Removal of heavy metals by tight γ-Al$_2$O$_3$ ultrafiltration membrane at low pressure

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ABSTRACT

The removal of chromate (Cr(VI)) and copper (Cu(II)) from water was investigated by using ultrafiltration (UF) as a possible alternative to the conventional methods of metal ions removal. The influence of experimental parameters such as pH, pressure and concentration was investigated on different solutions (K$_2$Cr$_2$O$_7$, CuSO$_4$ and Cu(NO$_3$)$_2$). The influence of salts' presence (NaNO$_3$ and Na$_2$SO$_4$), with different concentrations, on metal removal was studied. The rejection of Cr(VI) was found to be improved with the increase of pH (with high rejection of 97% at pH above 9), whereas for Cu(II) the best rejections were obtained at 2.60 (with high rejections of 80% and 50%, for Cu(NO$_3$)$_2$ and CuSO$_4$). The increase of the applied pressure causes an increase of metals' rejections and fluxes. Furthermore, an insignificant polarization concentration phenomenon was observed. The Cr(VI) rejection was observed to be independent from the increase in concentration (>90% for all concentrations, ranging from 10 to 150 mg (Cr(VI))/L) and a decrease in rejection with increasing concentration was observed for copper salts. The permeate flux was found to be lower at higher feed concentration, but varied only marginally with change in pH value. The metals' retentions depend strongly on the solute type (including charge valency and hydration energy). The γ-Al$_2$O$_3$ UF was found to be an efficient process to remove/recover heavy metals from industrial discharges.

Keywords: Chromium; Copper; Heavy metal contamination; γ-Al$_2$O$_3$; Ultrafiltration; Metalworking industries

1. Introduction

Water is the bloodstream of the biosphere and it is equally fundamental for humans and ecosystems. Consequently, the evolution of an economy is strongly dependent on our future patterns of water use. This evolution of economy has major (direct and indirect) implications on water [1]. According to Calzadilla et al. [2], nearly one in three people live in areas of moderate to high water stress and it is estimated that two-thirds of population could be living under water-stressed conditions by 2025 [3]. The increase of water problem with wastewaters primarily entails with the continuous development of the different industrial sectors [4,5]. The process wastes from industries such as ceramics, plating, glass, battery manufacturing and mining are considered as the primary sources of groundwater contamination by heavy metals [6,7]. In fact, metal can be classified as a heavy metal when it is toxic at low concentrations and has a high density that is five times bigger than that of water [8,9]. Unlike organic pollutants, heavy metals are persistent contaminants, not biodegradable, with high solubility, high toxicity, and have the ability to accumulate in living organisms. In fact, the toxicity caused by heavy metal contamination is strongly dependent on the chemical form of the metal in question. Out of the existing heavy metals, Cr and its derivatives are used in a wide variety of industrial

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and manufacturing applications due its several beneficial features. As an active element of reduction–oxidation process, Cr can be discharged both in the form of cations chromium III (Cr(III)) and anions of hexavalent chromium (Cr(VI)) [10,11]. According to Fendorf [12] the presence of manganese facilitates the quick oxidation of Cr(III) ions to Cr(VI) ions. The intensity and seriousness of Cr(VI) effects lay on the possibility of causing hemorrhagic diathesis, gastrointestinal disorders, convulsions and even death after a cardiovascular shock [9,13]. Therefore, it was critical to set limits for effluents containing Cr before there are definitively disposed. According to the Moroccan official bulletin (NM 03.7.001) [14], the Russian federation, the Canadian drinking water quality guidelines and the World Health Organization (WHO), the maximum allowable limits for Cr in drinking and domestic water are 0.05 and 0.5 mg/L for Cr(VI) and Cr(III), respectively [15,16]. Whereas the European Union (EU) standards imply 0.5–5 mg/L and 0.1–0.5 mg/L for Cr(III) and Cr(VI), respectively [17,18]. Beside Cr, Cu is also found at high concentration in wastewater. It is commonly used in industries of metal finishing, electroplating, plastic and metal etching due to its good characteristic in terms of malleability, ductility and heat/electric conductivity [8,19]. The Cu is a transitional metal and occurs in four oxidation states [20]. Moreover, Cu is a very toxic metal even at low concentration for both human and environment. This toxicity is mainly due to Cu's catalytic role and also its capacity to accumulate in plants and animals [21]. Cu exposure (at concentrations above 1.3 mg/L) for short period of time causes stomach and intestinal problems. Whereas longer exposure leads to kidney and liver damage (known as Wilson's disease) [22,23]. Therefore, it is necessary to monitor its concentration in the biosphere. The permissible limit of Cu ions in water, for human consumption, was reported by the WHO to be 2.0 mg/L [24,25], and the same goes for the Moroccan regulation (NM 03.7.001). Whereas, the permissible limit in industrial effluents was reported by the USEPA to be 1.3 mg/L [8]. Thus, the need to develop efficient, cheap and environmentally friendly methods for removing metal pollutants has been the focus of many researches. In fact, several methods have been reported for Cr and Cu removal. The most widely used techniques are adsorption by a variety of natural and synthetic materials, ion exchange resin, chemical precipitation, electrochemical deposition and membrane filtration [26–29]. As an example, the use of alkyl-substituted polyaniline/chitosan (sPANIs/Ch-HCl) composite as adsorbent for Cr(VI) removal was studied by Yavuz et al. [30] and demonstrated 90% of rejection. Whereas Chowdhury et al. [31] studied the rejection of Cr through adsorption–desorption process using polyaniline nanoparticles grafted silanized silica gel. The separation of Cr(VI) by redox reaction with amino/imino groups on poly(m-phenylenediamine)/palygorskite (PmPD–PG) was also examined by Xie et al. [32]. However, these conventional treatment methods are very labor-intensive because of the different operations that must be performed periodically, such as analytical and cleaning tests. Membrane filtration has received considerable attention for the treatment of inorganic contaminants and offers a cost-effective option for the separation of heavy metal. Depending on the pore size, membranes could be

classified to microfiltration, ultrafiltration (UF), nanofiltration (NF) and reverse osmosis. Furthermore, based on material's type, membranes are divided into two basic categories: (i) organic membranes (or polymeric membrane) and (ii) inorganic membranes (referred to as ceramic or mineral membranes). Currently, polymeric membranes are the most commercially used. The use of polymer composite membrane (Nanomax 50) through an NF process has been studied for direct Cr(III) removal [33]. Tanninen et al. [34] investigated the rejection of Cu from acidic solution at high pressure (20–40 bar) by various polymeric NF membranes (e.g., NF270, Desal-5 DK). However, the disadvantages of polymeric membranes over ceramic membranes, such as low permeability, high operating and maintenance cost, low mechanical and thermal resistance as well as high fouling; have been confirmed and make ceramic membranes a promising alternative [35]. Charged ceramic membranes, especially UF, are growing popularly in pollutants removal due to their capacity for electrostatic interactions. The application of zeolite UF membranes into trivalent cation removal (88% and 83% for Fe^{3+} and Al^{3+}, respectively) was confirmed [36]. Pugazhenthi et al. [37] investigated the modified UF charged carbon membrane with a support of macroporous clay, which showed ≥90% rejection of Cr ions. Additionally, complexation of UF to technologies based on precipitation and ion exchange proves to be a promising alternative. However, the potential use of ceramic UF membranes as single-treatment step for heavy metal removal has not been fully realized and still requires improvement in terms of selectivity and antifouling properties especially for the several Moroccan estuaries and watercourses that are contaminated by metallic cations [21,38–41]. Indeed, the efficiency of a UF membrane over another depends on membrane's material, operating parameters (pH solution, ionic composition and solute concentration), economic parameters and the environmental impact. The main target of this work is to evaluate the performance of gamma alumina UF (γ-Al_2O_3 UF) membrane in reducing heavy metals (Cr(VI) and Cu(II)) in different metal solutions. The investigation was focused on obtaining permeates with lower metal concentrations, high permeability, and low fouling and/or concentration polarization. The influence of different operating conditions as feed solution pH, applied pressure, feed concentration and effect of co-counter ions was investigated. The membrane selectivity was studied using a real wastewater containing metallic ions. Eventually, the present experiments allow identifying the operating conditions in which γ-Al_2O_3 UF assure an excellent performance and can be applied on an industrial scale.

