



Performances of nanofiltration on industrial phosphoric acid purification

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Abstract

Phosphoric acid production is of major importance to the Tunisian economy. However, the quality produced is not suitable for other than agricultural use due to mineral and organic impurities. In this study, the purification of industrial phosphoric acid with a maximum P_2O_5 concentration of 25% was achieved by nanofiltration. Six solutions of different P_2O_5 concentration were used. The removal of organic (total carbon) and inorganic impurities such as magnesium, iron, chrome, zinc, cadmium and vanadium, were studied.

The performances of nanofiltration (NF) Nadir NP 30 membrane were determined in terms of permeate flux and P_2O_5 and impurities retention taking into account the effect of transmembrane pressure, P_2O_5 concentration and membrane pre-treatment by purified phosphoric acid solution.

Results showed that for the industrial 25% P_2O_5 acid solution, the use of NF membrane achieved a retention of 87.35%, 86.73%, 87.57%, 78.41% and 73.17%, respectively, for iron, aluminum, chrome, magnesium, vanadium and organic matter (kerogen and humic acids) under a pressure of 20 bar. P_2O_5 permeation increased with the increase of its concentration in the acidic feed solution. The best permeation is provided by 25% P_2O_5 feeding acid solution which is of almost 98%.

Keywords: Industrial phosphoric acid, 25% P_2O_5 , purification, heavy metals, Nanofiltration

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1 Introduction

Phosphoric acid purification is the aim of many industries not only due to its application in many fields, especially in agriculture as a fertilizer, food industries as an additive but also due to constraining purity regulations[1].

The synthesis of phosphoric acid by wet process, where phosphates are solubilized by mineral acids, often gives a contaminated product with several heavy metals present in the rock [2]. Phosphoric acid obtained by this process is of low cost due to its high content of mineral impurities, such as Mg, Fe, Al, Ca, Cd and Zn and in some case its high load on organic substances of very low molecular weight.

Many separation techniques have been used to purify phosphoric acid, among which are liquid–liquid extraction [3-4-5] precipitation [6-7], solid–liquid extraction [8-9] and adsorption on activated carbon [10-11].

The use of these techniques was limited due to a number of disadvantages such as low efficiency, high cost of organic solvents, difficulty in recovering the residual solvent from both the raffinate and the purified acid and environmental pollution by some by-products.

Currently, several studies are focusing on the use of membrane processes on phosphoric acid purification such as electrodialysis (ED) [12], ultrafiltration, reverse osmosis and nanofiltration [13-14]. The advantage of membrane processes compared to conventional separation processes is related to their simplicity, the possibility of high temperature use and operating automation.

Jie Gao et al [15] studied the retention performance of Pb^{2+} , Mg^{2+} and glucose using modified polyethyleneimine (PEI) NF membrane. They showed that the retention of each solute is controlled by the membrane pore size and the charge properties of the selective layer. So, it is possible to develop NF membranes for various purposes including not only heavy metal removal but also molecular separation of ion and neutral solutes.

Maxime and al. [13] used two types of UF membranes made from polyethersulfone (PES) and regenerated cellulose (RC) to purify 5.5 M (30% P_2O_5) phosphoric acid by coupling precipitation and ultrafiltration (UF) (PUFprocess). The results showed that both membranes showed a good chemical resistance and an increase of P_2O_5 acid permeability after a pretreatment by immersion in 5.5 M phosphoric acid for several days.

By an other hand, the regenerated cellulose membrane led to the best performances with an abatement of 84% for Cadmium, 30% for alumina and over 60% for Arsenic.

Recent studies on the nanofiltration treatment of industrial phosphoric acid were carried out at various pressures ranging from 30 to 100 bars, using Osmonics nanofiltration membranes based on cellulose acetate with weight cut-off between 300 and 500 Da (DS5DL, DS51HL MPF-34 SX 01, SP-28 and BQ01) pretreated by immersion for 15 hours in a commercial solution of phosphoric acid of the same concentration as the industrial solution [14]. The best flow was obtained with DS5DL membrane (3.02 l/h.m^2) at 70bar. Permeation of the acid in terms of P_2O_5 was 94.2% and the retention of heavy metals was 99.2%. For the SX01 membrane, the best impurities retention performance was obtained with 2M (8.58% P_2O_5) acid and pretreated membrane by immersion in the following solution : phosphoric acid / ethanol / water. The permeate flux obtained at a pressure of 126 bar was of 13 l/h.m^2 and 18 l/h.m^2 without and with membrane pretreatment. The acid permeation in term of P_2O_5 and the impurities retention were of 60.8% and 99% respectively. These studies also showed that increasing the concentration of the acid led to a drop in the permeate flow and a decrease in selectivity.

M.P. Gonzalez et al. [16] had reported that the immersion of DS5DL membrane in phosphoric acid solutions (8M \approx 33.4% P_2O_5) following by hydrofluoric acid and in H_3PO_4/HF mixture under fixed conditions increases the selectivity regarding acid permeation and impurities retention. They concluded that retention controlled by the charge density was maximum in the presence of HF.

The present work deals with the purification of industrial phosphoric acid solution produced in Tunisia according to the wet process using nanofiltration under different conditions. So, the effect of P_2O_5 concentration, transmembrane pressure and the acidic pretreatment of NF membrane on filtration performances regarding P_2O_5 and mineral and organic impurities retention are then studied.

