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Wastewater Purification by Nanofiltration Technology

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Abstract

The removal of two different heavy metals in aqueous solutions was investigated with polyamide nanofiltration membrane SNTE NF270-2540, the results show that the retention of iron ions was total (100%). Depending of the experimental conditions, the retention of copper ions was varied from 82% to 94%. It was observed that the pH has no influence in the iron retention. The retention of ions by nanofiltration was done by Donnan effect (electrostatic repulsion) and counter-ion volume effect (steric exclusion).

Keywords: Nanofiltration, Extraction, Iron, Copper, membrane SNTE NF270-2540.

1. Introduction

In industry heavy metals have a lot of uses. To this end, many wastewaters are treated; its treatment and recovery are a major economic challenge. Heavy metals are the main environment contaminants. Several techniques have been studied to extract these metals such as: solvent extraction [1], precipitation [2], ion exchange [3], liquid-liquid extraction [4], and adsorption [5]. These methods have many drawbacks, such as the need for organic solvents that are toxic to the environment and a lot of time. Today, membrane technology has many advantages over other conventional techniques, it includes supported membrane [6,7], nanofiltration (NF) [8], ultrafiltration (UF) [9], reverse osmosis (RO) [10] and microfiltration [11]. In recent years, nanofiltration has been developed in many fields [12,13]. The present work examined the ability of the NF270 membrane to extract copper, iron, and their mixtures under various operating conditions. The effects of pH, pressure and feed concentration on membrane performance were studied.

2. Experimental

2.1. Reagents

Iron nitrate salt, copper nitrate salt, sodium Hydroxide, and hydrochloric acid (38%) were supplied by Sigma Aldrich.

2.2. Materials

A commercially spiral nanofiltration membrane SNTE NF270-2540, was used in this study, all the experimental conditions of this membrane are summarized in Table 1.

All solutions were prepared by dissolving the appropriate weight of the salt in water and made to a volume of 40 L.

Table 1.
Main characteristics of the NF membrane used

Membrane structural parameters	
Membrane type	thin-film composite
Active area	2.6 m^2
Maximum operating Temperature	113°F (45°C)
Maximum operating pressure	600 psi (41 bar)
pH range	2-11
Free chlorine tolerance	< 0.1 ppm
Water permeability Lp (m/s bar)	0.366 x 10^{-6}

2.3. Apparatus

The weightings were made with an electronic analytical balance type OHAUS. The concentration of the Cu(II) and Fe(III) was determined by a flame atomic absorption spectrophotometer type PERKIN ELMER Pin AAcle 900H. The pH measurements were performed by ADWA AD 1030 pH meter.

2.4. Experimental setup

The experiments were performed with separation unit illustrated in figure 1.