2. Materials and methods

2.1. Studied membrane

Ceramic Al_2O_3 membrane, manufactured by Pall Corporation (Port Washington, New York), was selected as the UF membrane model. The membrane was supplied in tubular form and mounted in tangential module. The membrane characteristics are reported in Table 1.

The active layer of UF is a thin homogeneous γ-Al_2O_3 layer on the inner surface of a tubular α-Al_2O_3 microfiltration

Table 1
Characteristics of the used γ-Al$_2$O$_3$ UF membrane

Parameters	Values
Length	150 mm
Inner diameter	7 mm
Outer diameter	10 mm
Pore diameter	5 nm
pH$_{pzc}$	8–9 [51]
Surface charge	Amphoteric behavior
Surface area cm^2	24.5
ΔP Max (bar)	100
pH range	1–14

(α-Al$_2$O$_3$ MF) support (the UF morphological examination was investigated and presented in our previous paper, [42] as shown in Fig. 1). The isoelectric point (IEP) (8–9) and implicitly the surface charge of γ-Al$_2$O$_3$ UF have been previously noted by many researchers [42].

2.2. Chemicals

The salts of heavy metals used to evaluate the membrane performance are potassium dichromate K$_2$Cr$_2$O$_7$, copper sulfate (CuSO$_4$) and copper nitrate (Cu(NO$_3$)$_2$)·K$_2$Cr$_2$O$_7$ (99.8% purity) was used as a source of Cr(VI), whereas CuSO$_4$ (98.5% purity) and Cu(NO$_3$)$_2$ (99% purity) were used as source of Cu(II). All soluble salts and reagents utilized in experiments were of analytical grade and purchased from Sigma–Aldrich (Darmstadt, Germany). Furthermore, these solutions were prepared with fresh pure water (ultrapure water type I produced by PURELAB Ultra, ELGA (High Wycombe, United Kingdom), with resistivity of 18.2 MΩ-cm).

2.3. UF pilot

The experiments were carried out using tangential filtration pilot (as in Fig. 2). For each experiment, a feed volume of 3 L (to avoid concentration of solution) was filled into the tank setup. This latter is equipped with a cooling system to keep the feed solution temperature at constant value of 20°C. The system was operated by applying a pressure (ΔP) from 2 to 6 bar.

UF experiments were run for 90 min and an overall of six permeate samples were collected and analyzed. The operating time required for the membrane system to reach steady state was about 40–50 min. The concentrates' samples were also collected and analyzed at the end of each experiment. In addition, the experiments were started after a thorough washing and rinsing of the membrane (with pure water during 1 h), thereby eliminating impurities and maintaining the membrane initial performance.

Performances of the γ-Al$_2$O$_3$ UF membrane was characterized by three important parameters which are the permeate flux J_p (L/h m^2), observed rejection rate R_{obs} (%) and the real rejection rate (or intrinsic rejection) R_{int}, that are, respectively, defined by Eqs. (1)–(3).

The J_p was determined by measuring the volume of permeate collected in a given time interval.

$$J_p = \frac{V}{A \times t} \quad (1)$$

where V (L) is the volume of permeate collected during a time interval t (h) and A (m^2) is the effective membrane area. On the other hand, the observed salt rejection (R_{obs}) was determined according to the following expression:

$$R_{obs} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where C_p and C_f are the concentrations in the permeate and feed, respectively. Yet, this definition of R_{obs} is not accurate when concentration polarization is present. Indeed, polarization leads to higher solute concentration at the membrane surface (C_m), than the feed concentration C_f. It has been confirmed that in the presence of concentration polarization, the real rejection (or intrinsic rejection (R_{int})) of solute is always higher than observed rejection [43,44] and defined as in Eq. (3):

$$R_{int} = \left(1 - \frac{C_p}{C_m}\right) \times 100 \quad (3)$$

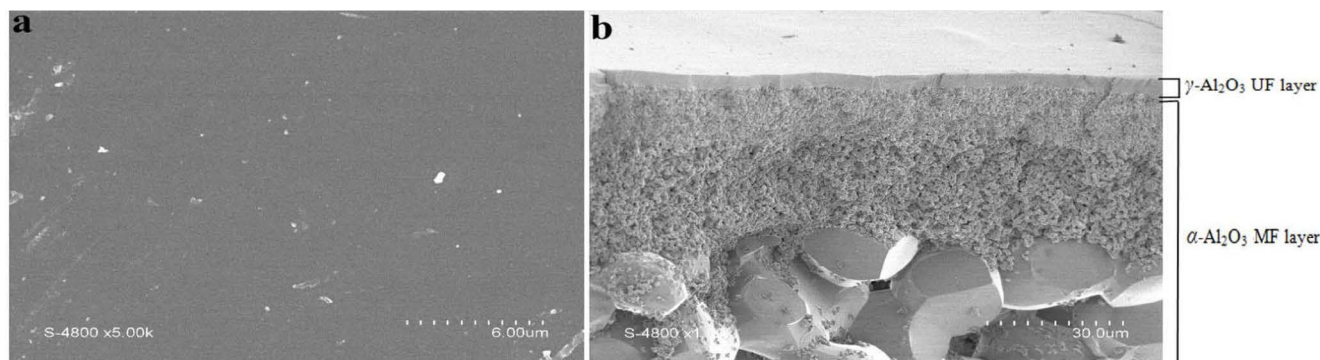According to the film theory, the relation between R_{obs} rate and R_{int} may be expressed as in Eq. (4):

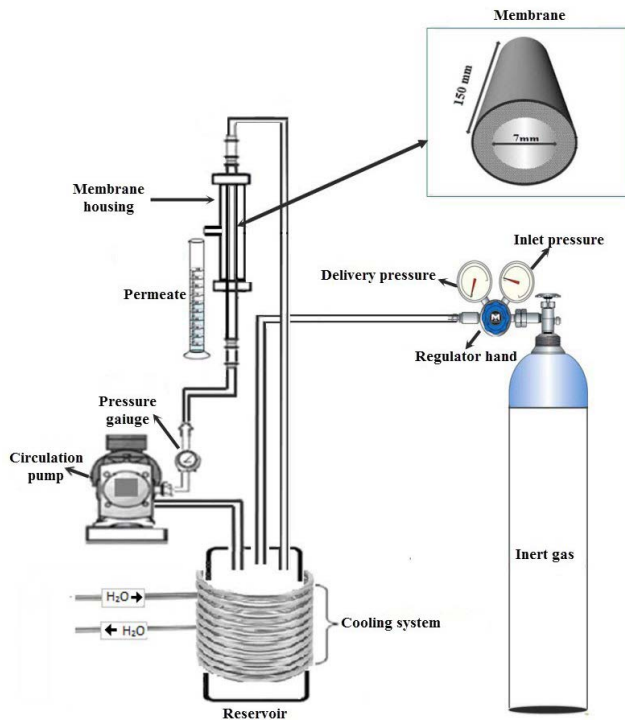Fig. 1. SEM of γ-Al$_2$O$_3$ membrane: (a) top surface and (b) cross-section [42].

Fig. 2. UF pilot.

$$\ln\left(\frac{1-R_{\mathrm{obs}}}{R_{\mathrm{obs}}}\right) = \ln\left(\frac{1-R_{\mathrm{int}}}{R_{\mathrm{int}}}\right) + \frac{J_p}{K} \qquad (4)$$

where K is the mass transfer coefficient in the polarized boundary layer. Hence, the real rejection may be determined from the experimentally observed rejection by plotting $\ln[(1 − R_{\mathrm{obs}})/R_{\mathrm{obs}}]$ against J_V.

