / 100 mL)
1	Phenol	8.3
2	o- Chlorophenol	2.8
3	p- Chlorophenol	Soluble
4	2- Chlorophenol	2
5	3- Chlorophenol	2.6
6	4- Chlorophenol	2.7
7	2,4-Dichlorophenol	0.45
8	2,6-Dichlorophenol	0.19
9	2,3,4-Trichlorophenol	In soluble
10	2,4,6-Trichlorophenol	0.05
11	Pentachlorophenol	0.001
12	m-Nitrophenol	1.35
13	o- Nitrophenol	0.26
14	p-Nitrophenol	1.80
15	2,4-Dinitrophenol	1.70
16	m-Cresol	2.35
17	o-Cresol	2.37
18	p-Cresol	2.4

Table 1
SOLUBILITY IN WATER OF SOME INTERESTS
PHENOLIC COMPOUNDS

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Nitrophenols separation and removal of watery effluent is primarily an environmental issue, but also can be an important technological application, technical and economic [15, 16].

If in terms of environmental impact is the removal of nitrophenols in aqueous solutions tend to be achieved by the complete destruction: oxidative and photo-oxidative [17, 18], in terms of chemical technology recuperative prefer: concentration, separation, purification and recovery nitrophenols mixed or components: extraction, ion exchange, membrane and emulsion liquid [19-22].

Both extraction and liquid membranes use solvents, which can be found later in the treated aqueous solution, thus changing a pollutant (nitrophenols) with another (solvent extraction) [22, 23].

Removal and separation of regenerative nitrophenols was at the same time, and a permanent objective of membranologys, who developed many techniques, methods and processes: electro-dialysis and dialysis, nanofiltration and reverse osmosis, distillation and membrane pervaporation [24-28].

Membrane separation processes nitrophenols limitations are related to technical and economic aspects: expensive membrane materials, high working pressure, heat consumption, productivity (flux and selectivity) low.

Building on the excellent results of extraction on a solid phase (polymer) [29-33], this work, combine nitrophenols adsorption nanoparticle with colloidal polymer ultrafiltration. The study aims at increasing performance nitrophenols ultrafiltration with colloidal nanoparticles, on composite polysulfone membrane-polyaniline (PANI-NP-PSf).

Experimental part

Materials and methods

Materials and membranes

Aniline, dimethylformamide (DMF), methanol, hydrochloric acid, calcium hydroxide, ammonium persulfate, and nitrophenols (table 2) were originated from Sigma-Aldrich [34]. The pure water used for preparing

synthetic solutions of copper sulphate and nitrophenols (10^{-7} - 10^{-4} Mmol/L) was obtained through Millipore system.

Membranes and nanoparticles preparation

The membranes of polysulfone-polyaniline (PSf-PANI) were made from 10-14% solution Udel polysulfone (PSf), dissolved in dimethylformamide (DMF) containing 3% aniline (A). This composite membranes used in ultrafiltration were prepared by phase inversion method, immersion precipitation techniques from polysulfone solution (Udel) 10-14% in dimethylformamide (DMF) by coagulation with 1: 1 methanol-water, and after oxidized in the coagulation bath with acidic solution of ammonium persulfate [35-38].

The composite nanoparticles of polysulfone-polyaniline (NP-PSf-PANI) were made from 5% solution Udel polysulfone (PSf), dissolved in dimethylformamide (DMF) containing 3% aniline (A) [39,40].

1000 mL of PSf-DMF-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 solution of methanol:water (1:1) and methanol.

The obtained nanoparticles were transferred to 1000 mL solution of 10% hydrochloric acid and 5% ammonium persulfate, for 3 h, and washed with pure water.

Ultrafiltration processes

Ultrafiltration colloidal solutions of nitrophenols (fig.1) is done in a plant ultrafiltration CELF System, with a capacity of 500 mL, variable working pressure (1-10 atmospheres), turbulent flow regime and usable filter 15 cm².

