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Membrane separation processes applied to the treatment of effluents from nanoceramic coating operations

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ABSTRACT

In this work, the use of membrane separation processes (MSP) for the treatment of a synthetic effluent from a nanoceramic coating line was evaluated. Three MSP were tested: electrodialysis, microfiltration, and nanofiltration (NF). The presence of zirconium, a chemical element able to combine with different compounds producing complexes, and pH variations in the nanoceramic effluent are responsible for the different efficiency levels of the MSP in treating this effluent. The better results were reached with NF, making this process an option for the treatment of this new effluent.

Keywords: Nanoceramic effluent; Hexafluorozirconic acid; Electrodialysis; Microfiltration; Nanofiltration

1. Introduction

New surface treatment processes have been developed in recent decades in order to replace the existing galvanic processes. These new processes should present advantages: fewer steps, operations at room temperature, and the absence of potentially toxic constituents such as chromium (Cr), cadmium (Cd), and phosphate (PO_4^{3-}) [1,2].

Nanoceramic coating is an example of these new methodologies and it is gaining more space in the galvanizing industry. The nanoceramic coating bath is used as a pretreatment of metal surfaces, and has, as its main components, hexafluorozirconic acid (H_2ZrF_6) and/or hexafluorotitanic acid (H_2TiF_6). The process is based on surface activation by a conversion reaction that leads to a protective oxide [2–4].

Studies of the use of nanoceramic coatings based on hexafluorozirconic acid in different metal substrates have been conducted and the results obtained so far show that this type of coating is a good option to replace those that have Cr, Cd, and PO_4^{3-} [2–6]. For best results associated to the environmental issues, besides the changes in the method of obtaining anticorrosive coatings, it is important to develop an effluent treatment process that is different from the conventional ones, namely coagulation, precipitation, and complexation, which are major consumers of water, chemicals, and sludge generators, characteristics that do not fit in an environmentally correct proposal.

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Among the wastewater treatment processes that currently exist, the membrane separation processes (MSP) are receiving more attention due to the good results when compared to conventional treatments [7–19]. So in this work, the use of three MSP was evaluated: electrodialysis (ED), microfiltration (MF), and nanofiltration (NF).

The presence of Zr in an aqueous solution is the determining factor for the choice of the process to be used in the treatment of this new effluent, as well as its efficiency, since it has a complex chemistry in aqueous solutions that has been studied since 1950 [20,21].

The ED process is an MSP, where ions are transported through selective membranes from one solution to another under the influence of an electric field [22–25]. Considering that this wastewater is mainly composed of ions in solution, the use of ED in its treatment would allow the concentration of compounds and reuse.

Besides the ions in solution, the presence of precipitates in this nanoceramic effluent, according to the pH [20,21], makes it interesting to use pressure-driven membrane processes such as MF and NF [26–29]. Along with ED, these processes would enable the concentration and reuse of the compounds and water. The kind of solute transport through the membrane, presented in these two processes, would make it possible to determine which process will be more efficient in the treatment of nanoceramic coating effluent [27,29].

Considering that there is no systematic study on the treatment of the effluent generated on nanoceramics coating lines based on hexafluorozirconic acid, the goal of this work is to develop an appropriate treatment method for this type of effluent that enables the separation, removal, and reuse of water and chemicals in the process. It is assumed that an effluent originated in a nanoceramic coating line, whose base component is hexafluorozirconic acid, would consist of water, zirconium (Zr), and fluorine (F). However, there are no data in the literature to report speciation of compounds in the effluent. So, for a better development of an effective process for treating this effluent, a characterization and a study on the behavior of the species present in the solution must be performed.

2. Materials and methods

2.1. Work solutions

In this paper, the work solutions were dilutions of a commercial ZR14 nanoceramic bath (NB9) in ultrapure water, alkalized with a commercial additive ZR30 to a pH of around 4 (4–4.5). This nanoceramic bath was prepared at the same concentration used in an industrial galvanic process. Dilutions of this bath were accomplished as a surrogate of wastewaters generated on the galvanic line. These dilutions are the solutions studied in this research and are presented in Table 1.

The first step of this study was to characterize the commercial products used and the work solutions, as described in Table 2.

