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Removal of heavy metals by ultrafiltration

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Abstract

Large amounts of polluted water are often obtained from the chemical process industry, which require a mandatory treatment before being disposed of. Heavy metals are employed as homogeneous catalyst in numerous processes, so that recovering and/or recycling of those metals to the reaction unit is essential.

In this study, ultrafiltration is presented as a useful technique to recover heavy metals present in aqueous solutions, without the need of adding further substances. Specifically, recovery of mixtures of iron (II) and iron (III), copper (II) and chromium (III) is presented. Ceramic membranes are mechanically, chemically and thermally more resistant than those polymeric. Thus, given the acidic nature of the studied effluents, a 5-kDa commercial ceramic membrane has been selected for this investigation. The effect of transmembrane pressure and pH are presented. The results show that chemical speciation of metals in aqueous solution is strongly correlated with the retention, which suggests a possible interaction between metallic species and membrane material.

Keywords: ceramic membrane, ultrafiltration, heavy metal recovery, wastewater treatment

1. Introduction

Chemical processes produce large amounts of polluted waters. Therefore, in order to assure water availability to future population, the application of wastewater treatments is mandatory. Biological wastewater treatment plants (BWWTP) are being widely used to achieve this objective. However, there exist some organic compounds which are recalcitrant to this treatment due to their specific chemical nature. Phenolic compounds are one example of these refractory substances and they have to be partially mineralised before being sent to a BWWTP (Arslan-Alaton et al. 2007, Jeworski and Heinzle 2000, Sangave et al. 2007). Among all the existing processes able to deal with this environmental problem, advanced oxidation processes (AOP's) have been widely studied (Catalkaya and Kargi 2007, Pera-Titus et al. 2004). These AOP's are based on the generation of hydroxyl radicals (·OH) which are powerful oxidants capable to attack a wide variety of refractory organic compounds (Chamarro et al. 2000). AOP's include a large variety of processes such as the Fenton-like processes, ozonation, photocatalysis, UV-based techniques, etc. The Fenton process is possibly the most popular AOP because of the simplicity of their reactants and operating conditions. This oxidation technology uses the addition of both hydrogen peroxide as oxidant and iron salts (usually ferrous iron salts) as catalyst. In addition, the Fenton process usually satisfactorily works at room temperature and atmospheric pressure. Phenolic compounds such as phenol, chlorophenols, cresols, nitrophenols between others have been partially mineralised by using this oxidation process (Du et al. 2006, Kavitha and Palanivelu 2005, Pérez-Moya et al. 2007). As abovementioned, the Fenton process uses iron (II) ions to generate the hydroxyl radicals from hydrogen peroxide but, in the so-called Fenton-like processes, other heavy metals could be successfully used as catalyst for the AOP (Anipsitakis et al. 2004). The main environmental drawback of the Fenton process and the Fenton-like processes is that the metallic ions added to the media leave the reaction step and are released to the media or are driven to the BWWTP. Thus, the Fenton or Fenton-like processes assure a partial (or total) mineralisation of a biorefractory organic compound but they cause a constant release of iron (or other active metals) species to the nature. In addition, there is also an economic problem linked with these processes because of the necessity of a continuous addition of catalyst during the oxidation step.

Even though the Fenton process and Fenton-like processes have been widely studied, there is a lack of information about the recovery and re-use of the homogeneous catalysts. Precipitation and decantation processes have been proposed to recover and reuse the iron ions (Kavitha and Palanivelu 2004). However, further acidification is required in order to retrieve the iron species in ionic form, which is how they are active for the hydroxyl radical production. Another technique that could be selected is the so-called enhanced ultrafiltration technique (Pramauro et al. 1992, Tung et al. 2002). This filtration technology uses the addition of a macroligand to enlarge the size of the targeted species (in this case, metal ions) and be retained with an ultrafiltration membrane. Nevertheless, this technique needs a further recovery process in order to re-use the macroligand and a readjustment of the pH of the solution to be filtered would be required (Kim et al. 2006, Sanli and Asman 2000). Nanofiltration membranes could also be used for the recovery of heavy metals (Choo et al. 2002). Nonetheless, the system should perform at not extremely low pH due to the resistances of the polymeric membranes, material which the greater part of the nanofiltration membranes are made of. In this case, the pH of the effluents of the Fenton process should be adjusted causing an increase of the treatment cost.