Permeate flow volume equation (1) is determined to establish the productivity of system:

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

where:

V = permeate volume (L)

S = the effective area of the membrane (m²)

t = the amount of time needed to collect the permeate (h)

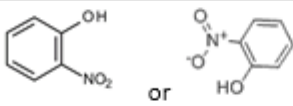
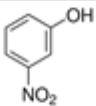
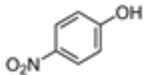
Chemical formula	<i>o</i> -C ₆ H ₅ NO ₃	<i>m</i> -C ₆ H ₅ NO ₃	<i>p</i> -C ₆ H ₅ NO ₃
Chemical structure			
Molar mass	139.11 g·mol ⁻¹	139.11 g·mol ⁻¹	139.11 g·mol ⁻¹
Appearance	Colorless or yellow pillars	Colorless or yellow pillars	Colorless or yellow pillars
Melting point	42-45 °C	96-98 °C	110-115 °C
Boiling point	214-216 °C	194 °C	279 °C
Solubility in water (g/L)	2.1 (25 °C) 10.8 (100 °C)	13.5 (25 °C)	10.0 (15 °C) 11.6 (20 °C) 16.0 (25 °C)
Acidity in water (pK _a)	7.23	8.36	7.15

Table 2
SOME
PHYSICO-
CHEMICAL
CHARACTERISTICS
OF USED
NITROPHENOLS
[34]

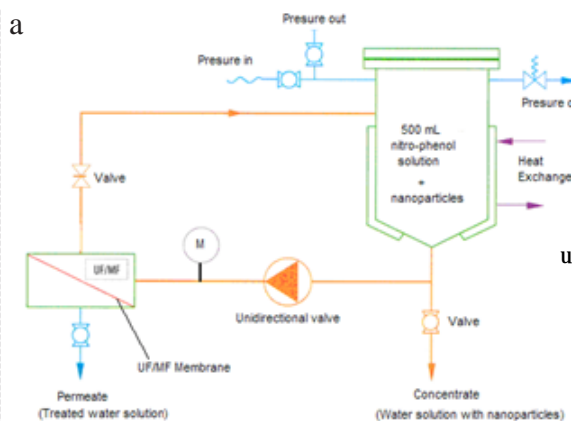


Fig. 1. CELFA ultrafiltration system: overview (a) and scheme colloidal ultrafiltration (b)

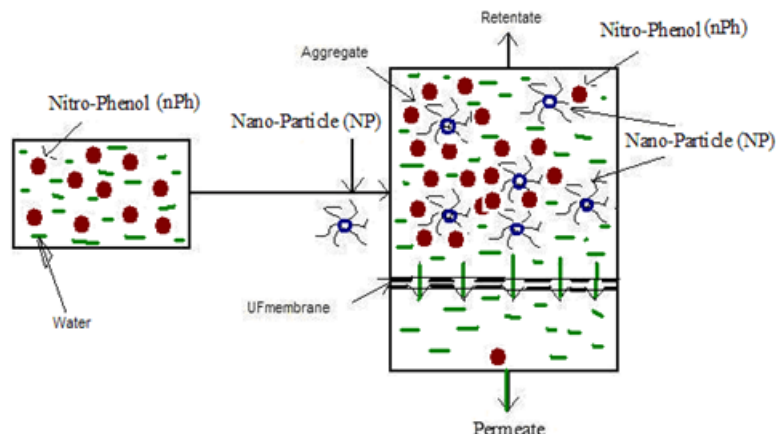


Fig. 2. Ultrafiltration colloidal solutions of nitrophenols with polymeric nanoparticles

Dimensional and functional characteristics of the system used in the experiments are as follows [41, 42]:

- membrane diameter: 50 mm;
- effective membrane area: 15cm²;
- volume supply tank: 750 mL;
- speed liquid (leakage tangential): 2- 4m/s;
- maximum working pressure: 40 atm;
- working pressure: 1-10 atm;
- maximum working temperature: 30°C;
- flow pump - 1.5-2.5 L/min;
- material - stainless steel.