Table 1
Work solutions and, respectively, pH, conductivity, and MSP used

	Work solutions	pH	λ (mS cm^{-1})	MSP
NB9	Nanoceramic bath: 9% of ZR14 alkalized with ZR30	4.5	1.18	
		3.0	0.18	NF
NB1	NB9 diluted to 1%	4.5	0.03	MF and NF
		9.0	0.06	NF
NB9 HCl 1.8	NB9 acidified with HCl 0.3 mol L^{-1}	1.8	6.0	ED

Table 2
Characterization of commercial products (ZR14 and ZR30) and work solutions

Solutions	Zr (mg L^{-1})	Na^+ (mg L^{-1})	F^- (mg L^{-1})	Cl^- (mg L^{-1})	$(SO_4)^{2-}$ (mg L^{-1})	$NH_4{}^+$ (mg L^{-1})
ZR14	5,520	260.1	10,571	364.8	<0.1	<0.25
ZR30	<10	<0.2	<0.02	<0.1	<0.1	5,933
NB9	478.8	23.84	907.2	33.12	<0.1	<0.25
NB1	0.932	<0.2	12.04	3.12	<0.1	<0.25

2.2. Membranes

For the ED experiments, Chinese commercial membranes HDX100 (cationic) and HDX 200 (anionic), supplied by Hydrodex, were used.

An MF test was carried out with a PVDF 0.2 µm commercial membrane supplied by Synder Filtration.

NF permeation experiments were carried out with a commercial NF270 membrane supplied by Filmtec Corp. from Minneapolis, MN (USA).

2.3. Membranes characterization

A characterization of the membranes is necessary for the MF and NF experiments [27,30]. The MF membrane was characterized in terms of pure water permeability (Lp).

The pure water permeation flux (PWP) was measured at transmembrane pressures (ΔP) of 0.3, 0.5, 0.7, and 1 bar. The membrane hydraulic permeability (Lp) is given by the slope of the straight line, PWP vs. ΔP.

For the characterization of the NF membrane, beyond the Lp measured ΔP range of 5–12 bar, the rejection coefficients were measured to reference solutes: NaCl and Na_2SO_4. The permeation of reference solutions for NF membrane characterization was performed at a transmembrane pressure of 10 bar, feed solution of 2,000 mg L^{-1}, and at a feed flowrate of 200 L h^{-1}.

The solute rejection coefficient (f) was defined as: $f = [(C_{\text{Afeed}} - C_{\text{Apermeate}})/C_{\text{Afeed}}] \times 100$, where C_{Afeed} represents the solute concentration in the feed and $C_{\text{Apermeate}}$ represents the solute concentration in the permeate [30–32].

2.4. ED experiments

The synthetic nanoceramic effluent NB1 has a conductivity of 300 µS cm^{-1}, which is similar to municipally supplied water, and a pH of 4.5. At these conditions, Zr is present forming precipitates [20,21], which makes the ED process not a viable option. So a modified nanoceramic bath, NB9 HCl 1.8, was used for the ED tests. At a pH of 1.8, the Zr is present in the Zr^{+4} ionic form and ionic complex forms, as shown in Fig. 1, obtained by Hydramedusa software.

The ED experiments with the solution NB9 HCl 1.8 were performed in a five-compartment bench cell, using titanium electrodes covered with titanium and ruthenium oxides in a ratio of 70/30 as the anode and cathode, both with active areas of 16×10^{-4} m^2. The membrane (HDX 100 and HDX 200) area was 16×10^{-4} m^2. The distance between the two membranes was 10×10^{-3} m. The ED stack is shown schematically in Fig. 2.

Two membrane pairs were used in all ED experiments. During each experiment, the solution conductivity and pH were measured in each solution reservoir. The voltage drop across the membranes was also recorded as show in Fig. 3.

Sodium sulfate solutions at different concentrations were used as the electrode rinsing solution in all experiments. The recirculation of the solution occurred in the diluate and in the concentrate streams (600 mL). A constant current of 40 mA, established previously by current–voltage curves, was applied. Samples were obtained for analysis at the beginning and at the end of the test to evaluate the variation of concentration of the ionic species.

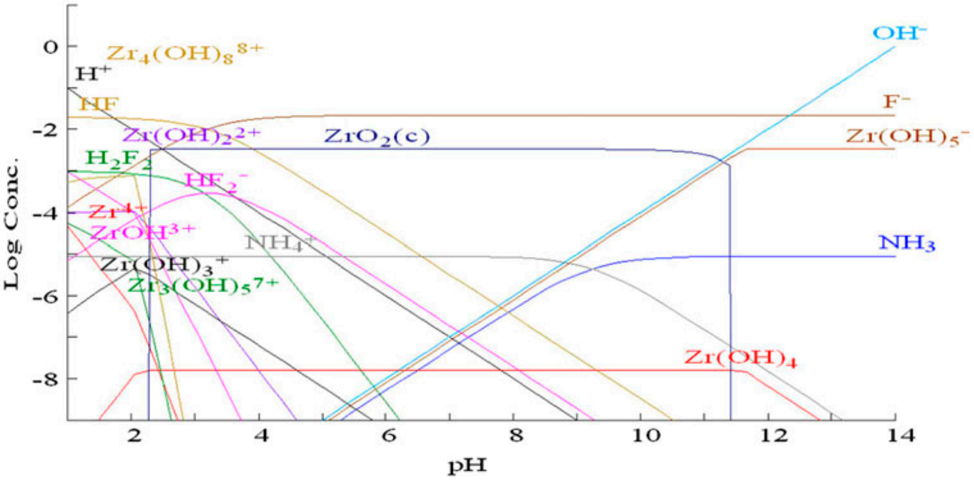


Fig. 1. Behavior of chemical species of Zr and F at pH range (0–14).

