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REMOVAL OF COPPER (II) AND IRON (III) MIXTURE BY PILOT NANOFILTRATION

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ABSTRACT
In the current study, the effect of operating conditions such as pH value, feed flow, concentration of the solution and the applied pressure for the removal of copper(II) and iron(III) mixtures for the production of drinking water by nanofiltration membrane was investigated. The results show that it is possible to extract all of the iron (III) and copper (II) at the same time to a salt mixture of Fe 50% - salt Cu 50% for concentration 4 ppm, pH = 4.5 and pressure = 6 bars. The best results for the copper (II) were obtained for the various mixtures at the pressure of 6 bars at varying pH.

Keywords: Extraction, nanofiltration, copper (II), iron (III), mixture, synergism.

1. INTRODUCTION

The use of membrane technology has gained momentum in recent times and is preferred over conventional techniques like chemical precipitation or solvent extraction [1]. Advances over the last 10 years have shown a significant growth of papers published on nanofiltration (NF) membranes in many different areas. NF membranes in contact with aqueous solution are slightly charged due to the dissociation of surface functional groups or adsorption of charge solute. These properties have allowed NF to be used in niche applications in several areas especially for water and wastewater treatment, pharmaceutical and biotechnology, and food engineering [2]. in recent years, the use of nanofiltration membranes (NF) has increased rapidly in the chemical, petrochemical, biotech and desalination industries, since the NF technology over comes operational problems that are associated with conventional techniques. Several studies have been reported in which NF membranes have been used as tools for heavy metal removal [3].

Nanofiltration has some advantages over other membrane techniques, for example it has higher rejection of divalent ions and lower rejection of monovalent ions, lower operating pressure, higher flux and lower energy consumption compared with RO[4].

The aim of this work was to study the efficiency of copper (II) and iron (III) mixtures retention by using the SNTE NF270-2540. The effects of pressure and initial feed concentration on the membrane performance were studied.

2. EXPERIMENTAL

2.1 Apparatus

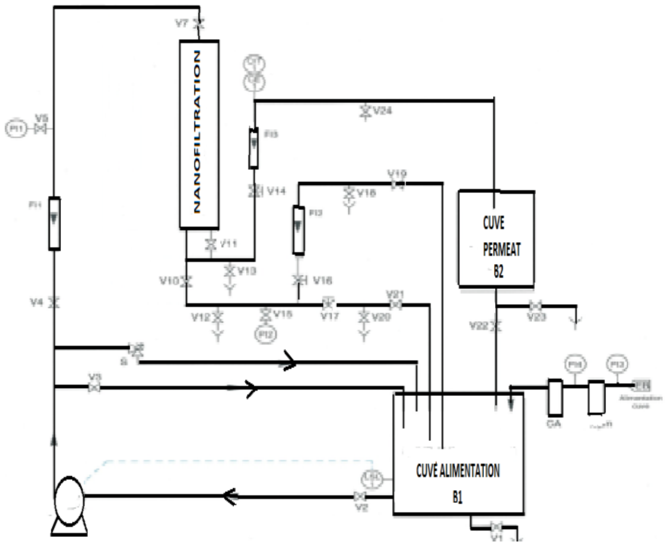
All chemicals used in this research were of analytical grade. All metal salt solutions were prepared by dissolving the appropriate weight of the salt of each metal in distilled water and made to a total volume of 50 L. The pH of solutions was measured using a pH-meter (Adwa), provided with a glass combine electrode. The conductivity measurements were carried by using MC126 Conductivity meter provided with an electrode.

The metal ion concentrations were determined by atomic absorption spectrophotometer (PINA cle 900 H - Perkin Elmer), using an air acetylene flame, two wavelengths were used 327.40 nm (linearity: 0.17 - 8 ppm) for copper and 302.06 nm (linearity: 0.4-20 ppm) for iron a range of standards solutions for various concentrations were prepared from a standard solution of 10 ppm for iron and 8 ppm for copper.