2 Experimental procedures

2.1 Materials

2.1.1 Membrane

A commercial membrane manufactured by Nadir 'NP 030' ($MWCO300 \text{ g mol}^{-1}$) (Table 1) was used in all experiments.

Prior to use, the membrane was rinsed by ethanol to remove preservatives. Then the membrane was compacted in water under 20 bar for one hour which is sufficient to reach permeability.

Data provided by manufacturers are listed in Table 1.

**Table 1. Chemical and physical characteristics of NF membranes used**

Membrane	NADIR NP030 P
Membrane material I	PES
MWCO/ gmol ⁻¹	300
Water flux [l/ (m ² h)]	> 40
Rejection Na ₂ SO ₄ [%]	80-95
Thickness [μm]	210-250
pH range	0 – 14
Allowable operating conditions	
pH range	0 – 14
Processing temperature [°C]	5 – 95
Surface used	44 cm ²

2.2 Reactive chemicals

2.2.1 Industrial solution

An industrial phosphoric acid solution obtained from the wet process was purchased from the SIAP (Tunisian Chemical Company) to which water was added to obtain 2.5, 3, 4, 6, 12.5 and 25% P₂O₅. These dilutions were chosen to study the effect of the concentration. The industrial solution used was a 25% P₂O₅ (about 4.38M H₃PO₄) containing various impurities (Table 2).

Table 2. Composition of 25% P₂O₅ industrial acid solution

P ₂ O ₅ (wt. %)	Al (mg/l)	Cd(mg/l)	Mg(mg/l)	Fe(mg/l)	Mn(mg/l)	Zn(mg/l)	Cr(mg/l)	V(mg/l)	F(mg/l)
25	3054	8	4382	1685	19	80	161	41	500

2.2.2 Phosphoric acid synthetic solution

Phosphoric acid synthetic solutions was used. They were made from a commercial product (Prolabo, 85% mass, 1.71 density, 0.007% of heavy metals).

Deionized water (conductivity lower than 1 μS cm⁻¹) was used both for solution preparation and membrane washing.

2.3 Experimental set-up

The evaluation of the membrane performance was carried out as follows: the membrane was washed with high purity water. It was then submerged into an analytical grade solution of phosphoric acid at the same concentration of the feeding solution during 15 h [17], then placed in the separation cell with the feeding solution.

The stainless steel cell was used in all cases. It works with magnetic stirring under the pressure of an inert gas (N₂). First, phosphoric acid solutions of analytical grade at the same concentration as the industrial phosphoric acid solution (25% P₂O₅) at a temperature of 25°C were used to determine the acid permeation parameters in simple water/acid systems. Then, industrial phosphoric acid solutions were used to evaluate the membrane selectivity and mineral impurities retention. When the permeate solution was obtained, the cell was depressurized and the resulting concentrate was recovered. Finally, the feeding and the permeate solutions were analyzed. The duration of each test was between 5 and 6 hours.

A scheme of the laboratory pilot unit is presented in Figure 1.

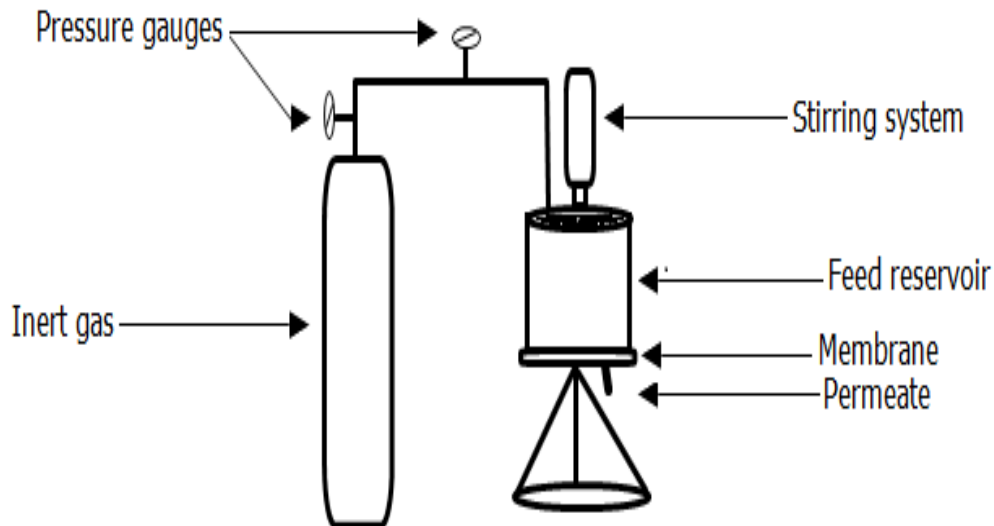


Fig 1: Scheme of the unit used

The transmembrane pressure was varied between 15 and 20 bar. The permeate flow calculated from the time taken to collect involved a volume of solution determined after weighing [18].

2.4 Characterization

P_2O_5 content was determined by volumetric titration with NaOH using bromocresol green and phenolphthalein indicators with an accuracy of $\pm 0.2\%$.

The organic matter content expressed in term of TOC was determined by a redox titrimetric method using a hot mixture of $K_2Cr_2O_7$ in sulfuric medium [5].

The analytical control of the cationic impurities (Al, Fe, Mg, Cd, Zn, Cr, Mn and V) was made by flame atomic absorption spectrometry with a Perkin-Elmer 3110 spectrophotometer. All analysis were carried out at $25^\circ C$.