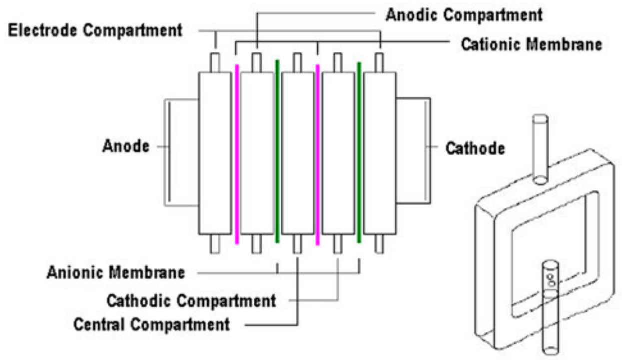


Fig. 2. Schematic ED bench cell with all compartments and the ionic exchange membranes alternately arranged being represented.

Table 3 displays the experimental conditions of the ED test. The electrode reusing solutions as well as the cathodic and anodic compartments were initially filled up with sodium sulfate solutions. The work solution (NB9 HCl 1.8) was added to the central compartment of the cell. The cationic and anionic membranes were alternately arranged.

2.5. MF and NF permeation experiments

Both permeation experiments were performed in bench scale in a permeation module of *PAM Membranas Seletivas* with a flat-cell unit. A schematic illustration is presented in Fig. 4. The membrane surface area is $13.2 \times 10^{-4}\,m^2$. The feed temperature was kept at 25℃ (± 2℃) in all the experiments by an ultratermostate bath (Nova Ética) attached to the permeation module.

The permeation experiments were conducted in total recirculation mode and in concentration mode. The experiments in total recirculation mode were carried out to determine the experimental parameters for the MF and NF that would be applied in concentration mode. At the experiments in concentration mode, it was calculated the volumetric concentration factor (VCF) which was defined as: $VCF = [Volume_{Feed}/(Volume_{Feed} - Volume_{Permeate})]$.

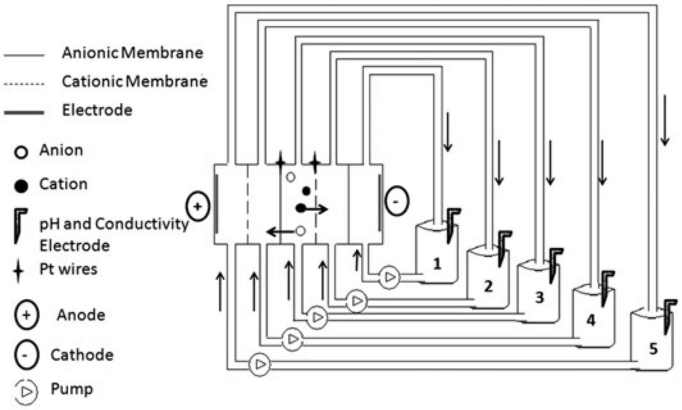


Fig. 3. Setup of the ED module. 1—Electrode compartment (cathode), 2—Cathodic compartment, 3—Central compartment, 4—Anodic compartment, and 5—Electrode compartment (anode).

Table 3
Experimental conditions of ED experiment

	Parameters						
	I (mA)	Initial potential cell (V)	Time (h)	Work solution (BN9 HCl 1.8)		Conductive solution (Na_2SO_4)	
				pH	λ (mS cm^{-1})	pH	λ (mS cm^{-1})
ED	40	7.3	30	1.8	6.0	7.0	9.0

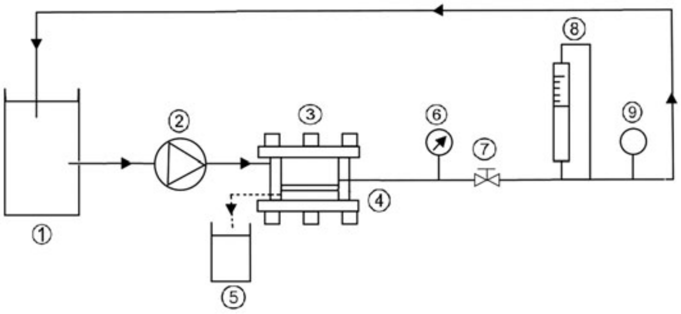


Fig. 4. Setup of the permeation module. 1—Feed tank, 2—Pump, 3—Permeation cell, 4—Membrane, 5—Permeate sample, 6—Manometer, 7—Pressure regulation valve, 8—Rotameter, and 9—Thermometer.