2.2 Pilot Equipment

Filtration was performed with a tangential filtration, capacity100 L (Figure 1). All the experiments were carried out in a closed system, where the permeate does not return to the tank whereas the retained liquid returns to the tank.

Figure 1: Schematic Diagram of Nanofiltration Pilot



2.3 Membrane Description

The module membrane spiral used was 1016 mm long and has a width of 61 mm. The nanofiltration membrane is a thin film composite membrane. All is established by three layers: A layer support in polyester (120 µm); a micro porous intercalary layer Polysulfone (40 µm) and a layer barrier (active layer) ultrathin of polyamide on the superior surface (0.2 µm).

Table 1: Characteristique of Membrane

Data from manufacturer		
Reference	Material	Cut-off (Dalton)
AFC 30	Polyamide on polyethersulfone	100
MRT 10	Polysulfone on polypropylene	200
MPT 08	Polyamide on polyethersulfone	200
MPT 34	Polysulfone on polypropylene	300
MPT 31	Polysulfone on polypropylene	400
MPT 04	polyethersulfone	>1000
SNTE NF270-2540 (used in present work)	**polyamide**	**200-400**

2.4 Extraction Procedure

The experiments were carried out at the Laboratory of Separation and Purification Technologies. After each experiment the membrane is cleaned by a hydrochloric acid solution for 10 min, and then it is rinsed with distilled water.

2.5 Analytical Methods

The volumetric flux was determined by measuring the permeate volume collected in given times interval. Owing to electro neutrality conditions, it was observed that both cation and anion rejection rates were the same, that is to say $R_{cation} = R_{anion} = R$. Consequently, the rejection rate can be calculated by Eq. (1):

$$R = 100\left(1 - \frac{C_p}{C_0}\right) \quad (1)$$

C_p concentration of salt in the permeate (ppm),

C_0 concentration of salt in the feed solution (ppm).

2.6 Results and Discussion

2.7 Determination of the Hydraulic Membrane Permeation

The permeability of the membrane is given by the slope of the Figure 3 which is equal with L_P= 3.95 m s^{-1} bar^{-1} and the resistance, R_m = 0.253 bar m^{-1} s, Eqn. (2).

$$R_m = \frac{1}{A} = \frac{S\Delta P_m}{Q_P} \qquad (2)$$

A permeability of the membrane

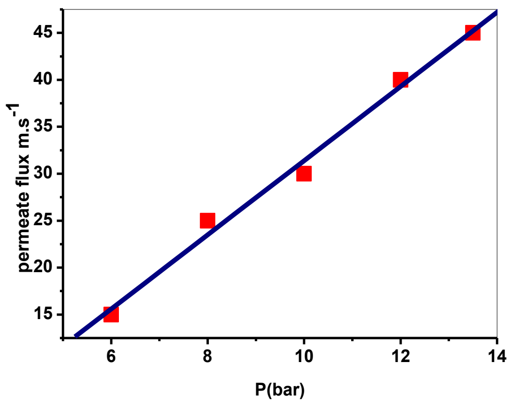
S membrane area

ΔPm the effective transmembrane pressure

Q_P permeation volume flow rate.

The value of the L_p obtained on the used membrane (SNTE NF270-2540) was proved to be 1.457; 106 times as large as that obtained on the membrane Nanomax-50 (Millipore USA)[5]. and on the Duramem MWCO 900, where L_P is 0.028 x 10^{-6} m s^{-1} bar what shows that our membrane is very successful, and can be used in the industrial scale[6] .