The surface characterization of the membranes before and after their use in the purification of industrial phosphoric acid solutions was examined using a scanning electron microscopy (SEM) (microscope Phillips, XL 300).

A viscometer (LAMY of TVe-0.5) was used to measure viscosity.

2.3 Methodology

For the purification of phosphoric acid solutions, permeate flux, P_2O_5 permeation and impurities retention were determined.

To assess the separation efficiency of the membrane against each parameter, the retention of the element X (R_x (%)) was calculated according to the formula:

$$R_x = \left(1 - \frac{C_{p_x}}{C_{f_x}}\right) 100 \quad (1)$$

Where C_{p_x} and C_{f_x} are, respectively, the concentration of the element in the permeate and in the feed solution.

- **Determination of real retention**

Phosphoric acid permeation is defined as the ratio of the acid concentration in the permeate to the feed concentration.

Since phosphoric acid has undergone a degree of dilution, so it is necessary to take into account of this dilution (D_f) when calculating the retention of the element, according to equation 3.

$$\text{Dilution factor } (D_f) = \frac{P_2O_5(\text{befort purification})}{P_2O_5(\text{after purification})} \quad (2)$$



So, the real retention R'_x will be

$$R'_x = 1 - \frac{Cp_x}{Cf_x} \quad (3)$$

With $Cp_x = D_f \cdot Cp_x$

Cp_x is the real concentration of the element in the permeate (mg/l)

The global purification and real global purification percentage were calculated respectively using the following expressions:

$$\% \text{ global purification} = \frac{\sum Cf_x - \sum Cp_x}{\sum Cf_x} 100 \quad (4)$$

$$\% \text{ real global purification} = \frac{\sum Cf_x - \sum Cp_x}{\sum Cf_x} 100 \quad (5)$$

3 Results and discussion

The effect of the applied pressure, initial P_2O_5 concentration, viscosity and membrane pretreatment on the retention of heavy metals, TOC and P_2O_5 was studied.

3.1 Retention of heavy metals and P_2O_5

3.1.1 Effect of the P_2O_5 concentration

In order to vary the initial concentration of industrial phosphoric acid, different H_3PO_4 solutions having concentrations of: 2.5, 3, 4, 6, 12.5 and 25% P_2O_5 or 0.438, 0.5475, 0.73, 1.095, 2.19 and 4.38M respectively, were prepared.

The variation of the apparent and real retention of different heavy metals was then studied (Fig. 2a and Fig.2b).

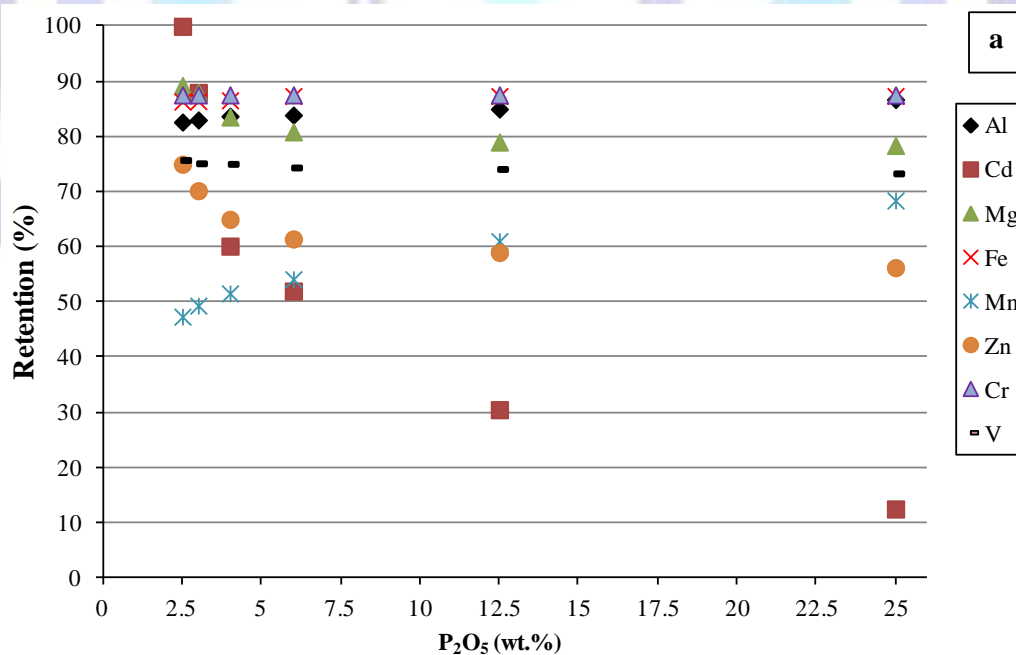


Fig 2a: Variation of apparent heavy metals retention with initial P_2O_5 concentration

