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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.4, pp 2201-2218, 2015

Study of the Tangential Nanofiltration of Orthophosphate Ions in Batch: Effects of Concentration, pH and Ionic Composition

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Abstract: As part of understanding the mechanisms of orthophosphates ion transfer through a Nanomax-50 type nanofiltration membrane, a study of retention behavior of simple solutions was carried out according to the tangential flow velocity and concentration. The behaviour of charged membranes vis-à-vis a particular ion may be significantly affected by the presence of other ions in the feed solution. For this, we compared the retention behaviour of orthophosphates in complex solution with the shape of retention rates of these same species placed in a simple solution. In this context, nanofiltration experiments were conducted on model salt solutions of various proportions. These mixtures were prepared from an initial solution of sodium dihydrogenophosphate NaH_2PO_4, disodium hydrogenophosphate Na_2HPO_4 supplemented by sodium chloride. The effect of pH on the retention of ions $H_2PO_4^-$, HPO_4^{2-}, Cl^- and the permeate flux was also investigated in mixed solutions.

Keywords: Nanofiltration, charged Membrane, Orthophosphates, Chlorides, pH.

Introduction

The physicochemical analyses performed on the urban and industrial wastewaters in eastern Algeria (Annaba city) have revealed the presence of phosphate species in high concentration [1]. Algerian recommended standards are often exceeded especially in wastewaters released from the phosphate fertilizer plant FERTIAL [2]. The remedy of such a problem lies in an eco-efficient treatment of the emission sources that are responsible for this excessive content.

The increasing demand of the use of phosphates led to a drastic shortage of this natural resource [3-5]. Several studies have been conducted to explore the practical and economic recovery of these species from urban and industrial wastewaters so as to generate a useful product [3]. In addition, the discharged water should comply with environmental directives in such a way that the phosphate should not exceed 0.15 mg/L [6].

The development of separation techniques in process engineering has put into competition several ways to realize phosphate recovery aiming to improve the performance and the economic cost. The available literature on phosphate recovery from urban and industrial wastewaters had focused on performance and effectiveness of removal processes so as to meet the stringent regulatory requirements. The two major and most commonly used routes of elimination treatments are: the physicochemical phosphorus removal and the biological phosphorus removal [7, 8].

Faced with the conventional treatment methods, membrane processes could present an interesting alternative, with three main advantages: they are clean processes, compatible with sustainable development, sober as little energy is needed (a few kWh m^{-2}), and safe, since cleaning and disinfection are controlled [6]. Membrane separation techniques have been developed considerably in recent years. Thanks to the implementation of new materials, membranes are getting more and more efficient and are gradually replacing the reserved areas of distillation, adsorption, ion exchange or chemical treatments. Unlike competing processes, the membrane techniques allow a continuous operation without passing through an intermediate phase [9].

The most recent technique, the cheapest and easiest to implement is nanofiltration (NF). This technique offers much broader opportunities in separation level between the different solutes due to the fact that it uses two transfer mechanisms with very different selectivities:

(i) One is a convective like in ultrafiltration (UF)

(ii) The other is diffusive like reverse osmosis (RO) [9].

The nanofiltration is a membrane process that has already shown its effectiveness in eliminating a wide variety of compounds present in water (dissolved organic matter[10], fluorides[11], , , nitrates [12], bicarbonates[13], nickel[14], and zinc[15]. It has many advantages including lower operating pressure range than that of reverse osmosis [9].

Nanofiltration seems to be interesting for a selective retention of phosphates. Some authors have successfully tested the efficient separation on NC 200 type membrane [16] [17]. A preliminary study was conducted in the Chemistry laboratory at Rennes University (France) and dealt with the characterization of a commercial spiral organic membrane (Nanomax-50). This study allowed the identification of pore size and the hydraulic permeability of the membrane, then the influence of operating conditions (applied transmembrane pressure, ionic strength, pH, etc) on the retention of orthophosphate ions $H_2PO_4^-$,HPO_4^{2-} and PO_4^{3-} [18]

The development of NF for the recovery of phosphate requires the selection of highly permeable membranes that reject phosphates selectively while passing other anions such as chlorides and nitrates. The present study investigates the selectivity of a commercial nanofiltration membrane, type Nanomax-50 (Millipore) for phosphate transfer in the presence of chloride ions. For this, experiments were carried out on synthetic solutions of increasing complexity (simple solutions then mixed with ions for various concentrations) in order to characterize the effect of cations associated with anions and understand the identity of transfer mechanisms that govern these anions and highlight the possible interactions in the experimental matrix.

The experiments were performed using various phosphate solutions:

- With binary mixtures, we were mainly interested in the effect of tangential velocity and concentration and the characterization of the solution-membrane interactions.
- With ternary mixtures, we studied the effect of the ionic composition and pH in order to reveal possible interactions between phosphate and other ions in solution. This approach was chosen to progressively identify the various factors involved in phosphate retention by nanofiltration.

2. Materials and methods

2.1. Solutions to be treated

The solutions to be treated were prepared from deionised water by adding NaH_2PO_4, Na_2HPO_4, NaCl, of analytical grade (Acros Organics, Fluka Analytical). The pH of solutions was modified with H_3PO_4 and NaOH.

2.2. The pilot of nanofiltration

Figure 1 shows the used nanofiltration pilot. It included a module, a tray of 12 litres a variable speed pump, valves for regulating the pressure, flow meters on the permeate circuits, the retentate and the supply. The pilot is a commercial Proscale Millipore of a capacity of 12 litres. All experiments were carried out in discontinuous mode with a total return of retentate and permeate to the feed tray to maintain constant concentration in the solution to be treated.

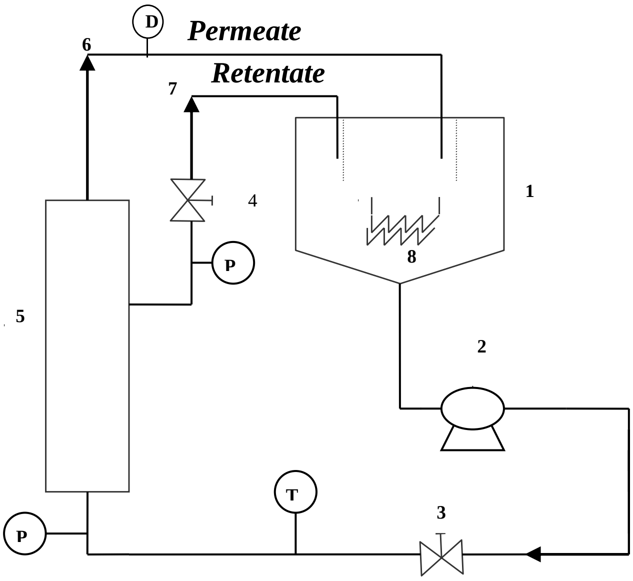

Figure .1: Synoptic diagram of the nanofiltration pilot

1. feed tray. **2**. Positive-displacement pump. **3 and 4.** pressure regulation Valves**. 5**. Nanofiltration module. **6.** Recirculation of permeate. **7.** Recirculation of retentate. **8.** heat Exchanger. **D**. Flowmeter. **P**. Pressure sensor. **T**. Temperature sensor