The aim of this work is to study the recovery of mixtures of iron (II) and iron (III), copper (II) and chromium (III) by using a ceramic ultrafiltration membrane. As it is well known, ultrafiltration membranes deal with the recovery of macromolecules. However, in a previous work (Bernat et al. accepted), it was observed that a 5-kDa ceramic membrane was able to recover iron species from aqueous solutions when soluble charged iron hydroxides were present. Thus, the present work aims to test this phenomenon when other heavy metals are present. If the membrane is able to recover these metallic species, the use of nanofiltration or reverse osmosis membranes could be avoided, reducing the costs of the recovery process because of the moderate pressures usually applied in the ultrafiltration range. On the other hand, the enhanced ultrafiltration processes should be only desirable when the nature of the heavy metals solutions does not allow a direct membrane separation. With this goal, the behaviour of iron, copper and chromium solutions has been inspected.

2. Experimental section

2.1. Chemicals

Iron (III) nitrate nonahydrate was analytical reagent grade (purity higher than 98.0%) and was supplied by Riedel-de Häen. Iron (II) sulphate heptahydrate was analytical reagent grade (purity of 99.0%) and was supplied by Panreac. Copper (II) sulphate pentahydrate and chromium chloride hexahydrate were also analytical reagent grade and were supplied by Fluka with a purity of 99.0% and 98.0% respectively. Concentrated hydrochloric acid solution (37%), supplied by Fluka, and sodium hydroxide (purity of 98%), supplied by Sigma, were used to adjust the pH of solutions when needed. All reagents were used as received. Deionised water was used in the water permeability tests and to prepare the solutions containing heavy metals.

2.2. Apparatus, experimental methods and analysis

The experimental set-up was a home-made tangential flow filtration plant designed to work with tubular ceramic membranes. A 5-L reservoir was used to contain the solutions to be filtered. After this, a pump, a pulse dampener, a pressure gauge and a ball valve were installed before the membrane module. Another pressure gauge and a backpressure were installed after the membrane module in order to fix and maintain the transmembrane pressure (TMP). A detailed scheme of the experimental assembling can be seen elsewhere (Bernat et al. accepted). The system worked at continuous operating mode. Thus, both permeate and retentate were driven to the feed reservoir to keep constant the concentration along the experiments and simulate a continuous filtration process.

The selected membrane was a commercial 5-kDa molecular weight cutt-off (MWCO) ceramic membrane purchased at Tami Industries (France). It was a trichannel membrane having an external diameter of 10 mm and a hydraulic diameter of each channel of 3.6 mm. The length of the membrane tube was 250 mm and the available filtration area 94 cm^2. The average pure water permeability tested in our laboratories was around 24 $L/h\cdot m^2\cdot bar$.

The experimental procedure consisted of different steps. In all them, the feed flow rate was 31.4 L/h corresponding to 27 cm/s of tangential flow velocity. The TMP was successively fixed at 2, 4, 6 and 8 bar in each experiment. The first step consisted of the measurement of the pure water flux (J_w) before any filtration of the solutions containing heavy metals. After this, the reservoir was filled up with 3 L of the solution to be filtered. The pump was switched on and the TMP fixed to 2 bar. The permeate flow (J_p) was periodically measured and at each measurement point, about 10 mL of sample were taken for determining the metal concentration. After one hour operation, the TMP was increased to the next value. The procedure above described was repeated for each TMP. At the end, the pure water flux was measured again with deionised water. When a difference between this final water flux and the initial J_w was detected, the membrane was subjected to chemical cleaning. The membrane was treated in-situ with a 10 g/L oxalic acid solution at 50ºC for 1 h. Subsequently, the membrane was rinsed with deionised water until neutrality of both permeate and retentate. If needed, the cleaning method was repeatedly applied until the original permeate flux was restored. By using this method, the elimination of the species, which could have interacted with the membrane material, was completely guaranteed.

The permeate fluxes were directly measured with a balance (A&D Instruments, GF-1200). The heavy metal concentration in the permeate stream (C_P) and in the feed solution (C_f) were analysed by atomic absorption spectrometry (Perkin Elmer, model 3110) when copper and iron solutions were studied. In turn, when dealing with chromium, an UV-VIS spectrophotometer (Dinko Instruments, model 8500) was used at a wavelength of 575.5 nm.

