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Analysis of membrane performance in Ni and Co removal from liquid wastes by means of micellar-enhanced ultrafiltration

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ABSTRACT

Heavy metal pollution of civil and industrial wastewaters represents a major problem for the environment since metal ions are non-biodegradable, have a very high toxicity, and some of them have proved to be carcinogenic. If directly discharged in sewers, metal ions may seriously damage the subsequent biological treatments in depuration plants and render treatment sludge not reusable for agriculture. On the contrary, water and sludge reuse should be a primary criterion when planning improvements for wastewater treatment plants and their adaptation to new standards. In this paper, the membrane performance (a monotubular ceramic membrane of molecular weight cutoff: 210 kDa) is investigated in the removal of nickel and cobalt ions from synthetic liquid wastes aimed at water reuse using a micellar-enhanced ultrafiltration process. The ultrafiltration membrane is used with adding an anionic surfactant (sodium dodecyl sulfate (SDS)) in a laboratory scale experimental device. The synthetic liquid waste contains metal ions in a concentration range 10–100 mg/L, and the SDS concentration was 1.15 mg/L, under the critical micellar concentration (CMC). The experiments have been carried out at a fixed temperature of 20˚C. The preliminary results show that very good percentage removals of these metal ions are achieved, even if the surfactant was below its CMC.

Keywords: Micellar-enhanced ultrafiltration (MEUF); Membranes; Surfactant; Wastewaters; Heavy metals; Nickel; Cobalt

1. Introduction

Water use and wastewater production are part of nearly every type of production process, including urban, industrial, and, of course, agricultural (EPA, 2012). As a result, it is no longer advisable to use water once and dispose of it; it is important to identify ways to reuse water. The need to protect available water resources and to optimize water management is contained in the legislation in force that establishes precise rules for the protection of waters from the

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pollution and for regulation of the discharges. Wastewater treatment is therefore a duty.

At present, all treated water except for a few cases of industrial reuse enters in surface or marine waters. An Italian Ministerial Decree about water reuse, D. Lgs 152/06 (art.112), establishes allowed uses for treated water, and it states technologies that produce water with physicochemical and microbiological characteristics for reuse at low cost. Moreover, wastewater treatment sludge can and should be reused. And, of course, it is a matter of public concern to create and develop new and advanced processes for the treatment of wastewater in order to safely reuse it [1–3]. In the field of wastewater treatment, a great step forward can be done by the reuse of industrial wastewaters, mainly for internal uses. A lot of industrial productions make use of a huge water quantity, thus producing a lot of wastewaters that have to be treated and, if they reach a sufficient level quality, reused. Liquid wastes produced as effluents by several industrial activities often contain metals ions, their nature and concentrations depending on the type of treated waste. As for example, the residual solutions from anaerobic digestion of several biomasses can contain metals as nickel and cobalt and other heavy and dangerous elements. Precipitation [4,5], ion exchange [6], and reverse osmosis [7] are frequently used for heavy metal removal. However, precipitation cannot remove metal ions completely and the cost of ion exchange resin and the low permeate flux of reverse osmosis are the problems. Ultrafiltration process combined with surfactant micelle (micellar-enhanced ultrafiltration, MEUF) is a reliable technique for efficient heavy metal removal. This research group has already applied with success this method for arsenic and lead removal from a real wastewater treatment plant effluent, aimed at water reuse [8,9]. However, since surfactants are expensive and non-biodegradable, the environmental hazard of them remained in effluent is a serious disadvantage of complexation-membrane separation methods and has to be faced.