2.4. Analytical methods

The concentrations of Cr(VI) in the feed solution, permeate and retentate samples were determined by the standard colorimetric method with 1,5-diphenylcarbazide (international standard, ISO 11083) [45]. In this method, 1,5-diphenylcarbazide was added to the samples containing Cr(VI) to reach a reddish purple color and then the amount of absorbance was measured at a visible wavelength of 540 nm via V-730 UV-visible/NIR spectrophotometer (JASCO, Tokyo, Japan). Cr(VI) calibration curve was linear over the concentration range of 0.025–0.25 mg/L with regression coefficients superior to 0.999. A quantitative analysis of Cu was performed by complex-metric titration. The complexing agent was ethylenediaminetetraacetic acid (EDTA) in the form of its disodium dehydrate salt ($Na_2C_{10}H_{18}N_2O_{10}$), and the indicator used for the titration is called murexide ($C_8H_8N_6O_6$) (ISO 6059 and Standard methods for water 18th edition 2.36 2340C [46]).

NO_3^- concentration in samples was calorimetrically analyzed before and after filtration, by means of V-730 UV-visible/NIR spectrophotometer (JASCO, Tokyo, Japan) at wavelength of 415 nm, according to the international organization for standardization (ISO 78903 [47]). The method has a limit of detection of 0.013 mg/L. The concentrations of sodium (Na^+) were analyzed by flame photometer model PFP7 with limit of detection of 0.2 mg/L.

The sulfate (SO_4^{2-}) ions in solutions were detected with titration by precipitation using barium chloride ($BaCl_2$) solution. A white precipitate of barium sulfate forms if sulfate ions are present. SO_4^{2-} calibration curve was linear over the concentration range of 3–30 mg/L with regression coefficients superior to 0.995 (standard deviation of 0.11689). The pH of solution was measured by pH meter-Seven compact (Mettler Toledo GmbH, Analytical, Giessen, Germany), with accuracy of ±0.05.

The real water characterization was analyzed via ICP-AES (ICP-AES, model iCAP 6300 series thermo, spectrometer echelle type 52.91, the samples were subjected to the action of aqua regia (mixture of HCl and HNO_3) by microwaves according to a defined program and the analysis of all the elements is made by standards of 1,000 mg/L obtained from Sigma-Aldrich, Darmstadt, Germany).

2.5. Operating procedure

Performances of a UF module depend not only on physico-chemical conditions of solution but also on operating parameters, themselves under the dependence of experiment. The effects of different parameters on the removal of Cu(II) and Cr(VI) were studied; the parameters investigated included pH of feed solutions, applied pressure ΔP, metals' concentration and the presence of different salts in feed solutions. Only one parameter was changed at a time, whereas others were maintained constant. Furthermore, six samples were taken for every set of run with the desired feed solution (stabilization time required for each run was about 45 min). The experimental procedure for each parameter studied is given below.

2.5.1. Effect of pH of solution on Cu(II) and Cr(VI) removal

In order to determine the effect of pH on metal ions' retention and flux, the experiments were performed with a fixed metal concentration of 50 mg/L, time = 75 min, transmembrane pressure of 6 bar at different pH solutions. The tests were performed at room temperature (20°C ± 2°C). The effect of the feed pH on Cr(VI) was studied in the pH range 2.63–11.44. With regards to Cu(II) (from the two salts $CuSO_4$, $Cu(NO_3)_2$), the study of pH effect was made in the range of 2.68–5.69. The desired pH of the feed was adjusted using either NaOH (1.0 N) or HCl (1.0 N). It should be mentioned that the best result out of the experiment was applied for the other effects. Furthermore, between each experiment the membrane was rinsed and cleaned with pure water under an applied pressure of 4 bar.

2.5.2. Effect of applied pressure on Cu(II) and Cr(VI) removal

The effect of the applied pressure on metal ion removal, as well as the influence of the associated cation/anion was investigated. The experimental conditions for this study were an initial concentration of 50 mg/L (for both Cr(VI) and Cu(II)), time = 75 min, temperature (T) = 20°C and pH around 10.46–10.56 and pH 2.8–3.2, respectively, for Cr(VI) and Cu(II).

2.5.3. Effect of metal concentration in the feed on metal removal

The effect of metal concentration was investigated by varying the Cr(VI) and Cu(II) amount independently in feed solutions, in the range of 10–150 mg/L at a fixed pressure of 6 bar, time = 75 min, *T* = 20°C, fixed pH (between 10.46 and 10.56) for Cr(VI) and pH around 3 for Cu(II).

2.5.4. Effect of salt presence on Cu(II) and Cr(VI) removal

To study the effect of salt presence in the feed solutions on metal removal, the experiments were carried out by adding different salts to Cr(VI) and Cu(II) solutions. The effect of the anions on Cr(VI) removal was studied by mixing a known amount of Cr(VI) with defined concentrations of SO_4^{2-} from Na_2SO_4 salt, or a well-known concentrations of NO_3^- from $NaNO_3$ salt. Furthermore, a mixture of the three salts ($K_2Cr_2O_7$ + Na_2SO_4 + $NaNO_3$) was investigated. For all Cr(VI) experiments, the pH was fixed around 10.66–10.68, ΔP = 6 bar, time = 75 min and *T* of 20°C. In a similar procedure, the effect of anion was investigated for Cu(II) removal by mixing the two salts together ($CuSO_4$ + $Cu(NO_3)_2$) at pH between 2.83 and 2.90 and pressure of 6 bar. The variation of salt portion was studied, the detail of the experiments is explained in Table 2. The cations concentrations were measured.

2.5.5. Membrane performance in treating real metallic wastewater

The separation properties of the membrane were finally determined by testing it with real wastewater from sheet metal and metalwork industry. The metallic wastewater was previously treated by passing it through a glass fiber (GF/C) filter paper of pore size 0.45 μm before experiments were conducted. The characteristics of the wastewater as well as the filtering results are presented in section 3.4.

Table 2
Variation of salt portion in the tertiary, quaternary and quinary metals' solutions

$K_2Cr_2O_7$ + $NaNO_3$ at pH 10.66–10.68			
[Cr(VI)] from $K_2Cr_2O_7$ salt %	25	50	75
[NO_3^-] from $NaNO_3$ salt %	75	50	25
$K_2Cr_2O_7$ + Na_2SO_4 at pH 10.66–10.68			
[Cr(VI)] from $K_2Cr_2O_7$ salt %	25	50	75
[SO_4^{2-}] from Na_2SO_4 salt %	75	50	25
$Cu(NO_3)_2$ + $CuSO_4$ at pH 2.83–2.90			
[NO_3^-] from $Cu(NO_3)_2$ salt %	25	50	75
[SO_4^{2-}] from $CuSO_4$ salt %	75	50	25
$K_2Cr_2O_7$ + $NaNO_3$ + Na_2SO_4 at pH 10.60			
[Cr(VI)] from $K_2Cr_2O_7$ salt %	50		
[NO_3^-] from $NaNO_3$ salt %	25		
[SO_4^{2-}] from Na_2SO_4 salt %	25		

The filtration was done at a natural pH ≈ 8.34, ΔP = 6 bar for time = 60 min.

2.5.6. Antifouling performance

The antifouling behavior of γ-Al_2O_3 UF membrane was determined according to the procedure described by Ahmad et al. [48]. In this study, solution of Cr(VI) salt with concentration equal to 150 ppm (which represents the highest concentration used in our experiments), pressure of 3 bar, natural pH ≈ 4.89 and duration of 90 min of filtration were applied to measure the permeate flux (J_p). Prior to the measurement of J_p of Cr(VI), the pure water flux (J_{w1}) was measured at ΔP of 3 bar, time = 90 min and natural pH. Furthermore, after the filtration of Cr(VI) solution, the membrane was washed with distilled water for 10 min and a second measure of pure water flux was conducted (J_{w2}) under the same condition as J_{w1}. The flux recovery ratio (FRR), total flux decline ratio (TFR), reversible flux decline ratio (RFR) and irreversible flux decline ratio (IFR), which are the parameters determining the membrane antifouling behavior, were identified using the following equations:

$$\text{FRR}\left(\%\right) = \frac{J_{w2}}{J_{w1}} \times 100 \tag{5}$$

$$\text{TFR}\left(\%\right) = \left(1 - \frac{J_p}{J_{w1}}\right) \times 100 \tag{6}$$

$$\text{REF}\left(\%\right) = \left(\frac{J_{w2} - J_p}{J_{w1}}\right) \times 100 \tag{7}$$

$$\text{IFR}\left(\%\right) = \left(\frac{J_{w1} - J_{w2}}{J_{w1}}\right) \times 100 \tag{8}$$

3. Result and discussion

3.1. Effects of solution pH on metal removal and flux

It has been acknowledged that two important factors affect the performance of a membrane, which are, the speciation of the chemical species in the feed solutions and the physical nature of the membrane surface (either its charge or its pore size) [49,50]. The pH has a remarkable influence on the process of removing metallic ions in aqueous solutions, as it has the capacity to change the membrane surface charge and the nature of the ionic metallic species [16,28]. Fig. 3 demonstrates the effect of pH values on the removal efficiency of Cr(VI) and Cu(II) as well as the variation of salt permeate flux.