To achieve the ultrafiltration of colloidal solution using 500 mL of nitrophenols concentration 0.1-10 g / L (depending on the solubility of the particular nitrophenols) and 1-50 g polysulfone type polymer nanoparticles (NP-PSf), and polyaniline, polysulfone (PSF NP -Up) and duration of the process is 25 to 200 min (fig. 2).

After ultrafiltration the retention of the species of interest (**R**) was determined using the solutions' absorbance and concentration [41-44]:

$$R = (c_o - c_f) / c_o \quad (2)$$

where:

- c_f - the final concentration of the solute (nitrophenols),
- c_o - the initial concentration of solute (nitrophenols)

$$R = (A_o - A_{sample}) / A_o \quad (3)$$

where:

- A_o - initial sample solutions absorbance
- A_{sample} - current sample absorbance

Analytical methods

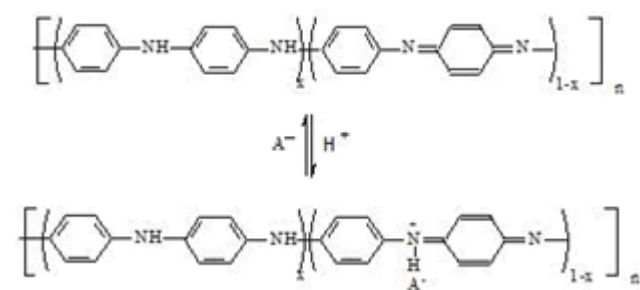
The solutions pH was adjusted by hydrochloric acid a calcium hydroxide 0.1 Mol/L solution.

The determination of phenol is accomplished through the spectrophotometric method Spectrometer CAMSPEC [45-47].

Morphological analyses of membrane and nanoparticles samples were performed by scanning electron microscopy (SEM) [48-50].

Results and discussions

Ultra-filtration of aqueous solutions has been extensively studied as in the case of composite membranes on the basis of polyaniline, the pH of the feed solution can influence the permeate flow [38]. The experimental results obtained at the passage of flows of aqueous solutions of different pH concentration of composite membranes 10%, 12% and 14% PSf-PANI prepared in the experimental conditions set out are shown in table 3 and confirm the historical data [37, 38].



Scheme 1

Thus, the permeate flow increases with increasing operating pressure and shows a peak at pH between 5 and 9, which indicates a clear influence of protonated polyaniline in the composite membranes according to the reaction of scheme 1.

For tests of colloidal ultrafiltration with polymeric nanoparticles of nitrophenols solutions a 10% PSf membrane-PANI has been selected. The main process and morphological characteristics are indicated in figures 3 and 4.

Table 3
WATER FLOWS AT DIFFERENT pH AND PRESSURE OF TESTED IN COMPOSITE MEMBRANES

Membrane	Transmembrane pressure (P) (atm)	Water flux (J) (L/m ² xh)					
		pH=1	pH=3	pH=5	pH=7	pH=9	pH=11
10%PSf+PANI	2	69.1	85.4	99.3	128.5	141.1	105
	4	157.6	175.9	167.5	287.1	304.3	165.7
	5	215.2	234.6	187.5	444.8	393.1	349.9
	6	253.9	287.1	459.6	548.8	499.0	423.5
12%PSf+PANI	2	19.8	23.8	24.5	49.8	37.8	34.5
	4	45.1	46.8	48.9	89.2	76.4	71.8
	5	53.6	59.7	66.9	110.3	120.1	111.4
	6	72.4	78.5	86.4	137.9	141.0	131.1
14%PSf+PANI	2	12.3	14.4	15.1	17.2	14.0	12.1
	4	27.8	28.9	32.3	35.1	31.3	28.4
	5	36.2	37.4	40.5	47.2	41.7	41.3
	6	46.5	49.8	57.6	59.3	53.7	51.9