Vibhandik and Marathe [10] studied the removal of Ni(II) ions from wastewater by micellar-enhanced ultrafiltration; the surfactant mixture was the nonionic surfactant Tween-80 (TW80) mixed with the anionic surfactant sodium dodecyl sulfate (SDS), and rejection of Ni and TW80 was 99 and 98%, respectively, whereas that for SDS was 65%. SDS and linear alkylbenzene sulfonate (LAS) were used in nickel removal by Samper et al. [11]; the effects of pH, conductivity, and surfactant concentration on the permeate flow, retention of surfactants and nickel by MEUF were studied. Results showed that for surfactant concentrations beyond the CMC, Ni(II) retention with SDS was slightly higher than with LAS ($S/M = 45$: Ni(II) retention was 70 and 55% for SDS and LAS, respectively). Cobalt and nickel removal was conducted by Akita et al. [12]; they used polyoxyethylenenonyl phenyl ether with 10 ethylene oxide units (PONPE10) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPNA) as a nonionic surfactant and an extractant, respectively. The selective rejection of Co(II) over Ni (II) can be attained; the separation was enhanced with increasing solution pH and the extractant concentration. On the other hand, it was found that SDS as a surfactant and di-2-ethylhexyl phosphoric acid (D2EHPA) as an extractant give no selectivity between these heavy metals in the same operation. Simultaneous removal of nickel and cobalt was also conducted by Karate et al. [13] by 20 kDa polysulfone membrane, and the rejection more than 99% was obtained; the presence of salt in the aqueous feed results in drop in rejection from 99 to 88%. Various researchers have demonstrated significant effect of pH on heavy metal removal. Juang et al. [14] reported that cationic heavy metals (Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, and Cr^{3+}) removal reached over 80% with SDS as the pH increased from 2 to 12. At the lower pH, lower heavy metal removal efficiency was due to the competition between H^+ ions and cationic metal ions to get adsorbed on the anionic micelle surface of SDS. Some review works explain the influence of operative parameters on MEUF processes [15,16]. In particular, Ghosh and Bhattacharya [17] explained that permeate flux reduced due to the formation of micelle aggregation layer (MAL) on the membrane surface. With a view of the permeation flux, CMC of SDS (8 mM) was the appropriate SDS concentration [18]. Permeate flux reduction was higher at the lower SDS concentration (<CMC) than higher SDS concentration (>CMC) due to the adsorption phenomenon and the interaction between ionic species and membrane with opposite charge. The size of micelle has an important role in the removal efficiency. Xu et al. [18] reported that at CMC of SDS, the micelle has normal size of 5.07 nm. Beyond the CMC value, the size of micelle decreases and shape of it also changes. Linear molecule passes through a membrane, whereas globular molecules of the same molecular weight may be retained [19]. CMC of surfactant can be affected by the changes in temperature, pH, presence of non-ionic surfactant, and inorganic salt.

In this paper, the membrane performance in the removal of nickel and cobalt ions from synthetic liquid wastes aimed at water reuse is carried out using a micellar-enhanced ultrafiltration (MEUF) process, in which a ultrafiltration (UF) membrane (a monotubular ceramic membrane of molecular weight cutoff:

210 kDa) is used with adding an anionic surfactant (SDS) in a laboratory scale experimental device. Experiments are carried out to evaluate the membrane resistances during the ultrafiltration process and to verify the influence of surfactant on the metal ion percentage removal.

2. Materials and methods

2.1. Apparatus description

Experimental studies have been carried out in a tangential flow Membralox® XLAB 3 (Exekia, Bazet, France) laboratory pilot plant with a single tube Membralox® Tl-70 ceramic ultrafiltration membrane (Fig. 1). The recirculation pump gives a fixed tangential velocity of about 7 m/s. All experiments were performed at room temperature; for the cleaning procedure, in which water was at 40˚C, temperature was controlled by the tank jacket connected to a Crioterm 10–80 thermostat. The plant is equipped with a backflush system BF3, controlled by an electrovalve (pressure 7 bar, reinjected volume 3 ml). Backflush was utilized only during membrane cleaning, with intervals and lengths regulated manually (frequency 2 min, length 1 s, approximately). The pore size of membrane used in experimental work was 20 nm (MWCO 210 kDa).

2.2. Feed water characteristics

Wastewater utilized in this study was a synthetic liquid solution. In detail, distilled water was produced by a D10-T distiller (Enrico Bruno Company), depending on the solution to be tested, cobalt, nickel, and then SDS as surfactant. As shown in Table 1, for each ultrafiltration procedure, a different solution was used:

(1) Only surfactant solution, under critical micellar concentration (CMC) for F1 test.
(2) Solution with 10 mg/l of cobalt in distilled water for F2 test.
(3) Solution with 10 mg/l of nickel in distilled water for F3 test.
(4) Solution with 10 mg/l of cobalt and SDS under CMC in distilled water for F4 test.
(5) Solution with 10 mg/l of nickel and SDS under CMC in distilled water for F5 test.