Figure 2: Permeate Flux Variation as a Function of Pressure for Distilled Water

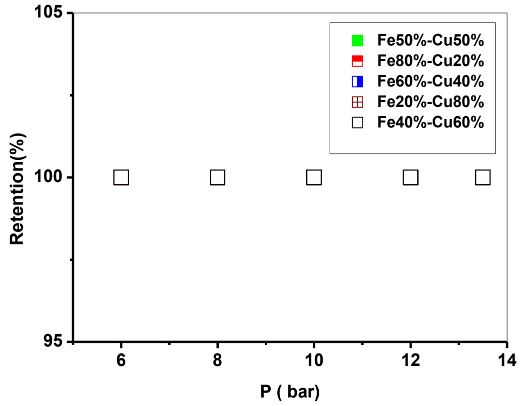


2.8 Effect of Pressure and Concentration for Mixtures

2.9 Effect of Pressure and Concentration for Iron

Figure 3 shows that, for variations of pressure from 6 - 13.5 bars, the retention is quantitative (100 %) for iron and copper at different proportions, while maintaining a total concentration of 4 ppm for the mixture. A pressure of 6 bars is enough for a full purification of iron. The difference between the iron and the copper is not observable, because the presence of the copper in the mixture does not influence the retention of the iron.

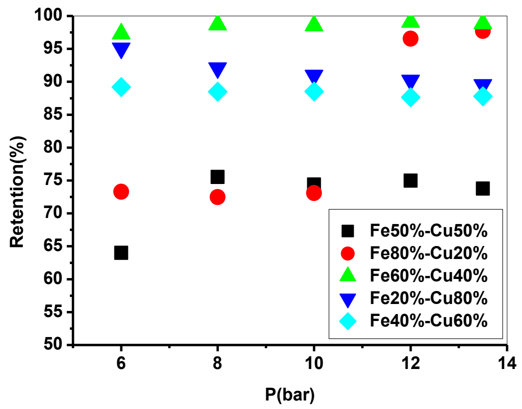
Figure 3: Variation of Iron Retention as a Function of the Pressure for Different Mixtures



3. Effect of Pressure and Concentration for Copper

The presence of iron influences the retention of the copper as seen from the results presented in Figure 4. The best retentions were obtained for the mixture Fe 60 % + Cu 40 % about pressure from 12 bars. For the mixture Fe 80 % + Cu 20 %, pressure up to 10 bars, the retention is constant (around 74 %) then increases exponentially until 97 % beyond this pressure. The effect of pressure was important on the retention, whatever the proportions of the mixture; the total concentration being always maintained at 4 ppm.

Figure 4: Variation of Copper Retention as a Function of the Pressure for Different Mixtures



Effect of pH

Effect of pH for the retention of iron and copper in the different mixtures

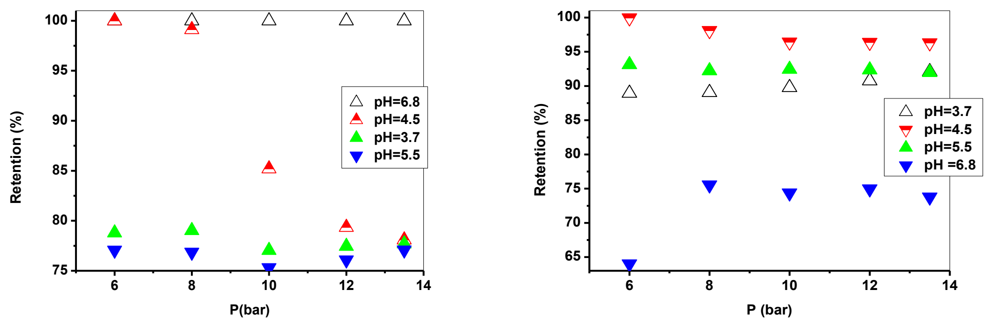
Mixture iron salt 50% - copper salt 50%

In view of the figure 5 (A), the obtained results show that the accepted pressure is about (6 - 13.5 bars) and the pH = 6.8; the retention of the iron is total (100 %). With pressure 6 bars, the retention of the iron is also total, in pH = 4.5. The difference at pH = 6.8 and pH = 3.7 then 5.5 becomes important. The best conditions of extraction of the iron correspond to pH = 4.5 and the pressure of 6 bars, with the addition of some mL of HCl. Without the addition of HCl, the best conditions are pH = 6.8 and the pressure of 6 bars.