From Fig. 3a it appears that until pH 7, the Cr(VI) rejection was found to decrease constantly (rejection rate of 6%), which then increased after a point was attained (around 8 with a rate rejection of 20%). Beyond pH 9, the rejection reached a plateau around 97%. This result is in conformity with the evolution of speciation of Cr(VI) with the pH [51–53]. In fact, the speciation profiles (as in Fig. 4) are a major factor to understand and interpret the reactivity of
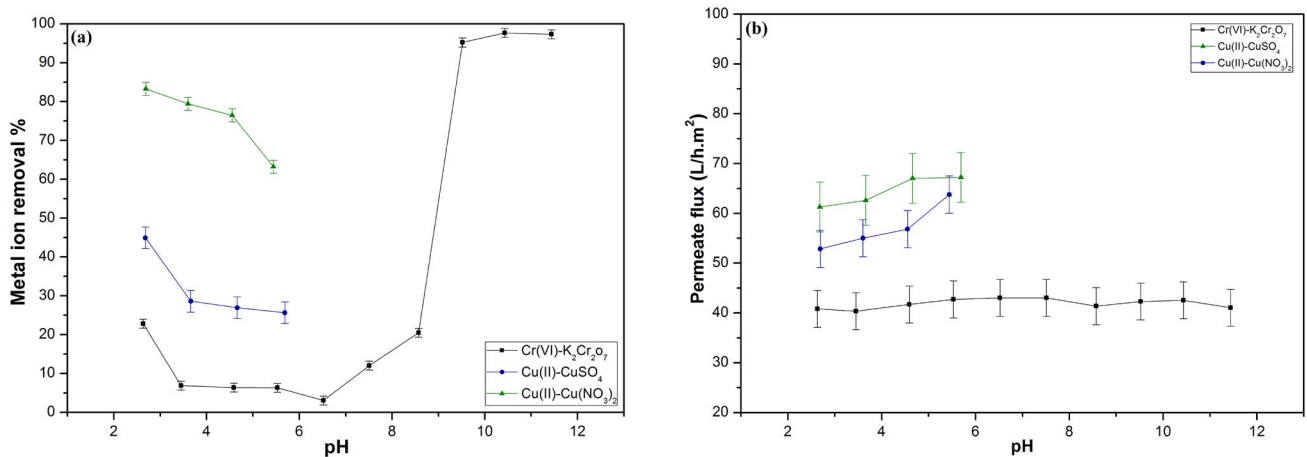
Fig. 3. Effect of pH on metal ions removal (a) and flux (b) (at ΔP = 6 bar, [Metal] = 50 mg/L, T = 20°C and time = 75 min).
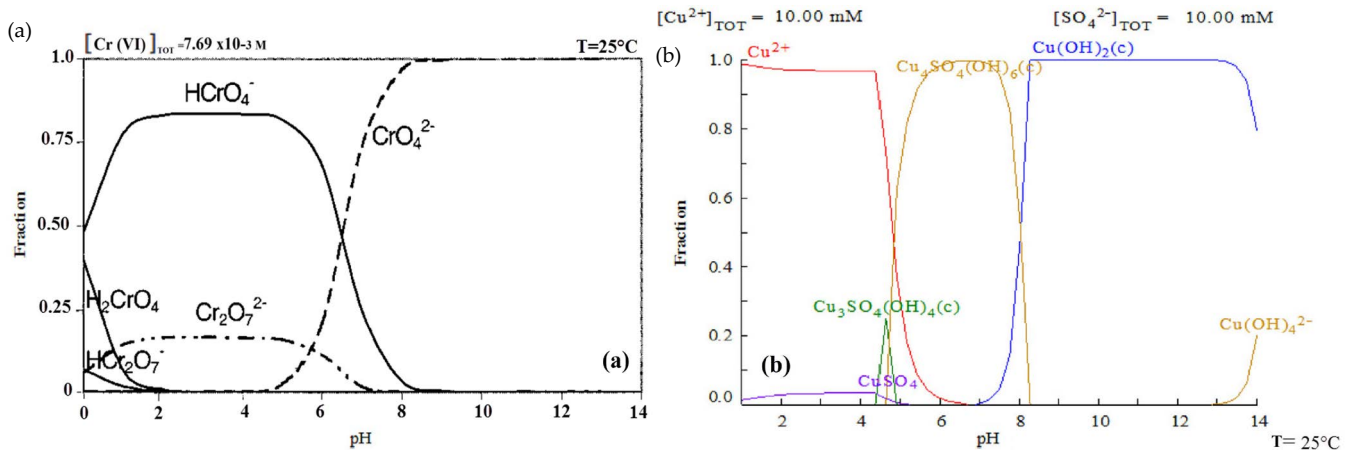

Fig. 4. Speciation forms of Cr(VI) (a) [11], and Cu(II) (b) [54].

Cr species with the membrane charge and consequently the results obtained in Fig. 3a. These profiles allow the identification of Cr(VI) forms in which ions are present in solution as a function of the pH, as shown in Fig. 4a [11,54].

In solutions, Cr(VI) exists in four different soluble species and the proportions of these species vary with pH. At acidic pH range (between 1 and 6), $HCrO_4^-$ is the predominant species at low concentration. Furthermore, $Cr_2O_7^{2-}$ which represents ≈17% of the total Cr also appears at pH < 6.5 and disappears at pH 8. For pH higher than 8, the CrO_4^{2-} species starts to form to become the only species at pH ≥ 10 and this independently of the concentration of Cr(VI). The natural species H_2CrO_4 (aq) appears with a low concentration at pH 2.0 and 3.0 only [4,15,55]. Furthermore, the variation of Cr(VI) radius depends on coordination type, species, spin (as reported in Table 3) and plays an important factor in membrane separation [9,56,57]. The variation of Cr(VI) rejection with pH change can be mainly explained by the electrostatic interactions. The membrane surface charge can form an appropriate electrostatic potential, which could interact (either by attracting or rejecting) with the metal ions in solutions.

In fact, the hydrated surface of alumina is known by amphoteric behavior that explained, in part, the choice of using γ-Al_2O_3 membrane [42]. As mentioned in Table 1, the IEP of γ-Al_2O_3 UF is in the range of 8–9. At pH beyond pH_{IEP}, the membrane is negatively charged due to the presence of AlO^- groups at the membrane surface, and it is positively charged in solution below pH_{IEP} due to the presence of $AlOH_2^+$ groups, based on the following reactions:

$$Al-OH + H_2O \leftrightarrow Al-OH_2^+ + OH^- \tag{9}$$

$$Al-OH + H_2O \leftrightarrow Al-O^- + H_3O^+ \tag{10}$$
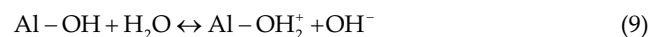
Therefore, the high rejection obtained at pH > 9 is due to the high repulsion force between the negative charge of both membrane (AlO^-) and Cr(VI). Meanwhile, the lower rejection at acidic pH (pH < 7) is due to the attraction force between the positive charge of the membrane and the negative charge of Cr(VI) anions. In addition, the lower charge density of the monovalent anion ($HCrO_4^-$) compared with the divalent chromic anion (CrO_4^{2-}) emphasizes the low retention

of the Cr(VI). In fact, the low valence of $HCrO_4^-$ may reduce the overall size of the hydrated ion, which results in a higher diffusivity and lower retention [58].