The permeate flux decrease (J_P/J_w) and the heavy metal retention (R) were chosen as key parameters to describe the filtration process. The permeate flux decrease was calculated as the ratio of the J_P to J_w and the heavy metal retention was calculated as usual:

$$R\,(\%) = \left(1 - \frac{C_P}{C_f}\right) \cdot 100 \qquad (1)$$

3. Results and discussion

3.1. Iron (II) and iron (III) filtration

As demonstrated in a previous work (Bernat et al. accepted), iron (III) could be retained by the selected ceramic ultrafiltration membrane due to the presence of iron (III) soluble charged hydroxides which could interact with the membrane material forming a layer over the membrane surface, which could act as an actual different membrane. Contrarily, iron (II) species could not be retained by the same membrane due to the absence of these hydroxilated species. In this section, it is studied the behaviour when mixtures of iron (II) and iron (III) are filtrated. Hence, three solutions containing different concentrations of iron (II) and iron (III) were filtered. All these solutions had a total iron concentration of 2.0 mM and pH was fixed at 2. The ratios of iron (III) to iron (II) were 1:3, 1:1 and 3:1. These ratios were chosen in order to see the influence of the presence of retainable species (ferric ion) and non-retainable species (ferrous ion) in the same solution on the separation performance.

The permeate flux decrease for the three mixtures of iron is displayed in the Figure 1. As it can be seen, the higher the iron (III) content, the higher the permeate flux decrease. However, when the ratio of iron (III) to iron (II) is higher than one, the permeate flux decrease is almost independent on the iron (II) and (III) concentrations. Additionally, the TMP has a low effect on the permeate flux decrease at the ratio Fe(III)/Fe(II) equal to 1:3. However, when this ratio increases, the TMP becomes more important. This could be explained if higher iron deposition over the membrane occurred when the iron (III) content is higher causing a subsequent reduction of the permeate flux. This is in agreement with the fact that, the higher the iron (III) concentration in the media, the higher the iron (III) soluble charged hydroxides and, consequently, the higher the interaction between these charged species and the membrane material.

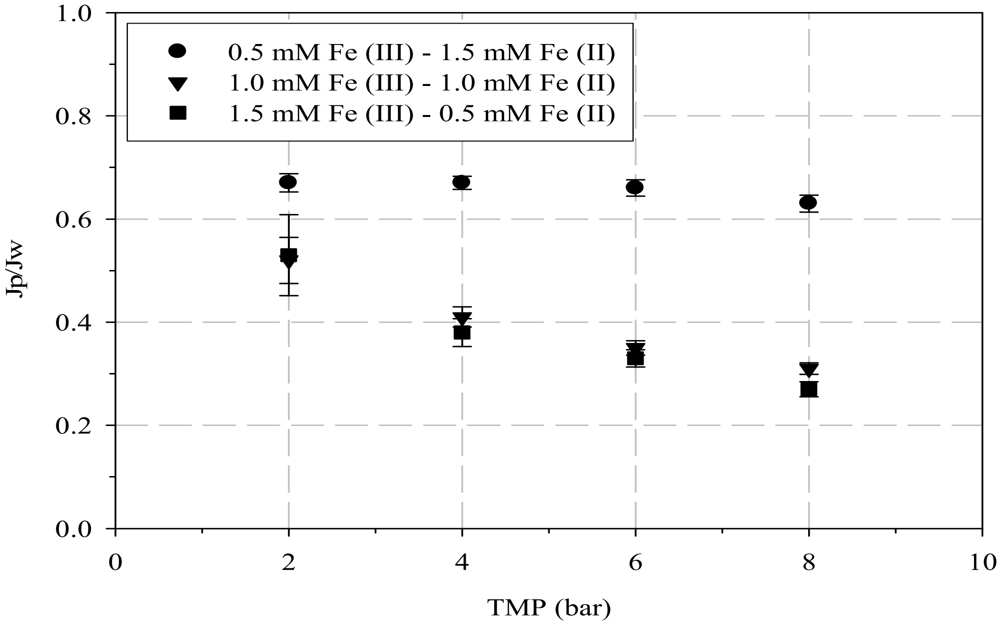

Figure 1. Effect of the TMP and Fe (III)/Fe (II) ratio on the permeate flux decrease at pH 2.0

Figure 2 shows the iron retentions achieved for the same tests. As it can be deducted from Figure 2, the iron retention increases as long as iron (III) concentration is higher. Furthermore, the TMP has a remarkable impact on the iron retention only at the highest Fe (III)/Fe (II) ratio.