SDS of Merck Millipore was used as a surfactant (molecular mass 288.38 g/mol), cobalt(II) nitrate-hexahydrate (molecular mass 291.3 g/mol) (Acros Organics), and a nickel(II) sulfate-heptahydrate (molecular mass 280.86 g/mol) (Riedel-de Haen) were the metal salt used in the sample preparation. The CMC of SDS at 25˚C is 6 to 8mM, and for the

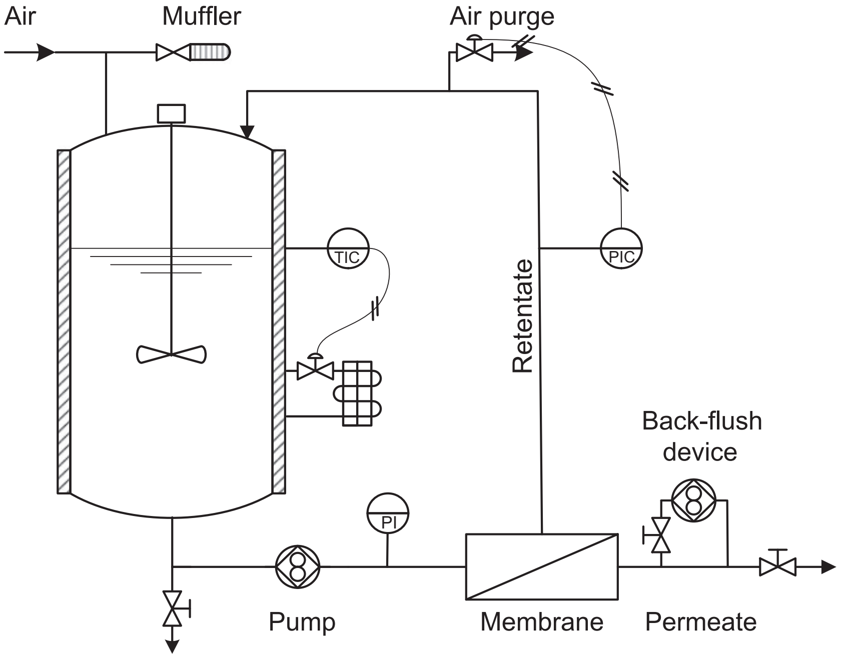

Fig. 1. Experimental plant (tubular ceramic membrane, 20 nm).

Table 1
Experimental plan (tubular ceramics membrane, 20 nm)

Test	Surfactant SDS (mg/l)	Co (mg/l)	Ni (mg/l)
F1	X1	–	–
F2	–	10	–
F3	–	–	10
F4	X1	10	–
F5	X1	–	10

calculations of the concentration of SDS under CMC, we considered 4 mM that corresponds to a concentration of 1.15 mg/L and 4.025 g of SDS for 3.5 L of solution. The concentration of 10 mg/L corresponds to 0.173 and 0.168 g for Ni and Co, respectively, for 3.5 L of solution.

2.3. Ultrafiltration procedure

Five ultrafiltration experiments have been carried out; a summary of this experimental plan is shown in Table 1.

The membrane was stored in 3% hydrogen peroxide solution to protect it during storage at low temperature (5°C) preventing microbial growth. Before each experiment, distilled water flux was measured for different values (0.8, 1.3, 1.8, 2.3, 2.8 bar) of transmembrane pressure to control if membrane was clean. After this measurement, feed tank was filled with 3 L of wastewater solution and TMP is adjusted at the first point of 0.8 bar with permeate and retentate valves closed; the apparatus is pressurized by nitrogen, so it was not possible to work in a continuous way. After 10 min, permeate valve was open and flux is checked manually. After this, valve was closed and system is pressurized to the second TMP value and so on until the last value of 2.8 bar, when 1 L of permeate is withdrawn for the analyses. After the feed tank was empty, 3 L of distilled water was put inside to estimate flux decline. After each experiment, equipment and membrane were washed with alkaline detergents (P3-Ultrasil 25) and rinsed with distilled water until pH returned to the value of about 7. Chemical cleaning was necessary in order to get outlet fluxes similar to those obtained with distilled water; the cleaning procedure is described in Table 2.

3. Results and discussion

3.1. Flux decay experiments

Fig. 2 reports the flux pattern at various transmembrane pressures for the cobalt test without surfactant.

The analysis of the figure shows that for each tested pressure, there was a higher flux for the clean membrane, followed by the dirty membrane and finally by the cobalt solution; this is a logical consequence of different fouling of the membrane. However, the profiles of the flux for dirty membrane and cobalt solution appear nearly overlapped.

Fig. 3 reports the flux pattern at various transmembrane pressures, for the cobalt test with SDS under CMC.