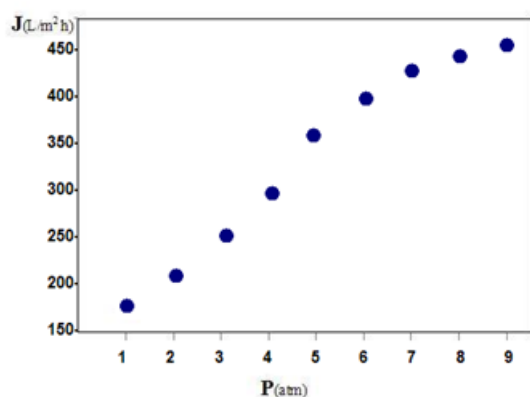


Fig. 3. Nitrophenols flow of solution and nanoparticles depending on the pressure membrane 10%PSf/DMF/methanol

This membrane has the classic behaviour of an asymmetric micro porous membrane (fig. 3): permeate flow increases with pressure up to 7 atmospheres and when it compacts it leads to a quasi-cap specific flow ultrafiltration. Therefore, recommended optimum working pressure for the membrane not to be deformed is 5 atmospheres.

PSf-PANI composite membrane has an asymmetric structure highlighted by the Scanning electron microscopy (fig. 4) with an active layer of SiO nearly 10 µm and total thickness of 100-110 µm.

As demonstrated by KESTING [48] a membrane can trap particles almost 10 times smaller than the pore diameter. In this way, the achievement of colloidal ultrafiltration of 20-40 nm colloidal nanoparticles can be

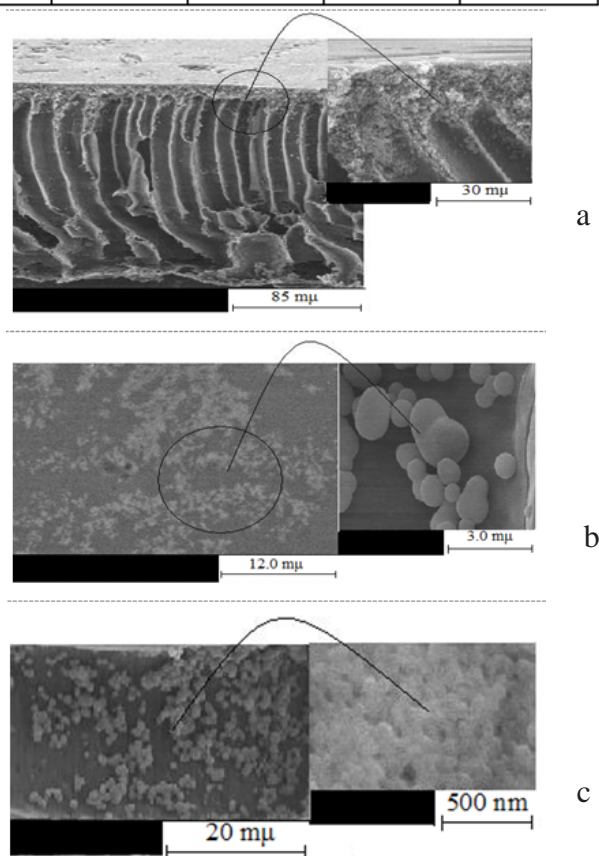


Fig. 4. The morphology of the 10% PSf / DMF / methanol membrane: *a*-composite membrane section, *b*- composite membrane with polymeric nanoparticles on surface, *c*-polymeric nanoparticles aggregates)

performed efficiently, as they will be retained by the membrane for the micro- or ultra-filtration chosen (fig. 4 b and c). Basically, the entire amount of nanoparticles used in order to retain through adsorption of nitrophenols will be found in the retentive (fig. 2), but it also accumulates and aggregates, in part, also on the active surface of the membrane (fig. 4c). Turbulent flow regime (on the membrane surface flow velocity 2-4 m / s) will lead to maintaining the flow of permeate at least 80% from baseline [49, 50].