Due to the fact that free Cu ions can precipitate in neutral and alkaline solution, the study of Cu(II) rejection was conducted in acidic solutions of various pH levels (2.68–5.69) with the existence of different counter-ion (NO_3^- and SO_4^{2-}) as illustrated in Fig. 3a. Generally, as the pH increases from 2.68 to 5.69, the rejection of Cu metals decreased. The high rate rejections (equal to 83% for $Cu(NO_3)_2$ and 45% for $CuSO_4$) obtained for Cu metals at pH ≈ 2.68 could be due to mutual electrostatic repulsion between the positive charge of γ-Al_2O_3 and the metal cation. Furthermore, in the whole range of the studied pH values, the retention of $Cu(NO_3)_2$ was greater than $CuSO_4$ which demonstrated the major effect of counter-ion (NO_3^- and SO_4^{2-}) on Cu(II) rejection. Indeed, the attraction between the positive charge of the UF membrane and the negative charge of ions is greater for anions with high valency (divalent in our case (SO_4^{2-})), thereby respecting the Donnan principal. The observed trend is in accord with the results obtained for anions rejection, as in Table 4.

It is worth mentioning that some authors found the optimum Cu rejection at pH 6.80. The possible explanation for this finding is that, at higher pH, metal ions (namely Cu) are capable of forming complexes with OH^- ions and lead to the formation of the insoluble hydroxide. As a result, solute varied to a larger molecule and precipitate onto the membrane surface [23,59,60]. According to the Cu speciation profiles, the $CuSO_4$ starts to disappear and convert to $Cu_3SO_4(OH)_4$ complex as shown in Fig. 4b [54]. Mehiguene et al. [61] indicated that the increased anion in the acidic solution might neutralize the positive sites on the membrane surface and thus to reduce the cation repulsion effect caused by membrane surface charge.

Fig. 3b presents the effect of pH on the flux. It can be seen that for Cu(II) of both salts, the flux increases with an increase of pH. The maximum flux occurs at pH 5.69 (67.24 L/h m²) and the minimum flux occurred at pH 2.68 (61.28 L/h m²) for $CuSO_4$. Cations did not easily pass through the membrane for feed pH values below the IEP due to the electrostatic repulsion between the cations and the positively charged membrane surface.

In contrast, for Cr(VI) permeate flux is found to be approximately independent over the entire investigated pH range, and remains almost constant at about 40 L/h m². Indeed, the permeate flux increases slowly starting from the very acidic pH to the neutral point where it reaches maximum and decreases as the alkalinity increases, which can be explained by the speciation of metals that differs at different pH ranges,

as shown in Fig. 4a. The previous explanations hold good for the effect of pH on the flux. In general, the obtained results showed that the effect of pH depends mostly on the ionic nature of the membrane surface and on metals speciation that is in agreement with data reported in the literature.

3.2. Effect of pressure on metal ions' flux and removal

The effect of applied pressure (from 2 to 6 bar) on the permeate flux and the removal of metal ions was studied as shown in Fig. 5. The other conditions such as pH, initial concentration and temperature were constant during the experiment.

3.2.1. Effect of pressure on the permeate flux of metal ions

From Fig. 5a, the permeate fluxes increase with increasing pressure for all metals, this trend might be due to enhancement of driving force across the membrane [62]. At low pressure, diffusive transport becomes more important. Indeed, the enhanced water permeation under increased feed pressure can facilitate the diffusion of the metal hydrated ions [63]. Furthermore, the increase of flux varies almost linearly with increasing pressure, thereby demonstrating that there is no significant contribution of additional transport resistance from concentration polarization and adsorption. A similar observation was made for different metals either by organic or inorganic membranes [36,60,62]. Li et al. [63] explained the transport of molecule through a ceramic membrane (MFI zeolite membranes) by a five-step process, that includes: (i) diffusion from the bulk feed to the membrane surface, (ii) entering the pores from the membrane surface, (iii) diffusion through the pores, (iv) exiting from the pores to the membrane surface and (v) diffusion from surface to the bulk permeate stream.

3.2.2. Effect of pressure on metal ions rejection

Fig. 5b represents the variation of Cu(II) and Cr(IV) retentions as a function of the applied pressure (ΔP) for a

Table 4
Effect of pH on the rejection of copper counter ion

CuSO₄ salt		Cu(NO₃)₂ salt	
pH	SO_4^{2-} retention%	pH	NO_3^- retention%
2.68	35.97	2.69	41.28
3.66	25.22	3.6	61.82
4.66	22.75	4.55	72.90
5.69	28.92	5.44	69.02

Table 3
Cr(VI) ionic radii

Oxidation state	Coordination type[a]	Species	Spin	Radius (nm)	Molecular weight
Cr(VI)–CrO_4^{2-}	4	Tetrahedral	–	0.04	115.992 g/mol
Cr(VI)–$HCrO_4^-$	4	Tetrahedral	–	0.04	117.001 g/mol
Cr(VI)–$Cr_2O_7^{2-}$	8	Octahedral	Low	0.058	215.985 g/mol

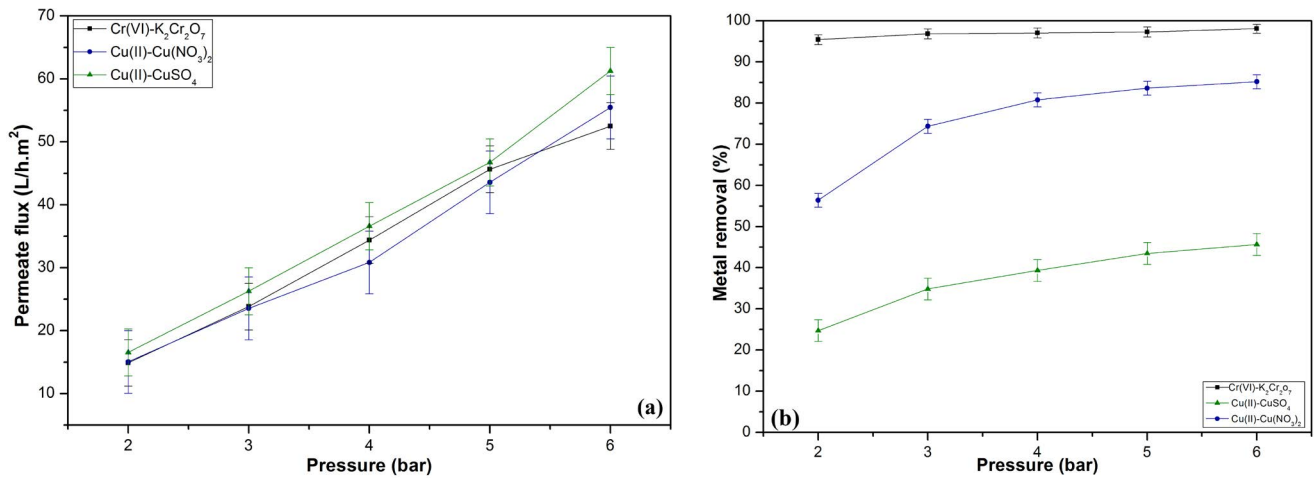[a]Coordination type refers to covalent bonding [58].

Fig. 5. Effect of pressure on metal flux (a) and rejection (b) (for time = 75 min, [Metal] = 50 mg/L and pH around 10.50 and 3, respectively, for Cr(VI) and Cu(II).

feed metal ion concentration equal to 50 mg/L at T = 20°C. As shown in Fig. 5b, Cu(II) rejection for experiments conducted in acidic solutions (pH ≈ 3) increases strongly with increasing ΔP from 56.4% to 85.17% and from 24.7% to 45.6%, respectively, for Cu(NO$_3$)$_2$, CuSO$_4$ at 2 and 6 bar. In contrast the rejection of Cr(VI) conducted in basic solutions (pH ≈ 10.50) remains nearly constant with a low growth rate of 2% between ΔP of 2 and 6 bar. Comparable experimental results were stated by several researchers [64–66].