The membranes were washed with deionized water between each run until the Lp reached 90% of the initial value.

2.5.1. Microfiltration

First, the PVDF membrane was compacted through the circulation of pure water (conductivity < 1 $\mu S.cm^{-1}$) pressurized during 3 h at 1 bar. This avoids pressure effects on membrane structure in subsequent experiments. After this a MF test with the feed solution NB1, characterized in Table 1, was performed at feed flowrate of 200 L $h^{-1}$and at four values of transmembrane pressures: 0.3, 0.5, 0.7, and 1.0 bar. The stabilization time for each run was 30 min. These experiments were carried out in total recirculation mode, where the permeate and the concentrate streams were recirculated to the feed tank.

After the optimization of the MF operating parameters, an MF was conducted in concentration mode. Feed samples were taken at the beginning and at the end of the experimental run and the average concentration of these two samples was considered as the feed. The feed and the permeate were analyzed for the Zr and F contents.

2.5.2. Nanofiltration

The NF270 membrane was compacted with the circulation of pure water, in total recirculation mode as the MF membrane, at 12 bar for 3 h, in order to prevent possible pressure effects at membrane structure.

The NF permeation run with the NB1 solution was performed at a feed flowrate of 200 $L.h^{-1}$, 25°C (± 2°C) and with the following transmembrane pressures: 5, 7, 10, and 12 bar. The stabilization time for each experimental run was 30 min. These tests were conducted in total recirculation mode.

As MF, the NF in concentration mode was performed based on data optimized from experiments in total recirculation mode. Feed samples were taken at the beginning and at the end of each experimental run and the average concentration of these two samples was considered as the feed. The feed and the permeate were analyzed for the following parameters: pH and concentration of Zr and F.

2.6. Analytical methods

Different parameters were evaluated during this work such as pH, conductivity at 25°C, and concentration of chemical species (Zr and F). The F and Zr concentrations were evaluated by ion chromatography (IC) for F, and optical emission spectroscopy with inductively coupled plasma (ICP-OES) for Zr. Images of scanning electron microscopy (SEM-EDS) were used to observe the presence and the possible formation of precipitates on membrane surface.

3. Results and discussion

3.1. Electrodialysis (ED)

During the ED experiment, pH and conductivity were monitored in all compartments of the bench cell. Fig. 5 shows the behavior of theses parameters, which are in accordance with literature [11,25]. Reactions occurring at the electrodes justify the changes of pH and conductivity in these compartments. The increased conductivity in the cathode concentrate and in the anode concentrate is associated to the passage of the ions from the central compartments to these ones. The cathode and the anode conductivity variations are due to the presence of ions H^+ and OH^- resulting from the following reactions:

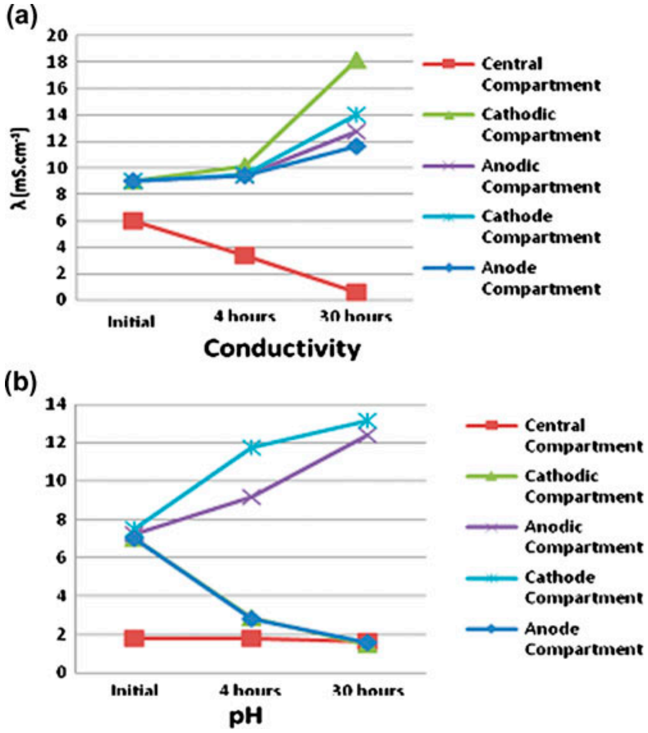


Fig. 5. Variation of the initial and final values of: (a) pH and (b) conductivity.

Cathode:

$$2H^+ + 2e^- \rightarrow H_{2(g)} \tag{1}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

Anode:

$$2H_2O \rightarrow 4H^+ + O_{2(g)} + 4e^- \tag{3}$$

Samples of the solutions of the ED cell compartments were obtained in the initial and end times of the experiments. These samples were analyzed by IC and ICP-OES for determining the F and Zr contents in the compartments as displayed in Table 4.