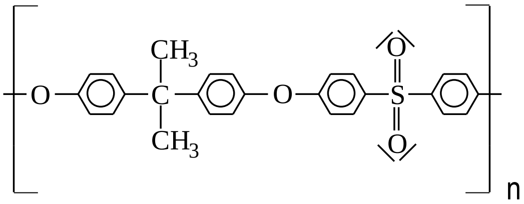

Figure 2. : **Structure of the mechanical support of the Nanomax-50 membrane.**

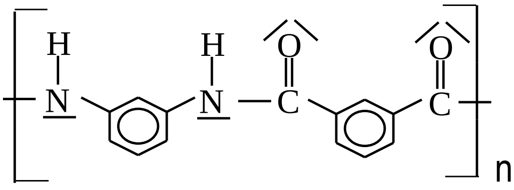

Figure 3. : Structure of the active layer of the Nanomax-50 membrane

2.3. The nanofiltration membrane

Nanomax-50 membrane is a membrane manufactured by the MILLIPORE Company (USA). It is assembled according to the spiral wound and has a filtration area of 0.37 m^2. This is an organic composite membrane with a polyester macroporous mechanical support, a polysulfone microporous mechanical support (**Figure 2**) and an active polybenzamide layer **(Figure 3**). The manufacturer's data state a cut-off threshold of about 300 Dalton for uncharged solutes and a pore diameter of 1 nm. The recommended application pressure ranges between 0 and 20 bars, the pH between 2 and 11 and the temperature must not exceed 40 °C.

2.4. Analyses

Analytical monitoring of the concentration of orthophosphates and chlorides in solution is carried out using a DIONEX ionic chromatography chain comprising a pump with a fixed flow rate of 1 mL min^{-1}, a conductivity detector and an anionic column. The system used is ICS: the first compact system integrating RFIC technology and controlled by Chromeleon software.

2.5. Operating Protocol

Membrane Cleaning was performed prior to testing with solutions of HCl (pH = 2) at a temperature of 25 °C, a transmembrane pressure of 2.5 ± 0.2 10^5 Pa and a tangential flow velocity of 380 Lh^{-1}. The sequence was as follows:

i) Filtration of the HCl solution for 15 min

ii) Open circuit rinsing with demineralised water until neutral (pH = 7) in both retentate and permeate

iii) The water permeability of the membrane was determined before and after the test by measuring the permeation flux (Jp) of demineralised water at a transmembrane pressure of 2 10^5 Pa. The experiments were performed on 6 litres of phosphate and chloride solutions during 30 min of filtration. Samples of retentate and permeate were taken after 10, 20, 30 min filtration. Since the concentrations did not vary after 20 min, this time was chosen and fixed for all subsequent experiments. Tests dealing with the influence of pressure were carried out in a range of 2 to 10 bar. The temperature of the solution is maintained at 25 °C and its initial pH was that of prepared solutions in demineralised water. During the tests, the tangential velocity was set at 380 L h^{-1}, then the transmembrane pressure was increased at a rate of 2 10^5 until 10 10^5 Pa depending on the tests. The temperature was, according to tests, 25 ± 2°C. the pH of the retentate and permeate were then measured. Retentate and permeate samples were collected at the same time.

2.6. Results Analysis

The considered parameters are:
- The permeation flux (*Jp*) deduced from experimental measurements of the volume (ΔV) collected during the given time interval (ΔT) by the equation:

$$Jp = \frac{\Delta V}{(\Delta t \times S)}$$

Where S represents the surface membrane area.
Some physical measurements are illustrated in **Table 1**.
The observed retention rate was calculated from the following relationship:

$$TR = 1 - \frac{Cp}{Co}$$

Where C_p and C_o denote respectively the concentration in the permeate and the initial concentration.

Table1: molar mass $M_{w,}$ stokes radius and diffusion coefficient D of anions **[19]**

Ions	M_w(g.mol^{-1}) D(m^2/s)	r_s(nm)
Cl^-	35.5	2.03 10^{-9}
$H_2PO_4^-$	97.0	0.96 10^{-9}
HPO_4^{2-}	96.0	0.76 10^{-9}

3. Results and discussions:

3.1. Simple model solutions

3.1.1. Effect of recirculation flux

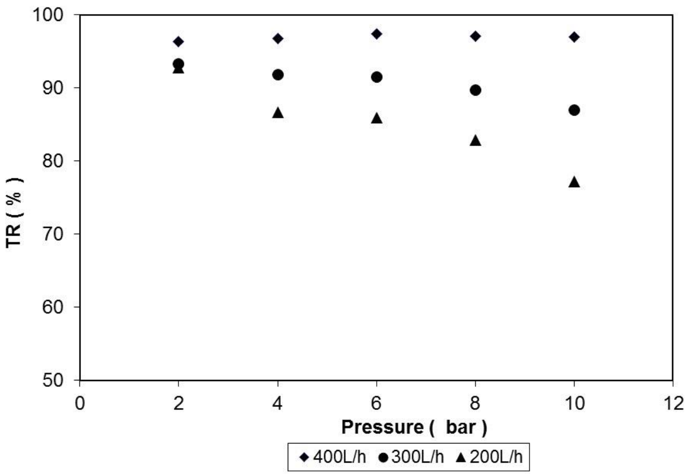

Figure 4 Effect of recirculation flux on the retention rate of Na_2HPO_4 (100 mg(PO_4^{3-}).L^{-1}).

The influence of the recirculation fluxs, which is equivalent to that of the tangential flow velocity, on the permeate flux and the retention rate was studied with solutions of NaH_2PO_4 and Na_2HPO_4 at 100 mg (PO_4^{3-}). L^{-1}. The results obtained are presented in **Figures 4, 5, 6 and 7** respectively. The permeate flux increases linearly with pressure and is not influenced by the recirculation flux. It remains practically independent of the tangential velocity and depends exclusively on the same transmembrane pressure. Similar results were found by Afonso et al [20], Gomez et al [21] and Ben Farese et al [15].

On the other hand, an increase of tangential velocity leads to higher retention rates. Indeed, the lower is the tangential flow velocity; the more the membrane-solute interactions would be facilitated. Therefore the amount of solute to penetrate into the pore will increase with decreasing velocity.

In this case, when the driving forces in the pore become stronger than the surface forces, the retention decreases rapidly as has been demonstrated previously. On the contrary, for a high velocity tangential flow, the driving of the solute to the retentate would be higher and the amount of solute entering the membrane pores is reduced. The lower the amount of solute in the pore, the less the pressure (driving forces) is influential because the surface forces would, in this case more efficient. Note that in the rest of our study and in order to overcome its effect, the tangential flow velocity was maintained constant at a feed rate of 280 L/h.