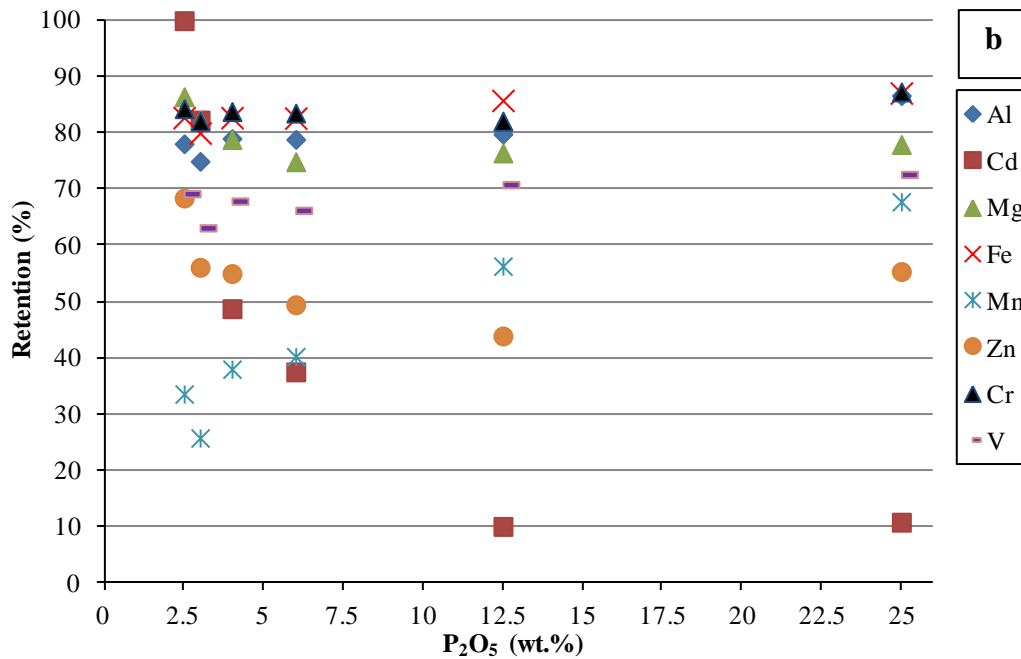


Fig 2b: Variation of real heavy metals retention with initial P₂O₅ concentration

From **Fig. 2a**, it appeared that the retention of ions was much higher at low P₂O₅ % concentration in the range 2.5%-6% which exceed 50%. At higher values of concentration, the retention is lower for Cd²⁺ following by Zn²⁺ and Mn²⁺ which was of 10%, 57% and 68% respectively for 25% P₂O₅ at which the retention of the other ions, remains higher than 70% (magnesium, manganese and vanadium).

For the industrial phosphoric acid solution 25% P₂O₅, it can be noticed that the best performances were obtained for the trivalent ions Al³⁺, Cr³⁺ and Fe³⁺.

In the same context, Gonzalez et al [19] studied the variation with time of the retention of Al, Fe and Mg by untreated DS5DL NF membrane. They showed that the rejection of metallic impurities increases during the first 30 h reaching values exceeding 80%.

For longer periods beyond 120h, the rejection of these impurities decreases considerably.

Considering the real retention (figure 2b), it appeared a decrease of performances in comparison with apparent retention (figure 2a). For example for Mn, the decrease is about 10% in the range of 2.5%-6% P₂O₅ concentration.

At high P₂O₅ concentration (25%), no difference regarding to ions retention rate was obtained considering the real and apparent retention.

It can be concluded then that the retention of the heavy metals by the membrane depends on the acid concentration regarding some ions such as Cd²⁺, Zn²⁺ and Mn²⁺. For the other ions especially the trivalent one and Mg²⁺, similar results was obtained considering apparent and real retention.

The influence of acid dissociation degree which is weakly dissociated at high concentration seems in relation to the ionic charge number. Indeed, for the bivalent ions such as Mn²⁺, the retention is much higher when the acid concentration is high [12]. Since the retention of Mn²⁺ depends on the acid concentration. It was of 67.77% for the industrial solution (25% P₂O₅), but only of 26% in the diluted one (3% P₂O₅). The retention order of bivalent ions is Cd²⁺ < Zn²⁺ < Mn²⁺ < V²⁺ < Mg²⁺. The reason of this observation is very simple: the ion rejection is mainly dependent on its hydration energy in the solution upstream and it will be more retained if it has higher hydration energy than the others (the case of magnesium et vanadium) while the retention of cadmium, zinc and manganese depends on the phosphoric acid concentration.

Considering 25% P₂O₅ concentration which corresponds to the concentration of industrial phosphoric acid, figure 2b shows the order of retention for the different ions.

This can be attributed to the charge density of the cations, which is given by $CD = z/r_{hi}$, where z is the ionic charge and r_{hi} the hydrated ionic radius. Therefore, assuming that in this medium (33.4% P₂O₅) the cations should be in their maximum oxidation state, with r_{hi} given in parenthesis: Fe³⁺ (4.57 Å), Al³⁺ (4.75 Å) and Mg²⁺ (4.28 Å) [16], these values coincide with the rejections order obtained with the different treatments: Fe > Al > Mg.

3. 1.1.1 Effect of the phosphoric acid concentration on P_2O_5 permeation

Fig.3 shows the effect of initial phosphoric acid concentration on P_2O_5 permeation using NF membrane at 20 bar. It can be seen that the permeation increased slightly with concentration from 70% for 6% P_2O_5 to almost 98% for 25% P_2O_5 .

The increase of acid solution concentration provides higher H concentration and leads to an electrical double layer of positive charges on the membrane surface. This phenomenon improves the transport of anions through the membrane. This explains partly why the retention of phosphoric acid decreases with the increasing concentration of the feeding solution [20].