The low retentions obtained for experiments conducted with Cu salts, at lower operating pressures, might be caused by a high diffusive transport of solute (Cu(II)) across the membrane compared with convective transport. With increasing pressure, convective transport becomes more important and retention will, therefore, increase. Furthermore, as previously explained, the surface charge is a major factor explaining the separation efficiency of the γ-Al$_2$O$_3$ UF with the different studied Cu solutions. Indeed, the obtained rejection rates can be explained by the Donnan effect, taking into account the strong interaction developed between the divalent metal cation (Cu(II)) and the positive surface charge of the γ-Al$_2$O$_3$ UF at pH 3. In addition, as can be seen from Fig. 5b, the membrane shows rejections (for fixed metal counter-ions (SO$_4^{2-}$ and NO$_3^-$)) in the following sequence: UF (SO$_4^{2-}$) < UF (NO$_3^-$). This finding has been found and explained by other authors based on charge pattern [67]. The rejection of the Cu metal depends on the associated anion and a decrease of the rejection was observed when the valency (charge) of the anion increases [68–70]. Furthermore, the SO$_4^{2-}$ anions are able to form surface complexes with the surface groups AlOH$_2^+$ or AlO$^-$. Certain parameters of ion, such as its hydration radius and diffusion coefficient, appear if we compare the rejection rates of Cr(VI) and Cu(II). Generally, more the ion is hydrated the more its transfer across the membrane become difficult and consequently it has high rejection as shown in Table 5 and Eq. (11).

$$k^+_{\text{Hydratedradius}} < NO^-_{3\text{Hydratederadius}} < Na^+_{\text{Hydratederadius}} < SO^{2-}_{4\text{Hydratederadius}}$$
$$< Cu^{2+}_{\text{Hydratedradius}} < CrO^{2+}_{7\text{Hydratedradius}} \qquad (11)$$

In addition, the Cr(VI) rejection has a very high value but which slowly increased with the increasing pressure. The small difference in Cr(VI) rejection can be attributed to the water permeation rate (that becomes more important at higher pressure) or to the solute diffusion (which is not considerably affected by higher pressure but rather by solute concentration). In other words, the increase in water flux which might be due to an increase of the preferential sorption of water at higher pressure, leads to an increase of the solvent permeability at high pressure compared with solute permeability. Consequently, the Cr(VI) rejection increases due to a difference in concentration (caused by dilution effect) [57,62,71]. The increase in Cr(VI) rejection can be attributed to the water permeation and/or to the solute diffusion rate that would not be expected to be remarkably effected by higher pressure but rather controlled by the solute concentration variation. Other authors explained the nearly constant Cr(VI) retention values because of the counteracting contributions of both convective transport and concentration polarization [61]. Muthumareeswaran et al. [72] demonstrated that the pressure effect plays an insignificant role for Cr ions removal at low feed concentration by a polyacrylonitrile-based UF membrane. Furthermore, Muthumareeswaran et al. [72] discovered that concentration polarization became important at higher feed concentration above ≥400 ppm. For this reason, it was important to explore the possibility of concentration polarization, to estimate the concentration of the metal ions at the membrane surface (identified by C_m) and also to estimate the intrinsic rejection (referred as R_{int}) of Cr(VI) and Cu(II).

According to film theory, and taking the results obtained from plotting $\ln[(1-R_{\text{obs}})/R_{\text{obs}}]$ against J_V (as shown in Fig. 6), the determination of R_{int} and the solute concentrations at the membrane surface for the two salts K$_2$Cr$_2$O$_7$ and CuSO$_4$ were possible. The results of this study are reported in Table 6. The results in the table confirm the absence of the concentration polarization phenomena and this for both salts, K$_2$Cr$_2$O$_7$ and CuSO$_4$, for a concentration of 50 mg/L. The C_m was found to be less than the initial concentration.

Table 5
Properties of related cations and anions

| Ion	Ionic weight (g/mol)	Ionic radius (nm)	Hydrated radius (nm)	Hydration energy (kJ/mol)	Diffusivity (10^{-9} m²/s)
Na^+	23	0.117 [51]	0.358 [51]	–405 [51]	1.334 [51]
K^+	39	0.149 [51]	0.331 [51]	–321 [51]	1.957 [51]
Mg^{2+}	24.3	0.072 [51]	0.428 [51]	–192 [51]	0.706 [51]
Ca^{2+}	40	0.100 [51]	0.412 [51]	–159 [51]	0.792 [51]
SO_4^{2-}	96	0.290 [51]	0.379 [51]	–114 [51]	1.065 [51]
NO_3^-	63	0.189 [51]	0.340 [51]	–328 [51]	1.902 [51]
Cu^{2+}	63.5	0.072 [72]	0.419 [72]	–216 [72]	0.62–0.75
		0.073 [72]			
		0.077 [72]			1.050 [74]
$Cr(VI)$	51.996	0.058 [58]	0.461	–1,301.1 [73]	1.270 [75]
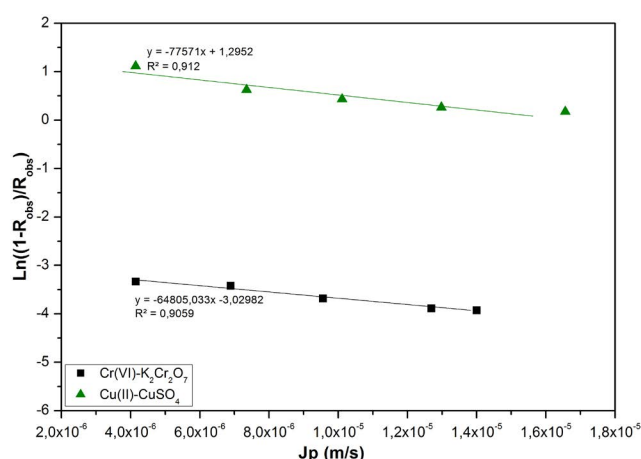
Fig. 6. Film theory equation.

3.3. Effect of concentration on metal ion removal

Among the factors known to influence retention rate of electrolytes as well as the effectiveness of UF processes, there is the concentration of metal and its competing ions.

This investigation was performed to observe the effect of various initial concentrations of Cr(VI) and Cu(II) on the permeate flux and metals' removal. In this experiments, all conditions such as pH, temperature and pressure were constant except for the initial concentration of Cr(VI) and Cu(II) which was increased from 10 to 150 mg/L. The results are shown in Fig. 7.

As shown in Fig. 7a, rejection of Cu(II) ion (for experiments conducted in $CuSO_4$ solutions) decreases with increasing initial solute concentration. The highest level of reduction is equal to 76.47% at 10 mg (Cu(II))/L and the minimum level is of 13.88% at 150 mg (Cu(II))/L. For experiments conducted on $Cu(NO_3)_2$ solutions, the Cu(II) rejection slightly decreased despite the variation of initial solute concentration (It passes from 88.23% to 76.92%, respectively, for 10 mg (Cu(II))/L and 150 mg (Cu(II))/L). Furthermore, Fig. 7a shows that Cr(VI) rejection (>90 mg (Cr(VI))/L) seems to be independent from the most concentrated $K_2Cr_2O_7$ solution (150 mg (Cr(VI))/L. Similar experimental observations were

reported in the literature for different membranes (organic and inorganic) and with different metals [23,64]. The small difference found for Cr(VI) was explained by Hafiane et al. [57] by the possibility that the density charge of the membrane was fixed by the salt concentration. Consequently, the electrostatic effect of the membrane diminished, and the steric hindrance of chromate ion must be taken into account.

The accumulation of solute's ions at the membrane/solution interface causes screening of the membrane surface charge and compression of the electric double layer [17,18]. This phenomenon was found to reduce the ability of the membranes to reject electrolyte by electrostatic effects, and thus explains the decrease in Cu(II) rejection. It is worth mentioning that authors such as Muthukrishnan and Guha [53], and Palmer and Puls [73] studied the variation of Cr species with concentration variation. The high Cr(VI) rejection was observed at low Cr concentration and at pH in the alkaline range (pH 6.5–11). However, the opposite trend was observed in the acidic range (pH < 6.5), with high rejection occurred at higher concentrations. In addition, from the different Cr species present in a solution, $Cr_2O_7^{2-}$ was found to be dominant at high Cr concentration and high acidic conditions (pH 1–7). The $Cr_2O_7^{2-}$ concentration is reduced with the presence of an increasing amount of CrO_4^{2-} ions caused by a further increase of pH. Therefore, variation in rejection with changes of Cr(VI) feed concentration is rather expected because of the changes in the relative amount of monovalent and multivalent ions present in solution.