In this case, a net difference between the test with dirty membrane-distilled water and the solution of cobalt and SDS is observed. The difference is probably due to the different fouling of the membrane that was previously dirtied in the cobalt-SDS test.

Fig. 4 reports the flux pattern at various transmembrane pressures for the nickel test without surfactant.

Also in this case like in Fig. 2, it is possible noting that for each pressure, we had a higher flux for the clean membrane followed by dirty membrane and finally the solution with nickel; this is a logical consequence of different fouling of the membrane.

Fig. 5 reports the flux pattern at various transmembrane pressures, for the nickel test with SDS under CMC.

Also in this case, we observed a net difference between the test with dirty membrane-distilled water and the solution of nickel and SDS. The difference is probably due to the different fouling of the membrane, which was previously dirtied in the nickel-SDS test.

Fig. 6 reports the compared flux at various transmembrane pressures, for the tests with cobalt (F2), cobalt together with the surfactant (F4), nickel (F3), and nickel together with the surfactant (F5).

The histogram shows the difference of flows between the tests with and without the use of surfactant. The major flows can be noticed in the F2 and F3 tests, because the solution was less fouled than the F4 and F5 tests.

3.2. Membrane resistances

Starting from the curves of permeability, it is possible to obtain the values of the resistances opposed from the membrane to the mass transfer, calculated as reciprocal permeability. The permeability is the slope "m" of the curve of permeability, therefore R is:

$$R = \frac{1}{m} \tag{1}$$

where R is expressed in $\left(\frac{\mathrm{m}^2 \cdot \mathrm{h} \cdot \mathrm{bar}}{\mathrm{l}}\right)$

Table 2
Cleaning procedure

Cleaning solution	Concentration	Backflush	PT (bar)	Time (min)	Permeate valve	Temperature (℃)
P3-Ultrasil 25	2%	Yes	1.3	30 + 30	Close/open	Room
Distilled Water	–	Yes	1.8	30	Open	50
Distilled Water	–	Yes	1.8	30	Open	50

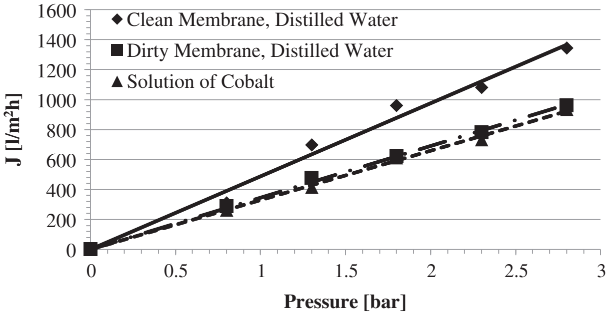

Fig. 2. Permeability curve of F2 test.

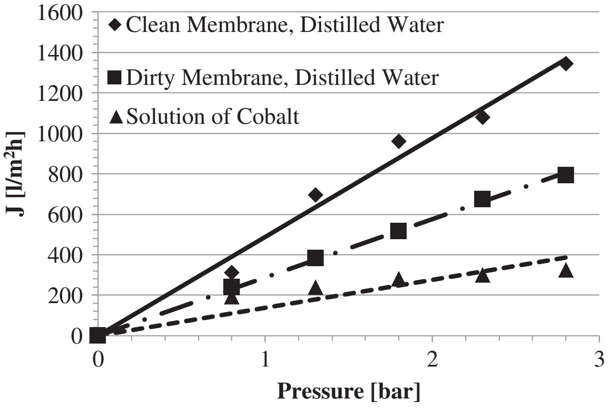

Fig. 3. Permeability curve of F4 test.

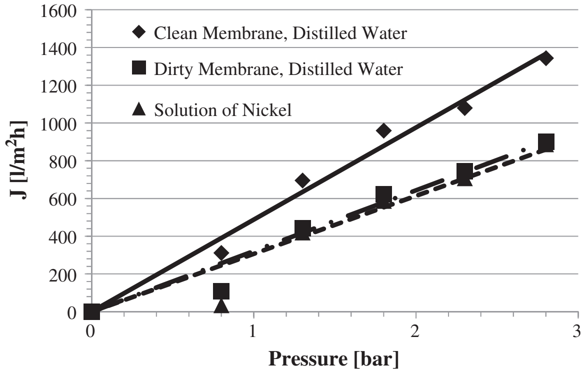

Fig. 4. Permeability curve of F3 test.