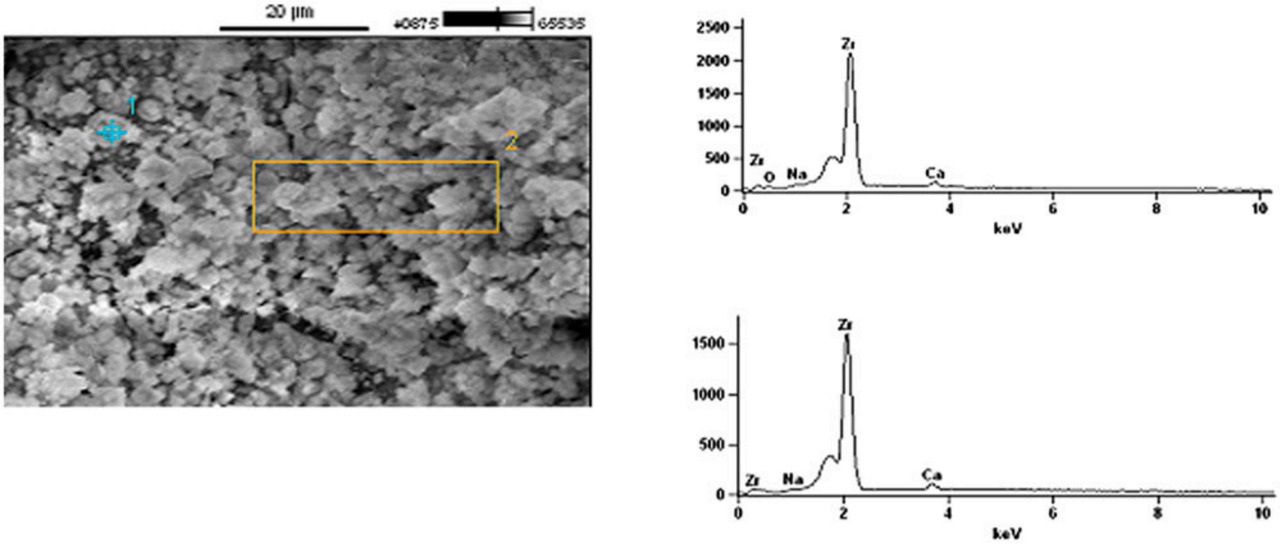
As shown in Table 4, there was a transport of Zr to the anodic and to the cathodic compartments. Showing that, this ion can be present both as a cation and as an anion. The transport of F occurred preferentially to the anodic compartment. The concentration of Zr and F in the dilute compartment decreased, as expected, but the concentration of these ionic species did not increase, at the same proportion, in the cathodic and anodic compartments. Visual analyses and SEM-EDS images of the membranes in contact with the dilute compartment were performed (Fig. 6). The presence of Zr precipitates at the surface and/or channels of both membranes can justify the lower concentration of this specie in the cathodic or anodic compartment. Furthermore, it indicates that the Zr element may be present either in the cationic complex form as well as anionic complex form [20,31].

Considering the precipitation of Zr compounds, the ED process, with the conditions utilized for this study, did not seem to be the best treatment process for nanoceramic effluents. Fig. 1 shows that from a pH of around 2, there is a possible formation of insoluble compounds such as $Zr(OH)_4$. The solution tested has an initial pH of 1.8. Nevertheless, considering the electrodes reactions, pH changes near the electrodes can cause small pH changes near the membranes. These changes would allow the precipitation of Zr compounds. For ED processes to be efficient on the treatment of this effluent, an acidification of the work solution (pH 0–1) and a strict control of the pH would be required. However, such a procedure is not advisable, firstly because working in an extreme pH is not recommended for the membranes and also because in this situation the main transport would be H^+ [25], and not Zr and F species.