Experimental tests were initially carried out with solution 1g/L 1-9 g polymeric nanoparticles nitrophenols and 500 mL of feed solution keeping the working pressure to 5 atm, supply tangential flow mode of 3 m/s and working temperature of 25°C (by cooling recirculation). The results show that nitrophenol retention in the colloidal ultrafiltration increases with increasing the amount of polymeric nanoparticles in the feed solution (fig. 5). Nitrophenol retention in nanoparticle composites ultrafiltration (NP-PSf-PANI) is higher than the retention of the nanoparticles in polysulfone (NP-PSf) (fig. 5), suggesting, throughout the study, a stronger interaction of nitrophenols with composite nanoparticles than with the polysulfone. Adsorption on

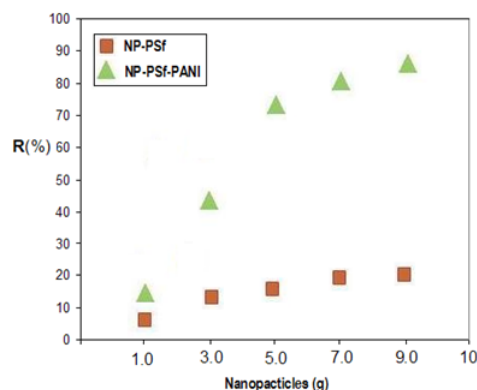


Fig. 5. Nitrophenols retention depending on the amount of polymeric nanoparticles to 100 mL solution of system

polysulfone nanoparticles is likely the hydrophobic-hydrophobic type and in the case of composite nanoparticles it is amplified by electrostatic interactions and hydrogen bonds that can provide polyaniline with nitrophenols groups.

Furthermore it was chosen an amount of 5 g to 500 mL nitrophenol solution, which would correspond to a concentration of 10g / L nanoparticles or 1% by weight of polymer mass in aqueous solution.

Varying, the amount of power nitrophenols in feed solution show that the retention decreases rapidly with increasing relative concentration of nitrophenols (fig. 6) for both types of nanoparticles. Basically, over the concentration of 0.50 g/L nitrophenols in food grain, retention drops below 50% for ultrafiltration composite nanoparticles and nanoparticles of less than 10% with polysulfone, making the process economically inefficient.

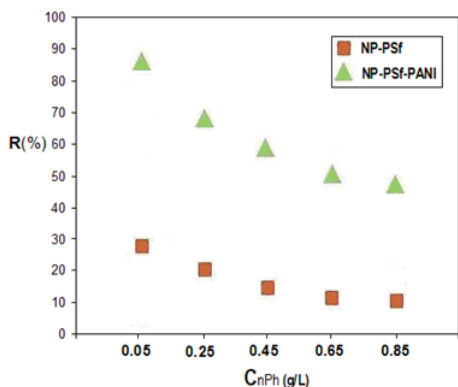


Fig. 6. Nitrophenols retention on polymeric nanoparticles (NP-PSf) depending on the concentration of supply

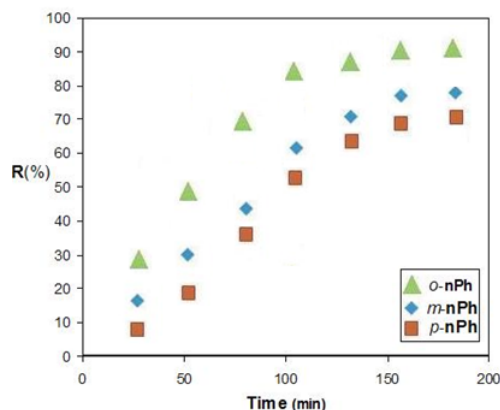


Fig. 7. Nitrophenols retention on composite polymeric nanoparticles (NP-PSf-PANI) depending on operating time

Of course concentrations chosen are close to saturation concentrations, which represents a major stress for specific membrane separation and recovery processes of chemical species in dilute solutions [35-37].

In the following tests of colloidal ultrafiltration (figs. 7-9) it was studied the influence of nitrophenols, nature, the operating time and pH) on retention.