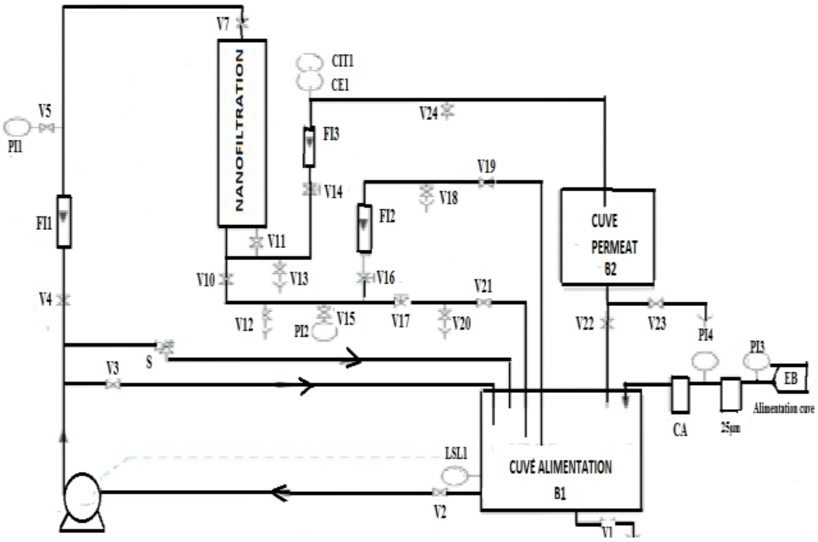


Figure 1. Nanofiltration pilot

CA is the cartridge filter with activated carbon and 25 µm of wound cartridge filter. S is the safety valve (14 bars). B1 is the feed tank (100 L). B2 is the permeate tank (20 L). C2 is the nanofiltration membrane. FI1 is the upstream flow meter (100–1000 l/h). FI2 is the downstream flow meter of retentive. FI3 is the downstream flow meter of permeate. PI1 and PI2 are the manometers at upstream and downstream of module (0–16 bars). PI3 and PI4 are the monitoring manometers of filters state (0–2.5 bars). LSL1 is the low-level sensor (pump safety). CE1 is the Sensor of permeate conductivity measuring. Y is the emptying, CIT1 to the electrical display cabinet. V1–5, 7, 10, 11, 14–16, 19 and 22 are the pressure regulation valves for nanofiltration process. P is the multistage centrifugal pump (high pressure).

2.5. Data analysis

$$R(\%)=(1-\frac{C_p}{C_0}).100 \qquad (1)$$

where R is the retention, C_p the permeate concentration (ppm) and C_0 the feed concentration (ppm).

3. Results and discussion

3.1. Determination of the membrane permeability

The permeability was calculated by the Darcy law equation (2):

$$J_V=L_P\,(\Delta P-\sigma\Delta\pi) \qquad (2)$$

In diluted solutions, $\sigma\Delta\pi$ has been neglected. The permeability of the membrane Lp was determined by the slope from figures 2. At 25°C, Lp=1.32 L/(m^2.h.bar) is close to those reported in literature [14].

Figures 2 represent the evolution of the permeate flux for distilled water (solvent) and metals solutions as a function of pressure. We observed that the permeate solute flux is lower than that of the solvent, for the solution containing 4 and 100 ppm in iron (Figure 2a) and the solution of 4 ppm in copper (Figure 2b), at a pressure higher to 6 bars. In this case, the transfer of solvent is preferred over the solute. This result is due to the concentration polarization increase, and is in agreement with that obtained by other authors [8].

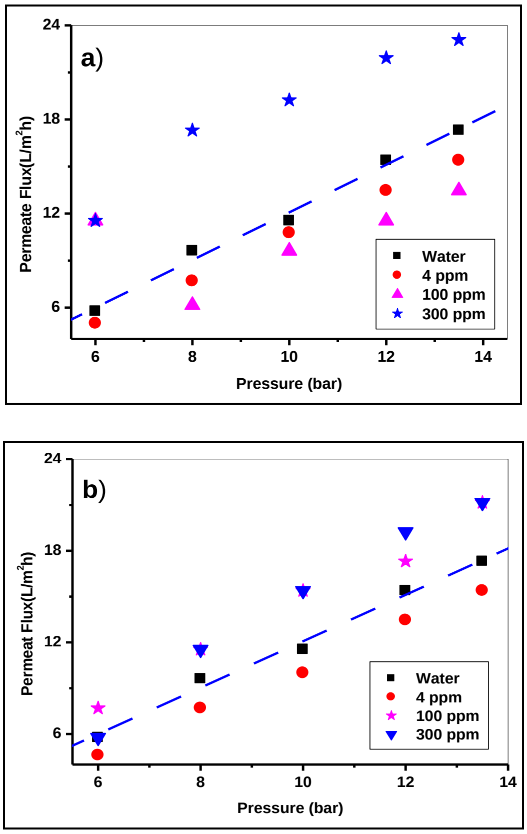


Figure 2. Influence of pressure on water and permeate flux for various concentrations of Fe(III) (a) and Cu(II) (b)