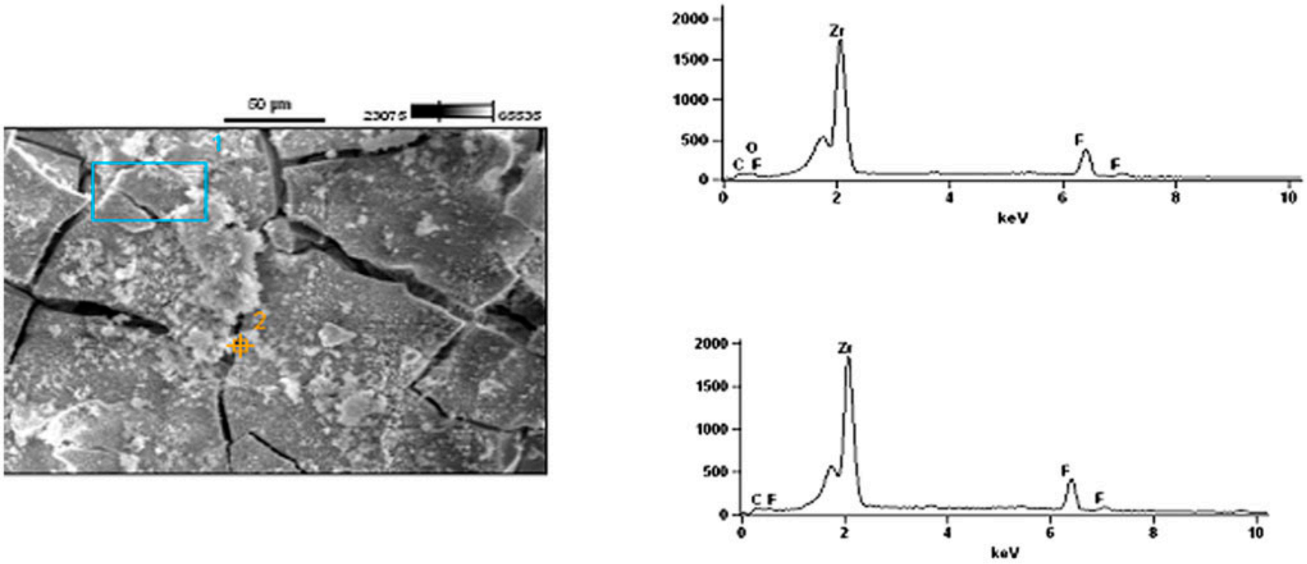
Based on these results, pressure-driven membrane processes were evaluated for the treatment of this effluent.

Table 4
Concentration of Zr and F species in compartments of ED cell

		Compartments of ED cell				
Species	Concentration ($mg\,L^{-1}$)	Anode	Anodic compartment	Central compartment	Cathodic compartment	Cathode
Zr	Initial	<3	<3	457.8 ± 0.05	<3	<3
	Final	<3	75.32 ± 0.01	126.1 ± 0.03	105.± 0.03	<3
F	Initial	< 0.02	<0.02	889.2 ± 0.4	<0.02	<0.02
	Final	6.23 ± 0.2	292.3 ± 0.3	35.78 ± 0.2	13.54 ± 0.3	8.52 ± 0.1



(a) SEM-EDS Anionic Membrane – HDX200 – Central Compartment



(b) SEM-EDS Cationic Membrane – HDX100 – Central Compartment

Fig. 6. Images of SEM-EDS confirming the presence of Zr on the membranes (a) HDX200 and (b) HDX100.

Table 5
Membranes characterization: hydraulic permeability and rejection coefficients

Membrane	Lp (kg h^{-1} m^{-2} bar^{-1})	fNaCl	fNa_2SO_4
PVDF 0.2 μm	278.3		
NF270	13.7	58.8%	98.4%

3.2. MF and NF membrane characterization

After membrane compaction, the Lp was determined for both MF and NF membranes. For the NF270, the rejection coefficients (*f*) of salts were evaluated. Table 5 presents these results, which are in agreement with literature data, of around 59% for NaCl and 98% for Na_2SO_4 [32,33].

3.3. Microfiltration (MF)

The work solution used on MF experiments was BN1 (pH 4.5), containing initially precipitates and with a conductivity similar to municipal water. Fig. 7 presents the behavior of permeation fluxes at each pressure during the MF in total recirculation mode.

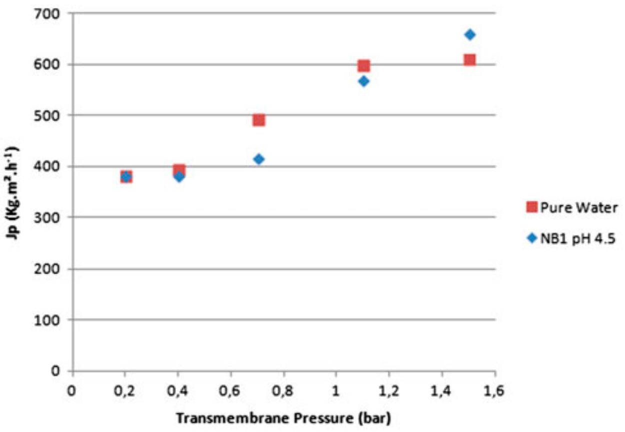


Fig. 7. Behavior of permeation fluxes at each pressure during the MF in total recirculation mode.

Table 6
Concentration of Zr specie in MF concentration test in each VCF

Sample	VCF	Zr (mg L^{-1})
Initial feed solution		0.706
Final feed solution		0.460
Permeate	1.5	0.034
Permeate	5	<0.005
Permeate	7	<0.005
Permeate	9	<0.005

Based on the results from Fig. 7, an MF in concentration mode was conducted at ΔP of 0.3 bar, 25˚C, at an operation time of 350 min and VCF of 9. At this pressure, the Jp for the NB1 is similar to Jp for pure water. Samples of feed solution and permeate were taken during the run. In these samples the concentration of Zr was analyzed by ICP-OES. The results are presented in Table 6.