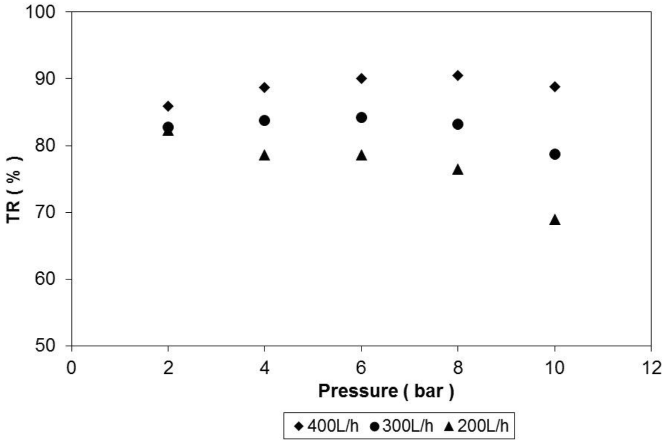

Figure 5: Effect of recirculation flux on the retention rate of NaH_2PO_4 (100 mg (PO_4^{3-}).L^{-1}).

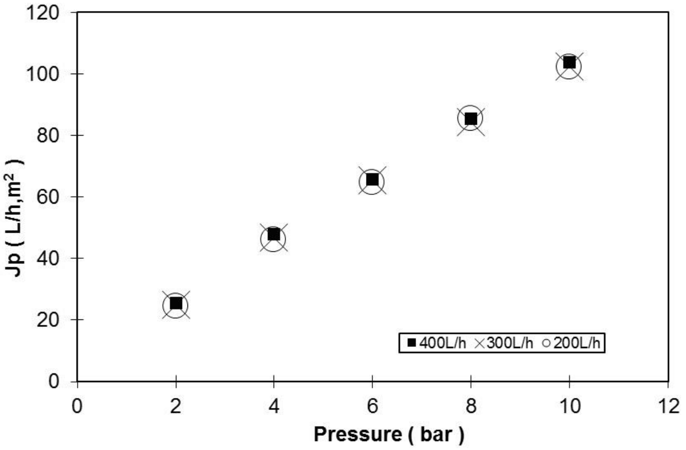

Figure 6: Effect of recirculation flux on the permeate fluxes of NaH_2PO_4 (100 mg (PO_4^{3-}).L^{-1}).

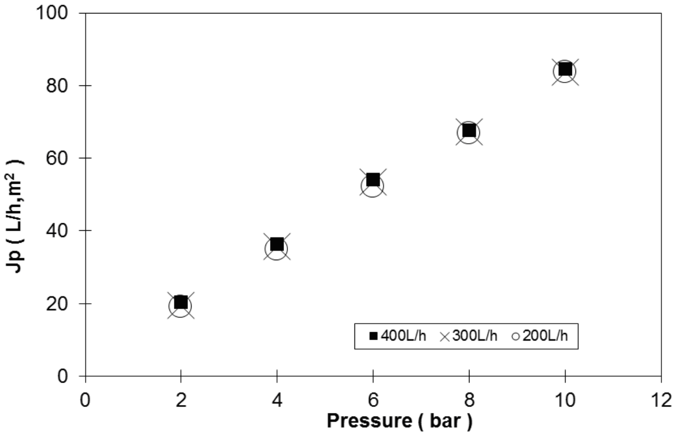

Figure 7: Effect of recirculation flux on the permeate fluxes of Na_2HPO_4 (100 mg (PO_4^{3-}).L^{-1}).

3.1.2. Effect of the concentration

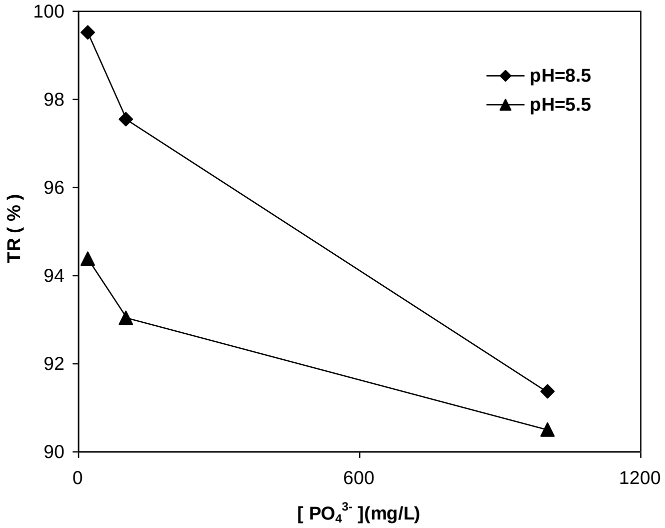

Figure 8: Effect of the concentration on the orthophosphates retention

Table 2: Values of the retention rates of the orthophosphate salts solutions NaH_2PO_4 and Na_2HPO_4 at a pressure of 6 bars for several concentrations.

Conc_(mg/L)	TR(%)NaH_2PO_4	TR(%) Na_2HPO_4
20	94.38	99.51
100	93.04	97.56
1000	90.5	91.37

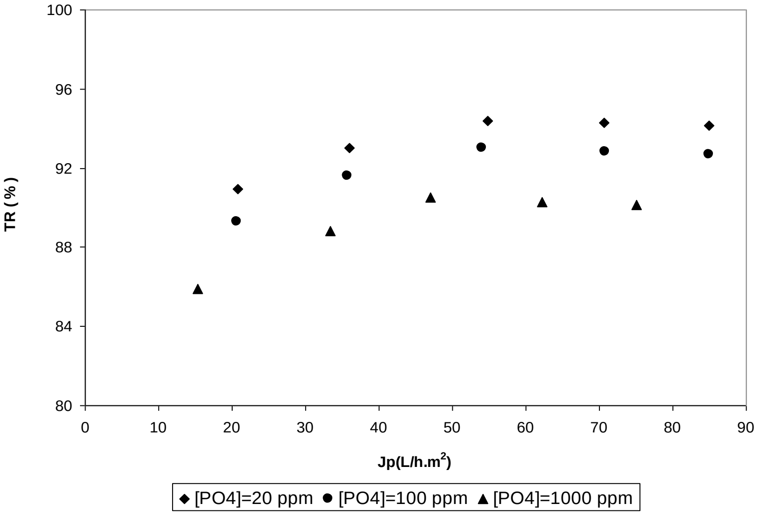

Figure 9: Variation of the retention rate of the ions $H_2PO_4^-$ according to the permeation flux for three different concentrations in PO_4^{3-}.

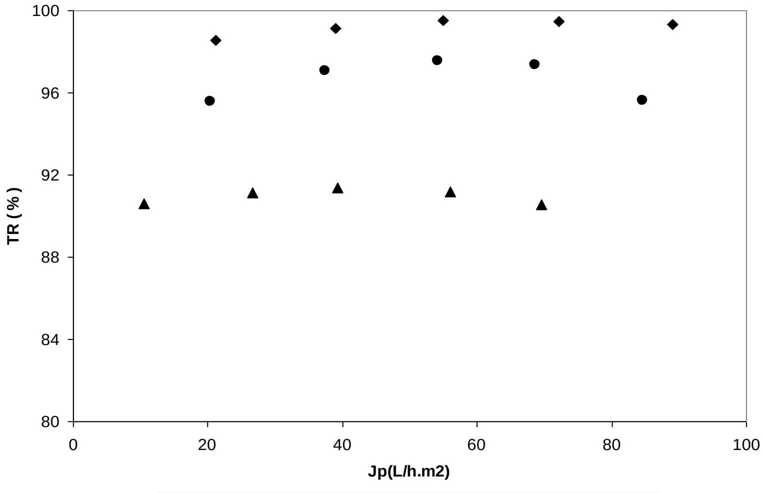

Figure 10: Variation of the retention rate of the ions HPO_4^{-2} according to the permeation flux for three different concentrations in PO_4^{3-}.