The increased concentration of SO_4^{2-} negatively affected Cu(II) rejection rather than NO_3^- concentration. The decreased Cu rejection with increased concentration in $CuSO_4$ solutions can be explained by taking into account the distribution of sulfate ion between membrane and solution phases [67]. In addition, the difference found for Cu rejection in two salts $(Cu(NO_3)_2$ and $CuSO_4)$ is based on the considerations of Donnan exclusion phenomena and electro-neutrality of aqueous solution.

Fig. 7b shows the values of the permeate flux (of $K_2Cr_2O_7$ and $CuSO_4$ which represent, respectively, salts with the highest and lowest retention) at various feed concentrations. It is clear from this figure that the permeate flux vs concentration

Table 6
Determination of R_{int} and C_m

| Salt solutions	ΔP (bar)	J_p (m/s)	C_p (g/L)	C_{int} (g/L)	R_{obs} (%)	$\ln (1-R_{obs})/R_{obs}$	R_{int} (%)	C_m (g/L)
	2	4.049 E-06	0.0426	0.0565	0.2472	1.1136	0.2189	0.0545
	3	7.574 E-06	0.0368	0.0565	0.3483	0.6264	0.2189	0.0471
Cu(II)–CuSO$_4$	4	1.037 E-05	0.0343	0.0565	0.3932	0.4336	0.2189	0.0439
	5	1.308 E-05	0.033	0.0584	0.4348	0.2623	0.2189	0.0423
	6	1.673 E-05	0.0317	0.0584	0.4565	0.1743	0.2189	0.0406
	2	4.140 E-06	0.0017	0.0501	0.9656	–3.3361	0.955	0.0386
	3	6.620 E-06	0.0015	0.0501	0.9684	–3.4227	0.955	0.0345
Cr(VI)–K$_2$Cr$_2$O$_7$	4	9.554 E-06	0.0012	0.0501	0.9755	–3.6837	0.955	0.0268
	5	1.286 E-05	0.001	0.0501	0.9799	–3.8896	0.955	0.0219
	6	1.463 E-05	0.001	0.0517	0.9806	–3.9259	0.955	0.0218
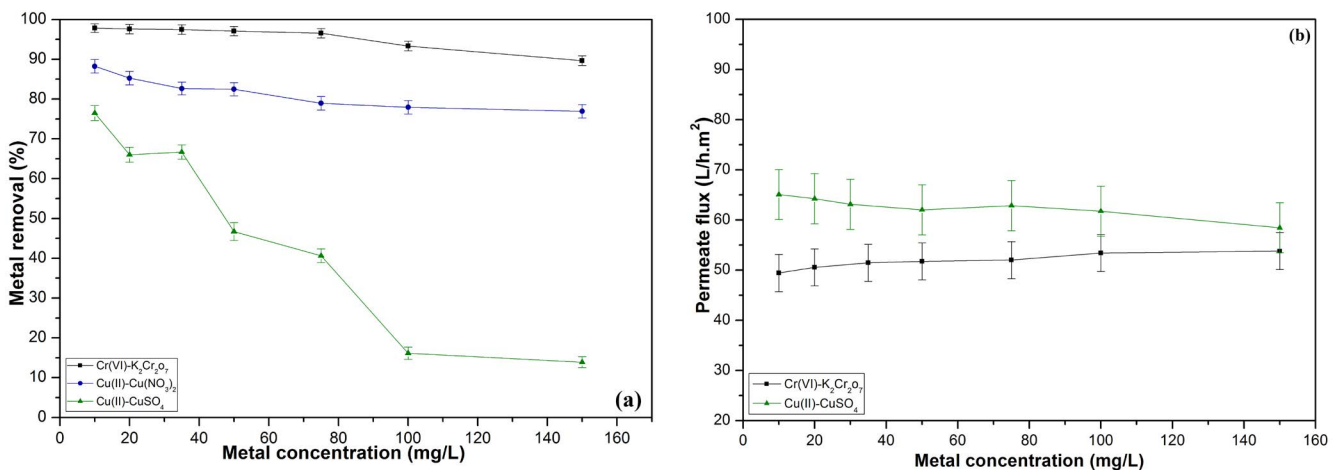
Fig. 7. Effect of concentration on metals' rejection (a), and metals' fluxes (b) (at pH ≈ 10.50 for Cr(VI) and pH ≈ 3 for Cu(NO$_3$)$_2$ and CuSO$_4$, ΔP = 6 bar, T = 20°C and time = 75 min of filtration).

has almost a linear dependence with a slightly negative slope. This negligible decrease in flux, observed as a function of ionic strength, demonstrates the unmarked effect of concentration polarization [17,18]. This result can be explained by an increase in osmotic pressure when increasing the feed concentration of metals. In fact, at high solute concentration, a decrease of the effective membrane pore size due to adsorption or deposition of solute on the membrane surface occur.

3.3.1. Effect of anions concentration on metal rejection rate

Salts such as NaCl, NaNO$_3$, Na$_2$SO$_4$ and MgSO$_4$ are common pollutants in industrial discharges from metal surface treatment sector. The effect of the presence of salts (namely NaNO$_3$, Na$_2$SO$_4$) on the rejection of Cr(VI) was investigated in quaternary ((K$_2$Cr$_2$O$_7$ + NaNO$_3$) and (K$_2$Cr$_2$O$_7$ + Na$_2$SO$_4$)) and quinary (K$_2$Cr$_2$O$_7$ + NaNO$_3$ + Na$_2$SO$_4$) solutions, with the variation of the molar ratio of anion in the following ratios: 3/1, 3/3, 1/3. Furthermore, the evolution of the retention of Cu(II) related to the variation of molar ratio of anions (NO$_3^-$ and SO$_4^{2-}$) was investigated in tertiary (Cu(NO$_3$)$_2$ + CuSO$_4$) solution. Experiments referring to this part of the study were performed at a constant pressure (ΔP = 6 bar) and at pH

10.66–10.68 for Cr(VI) salt and pH 2.83–2.90 for Cu(II) salts, T = 20°C and time = 75 min.

As reported in Table 7, the experimental results of those test runs reveal that the rejection of heavy metals tends to decrease with increase of feed concentration of divalent anion in solution. Nevertheless, the percentages of Cr(VI) rejection by UF membrane were moderately insensitive to the change of the molar ratio of anion, either in quaternary or quinary solutions (for all ratios, the Cr(VI) rejections were between 83% and 87%). Moreover, the rate rejections of Cr(VI) obtained for (K$_2$Cr$_2$O$_7$ + NaNO$_3$) were higher than those obtained for (K$_2$Cr$_2$O$_7$ + Na$_2$SO$_4$). These observations can be explained by the Donnan exclusion in which the difference in charge valency plays a major role. Indeed, divalent anions are strongly rejected given that the membrane is negatively charged at the studied pH (pH 10.66–10.68). However, in order to ensure electroneutrality at both sides of membrane; ions present in the feed solution are forced to pass through the membrane. Hydration energy and radius (Table 5) appear to be important factors that influence the selectivity of the UF membrane, and which explain the difference between the divalent anions CrO$_7^{2-}$ and SO$_4^{2-}$. The obtained results in case of Cu(II) are also in

Table 7
Influence of the concentration of the metals' co and counter ion (ΔP = 6 bar, time = 75 min, T = 20°C)