In the retentate, the Zr concentration decreased and in the permeate it was not detected. These results confirmed that Zr in precipitate form was retained on pore and/or surface of the membrane. In MF processes, the active transport mechanism is the steric exclusion [27]. This fact may be responsible for the inefficiency of this process on treatment of synthetic effluent of nanoceramic coatings.

3.4. Nanofiltration (NF)

Different authors discuss that the performance of NF membranes can suffer the influence of the pH. The reason for these studies is due to the fact that this parameter can have a direct influence on membrane structure such as pore size, permeate flux, salt rejection and, in some cases, changes in the charge density of NF membranes [34–36]. Thus, an NF with NB1 at different pH values (3, 4.5, and 9) were carried out in order to check if the negative charge density of the membrane, permeate fluxes, and solute rejection of Zr and F will be influenced by pH changes on nanofiltration with NF 270 membrane. Fig. 8 presents the results obtained. NB1 was acidified by an HCl solution (0.3 mol L^{-1}) and alkalized by an NaOH solution (0.5 mol L^{-1}).

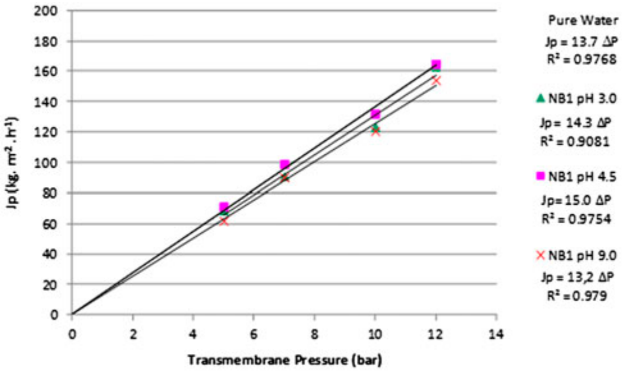


Fig. 8. Behavior of NB1 at different pH values in NF in total recirculation mode.

Table 7
Concentrations of zirconium and fluorine at different pH values in NF test at total recirculation mode

Samples	Pressure (bar)	Zr (mg L^{-1})	F^- (mg L^{-1})
Initial feed solution [BN1 pH 4.5]		0.93 ± 0.05	12.24 ± 0.1
Permeate [BN1 pH 4.5]	5	<LD	12.24 ± 0.2
Permeate [BN1 pH 4.5]	7	<LD	10.04 ± 0.3
Permeate [BN1 pH 4.5]	10	<LD	16.86 ± 0.1
Permeate [BN1 pH 4.5]	12	<LD	13.77 ± 0.3
Final feed solution [BN1 pH 4.5]		0.10 ± 0.02	15.32 ± 0.4
Initial feed solution [BN1 pH 3.0]		0.79 ± 0.01	12.22 ± 0.2
Permeate [BN1 pH 3.0]	5	<LD	12.0 ± 0.4
Permeate [BN1 pH 3.0]	7	<LD	13.37 ± 0.2
Permeate [BN1 pH 3.0]	10	<LD	10.18 ± 0.4
Permeate [BN1 pH 3.0]	12	<LD	9.80 ± 0.3
Final feed solution [BN1 pH 3.0]		0.07 ± 0.02	11.76 ± 0.3
Initial feed solution [BN1 pH 9.0]		1.24 ± 0.01	11.51 ± 0.1
Permeate [BN1 pH 9.0]	5	<LD	11.76 ± 0.5
Permeate [BN1 pH 9.0]	7	<LD	13.57 ± 0.1
Permeate [BN1 pH 9.0]	10	<LD	9.52 ± 0.2
Permeate [BN1 pH 9.0]	12	<LD	9.73 ± 0.2
Final feed solution [BN1 pH 9.0]		1.30 ± 0.06	12.70 ± 0.3

Permeate fluxes of NB1 at different pH values showed the same linear behavior over all pressure ranges (5–12 bar), showing that pH does not have an influence on the membrane structure, does not affect the pore size and does not promote a change in the negative surface charge of the membrane, as previously reported in some studies [34–36]. Based on this data, it was verified that a concentration polarization phenomenon does not occur on the membrane surface [37]. However, Zr and F rejections display distinct values according to the pH of the solution as indicated in Table 7.

Analyzing the Zr concentration present in Table 7, it is noted that the rejection is higher in pH 9 when compared to other pH values. This fact is consistent with the literature that reported an increase in the negative charge surface of the NF membrane when there is an increase in the pH of the solution [35]. The different results obtained are related to the presence of ionic complexes, containing Zr, present in the solution, which vary in their charge according to the pH values [20,21,38–40]. Fig. 1, obtained by Hydramedusa software, reports the possible zirconium ionic complexes present in NB1 at this pH range.