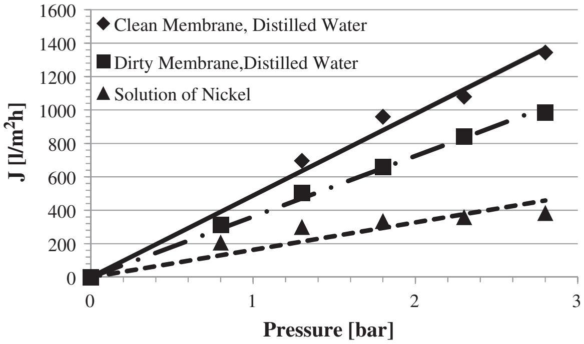

Fig. 5. Permeability curve of F5 test.

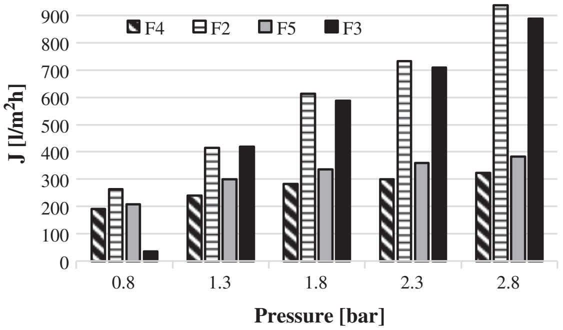

Fig. 6. Compared flows of F2, F4 tests and F3, F5 tests.

For example, considering the curves of permeability obtained in the F4 test and reported in Fig. 7, according to the model of the series resistances, the total resistance of the membrane to mass transfer can be considered as composed of three terms:

$$R_{\text{tot}} = R_{\text{m}} + R_{\text{f}} + R_{\text{p}} \tag{2}$$

where R_{tot} is the total resistance; R_{m} is the membrane resistance; R_{f} is the resistance of fouling; R_{p} is the resistance of concentration polarization.

In the test with distilled water, R_{m} is the only resistance and it can be calculated using the Eq. (3):

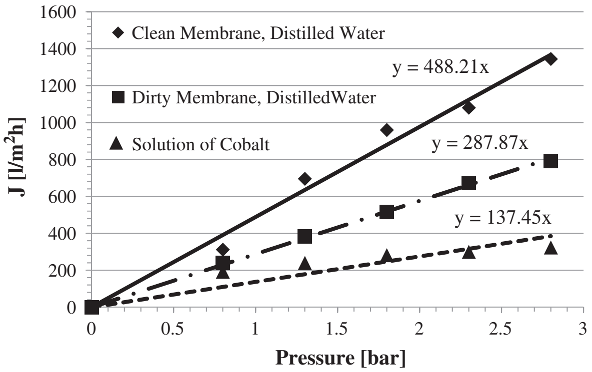

Fig. 7. Slope values for permeability curves in F4 test.

$$R_m = \frac{1}{m_W} \tag{3}$$

where m_W represents the slope of the straight line obtained in the test with distilled water and clean membrane. Referring to Fig. 7, m_W is equal to 488.21 $\left(\frac{1}{m^2 \cdot h \cdot bar}\right)$ and is thus $R_m = 0.002$ $\left(\frac{m^2 \cdot h \cdot bar}{1}\right)$.

By the straight line relating dirty membrane and distilled water, however, it is possible to calculate the resistance R_I equal to the sum of R_m and R_f.

$$R_I = R_m + R_f \tag{4}$$

As a matter of fact, during the test performed with distilled water and with using dirty membrane, the resistance due to the concentration polarization, while is that due to fouling, is lacking. If m_W^d is the slope of the relative membrane dirty and distilled water, R_I is calculated using the following equation:

$$R_I = \frac{1}{m_W^d} \tag{5}$$

According to the data of Fig. 7, m_W^d and R_I are equal to 287.87 $\left(\frac{1}{m^2 \cdot h \cdot bar}\right)$ and 0.0035 $\left(\frac{m^2 \cdot h \cdot bar}{1}\right)$, respectively.

Finally, the slope of the line relative to the solution, referred to as m_{SOL}, is the inverse of the resistance R_{tot}:

$$R_m = \frac{1}{m_{SOL}} \tag{6}$$

Referring to Fig. 7, m_{SOL} is 137.45 $\left(\frac{1}{m^2 \cdot h \cdot bar}\right)$ and R_t is 0.0073 $\left(\frac{m^2 \cdot h \cdot bar}{1}\right)$.