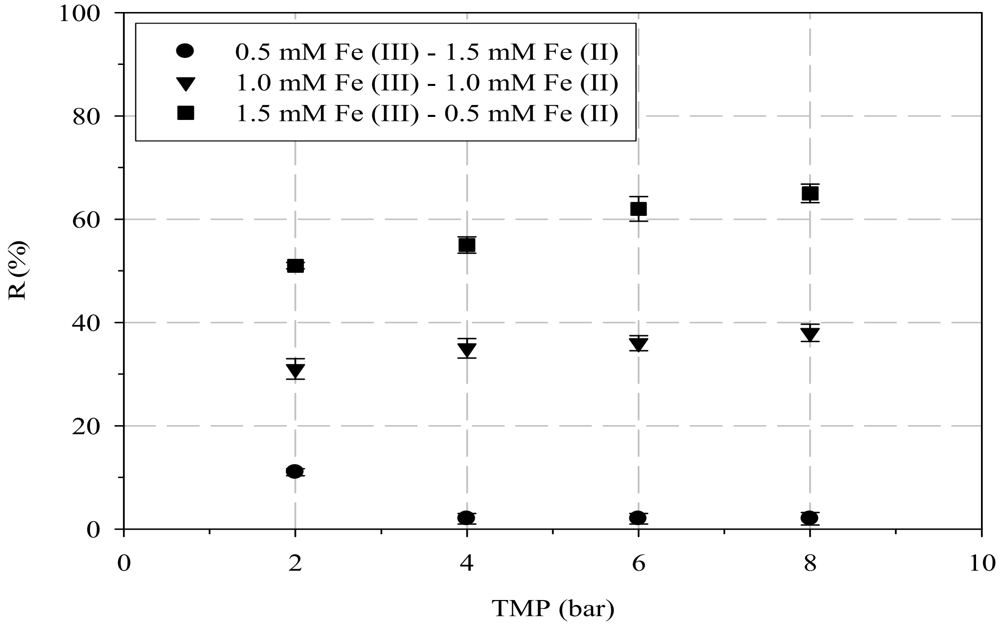

Figure 2. Effect of the TMP and Fe (III)/Fe (II) ratio on the iron retention at pH 2.0

Table 1 shows the theoretical iron retentions (R_{theo}) that could be achieved if considering that iron (II) is not retained and taking into account the iron (III) retentions obtained in a previous work (Bernat et al. accepted).

Table 1. Theoretical retentions assuming that only Fe(III) is retained

TMP (bar)	R_{theo} (%)			
	2	4	6	8
0.5 mM Fe (III) – 1.5 mM Fe (II)	22.9	20.9	19.7	20.4
1.0 mM Fe (III) – 1.0 mM Fe (II)	45.8	41.8	39.5	40.9
1.5 mM Fe (III) – 0.5 mM Fe (II)	68.7	62.7	59.2	61.3

A comparison of the R_{theo} with the actual retentions obtained shows that the experimental retentions are lower than those predicted theoretically. This can be explained by the possible difference on total iron concentration (the previous work dealt with 0.9 mM iron (III) solutions) which can affect the iron retention and on the formation of the active layer over the membrane surface. Furthermore, a negative effect on the iron retention, owing to the increase of the ionic strength, could also occur.

3.2. Copper (II) filtration

A solution containing 1.0 mM of copper (II) was filtered at its natural pH (5.2). As it can be seen in Figure 3, the permeate flux decrease was very low in comparison with that observed with the solutions containing iron (III) and iron (II). This behaviour agrees with the retentions obtained, which were always lower than 12%, as shown in Figure 4.