$K_2Cr_2O_7$ + $NaNO_3$ at pH 10.66–10.68			
$K_2Cr_2O_7$ salt %	25	50	75
$NaNO_3$ salt %	75	50	25
R(Cr(VI))%	83.16	89.20	87.55
R(Na^+)%	92	60	40.38
R(NO_3^-)%	40.86	44.61	35.02
$K_2Cr_2O_7$ + Na_2SO_4 at pH 10.66–10.68			
$K_2Cr_2O_7$ salt %	25	50	75
Na_2SO_4 salt %	75	50	25
R(Cr(VI))%	86.39	86.91	86.85
R(Na^+)%	63.7	60.1	40.00
R(SO_4^{2-})%	78.64	75.12	72.74
$Cu(NO_3)_2$ + $CuSO_4$ at pH 2.83–2.90			
$Cu(NO_3)_2$ salt %	25	50	75
$CuSO_4$ salt %	75	50	25
R(Cu^{2+})%	44.44	50.98	56.52
R(SO_4^{2-})%	52.26	39.66	32.29
R(NO_3^-)%	7.87	1.80	47.42
$K_2Cr_2O_7$ + $NaNO_3$ + Na_2SO_4 at pH 10.60			
$K_2Cr_2O_7$ salt %	50		
$NaNO_3$ salt %	25		
Na_2SO_4 salt %	25		
R(Cr(VI))%	82.17		
R(Na^+)%	58.75		
R(NO_3^-)%	35.64		
R(SO_4^{2-})%	80.90		

Table 8
Characterization of industrial discharge before and after ultrafiltration (at ΔP = 6 bar, natural pH and 60 min of filtration)

Ions' concentration	Effluent's concentration (mg/L) at pH 8.20	Permeate samples' concentration (mg/L) at pH 6.945
[Ca^{2+}]	145	24
[Mg^{2+}]	87.57	19.64
[Na^+]	215.21	102.45
[K^+]	4.25	1.023
[P]	<0.2	<0.2
[NH_4^+]	<0.4	<0.4
[SO_4^{2-}]	204	41
[NO_2]	67	18
[THT]	<0.4	<0.4
[Cu^{2+}]	2.125	0.215
[Zn]	1.375	0.842
[Fe]	3.214	0.024
[Mn]	<0.4	<0.4
[B]	<0.4	<0.4
[Cr]	22	<5
[Ni]	61	<5
[Pb]	17	<5
[As]	28	<5
[Ba]	80	21
[Sr]	302	19
[Se]	12	<5
[Cd]	<0.1	<0.1
[Hg]	<0.1	<0.1

agreement with Donnan exclusion and the electric equilibria. Furthermore, the overall rejections are lower than single metal solutions.

3.4. Rejection of heavy metals from industrial wastewater

The usability and efficiency of the UF membrane were further analyzed by its application in the filtration of real industrial metallic wastewater (from different metalwork and coating metal surfaces industries). The characteristics of the studied wastewater (which contains significant amounts of Cr, Ni and Ba) and the samples obtained after filtration are presented in Table 8.

From the obtained results, the rejection of some metals such as Cu, Zn, Fe, Cr, were found to be equal to 95%, 39%, 99% and 77%, respectively (as reported in Table 8). It can be said that the γ-Al_2O_3 UF can suitably be applied in the heavy metal industries to recover heavy metals and reclaim wastewater.

3.5. Antifouling properties of the membranes

The results in Fig. 8a show the comparison in flux of initial and final pure water measurement, including intermediate
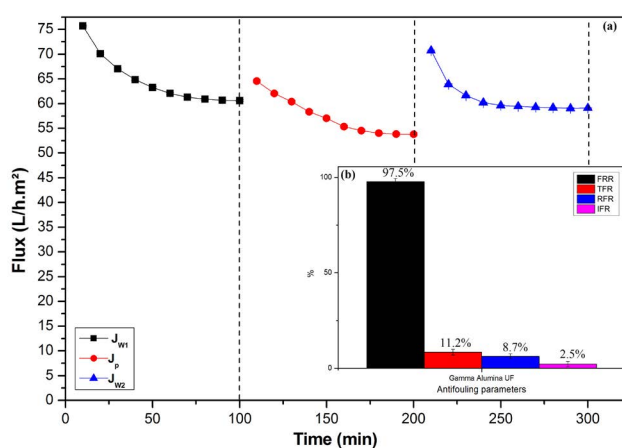

Fig. 8. (a) Flux of pure water and Cr(VI) permeate (the first flux matches pure water, the second matches Cr(VI) and the third for pure water after washing the membranes) and (b) Fouling parameters of γ-Al_2O_3 UF membrane.

flux of Cr(VI) permeate. As it can be seen in Fig. 8a, the water flux is nearly steady over 60 min of filtration and J_{w2} is almost in the same range as J_{w1}.

The results of the measurements of the antifouling parameters (FRR, TFR, RFR and IFR) using Eqs. (5)–(8) are shown

in Fig. 8b. FRR of the γ-Al$_2$O$_3$ UF membrane is found to be very high 97.5%, whereas TFR is found to be equal 11.2%, thus demonstrating the absence of fouling phenomenon and the potential use of this membrane in heavy metal removal.

4. Conclusion

The demand to eliminate or recover metal ions from industrial discharges is essential for both environment and economy. Environmentally speaking, the reduction of heavy metal toxicity can rescue living organisms, it also helps savings costs by metals' reuse or sale. In this study, the effectiveness of UF membrane as a function of, physicochemical properties of the ions, characteristics of the membrane and the various filtering parameters for metal ions removal, were investigated. The parameters such as pH, applied pressure, initial concentration of Cu(II) and Cr(VI), and effect of co-counter ion concentration had various effects on the percentage of metals removal. The experimental results show that UF is a very promising method for effluent treatment containing Cu(II) and Cr(VI). The following conclusions were obtained:

- The solution pH exerts a strong influence on the Cr(VI) and Cu(II) retention. For Cr(VI) salt, high rejections over 97% were obtained for pH values above 8. For Cu salts (Cu(NO$_3$)$_2$ and CuSO$_4$) retentions revealed a maximum values around, respectively, 80% and 50%, for pH $\approx$ 2.60. Furthermore, the rejections of Cr and Cu at acidic and alkaline pH have been thoroughly explained by their ionic dissociation and interaction with the charged γ-Al$_2$O$_3$ UF membrane. The variation of permeate fluxes as a function of pH were independent for Cr(VI), in contrast an increase of fluxes with pH growth were found for Cu(II).
- The increase of applied pressure results in an increase of metals' rejections and fluxes. The Cu rejections of Cu(NO$_3$)$_2$ and CuSO$_4$ at pH $\approx$ 3, increase, respectively, from 56.4% to 85.17% and from 24.7% to 45.6% for ΔP = 2 bar and ΔP = 6 bar, respectively. However, the rejection remains nearly constant for Cr(VI) in basic solutions (pH $\approx$ 10.50). Insignificant polarization concentration phenomenon was observed.
- The rejections were found to be dramatically decreasing with an increase in CuSO$_4$ concentrations (highest level of rejection was 76.47% at 10 mg(Cu(II))/L and the minimum level was 13.88% which occurred at 150 mg(Cu(II)/L). For Cu(NO$_3$)$_2$ solutions, the rejection slightly decreased with concentration (It passes from 88.23% to 76.92%, respectively, for 10 mg(Cu(II))/L and 150 mg(Cu(II))/L). Cr(VI) rejection seems to be independent from the increase in concentration (>90% for all concentrations).
- Solute retention depends strongly on the solute type (including charge valency and hydration energy), on the pH of the the studied solutions, the applied pressure and on salt concentration.
- Environmentally speaking, it seems that under given operating conditions, γ-Al$_2$O$_3$ UF can be seen as an efficient process to remove/recover heavy metals from industrial discharges. In addition, no fouling phenomenon was observed.

Symbols

ΔP	—	Applied pressure
J_p	—	Permeate flux
R_{obs}	—	Observed rejection rate
R_{int}	—	Intrinsic rejection
V	—	Volume
t	—	Time interval
T	—	Temperature
A	—	Effective membrane area
C_p	—	Permeate concentration
C_f	—	Feed concentration
C_{int}	—	Initial concentration
C_m	—	Concentration at the membrane surface
K	—	Mass transfer coefficient
NM	—	Moroccan Norm
WHO	—	World Health Organization
MCL	—	Maximum acceptable limit

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