The values of the resistances due to the fouling and to the concentration of polarization, respectively, can be calculated as follows:

$$R_f = R_I - R_m \tag{7}$$

$$R_p = R_{tot} - R_I \tag{8}$$

Table 3 and Fig. 8 summarize the values of the resistances.

It is possible to note that the values of R_m are the same for each test being the membrane equal for all. The values of R_{tot} in F2 and F3 tests are similar but this value is slightly higher for the F3 test.

In the presence of SDS with a concentration less than CMC (F4 and F5 tests), the total resistances are higher with respect to other experiments; this is a consequence of the ability of micelles to retain the cobalt and nickel ions, as already demonstrated by the rejection yields (Table 4).

3.3. Metal removal

Fig. 9 shows the concentration profile of cobalt as a function of time in the permeate as for test F4 (Co + SDS), it can be possible to observe that there is a decrease in metal ions' concentration of about 50% with respect to its initial value; a similar behavior was obtained also for nickel. Therefore, the removal of cobalt and nickel with the use of surfactant is reliable even if the surfactant is below its CMC, and it grows with the time or rather with the pressure increment.

Table 4 summarizes the rejection percentages for the metals in the absence and in the presence of SDS, showing that in the absence of surfactant, as expected, ultrafiltration is not able to retain metal ions (rejections less than 4%), while in the presence of surfactant even at a concentration below CMC, satisfactory rejections up to 53% are obtained.

Table 3
Calculated resistances $\left(\frac{m^2 \cdot h \cdot bar}{1}\right)$ during MEUF process

	Test			
	F2	F3	F4	F5
R_m	0.002	0.002	0.002	0.002
R_{tot}	0.003	0.00325	0.0073	0.0061
R_I	0.0029	0.0031	0.0035	0.0027
R_f	0.0009	0.0011	0.0015	0.0007
R_p	0.0001	0.00015	0.0038	0.0034

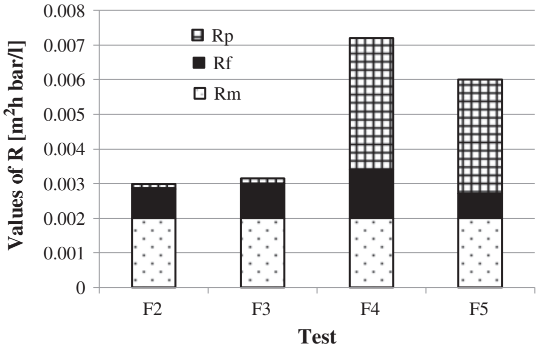

Fig. 8. Membrane resistances in cobalt and nickel ultrafiltration test.

Table 4
Rejection coefficients for metal removal

Metal	Percentage rejections (%)	
	Without SDS	With SDS
Cobalt	0.15	53
Nickel	3.93	51

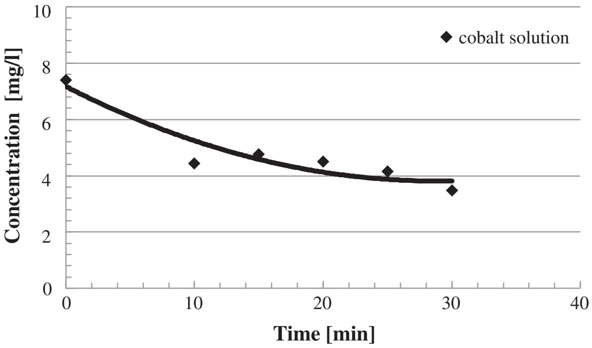

Fig. 9. Trend of Co concentrations in F4 test.

4. Conclusions

In this paper, the removal of Co and Ni ions from industrial wastewaters by surfactant-enhanced ultrafiltration has been investigated. The experimental results have shown that with the use of surfactant (SDS), a rejection percentage of 53% for Co and 51% for Ni was obtained, much higher with respect to the metal removal obtained without SDS. Moreover, all resistances to mass transfer have been calculated, showing that in the presence of SDS with a concentration less than CMC, the total resistances are higher, being is a consequence of the ability of micelles to retain the cobalt and nickel ions, thus confirming the rejections yields.

The future work will be aimed at using surfactant over CMC to recover the metals at a higher extent; the use of higher surfactant concentration will make mandatory the individuation of a reliable process for the surfactant recovery, as, for example, by means of a precipitation process. This will render more affordable costs of the whole process.

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