The study of the influence of feed concentration was performed on salt solutions of Na_2HPO_4 and NaH_2PO_4 at different concentrations: 20 ppm, 100 ppm and 1000 ppm, the **figures 9 and 10** illustrate the change in retention rate of orthophosphate ions $H_2PO_4^-$ et HPO_4^{2-} according to the voluminal flow of permeate at the applied transmembrane pressure and a temperature of 25°C.

When the concentration increases, the permeate flux increases and stabilizes first then it ends up with an apparent decrease. The figures also show that the increase of the concentration is accompanied by a decrease in the salts retention. the effect of concentration on the orthophosphate retention is manifested by a lower rejection rate of $H_2PO_4^-$ anions [94% → 88%] at pH = 8.5 and HPO_4^{2-}anions [99% → 91%] (**figure** 9) and (Table .1). This result can be attributed to the flux decrease at osmotic pressure. This later increases when the feed concentration increases. It opposes the fluid flow of the feed-out and therefore causes a decrease in the volume flow. Same results were obtained by Paugam et al [12].

Nevertheless, we attributed the decrease in the flux as a function of the concentration to the fact that when the concentration increases, it induces a reduction in the action of the repulsion electrostatic charge, allowing the passage of a greater number of ions in the pores, thus a reduction of the apparent size of the pores by simple steric hindrance thus leading to a reduction in membrane permeability. Similar results were found by [22] where they attributed this finding to the Donnan exclusion phenomenon, which is observed during filtration performed on charged membranes. Indeed, the Donnan exclusion globalises the interactions between attraction and repulsion forces exerted by the co-ions, the counter-ions and the fixed charge. During the increase of the feed solution concentration, there is a proportional neutralization of material fixed charges, thus a decrease in the Donnan potential.

3.2. Mixed model solutions

3.2.1. Effect of the ionic composition:

Interaction of the orthophosphate and chloride ions.

Unlike other anions, there are not many studies focusing on the effect of phosphate ion on the rejection of other anions in nanofiltration such as chlorides and nitrates. However, the influence of chloride anions on the retention rate of sodium dihydrogenophosphate salts, NaH2PO4, disodium hydrogenophosphate and Na_2HPO_4, was investigated successively. The orthophosphate ions concentration was kept constant whereas that of the added anion has been changed.

Chloride ion is one of the major anions of sea water and its concentration remains significant. In order to obtain specific information about the interaction of orthophosphate ions and chlorides, nanofiltration experiments were performed on Nanomax-50 membrane using solutions containing sodium, chlorides and orthophosphate ions.

The effect of chlorides on the retention of orthophosphates salts: NaH_2PO_4 and Na_2HPO_4, was successively examined. The PO_4^{3-} ion concentration is maintained constant, while that of the added anion was changed. The concentration was studied in the range of 0 to 500 mg/L for chloride ion by adding different concentrations of NaCl with a fixed PO_4^{3-} ion concentration of 100 mg/L for both phosphate salts NaH_2PO_4 and Na_2HPO_4.The results of orthophosphates and chlorides retention are shown in the **figure**s **(11-18**) respectively showing the evolution of anions $H_2PO_4^-$, HPO_4^{2-}et Cl^- depending on the transmembrane pressure. The overall observation of the curves is the same. the concentration of orthophosphate anions decreases with increasing NaCl concentration. The shape of the retention rate curves of orthophosphate ions versus pressure in the system [NaCl, NaH_2PO_4] at pH = 5.5 and in the system [NaCl, Na_2HPO_4] at pH = 8.5 has the same characteristics as that of a solution of orthophosphates only. In fact, the retention rate of orthophosphate ions increases with pressure initially, follows a plateau and then decreases slightly. The addition of Cl^- ions induced a general decrease in retention rate of orthophosphates. This behaviour is well known [12,16,18]: it is a characteristic of charged membranes and is generally explained by the screening phenomenon. The increase in the concentration of sodium cations in the solution involves the formation of a screen which gradually neutralizes the negative charge of the membrane. During the whole charge of the membrane decreases, the concentration of phosphate anions also decreases and the electrostatic effect of the membrane becomes lower. The screen phenomenon is lower in the case of divalent anions than monovalent reflecting strong retention of HPO_4^{2-} ions with respect to $H_2PO_4^-$ ions in one hand by electrostatic interactions with the negative charge of the membrane and on the other hand by the effect of size of the hydrated ion.

On the other hand and under a transmembrane pressure of 6 bar, the retention of Cl^- ions in the mixture [NaCl, Na_2HPO_4] (Table 4) is higher than that in the mixture [NaCl, NaH_2PO_4] (Table3) in all studied conditions. In fact, for the system [NaCl, NaH_2PO_4] at pH = 5.5, the rejection rate of the chloride ion varies between 25% and 56%, while that of $H_2PO_4^-$ ions varies between 88% and 96%. However for the system [NaCl,

Na_2HPO_4] at pH = 8.5 the rejection rate of the chloride ion varies between 34% and 71%, while that of HPO_4^{2-} ions varies between 96% and 99%. The ions behaviour observed in the mixture rises from the characteristics of the ions $H_2PO_4^-$, $HPO_4^{2-}$and Cl^- in the level of the ionic radius, the molecular weight rather than the ionic diffusion. **(**Table 1).

The decrease in orthophosphates retention with increasing the concentration of added Cl^- is allotted, as in the case of a simple salt, to the growth of the screening phenomenon of the membrane. The addition of NaCl leads to a stronger neutralization of the membrane charge by Na^+ ions and thus to a lower repulsions membrane-anions. The transfer of ions $H_2PO_4^-$, HPO_4^{2-} and Cl^- in the permeate is facilitated and their retention decreases.

The high retention of divalent orthophosphates co-ions, due to strong repulsive interactions with the membrane, would also cause a decrease in the monovalent Cl^-Co-ions retention in mixed solutions, according to a principle similar to that of Donnan dialysis. The contribution of this phenomenon to the separation selectivity is crucial. The ion exclusion of the membrane would be based on its repulsive interactions between ionized groups and co-ions, and between co-ions of different valence.

The ionic organization at the interface solution-membrane (surface and pores) can cause changes in membrane potential by a more or less important screening of charged groups of the membrane. The chemical potential difference in co-ions and counter-cons in the pores, called Donnan potential in the case of dilute solutions (concentrations lower at 100 mg/L), can be comparable to a difference in electrokinetic potential. Under the effect of this potential difference, which is the cause of the transmission of co-ions through the membrane, the system is globally balanced at all times (ie, cancellation of the electrokinetic potential difference). The transmission of co-ions occurs simultaneously with that of the counter-ions present in the membrane pores, in order to satisfy the condition of electrical neutrality. The potential difference is, however, restored by the convective addition of other co-ions and counter-ions to the membrane. Thus, the system membrane-solution, generally at equilibrium, is characterized locally by a succession of states of equilibrium / disequilibrium in the pores.