For pH 3.7, 4.5 and 5.5, the retention of the iron at the pressure of 13.5 bars is almost the same (78 %) We can conclude that there is an interaction between these two parameters. A study of plan of experience would allow quantifying this interaction. The purification is total for the mixture in the pressure of 6 bars and in pH = 4.5.Whereas the best selectivity is obtained for a pH = 6.8 (without addition of HCl) and the accepted pressure of 6 bars.

Figure 5: Variation of iron (A) and copper (B) retention as a function of the pressure for mixture salt iron 50%-salt copper 50%

(A) (B)

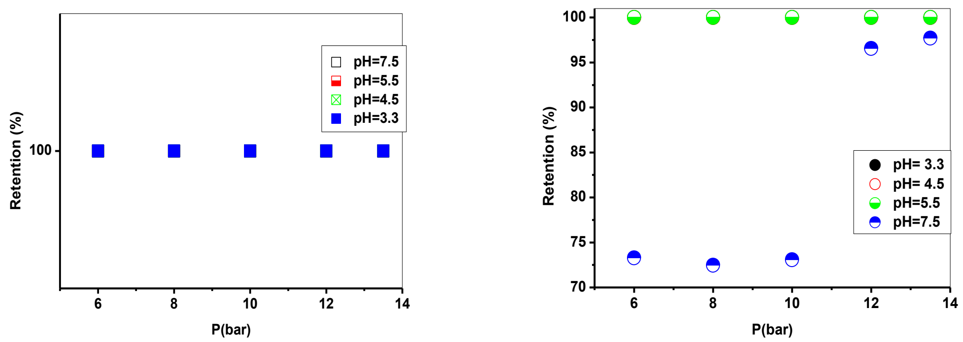


Mixture iron salt 80%-copper salt 20%

In view of the figure 6 (A), the obtained results show that the retention of iron is total (100 %) at pressure 6 - 13.5 bars and pH 3.3 - 7.5. In view of the figure 6 (B), for pH 3.3; 4.5 and 5.5 (with the addition of some mL of HCl) and a pressure from 6 - 13.5 bars the retention of copper is total (100 %). The membrane extracts the mixture without distinction between the iron and the copper, although these two metals have different physical-chemical properties; the iron Macke left some Ferromagnetic metals. The best selectivity is obtained for a pH = 7.5 (without addition of HCl) and the accepted pressure of 8 bars.

Figure 6: Variation of iron (A) and copper (B) retention as a function of the pressure for mixture salt iron 80%-salt copper 20%

(A) (B)

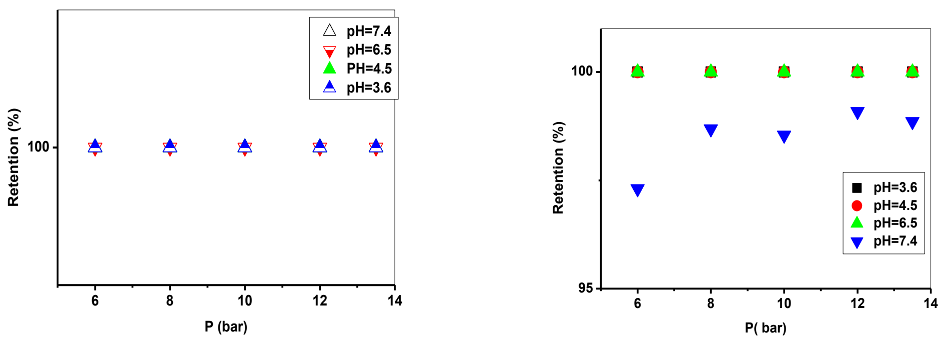


Mixture iron salt 60%-copper salt 40%

In view of the Figure7 (A), the obtained results show that the retention of the iron is total (100%) at pressures from 6 to 13.5 bars, and pH from 3.6 to 7.4. In view of the figure 14 (B), pH 3.6, 4.5, and 6.5 (with the addition of some mL of HCl) and a pressure from 6 to 13.5 bars the retention of the copper is total (100%). The separation takes place at P = 6 bars and pH = 7.4 which is a neutral pH. On these conditions of separation the speeds of diffusion through the membrane have different values.