Sun et al [21] found that for membrane (polyamide-imide) the retention of NaCl decreased while the effective charge density increased with an increase in electrolyte concentration. This is due to the reduction of the electrical double layer thickness within the pores with increases in the concentration of the electrolyte.

Diallo et al [17] found similar results regarding the behavior of phosphoric acid retention in the range 0.12–5.9 M by NF membrane and concluded that no steric retention of phosphoric acid can occur with the membrane (MPF34) at high acid concentration without the help of any concentration polarisation effect.

The process of phosphoric acid purification can be explained according the ion-exclusion model which assumes that the ions in the feed solution are rejected by the membrane, while the small neutral molecules pass through the membrane. Indeed, as phosphoric acid concentration is high, as acid dissociation is low [14].

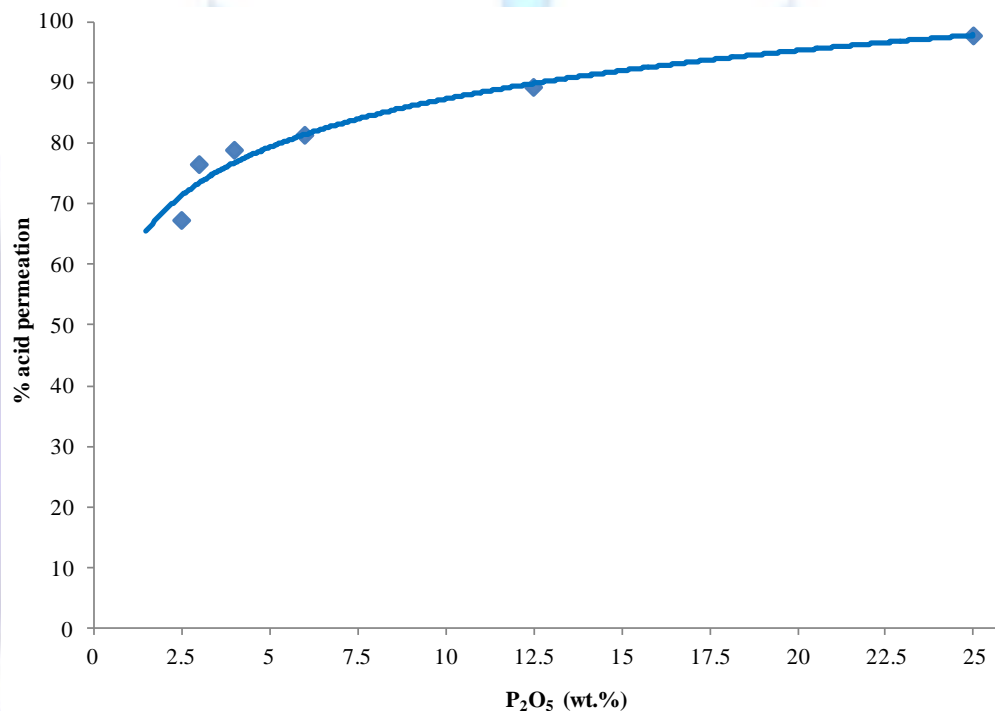


Fig 3: Evolution of acid permeation with initial phosphoric acid concentration

3. 1.1.2 Effect of P_2O_5 concentration on permeate flux

The performances of NF was determined also through the study of the variation of permeate flux with the phosphoric acid concentration in term of P_2O_5 .

Fig. 4 shows that the flux decreases dramatically when P_2O_5 concentration varies from 2.5 to 12 and then slightly until a concentration of 25. The increase of acid concentration leads to the increase of the viscosity as it can be shown by Fig.5 where the viscosity decreases from 6 mPa.s at 6% P_2O_5 to 13 mPa.s at 25% P_2O_5 . This result is in agreement with that found by Pontié et al [13] using a 100KDa UF membrane and industrial phosphoric acid. The highest decrease of permeate flux from 2.5l/h.m² (P_2O_5 = 2.5%) to 0.5 (P_2O_5 = 12.5%) is due to the membrane fouling caused in a great part by the increase of the phosphoric acid solution viscosity probably due to a phenomenon of pores clogging. In fact, the decreased level of dissociation at high concentration have a positive effect on the permeate flux since it retarded the osmotic pressure build-up.