Time is a decisive operational parameter when the membrane process is intended to be an alternative to a classic separation process (extraction, adsorption, ion exchange). In this case we observed whether reducing operating time can reach under 4 h, which would mean 2-4 production cycles per day depending on length of total working time: 8, 16 or 24 h. Taking into consideration that in a membrane processes outside the operating stage it also appears the necessity of nanoparticle regeneration and membrane laundering, which takes 2-3 h each, we have watched the evolution of nitrophenol retention in a range of 25-200 min (fig. 7).

As seen in figure 7, for nitrophenol retention by ultrafiltration of composite nanoparticles (NP-PSf-PANI), an operating time of about two hours ensures the achievement of efficiency and performance of a production cycle on the currency.

By choosing the most favorable working conditions: initial concentration of nitrophenols 1g / L, concentration of nanoparticles: 15g / L, flow rate of feed solution 3 m / s, operating time: 3 hours, temperature: 25°C, we obtained nitrophenol retention depending on the pH of the ultrafiltration colloidal supply. As seen in Figures 8 and 9 nitrophenol retention by ultrafiltration on polysulfone nanoparticle (NP-PSf) and composite (NP-PSf-PANI) depends on both the nature of nitrophenols and the working pH. Raising the pH disfavors the adsorption and retention of all nitrophenols on polysulfone nanoparticles. Also, ortho-nitrophenol retention is easier to obtain and behaves different than meta and para-nitrophenols in the case of nanoparticles over the entire range of pH (fig. 8).

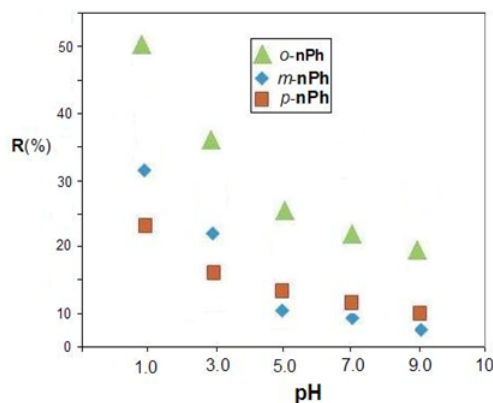


Fig. 8. Nitrophenol retention on polymeric nanoparticles (NP-PSf) depending on the pH supply

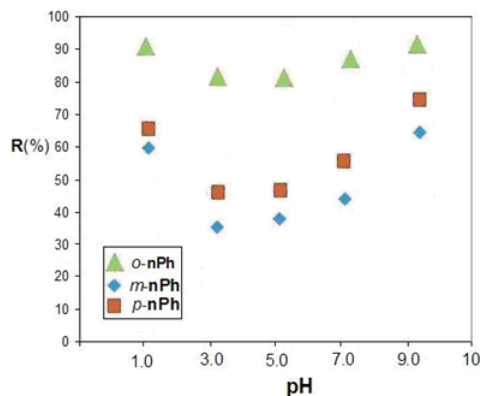
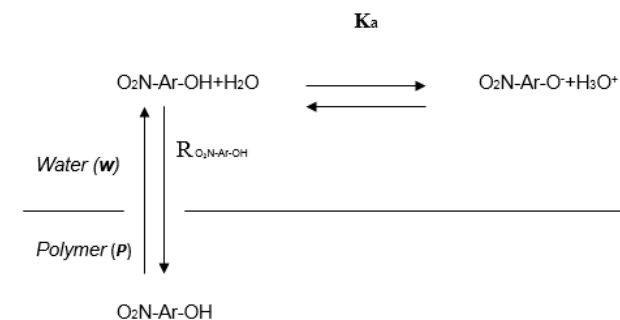


Fig. 9.
Nitrophenols
retention on
composite
polymeric
nanoparticles
(NP-PSf-PANI)
depending on
the pH supply