At a lower pH (1–5) just cationic complexes are observed, with charges ranging from +1 to +8. Beginning from pH 5, the presence of an anionic complex ($Zr(OH)_5^-$) is noted. Zirconium oxide (ZrO_2)—precipitate—and zirconium hydroxide ($Zr(OH)_4$) are present in the BN1 solution at any pH (3, 4.5, or 9).

Connecting this data with the negative charge density of NF270 surface [29,36,41,42], the results showed in Table 7 are consistent. Due to the negative charge density on the membrane surface, at a lower pH the Zr cationic complexes may interact with these membrane charges and be retained on the membrane surface, since the presence of Zr was not detected in the permeate. The inverse occurs at a higher pH, where the anionic complex is repulsed by the membranes' negative charges and returns to feed solution. Taking that into consideration, an NF in concentration mode was carried out at a transmembrane pressure of 10 bar with a controlled pH of 10 and at 25˚C (±2˚C). The pH was controlled by an NaOH solution addiction in the feed tank and monitored with a pH meter. The temperature was maintained by an ultratermostate

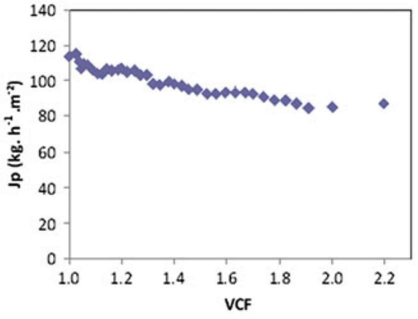


Fig. 9. Behavior of permeation flux in NF with controlled pH 10, in concentration mode.

Table 8
Zirconium and fluorine concentrations in NF test that controlled pH at concentration mode

Samples	VCF	Zr (mg L^{-1})	F^- (mg L^{-1})
Feed		1.51 ± 0.03	14.82 ± 0.2
Permeate	1.2	<LD	<LD
Permeate	1.6	<LD	<LD
Permeate	2.0	<LD	<LD
Permeate	2.2	<LD	<LD
Concentrate	1.2	1.82 ± 0.02	11.60 ± 0.3
Concentrate	1.6	2.14 ± 0.01	11.76 ± 0.2
Concentrate	2.0	2.64 ± 0.04	12.73 ± 0.5
Concentrate	2.2	2.70 ± 0.03	12.97 ± 0.3

bath. Fig. 9 presents the behavior of the permeation flux in the NF test with a controlled pH of 10, an operation time of 680 min, and VCF of 2.2.

During the NF test in concentration mode, samples of feed and permeate were taken at the following VCF: 1.2, 1.6, 2.0, and 2.2. These samples were analyzed by ICP-OES and IC and the results are shown in Table 8.

As an increase of pH leads to an increase of a negative charge surface, it also operates in the flow and retention, decreasing and increasing, respectively [35]. Analyzing Fig. 9 and Table 8 together, it is possible to understand the reason for the small decay in the flux during the NF test. Probably the Zr in precipitate form, which did not return to the feed solution, was retained on the membrane surface.

4. Conclusions

The experiment results obtained with the MSP make evident that three are the parameters that are the determinant ones for the positive or negative performance of each process: type of membrane, instability of the zirconium element, and pH of the solution. The instability of the Zr element against the pH changes produces different ionic complexes and also the hydroxide, which begins its formation and precipitation from a pH of 1.5. Depending on the pore size of the membrane and on the characteristics of the surface, the complex may be transported, retained, and/or rejected, and this behavior will determine if the concentrated solution concentrated in Zr and F, as well as the diluted solution, will be obtained.

The ED process did not provide a satisfactory result in the treatment of solutions containing Zr, indicating that in the working conditions evaluated here, the ED would not be applicable to this new type of effluent.

As for the ED, the MF process with the PVDF 0.2 μm membrane did not appear as appropriate to treat effluents from nanoceramic coating processes, since the element Zr was detected in the permeate and concentrate after the tests of MF in concentration mode.

Among the MSP related in this study, the NF is a promising process for the treatment of effluents from nanoceramic coatings. The NF270 membrane showed a linear variation of permeation fluxes vs. transmembrane pressures at different pH values. However, the rejection coefficient for Zr and F presents variation according to the pH values, which brings consequences to the efficiency of the NF process. The better result was obtained at an alkaline pH. Two factors explain this fact: (i) the negative charge density present on the NF270 surface and (ii) the presence of an anionic complex ($Zr(OH)_5^-$). There are no anionic complexes at lower pH, only cationic ones, which in turn interact with the negative charges present on the NF270 surface and were retained on the surface or trapped in the pores.

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