3.2. Effect of pH

From Figure 3 (a), the iron retention is very high (about 99% and 100%) whatever the pressure and the pH. At low pH, an increase in osmotic pressure has occurred due to the accumulation of solutes near the surface of the membrane, which could explain why the retention is higher [15]. The highest retention solute at higher pH values was interpreted by decreasing of pore size due to the dissociation and repulsion of the membrane carboxyl group [15,16], these results are similar to those given in the literature [8,14]. Unlike iron the figure 3(b) shows that the retention of copper was constant (80%) with the increase of pH from 3.5 to5.4 whatever the pressure, and the decrease (18%) at pH=6.7.

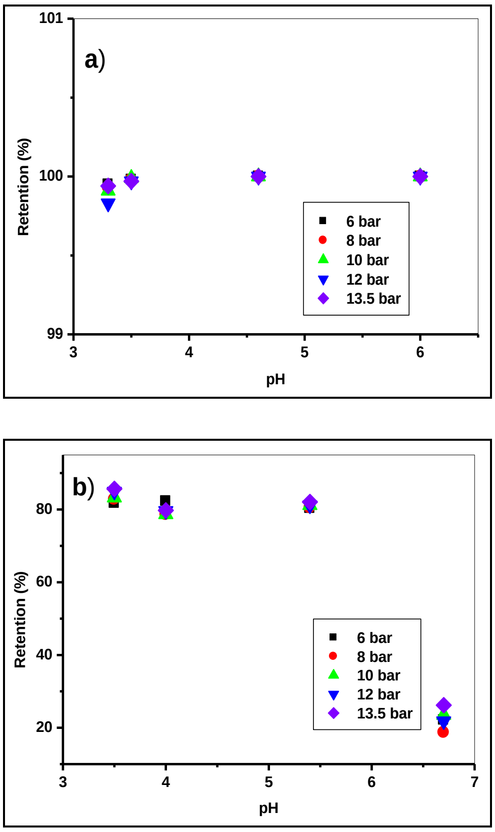


Figure 3. Influence initial pH on Fe(III) (a) and Cu(II) (b) retention.

Figure 4(a) shows that whatever the pressure and the pH the retention of iron in the mixture salt iron 20% - salt copper 80% was 100%. In figure 4 (b) the retention of copper was constant (100%) about pH=3.7, 4.9, 5.4 and it decrease when pH increases from 5.4 to 6.4. At pH=6.4 the retention of copper decrease (95% - 89%) with the increase of pressure, this phenomenon was explained by the neutralization of negatives sites of the membrane because of the increase of the positive charges.

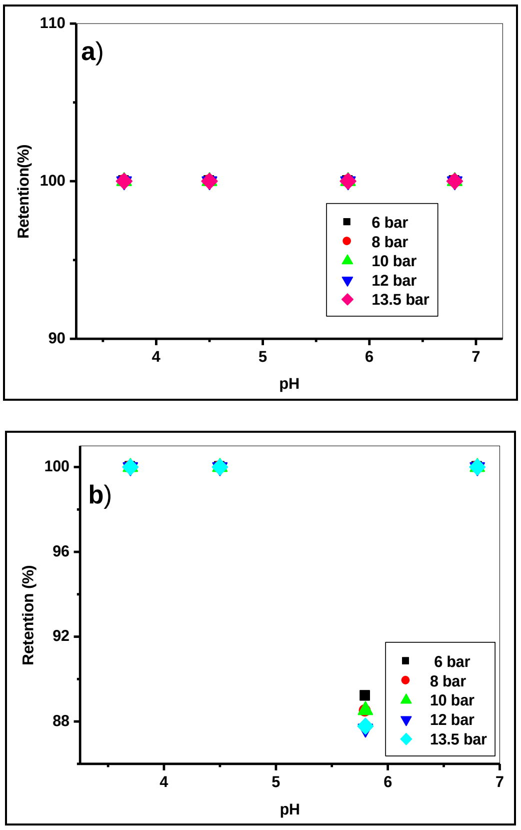
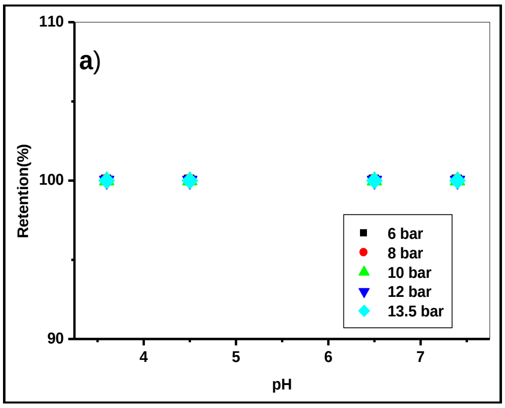