Scheme 2. Nitrophenols distribution between water and polymer nanoparticles

No.	Compound	Molecular formula	Mol.wt (g/mol)	λ_{max} (nm)	pKa
1	Phenol	C ₆ H ₆ O	94.11	269	9.95
2	o-nitrophenol	C ₆ H ₅ NO ₃	139.11	-	7.17
3	m-nitrophenol	C ₆ H ₅ NO ₃	139.11	-	8.36
4	p-nitrophenol	C ₆ H ₅ NO ₃	139.11	317	7.15
5	p-chlorophenol	C ₆ H ₅ ClO	128.6	279	9.41
6	p-cresol	C ₇ H ₈ O	108.13	276	10.26
7	p-tert-butylphenol	C ₁₀ H ₁₄ O	150	283	7

Table 4
SOME PHYSICO-
CHEMICAL PROPERTIES
OF THE PHENOLIC
COMPOUNDS [34]

In the case of composite nanoparticles (NP-PSf-PANI) orto phenol's retention is also different, but much lower than for the other two nitrophenols (fig. 9). It is interesting that this time, retention increases on the working range of pH, being more pronounced in meta nitrophenols.

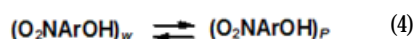
Nitrophenols separation from aqueous solutions has been extensively studied because these substances represent chemical species representative for both toxicity of this class of organic compounds and for UV-Vis spectrophotometric analysis to be easy and validated [51-53].

On the other hand Nitrophenols through their acid-base behavior, allowed in the colloidal ultrafiltration, besides the study of physical operational parameters: amount of phenol solution, the amount of polymeric nanoparticles, time and flow regime and varying chemical parameters: nitrophenol concentration (imposed by the different solubility of nitrophenols-table 1 and 2) and pH work (determined by different acidity constants (table 4).

Scheme 2 shows how the distribution of nitrophenols between aqueous and polymeric nanoparticles.

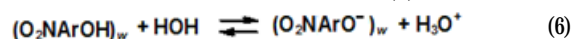
The distribution of nitro phenolic derivatives in the membrane system is a complex process [46-48]. Besides partition-diffusion balances and chemical competitive balances can occur.

Thus, in the feed solution (feed solution) nitro phenolic compounds may be involved in the proton transfer equilibrium of the form (4), characterized by a distribution constant, D (5):



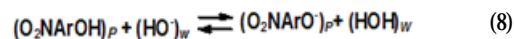
$$D_{O_2NArOH} = \frac{[O_2N-Ar-OH]_p}{[O_2N-Ar-OH]_w} \quad (5)$$

Nitrophenols ($O_2N-Ar-OH$) are recognized acidic organic compounds [35, 47]. Thus, while the Nitrophenols are brought into contact with two parts: water (w) and a nanoparticle polymeric composite (NP-PSf-PANI) water-insoluble (P), they will be distributed between the two phases in accordance with the balance (6), characterized by the acid dissociation constant K_a (7).



$$K_a = \frac{[O_2N-Ar-O^-][H_3O^+]}{[O_2N-Ar-OH]} \quad (7)$$

General equilibrium that involves nitrophenols (8) is incorporated in the distribution coefficient (d), which is dependent on pH, and which becomes an operational parameter (9).



$$d_{O_2NArOH} = \frac{D_{O_2NArOH}}{1 + 10^{pH - pK_a}} \quad (9)$$

Therefore, experiments of nitrophenol removal of (figs. 7 and 9) were intended to establish the optimal conditions of the process of separation composite membranes (PSf-PANI), taking into account the influence of nanoparticle polymer (NP-PSf-PANI) and the coupling process of proton transfer reactions with a separation capable of achieving induced. Through the study we can identify a constant of global acidity of the process dependent on the constant distribution of nitrophenols between nanoparticle (NP-PSf-PANI) and aqueous solution (10).

$$K_{a,Water-Polymer} = \frac{K_{a,Water}}{1 + D} \quad (10)$$

where: w represents the aqueous phase, and P represents polymer composite nanoparticle (NP-PSf-PANI).