Figure 7: Variation of iron (A) and copper (B) retention as a function of the pressure for mixture salt iron 60% - salt copper 40%.

(A) (B)



Mixture iron salt 20%-copper salt 80%.

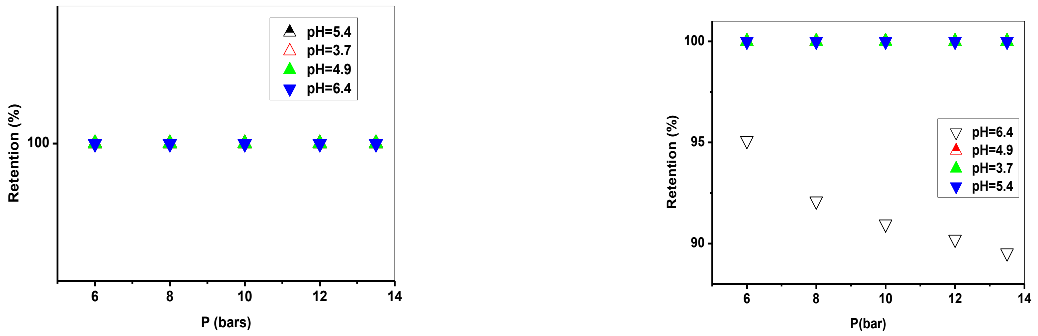
In view of the Figure 8(A), the results show that at pressures from 6 to 13.5 bars and pH from 3.7 to 6.4, the retention of the iron is total (100%). In view of the figure 8 (B), for pH 3.7, 4.9, and 5.4 (with the addition of some ml of HCl) and at pressures from 6 to 13.5 bars the retention of the copper is total (100 %). In these pH, the process does not make a difference between the iron and the copper.

In pH = 6.4 and at P =13.5 bars, the separation between both metals is the most important.

The retention decreases at pH = 6.4 with the increase of the pressure.

Figure 8: Variation of iron (A) and copper (B) retention as a function of the pressure for mixture salt iron 20%-salt copper 80%.

(A) (B)

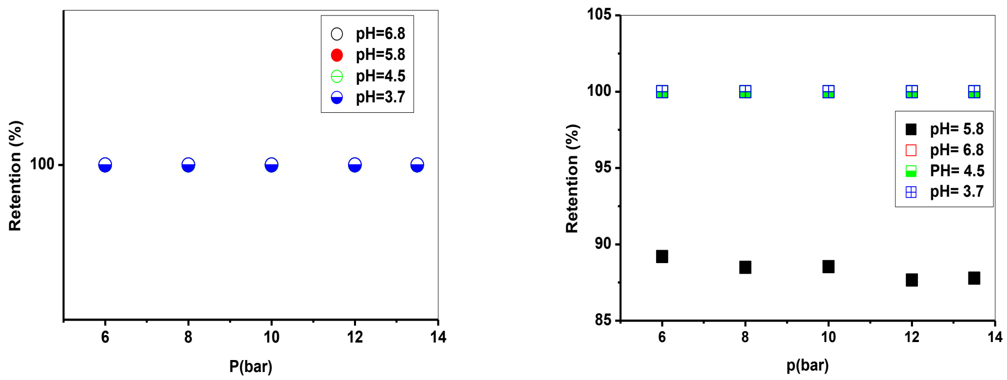


Mixture iron salt 40%-copper salt 60%

In view of the Figure 9 (A), the results show that the retention of the iron is total (100%) at pressure from 6 to 13.5 bars and at pH from 3.7 to 6.8. In view of the Figure 9 (B), the retention of the copper is total (100 %) for pH 3.7, 4.5, (with the addition of some ml of HCl) and 6.8 (with the addition of some ml of NaOH) at pressures from 6 to 13.5 bars. The difference of retention is obtained at pH = 5.8. In this pH, the effect of increase in pressure on the retention was weak.