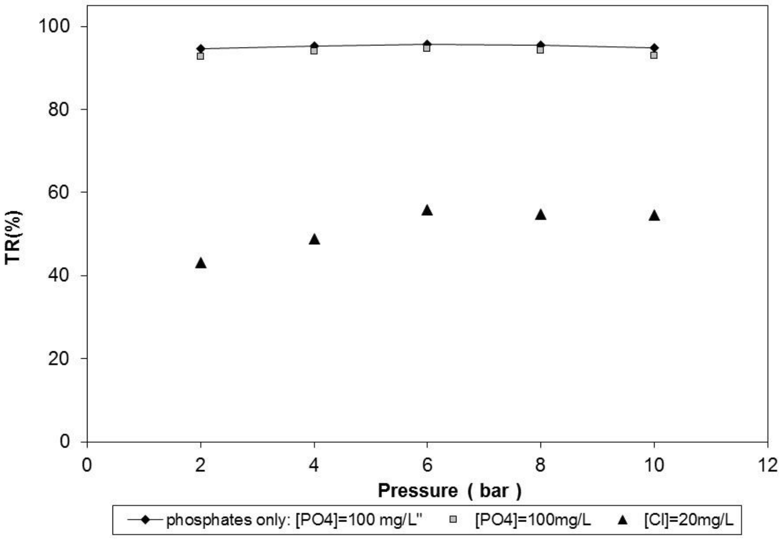

Figure 11 : Effect of the pressure on the retention rates of Cl^- and $H_2PO_4^-$ for a concentration in mass of Cl^- less than that of PO_4^{3-} at a pH = 5.5.

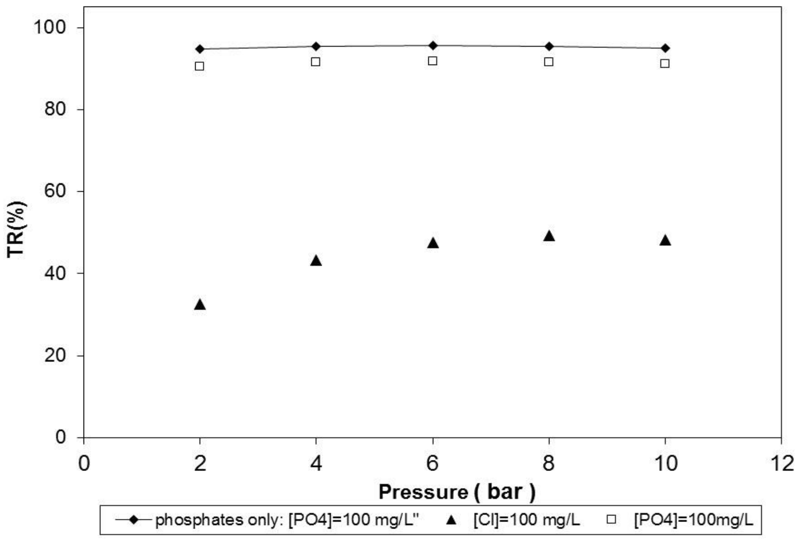

Figure 12: Effect of the pressure on the retention rates of Cl^- and $H_2PO_4^-$ for a mass concentration of Cl^- equal to that of PO_4^{3-} at a pH = 5.5.

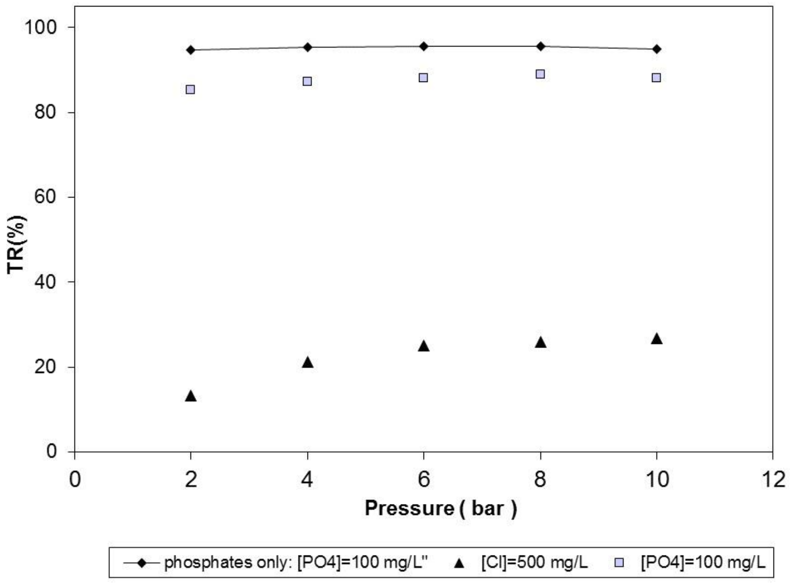

Figure 13 : Effect of the pressure on the retention rates of Cl^- and $H_2PO_4^-$ for a concentration in mass of Cl^- more than that of PO_4^{3-} at a pH = 5.5.

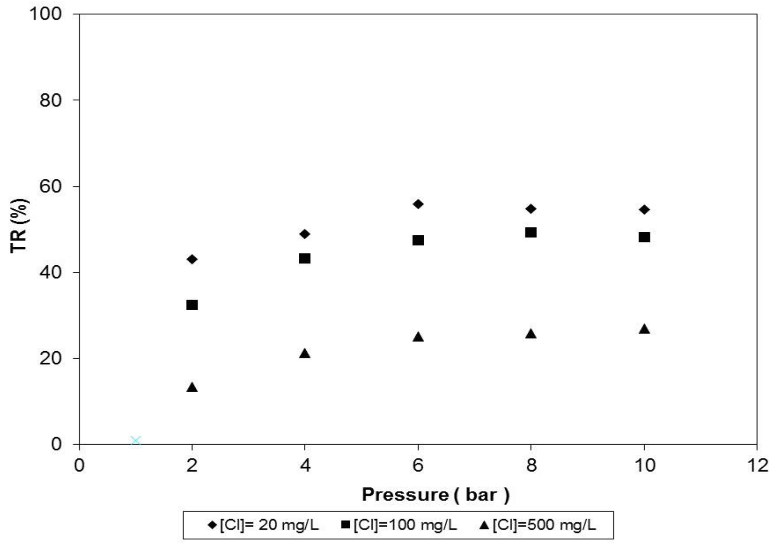

Figure 14 : Effect of the pressure and the concentration on the retention rates of the solutions of NaCl for the system [NaCl , NaH_2PO_4] at pH = 5.5.

Table 3: Values of the retention rates of the solutions of NaH_2PO_4 and NaCl when NaCl is added to a solution of NaH_2PO_4 100 mg (PO_4^{3-}).L^{-1} at a pressure of 6 bars.

[Cl^-] (mg/L)	TR ($H_2PO_4^-$) (%)	TR (Cl^-) (%)
0	95.61	0
20	94.62	55.94
100	91.73	47.56
500	88.15	25.05

Table 4: Values of the retention rates of the solutions of NaH_2PO_4 and NaCl when NaCl is added to a solution of Na_2HPO_4 100 mg (PO_4^{3-}).L^{-1} at a pressure of 6 bar.