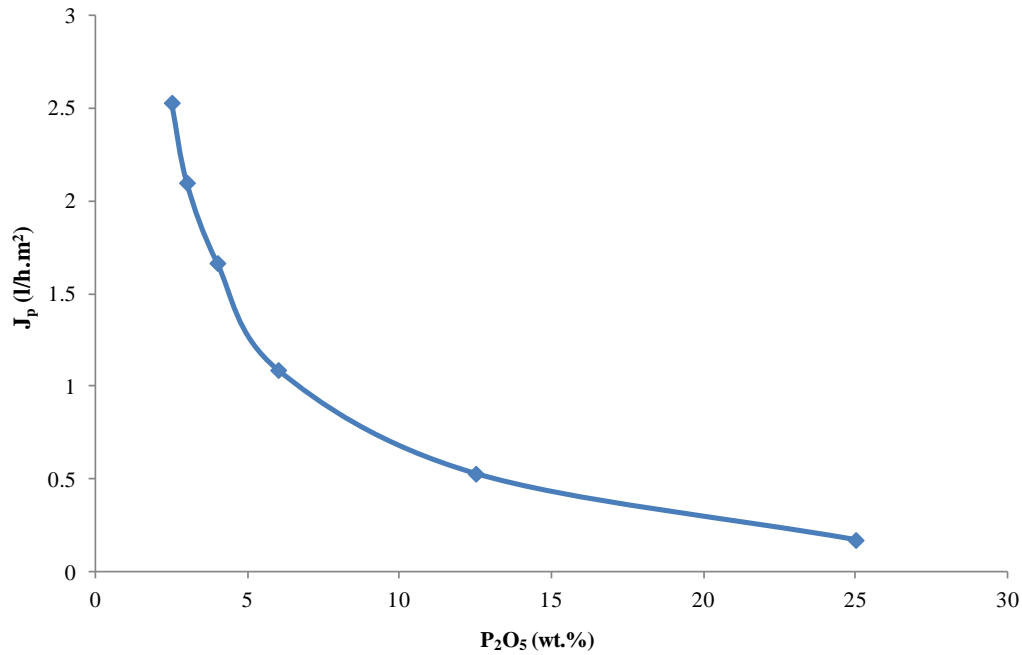


Fig 4: Flux variation as a function of P₂O₅ content

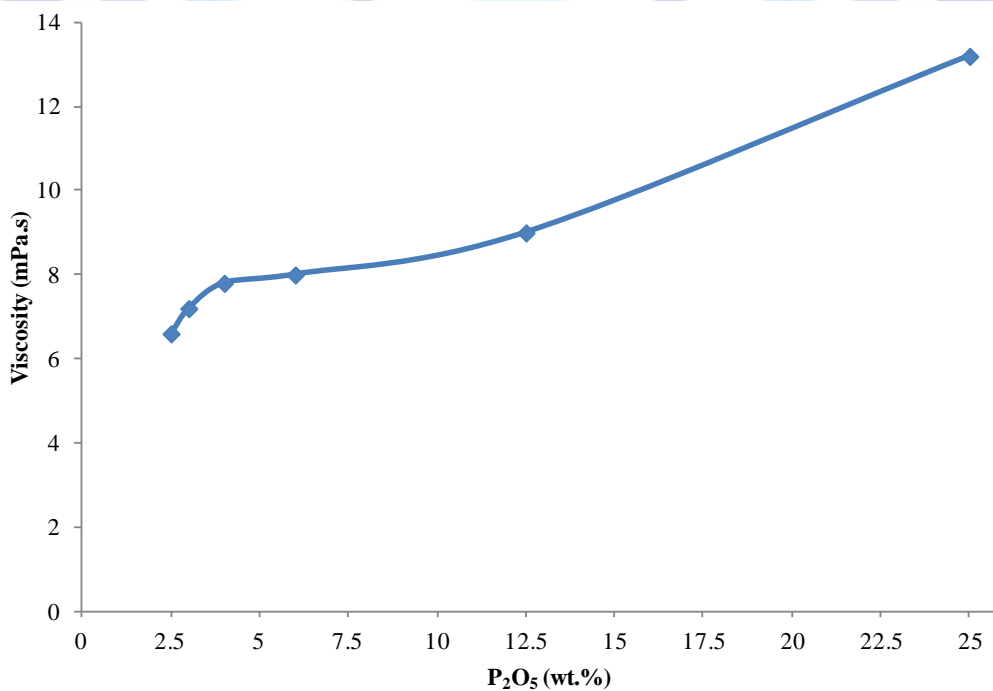


Fig 5: Variation of the phosphoric acid viscosity with P₂O₅ concentration

3. 1.2 Effect of pressure

The performances data are shown in table 3 at a constant acid solution concentration of 25% P₂O₅ (4.38M) and two different pressures of 20 bar and 16 bar. The retention of heavy metals increases with pressure while there was no significant influence of the pressure on phosphoric acid permeation in the range 16 - 20 bar due to the high concentration levels in the feed. The fact that the retention by membrane depends on the nature of species (metal ions or P₂O₅), shows that the pressure dependency is not equal for all components of a multi-components solution [20].

Pressure dependency on permeate flux is theoretically explained by the fact that the transfer through a nanofiltration membrane is a combination of diffusive and convective transport. In this case, the permeate flux increases with the pressure from 2 L/h.m² at 1 bar to 2.7 L/h.m² at 20 bar. It can be deduced then that higher pressure leads to a higher permeate flux due to a convective transport.

**Table 3. Effect of pressure on Nanofiltration performances**

	P ₂ O ₅ (%R)	Al(%R)	Cd(%R)	Mg(%R)	Fe(%R)	Mn(%R)	Zn(%R)	Cr(%R)	V(%R)	Flux (l/h.m ²)
Pressure 16 bar	2.09	75.11	0	61.84	75.51	46.24	28.51	75.25	52.66	0.10
Pressure 20 bar	2.03	86.66	10.68	78	87.12	67.77	55.34	87.31	72.61	0.17

3.1.3 Effect of membrane treatment on the performances retention

Membrane pretreated by immersion in aqueous solution of H₃PO₄ 8M (33.4 % P₂O₅) during 15 days has been used to evaluate the nanofiltration performances regarding 25% P₂O₅ industrial phosphoric acid purification under a transmembrane pressure of 20 bar. From table 4, it was observed that the order of retention was not affected by the treatment. From an other hand, it can be seen that the pretreatment has a positive effect on P₂O₅ permeation. Indeed, an increase of 33% was observed. However, it was observed a negative effect on the different cationic impurities retention except for Cd showing that the pretreatment did not have any effect on retention. The order of decrease of retention is as follows: Mg>V>Zn>Al>Fe=Cr>Cd. The Tunisian industrial phosphoric acid is characterized also by the presence of organic impurities which can be expressed by TOC parameter. Table 4 shows

retention of TOC exceeding 60% which is decreased by 11% when a pretreated NF membrane

was used. According to Gonzalez et al. [16], the H₃PO₄ treatment caused a decrease in the effective thickness and an increase in the pore size, as well as a decrease in the hydrophilic character.