Figure 4. Influence of pH on Fe(III) (a) and Cu(II) (b) retention for mixture salt iron 40%-salt copper 60%.

Figure 5(a) show that the iron retention was quantitative whatever the pressure and the pH.



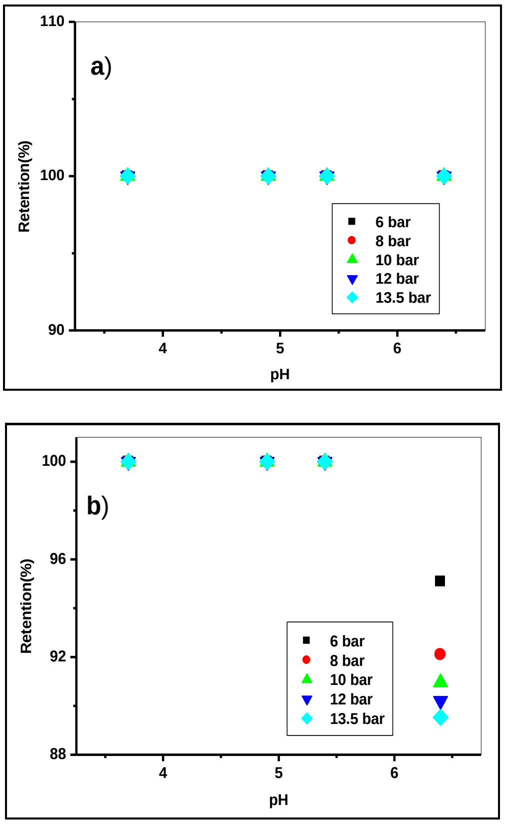


Figure 5. Influence of pH on Fe(III) (a) and Cu(II) (b) retention for mixture salt iron 20%-salt copper 80%.

About pH=3.3, 4.5 and 5.5, the membrane extracts the iron and the copper without distinction. The retention of copper decrease when pH increases to 7.5. This result is explained by the shape of the nanofiltered species at pH <6.8, copper is in its 99% free form so they are better ejected with the effect given by the membrane in the form of Cu ion pairs - Nitrate. When the pH increases the retention decreases because of the pairing of the complexes of metal hydroxides whose retention will be done with the steric and electrostatic exclusion [18].

The results obtained in the figure 6 show that whatever the allowed pressure and at pH=6.8 the iron retention is total and at the pressure equal to 6 bars and the pH=4.5. The retention of copper is 90% -100% for pH equal to 3.7, 4.5 and 5.5 and decreases when the pH increases to 6.8.