[Cl^-] (mg/L)	TR (HPO_4^{2-}) (%)	TR (Cl^-) (%)
0	99.53	0
20	99.15	71.48
100	98.24	64.30
500	96.37	34.71

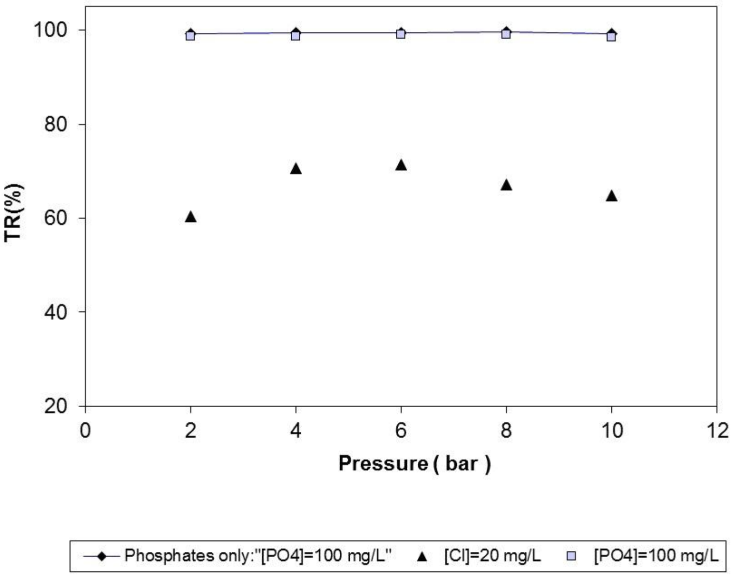

Figure 15 : Effect of the pressure on the retention rates of Cl^- and HPO_4^{2-} for a mass concentration of Cl^- less than that of PO_4^{3-} at a pH =8.5.

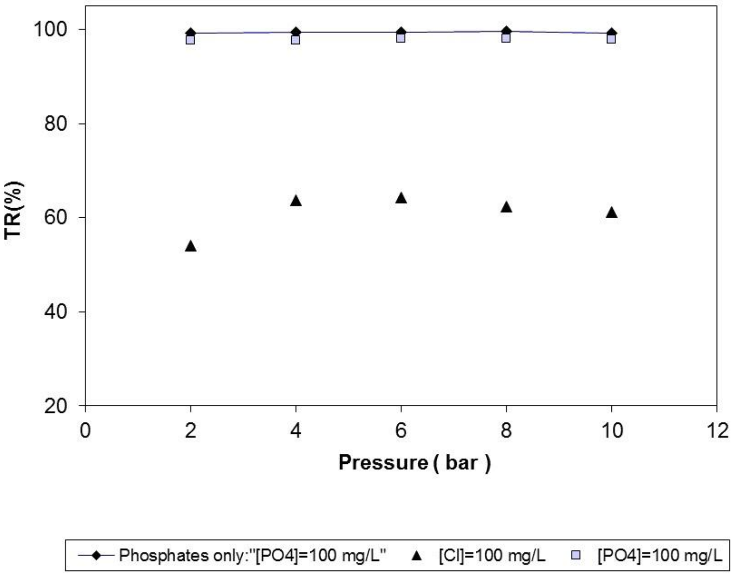

Figure 16 : Effect of the pressure on the retention rates of Cl^- and HPO_4^{2-} at a mass concentration of Cl^- equal to that of PO_4^{3-} at a pH = 8.5.

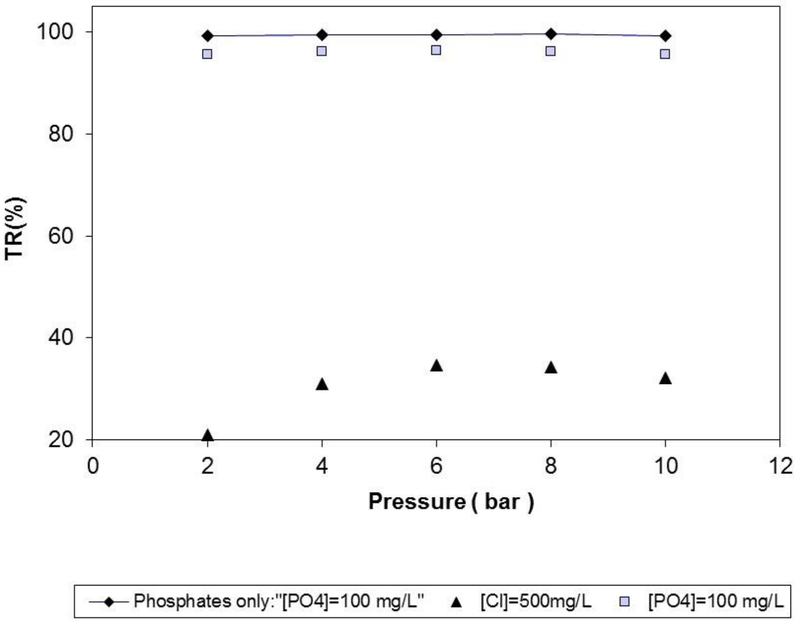

Figure 17 : Effect of the pressure on the retention rates of Cl$^-$ and HPO$_4^{2-}$ at a mass concentration of Cl$^-$ more than that de PO$_4^{3-}$ at a pH = 8.5.

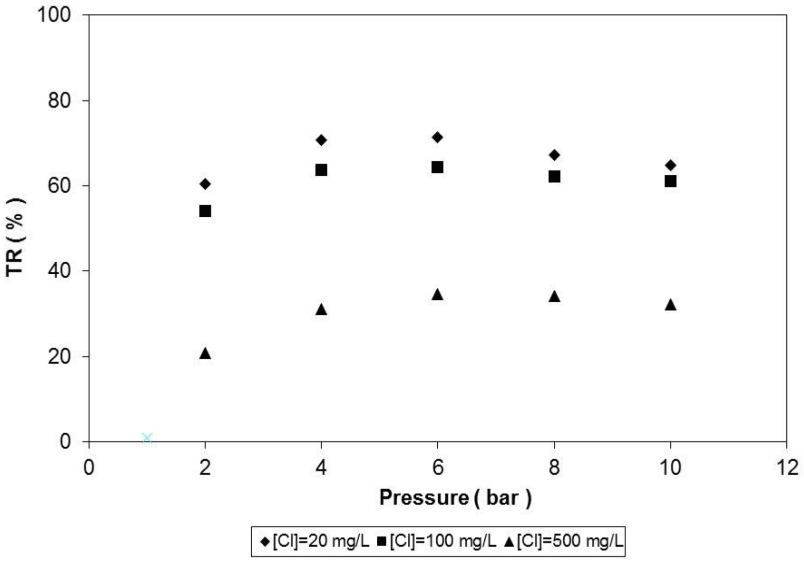

Figure 18: Effect of the pressure and the concentration on the retention rate of the NaCl solutions for the system [NaCl, Na$_2$HPO$_4$] at a pH = 8 .5.