As a consequence of these changes, a significant decrease of impurities retention from one side, increase of P₂O₅ permeation from other side, were observed. The permeate flux increases by about 170%. Gonzalez et al. [16] found that the permeate flux increases with the time of treatment. However, after 14 days of H₃PO₄ membrane treatment, the permeate flux becomes constant. The increase of the permeate flux can be attributed to the increase of the membrane permeability. Indeed, the water permeability increases from 0.029 l/h.m².bar without treatment to 0.82 l/h.m².bar after treatment (the permeability to the phosphoric acid solution 4.38M increases from 0.097 l/h.m².bar to 0.144 l/h.m².bar. To explain this result, Gonzalez et al. [16] showed that the membrane contact angle increased with H₃PO₄ treatment reflecting an increase of the hydrophobicity. So, it seems that the increase of membrane permeability and the loss of impurities retention are due in great part to the increase of the membrane pore size. The pretreatment seems has a positive effect on phosphoric acid permeability. This result is similar than that found by Gonzales and al. [16] whose explained this behavior by the presence of HF impurities in the industrial phosphoric acid solutions. The increase of the charge density of the after treated with H₃PO₄ caused by the increase in roughness low membrane which remains approximately constant over time largely explains the slight loss of the retention of the impurities due to the increase of pore radius of the membrane [16]. In fact, in this case, adsorption phenomena should be the main responsible of membrane fouling.

The purification of industrial phosphoric acid with NF membrane provides permeate flux of 0.17 l/h.m² for untreated membrane and of 0.47 l/h.m² for pretreated membrane. These values are similar with that obtained by Diallo et al. [17] whose found permeate flux se values.

Table 4. Effect of NF membrane treatment on the industrial phosphoric acid solution purification performances

R (%)	P ₂ O ₅	Al	Cd	Mg	Fe	Mn	Zn	Cr	V	F	COT	Flux (l/h.m ²)
Untreated membrane	2.0367	86.73	12.5	78.41	87.35	68.42	56.25	87.57	73.17	7.13	62.30	0.1732
treated membrane	1.36	67.68	12.5	49.61	69.67	47.36	41.25	69.56	48.78	6.2	55	0.4679
Increase or decrease rate(%)	-33	-21	0	-36	-20	-30	-26	-20	-33	-13	-11	+170

Figs. 6 and 7 show no damage caused by phosphoric acid and also the absence of fouling on the membrane surface. This is due to the effect of hydrofluoric acid on reducing membrane fouling and deterioration caused by H_3PO_4 [19], since the acid industrial solution contains ions of F^- .

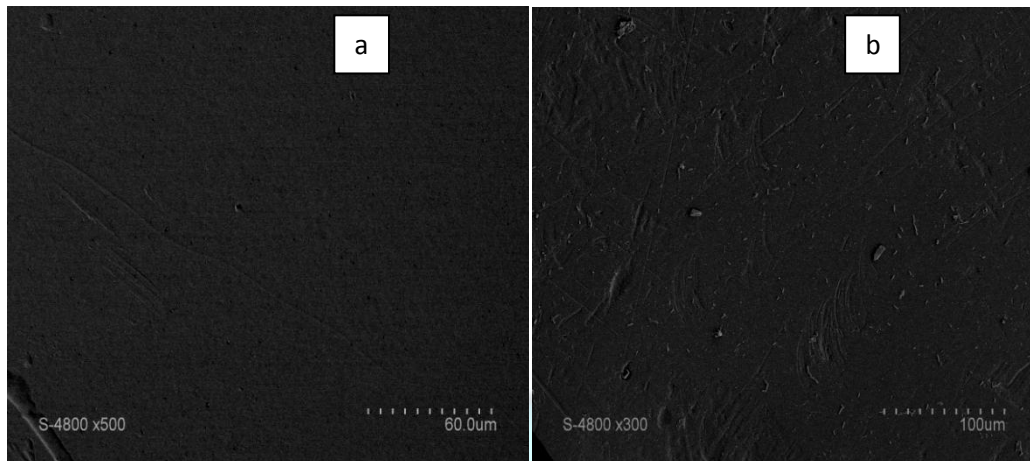


Fig 6: SEM images of the NP 30 membrane top surface non pretreated with acidic solution, prior to use (a) and after industrial phosphoric acid filtration (b)