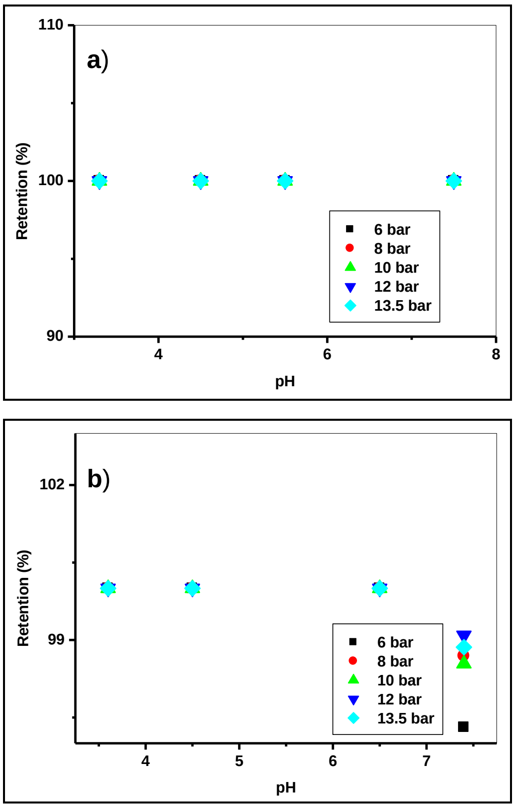


Figure 6. Influence of pH on Fe(III) (a) and Cu(II) (b) retention for mixture salt iron 60%-salt copper 40%.

The table 2 shows that the iron retention in the mixture salt iron 40%-salt copper 60%.was quantitative (100%) whatever the pressure and the pH. It also shows that the rejection of copper was quantitative for pH=3.7, 4.5 and 6.8.

Table 2.
Influence of pH on Fe(III) (a) and Cu(II) (b) retention for mixture salt iron 40%-salt copper 60%.

pH	**Pressure (bars)**	**Retention (%)**	
		Cu(II)	Fe(III)
3.7	6	100	100
	8	100	100
	10	100	100
	12	100	100
	13.5	100	100
4.5	6	100	100
	8	100	100
	10	100	100
	12	100	100
	13.5	100	100
5.8	6	89.2	100
	8	88.49	100
	10	88.53	100
	12	87.67	100
	13.5	87.78	100
6.8	6	100	100
	8	100	100
	10	100	100
	12	100	100
	13.5	100	100

Table 3 shows that the retention of iron was quantitative in the mixture salt iron 60% - salt copper 40% for pressure varied from 6 to 13.5 bars and whatever the pH. The retention of copper was also quantitative about pH equal 3.6, 4.5 and 6.5, and decrease about 97% at pH=7.4.

Table 3.
Influence of pH on Fe(III) (a) and Cu(II) (b) retention for mixture salt iron 60%-salt copper 40%.

pH	**Pressure (bars)**	**Retention (%)**	
		Cu(II)	**Fe(III)**
3.6	6	100	100
	8	100	100
	10	100	100
	12	100	100
	13.5	100	100
4.5	6	100	100
	8	100	100
	10	100	100
	12	100	100
	13.5	100	100
6.5	6	100	100
	8	100	100
	10	100	100
	12	100	100
	13.5	100	100
7.4	6	97.31	100
	8	98.69	100
	10	98.54	100
	12	99.09	100
	13.5	98.86-	100

3.3. Effect of concentration

The table 4 shows that iron retention was 100% at all pressures (6 bars -13.5 bars), for initial concentrations of 100 ppm and 300 ppm. These results are in agreement with those given in the literature. For the low concentrations (4 ppm) the extraction yield varied to 82% to 94% about 6 bars to 12 bars, after this pressure the retention decrease. It is noted for a concentration of 4 ppm of copper the pass from 92% to 94% for a variation of 6 bars to 10 bars. For the solution of 100 ppm the retention passes from 80% to 82% for a pressure varies from 6 bars to 13.5 bars. For the concentration of 300 ppm the retention varies from 82% to 84% for a pressure varies from 6 bars to 12 bars.

The decrease of retention with the increase of concentration was explained by the neutralization of the negative and by the polarization of concentration [8].

Table 4.
Influence of feed concentration on Fe(III) (a) and Cu(II) (b) retention.