3.2. 2. pH Effect :

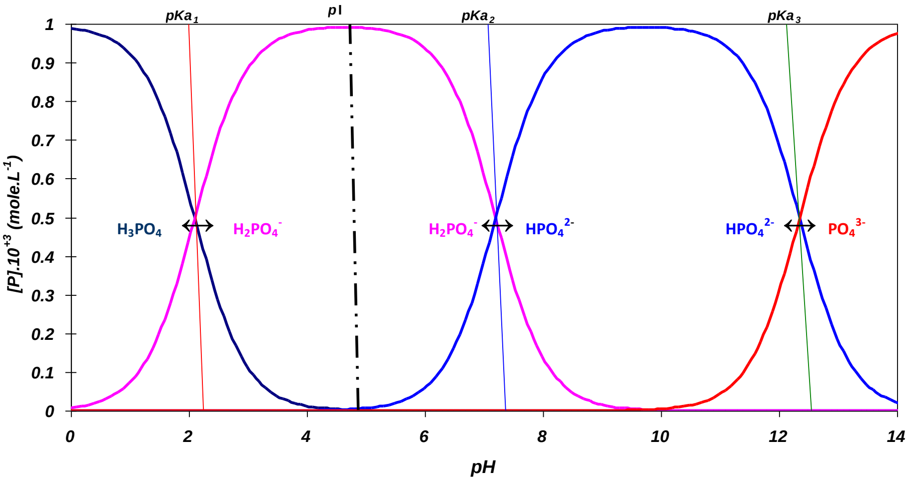

Figure 19: Diagram of prevalence of the various shapes of the Orthophosphoric acid according to the pH in aqueous solution.

The membrane Nanomax-50, like most commercial nanofiltration membranes, can be considered charged. In fact, its active layer consists of an aromatic polyamide whose partial hydrolysis will generates carboxylic acid groups RCOOH (pKa1 = 3.5) and ANH2 amine (pKa 2 = 6.3) which can be ionized according to pH. The ionization degree is a function of the nanofiltered solution pH which refers to the isoelectric point, pI = 4.9. This corresponds to the value of pH at which the electric charge of fixed cations neutralizes globally that of anions. The ionization degree of membrane groups depends on the pH of the nanofiltered solutions. According as it is above or below the pI, it highlights the intensity and the nature of interactions with the membrane. Similarly, the solution pH changes the mechanical and dimensional characteristics of the polymer, which is more expanded when these groups are ionized. The pH and the nature of the ions in solution have predominant effects on the observed selectivity of the studied Nanomax-50 membrane. The orthophosphates have the particularity of being the species of variable charges depending on pH and whose forms are interrelated through the acidity constants of phosphoric acid: $pKa_1 = 2.1$, $pKa_2 = 7.2$, pKa3 = 12.4 Figure.19. The pH effect on the nanofiltration of orthophosphates in simple mixture has been studied by Abidi et al [18] and Ballet et al [16]. This parameter can affect the properties of the membrane and the solutes chemical specificities by the distribution of molecules at the interface of membrane pores and the solution, coupled with the Donnan theory.

The study of the influence of pH was carried out for a phosphoric acid solution with a concentration of 100 mg L^{-1} in the presence of NaCl solution with a concentration of chloride ions of 200 mg (Cl^-). L-1, under a pressure of 10 bar, the temperature was fixed at 25 ° C. The recirculation flow was set at 280 Lh-1 and the acidity was adjusted by addition NaOH. The evolution of the retention of orthophosphates and chlorides ions in mixed models solutions is shown in figure 20. The discussion of results will be done on the basis of three ionization cases membrane groups distinguished according to the pH of the solution:

- *pH > 5* (pH more than pI)

Since the Nanomax-50 membrane being negatively charged, owing to the ionization of RCOO-groups, the co-ions (the anions of the solution) govern the retention of the ions, as they can not easily pass through the membrane due to repulsive interactions with membrane groups.

The divalent co-ions, such as HPO_4^{2-}, are better retained than monovalent co-ions $H_2PO_4^-$ et Cl^-, because their strong negative charge keeps them away from the pores. In contrast, the monovalent co-ions of higher ion mobility have lower retentions. Hence, for the same associated cation Na^+, Cl^- retention is lower than that of $H_2PO_4^-$. The increase of pH with respect to phosphoric acid pKa generates different forms of orthophosphates and the retention occurs in step with this variant.

In fact, with pH between 6 and $pKa_2 = 7.2$, the orthophosphates exist as $H_2PO_4^-$ and H_3PO_4 with a rejection rate of the order of 82% and 11% respectively. The rejection rate of the orthophosphates increases and reaches 97% in the form of $H_2PO_4^-$. The $H_2PO_4^-$ ions are increasingly rejected by the membrane, resulting in an increase of their retention rates. This observation is apparent for $pH > pKa_2$ with an equal coexistence of the two forms of phosphates $H_2PO_4^-$ (R=98%) et HPO_4^{2-} (R=98%) in the retentate at pH = 10.23. Beyond this pH value, the divalent form of orthophosphates anions HPO_4^{2-} dominates with a retention of about 98%. The increase in pH above the isoelectric point leads to a rise in negative charge of the membrane, hence it is the chloride ions that are increasingly rejected by the membrane, resulting in an increase in their retention rate up to a maximum value of about 56.5%

- ***4< pH<5*** (pH close to pl)

The retention of orthophosphates by the Nanomax-50 membrane in the mixed solution is close to those determined in the simple solution. This suggests that at the isoelectric point of the membrane, the anionic groups are only weakly ionized. The observed exclusion phenomena are limited to a steric exclusion. However, at its isoelectric point, the membrane has no charge, resulted from a balance between $A\text{-}NH_3^+$ et $R\text{-}COO^-$ionized groups.

Indeed the results presented in these figures show a minimum retention of chloride ions close to the isoelectric point (figure.19). The obtained results show that the values of the orthophosphates rejection rate increased from 40% to 80% when the solution pH varies from 2.9 to 5.9. This change reflects a fluctuation of sign (positive / negative) of the membrane at the isoelectric point (pI = 4.9). It would then the sieve effect which primarily governs the selectivity of the membrane due to the steric hindrance induced by the size of solute.

- *pH<4* (pH inférieur au pl).

the membrane is positively charged and this results in a rise in the overall retention of chloride ions CI-(R = 49.36), ion exclusion effects between Na^+ and $A\text{-}NH_3^+$ groups in addition to steric exclusion effects.

The reading in the diagram values shows that for pH <4 the orthophosphates are selected as H_3PO_4 $R(H_3PO_4)$=40% and a negative retention of monovalent phosphate anions $R(H_2PO_4^-)$ = -5 % to offset the imbalance charge created between the membrane and the solution when the pH decreases.

The positive charge of the membrane increases and Na^+ ions are increasingly rejected by the $A\text{-}NH_3^+$ groups of the membrane. Although the monovalent co-ions are repelled by divalent cations to the membrane, they cross the membrane at a higher level than their concentration in the retentate, so as to compensate the charge imbalance. This transmission occurs simultaneously with that of counter-ions, in order to satisfy the electroneutrality condition.