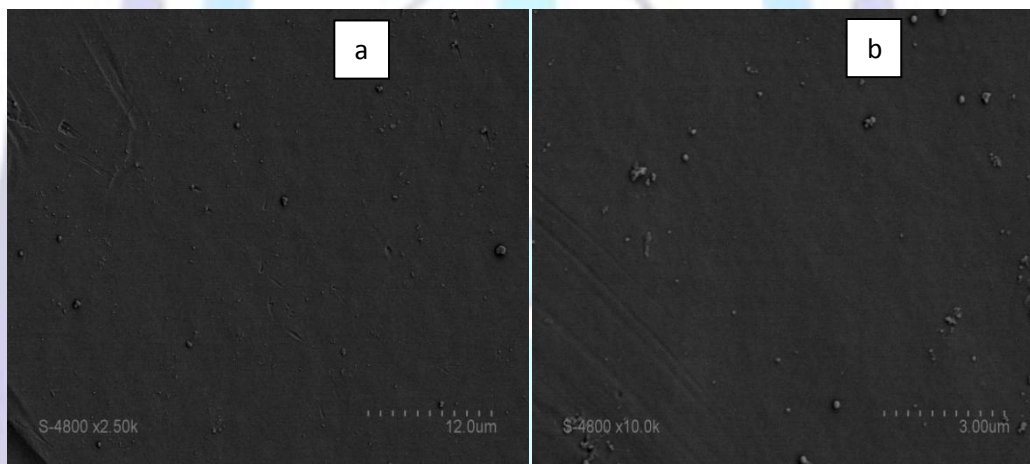


Fig 7: SEM images of NP 30 pretreated membrane top surface, prior to use (a) and after industrial phosphoric acid purification (b)

3. 2 Global performances of the NF membrane for the purification of industrial phosphoric acid solution

From the previous results, it can be concluded that the NF NADIR NP030 P membrane showed a good performances for purifying industrial phosphoric acid solution since a high rejection of impurities and a high P_2O_5 permeation were obtained.

The global purification percentage can be expressed by the following formula (5) [14]:

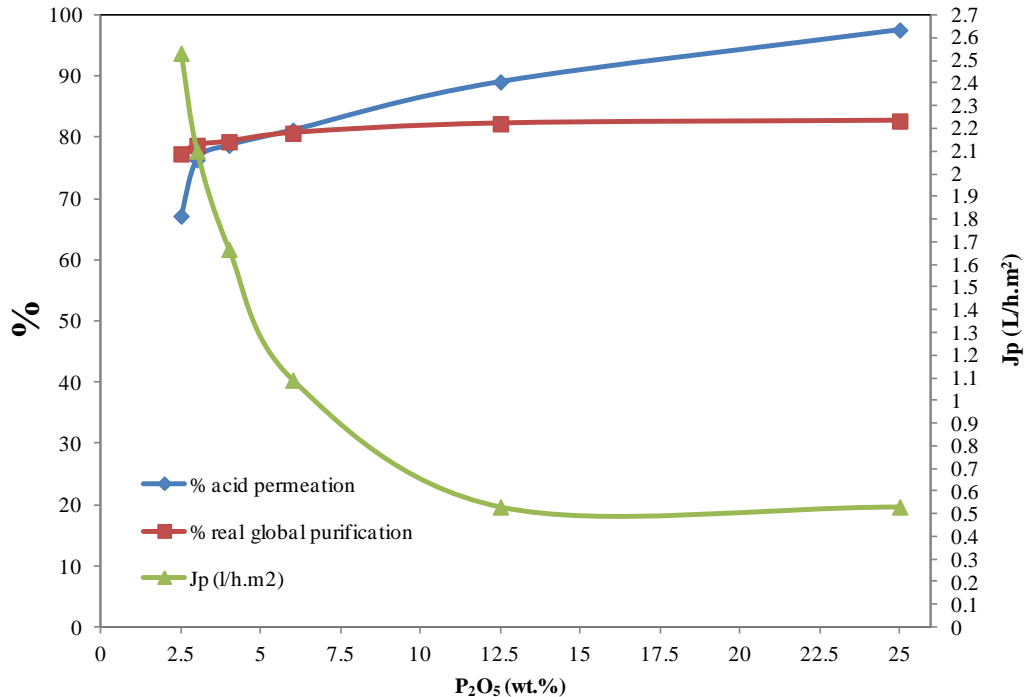


Fig 8: Variation of the global performances of the NF membrane with P₂O₅ concentration

Fig. 8 shows the evolution of the NF purification performances in term of acid permeation, global purification percentage and permeate flux with industrial H₃PO₄ acid solution concentration. It can be seen that the global purification percentage remains unchanged when the concentration increases from 2.5% to 25%. However, the flux decreased dramatically from 2.6 l/h.m² to 0.55 l/h.m² respectively. At the same time, the P₂O₅ permeation increases from 65% to 98%.

In this case, fouling by pore blocking and adsorption are the major contributors for flux decline at higher concentration.

4. Conclusions

Purification of industrial H₃PO₄ acid solution using NF has been studied. It can be concluded that NF is highly efficient to purify industrial phosphoric acid solutions by removing ionic impurities and TOC without a great P₂O₅ molecules loss. The selectivity of polyethersulfone nanofiltration membrane for the permeation of P₂O₅ molecules is significantly dependent on the effective pressure and concentration of industrial phosphoric acid solution. A high acid concentration leads to a significant increase in selectivity. The effect of the feed-solution composition is highly complex and should therefore be studied more in detail.

Generally, the experimental results show To increase the potentials for an effective retention of heavy metals, it seems beneficial to use effective pressure in order to gain high selectivity. Permeation acid in terms of P₂O₅ increases with increasing the feeding solution concentration. For all impurities, the retention of the heavy metals is much higher when the acid concentration is high. Relative purification is better for trivalent cations than for bivalent cations.

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