Concentration (ppm)	**Pressure (bars)**	**Retention (%)**	
		Cu(II)	Fe(III)
4	6	91.92	81.88
	8	93.44	84.39
	10	94.07	90.39
	12	93.94	90.07
	13.5	91.85	93.14
100	6	80.34	99.95
	8	80.45	99.93
	10	81.17	99.91
	12	81.15	99.83
	13.5	82.06	99.94
300	6	81.92	99.98
	8	82.16	99.98
	10	83.16	99.99
	12	83.58	99.97
	13.5	83.23	99.97

Table 5.
Influence of feed concentration on Fe(III) (a) and Cu(II) (b) retention in mixtures.

Mixture (ppm)	**Pressure (bars)**	**Retention (%)**	
		Cu(II)	**Fe(III)**
Salt iron 50%-salt copper 50%	6	63.99	100
	8	75.54	100
	10	74.37	100
	12	74.96	100
	13.5	73.77	100
Salt iron 80%-salt copper 20%	6	73.28	100
	8	72.46	100
	10	73.09	100
	12	96.56	100
	13.5	97.72	100
Salt iron 60%-salt copper 40%	6	97.31	100
	8	98.69	100
	10	98.54	100
	12	99.09	100
	13.5	98.86	100
Salt iron 20%-salt copper 80%	6	95.09	100
	8	92.10	100
	10	90.96	100
	12	90.21	100
	13.5	89.53	100
Salt iron 40%-salt copper 60%	6	89.20	100
	8	88.49	100
	10	88.53	100
	12	87.67	100
	13.5	87.78	100

In table 5, iron retention was 100% total whatever the pressure and composition of the mixture, the best copper retention is obtained for the mixture salt iron 60%- salt copper 20% whatever the pressure, for the mixture salt iron 80% - salt copper 20% up to 10 bars the retention is constant (74%) then increases to 97%. The retention increases with the increase of pressure this confirming that the metal ions do not penetrate in the membrane pores. In this case the retention of the ions was carried out by steric effects and charge [19].

3.4. Study of conversion parameter

The conversion was calculated by equation 2:

$$Y = \frac{Q_P}{Q_F} \times 100 \qquad (3)$$

where
Q_P: the permeate flow rate
Q_F: the feed flow rate

Figure 7 illustrates the evolution of the retention as a function of the conversion during the nanofiltration of Fe(III) and Cu(II), from their mixture at different concentration .The results show that the retention of iron decrease with the increase of the initial concentration from the mixture of salt iron 20%- salt copper 80%, To the mixture of salt iron 50%- salt copper 50%, and stay constant for the other mixture, but it is not proportional to the conversion, the copper retention will follow the same phenomenon as iron.

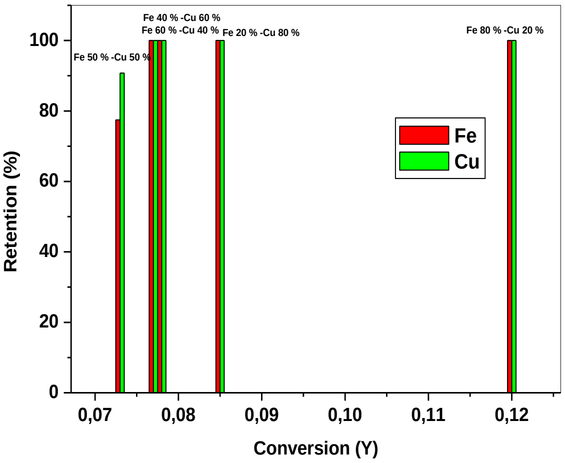


Figure 7. Evolution of Fe(III) and Cu(II) retention according to conversion P=12 bars, pH=3.5

4. Conclusion

In this study, we have tried to describe the performance of the NF270 polyamide membrane on the retention of iron, copper and their mixtures, Metal ion retention was 100% and 94% for iron and copper respectively, and in their mixture, it was 100% for both metals. The retention of ions by nanofiltration is done by Donnan effect (electrostatic repulsion) and counter-ion volume effect (steric exclusion).

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