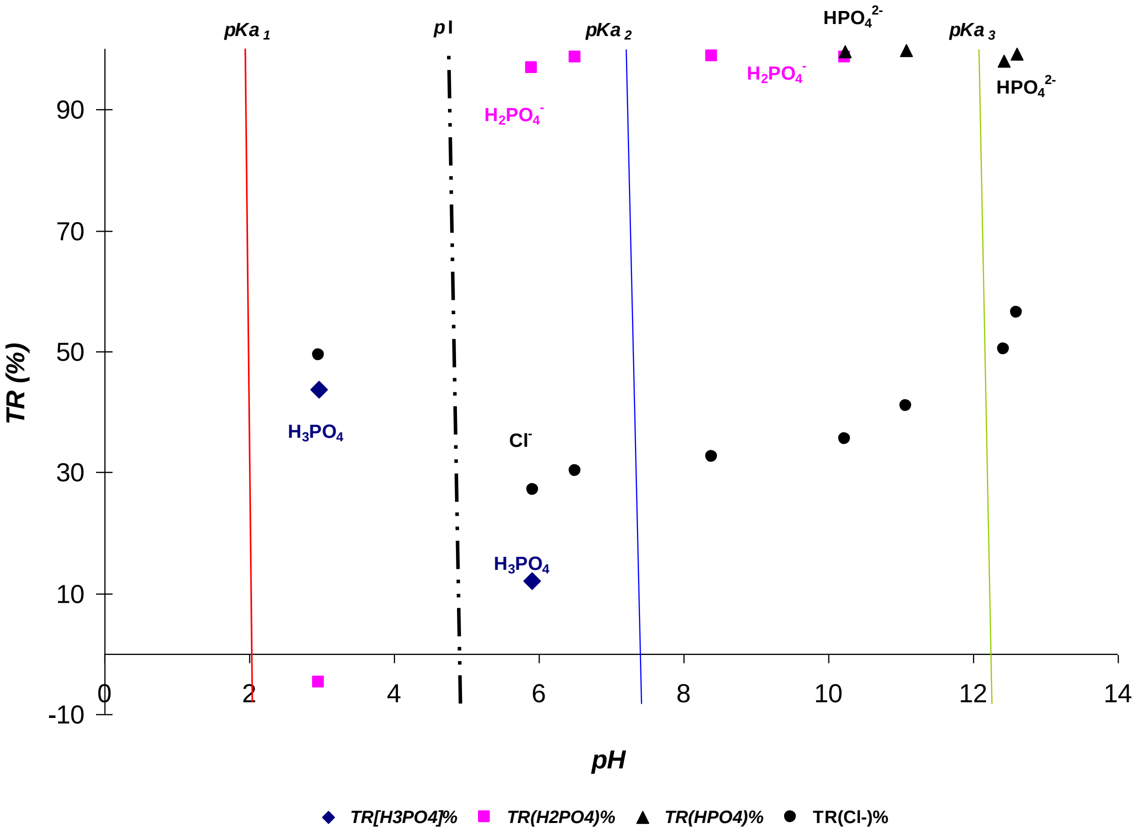

Figure 20. Retention Rates of the various orthophosphates and chlorides species in a mixed solution according to pH

The study on the Nanomax-50 membrane showed a significant drop in permeate flux between pH 3 (pH <pKa$_1$, forms RCOOH) and pH=7 (pH> pKa$_1$ forms RCOO-) **Figure.21**. The results show that the polymer conformation affects mainly the solvent transfer but does not explain the observed retention differences by changing the steric exclusion of the membrane. Thus, the membrane permeability is higher at pH=3 compared to pH=7 (lower expansion of the polymer), whereas orthophosphates retention increases between these two pH values. The contribution of steric exclusion in the membranes selectivity is thus limited, and slightly modified depending on the pH of solutions in contrast to that of ion exclusion and repulsive interaction.

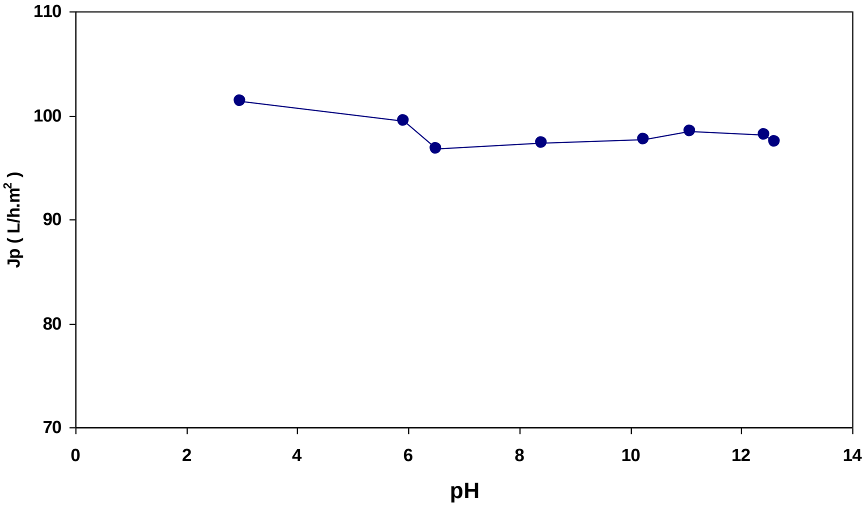

Figure 21. Evolution of the permeate flux according to the pH of a mixed model orthophosphates and chlorides solution.

Conclusion

This study outlined the influence of parameters such as the solute characteristics, the membrane-solute interaction, and the solute-solute interaction relative to apparent parameters such as tangential flow velocity, concentration, pH and ionic composition. In fact, retention is dependent on a ratio of the driving forces towards the retentate illustrated by the effect of the recirculation flow rate; a driving force towards the permeate illustrated by the effect of transmembrane pressure; a force reflecting surface membrane-solute interaction illustrated by the effect of the concentration and the nature of the counter-ion.

This study highlighted as well the importance of the valence of the associated anion on the removal of orthophosphate ions. In all tests, it was found that the retention rate is particularly important when the anion charge is high. The study of the concentration effect on the retention showed a charge effect for electrolytes (Na^+: $H_2PO_4^-$) and ($2Na^+$: HPO_4^{2-}). The orthophosphate salts retention decreases with increasing concentration. This behaviour was interpreted by the screening phenomenon of the membrane by the monovalent counter-ions. This interpretation is based on the ability of Na^+ cations to form a complex with the carboxylic groups of the membrane. For example, from a certain concentration of Na^+, the free $RCOO^-$ groups responsible for the negative charge of the membrane, are complexed in the form (R-COO-Na). In this context, the negative charge of the membrane is reduced and may even become slightly positive. The selectivity of the membrane would then be mainly due to the size effect of the solutes.

The pH of the solution, in particular, plays an important role in the selectivity of the membrane as it determines its charge and thus the intensity of interactions membrane-solute. The more the pH is far from the isoelectric point the greater the membrane charge and the orthophosphate ions retention.

Sometimes a very important change in the behaviour of orthophosphate ions was also demonstrated by varying the ionic composition upon the addition of another co-ion in a binary solution of sodium dihydrogenophosphate, NaH_2PO_4, disodium hydrogenophosphate Na_2HPO_4. The experimental matrix interferences with the chloride anion were considered important to the extent that the retention of orthophosphate has been particularly affected by the presence of this anion in solution. Their rejection rates decreased sharply and even reached negative values in an acidic medium. The effectiveness of nanofiltration in water treatment is strictly dependent phosphate on operating conditions, the ionic composition and membrane properties. The results obtained in the case of water with important chloride content appear logic with those already presented in the literature relating to the nanofiltration of ionic solutions with negatively charged membranes.

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