Figure 9: Variation of iron (A) and copper (B) retention as a function of the pressure for mixture salt iron 40% - salt copper 60%.

(A) (B)



Effect of synergism.

- $\frac{Cp_m}{Cp_s} > 1$ **synergism** (the effect of the mixture is greater each of the ion in the mixture).
- $\frac{Cp_m}{Cp_s} < 1$ **antagonism** (the effect of the mixture is less than that each of the ion in the mixture).
- $\frac{Cp_m}{Cp_s} = 1$ **non interaction** (interaction the mixture has no effect on the adsorption of each of the adsorbates in the mixture) [7,8].

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Table 2: Effect of Copper in the Mixture (*C*Ps = 0.22 ppm)

Mixture	$C_{P,m}$	$\frac{C_{p.m}}{C_{p,s}}$	Effect
Salt of Fe 50%- salt of Cu 50%	0.95	4.32	synergism
salt of Fe 80%- salt of Cu 20%	0.07	0.32	antagonism
salt of Fe 60%- salt of Cu 40%	0.03	0.14	antagonism
salt of Fe 20%- salt of Cu 80%	0.19	0.86	antagonism
salt of Fe 40%- salt of Cu 60%	0.40	1.82	synergism

Table 3: Effect of Iron in the Mixture (C_{Ps} = 0.21 ppm)

Mixture	$C_{P,m}$	$\frac{C_{p.m}}{C_{p,s}}$	Effect
salt of Fe 50%- salt of Cu 50%	0.00	0.00	antagonism
salt of Fe 80%- salt of Cu 20%	0.00	0.00	antagonism
salt of Fe 60%- salt of Cu 40%	0.00	0.00	antagonism
salt of Fe 20%- salt of Cu 80%	0.00	0.00	antagonism
salt of Fe 40%- salt of Cu 60%	0.00	0.00	antagonism

Several factors are considered to correlate metal ion uptake and metal ion properties. Factors like:

(i) electronagetivity of the metal ion,

(ii) electrostatic attrition due to charge to radius ratio,

(iii) ability to form metal hydroxide complex and

(İV) Suitable site for adsorption on adsorbent are responsible for competitive adsorption of one metal ion over another [9,10].

4. CONCLUSION

The results of the previous experiment show that NF270-2540 membrane is more efficient for copper and iron extraction due to its higher hydraulic permeability to distilled water (Lp = 3.95m s^{-1} bar^{-1}), A pressure of 6 bars is sufficient for such purification with respect to the iron, whatever the proportions Of the mixture and whatever the pH allowed.

The best results for copper (II) are obtained for the various mixtures of Pressure of 6 bar and variable pH . It is possible to extract all iron (III), copper (II) and at the same time for one

Mixture of 50% Fe salt - Cu 50% salt with a total concentration of 4 ppm, pH = 4.5 and the Pressure = 6 bar.

During the term of this study, the consideration of the difference (pH_r - pH_n), the retention of H^+ or of OH^- according to its sign, establishes a good descriptor of the imbalance of Ionic partitions realized between the solution and the pores of the membrane. The mechanisms of transfer of ions to be proposed in this study should allow a better understanding the selectivity observed during the nanofiltration.

Symbols

pH_r pH of permeate

pH_n pH of retentate.

Cp_m: concentration of an ion in the mixture (Fe^{3+}, Cu^{2+}).

Cp_S: concentration of a single ion in solution.

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