If we exclude the participation of nitrophenols in chemical reactions in the two phases of balance, for nanoparticles in polysulfone (NP-PSf), it is characterized by constant division R . Phenolic derivative molecular form hydrophobic ally penetrates or it is adsorbed onto the nanoparticle (NP-PSf) and at the nanoparticle interface (NP-PSf) water whose balance is the constant distribution, R (11) and partition coefficient, r (12) are:

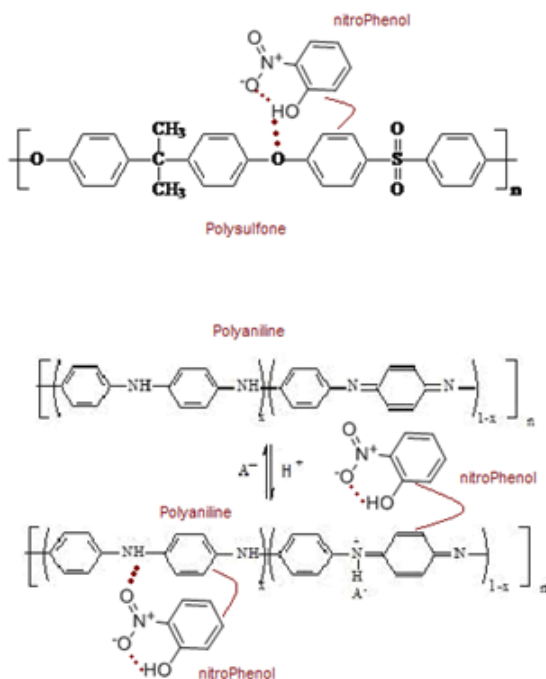
$$R_{O_2N-Ar-OH} = \frac{[O_2N-Ar-OH]_p}{[O_2N-Ar-OH]_w} \quad (11)$$

$$r_{O_2N-Ar-OH} = \frac{R_{O_2N-Ar-OH}}{1 + 10^{pH - pK_{a_w}}} \quad (12)$$

And in this case can be expressed in a constant acidity global system nitrophenols nanoparticle aqueous solution of polysulfone (13):

$$K_{a,Water-Polymer} = \frac{K_{a,Water}}{1 + R} \quad (13)$$

As such, the observations indicate that the pH of the aqueous phase is an optional parameter that may influence



Scheme 3. Interaction between nitrophenols and studied polymers (PSf and PANI)

the distribution of nitrophenols as demonstrated by the experimental data illustrated in figures 6 and 8.

In scheme 3 hydrophobic interactions are suggested to nanoparticles in polysulfone (NP-PSf) and complex interactions: hydrophobic, ion-ion and hydrogen bond to composite nanoparticles (NP-PSf-PANI).

For harnessing and applying the study at a larger scale, further research is needed on the influence of physico-chemical parameters: temperature, flow regime variable ionic strength and morphology of nanoparticles.

Conclusions

This study combines nitrophenol adsorption (a, m, p-nitrophenols) on polymeric nanoparticles (NP-PSf) and composite (NP-PSf-PANI) with the colloidal ultrafiltration 10% polysulfone-membrane composite polyaniline / methanol. Operational parameters of the process: the

concentration of nitrophenols, the concentration of the nanoparticles, the pH of the feed solution (feed solution) have been studied and tried and the results correlate with the nature of the ultrafiltration of colloidal nanoparticles. The flow of permeate is positioned at a pressure of 5 atm, and the retention depends on the nature of the nitrophenols. Good results have been obtained at $pH = 3.1$ for polysulfone nanoparticles (NP) and excellent retention at $pH = 1.3$ or $pH > 7$, for composite nanoparticles (NP-PSf-PANI). Rejection o-nitrophenols is superior to the others two nitrophenols in all experiments.

Acknowledgements: The authors have a gratefully acknowledge of Hybrid installation for water treatment using low pressure reverse osmosis and denitrification of the wastewater with bio-fuel cells, PN-II-PT-PCCA-2013-4-0742 Research Project.

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Manuscript received: 14.10.2016