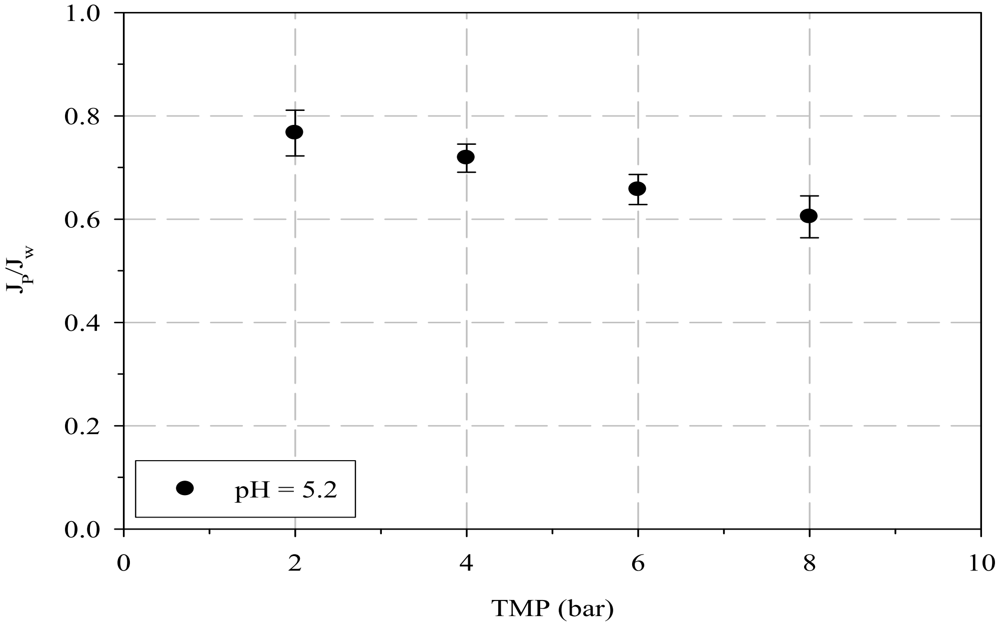

Figure 3. Effect of the TMP on the permeate flux decrease of a 1.0 mM Cu (II) solution at pH 5.2

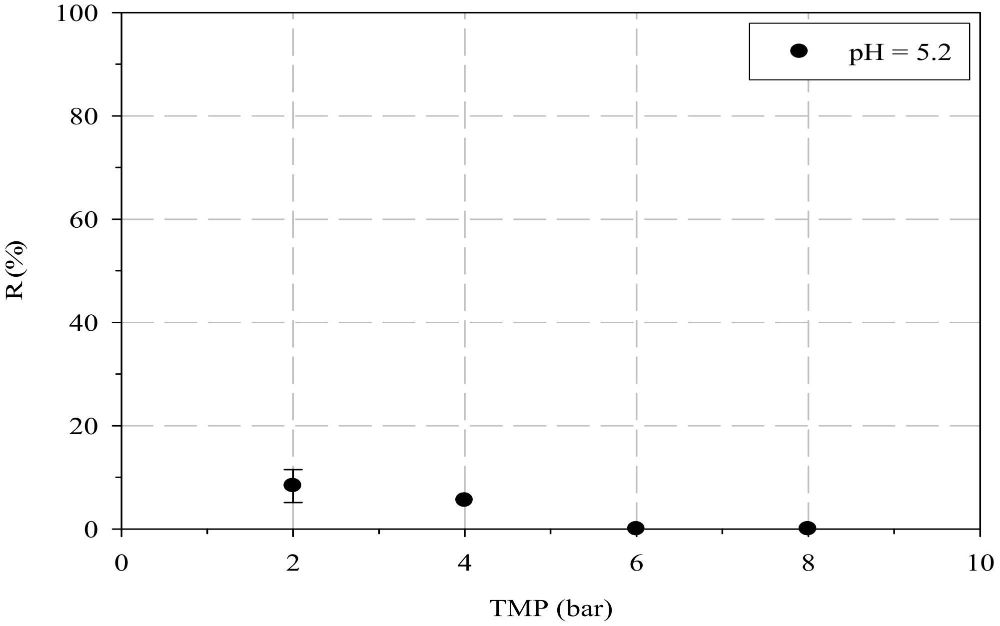

Figure 4. Effect of the TMP on the copper retention of a 1.0 mM Cu (II) solution at pH 5.2

The low retention of copper ions can be ascribed once more to the, this time, inexistence of soluble charged hydroxides, unlike for the iron (III) case. The speciation diagram for copper, shown in Figure 5, (the diagram was obtained using a freely available chemical speciation diagram software, Puigdomenech 2004) demonstrates that, at the working pH, only free copper ions exists so there is no possibility of forming an active layer of charged hydroxides over the membrane surface.

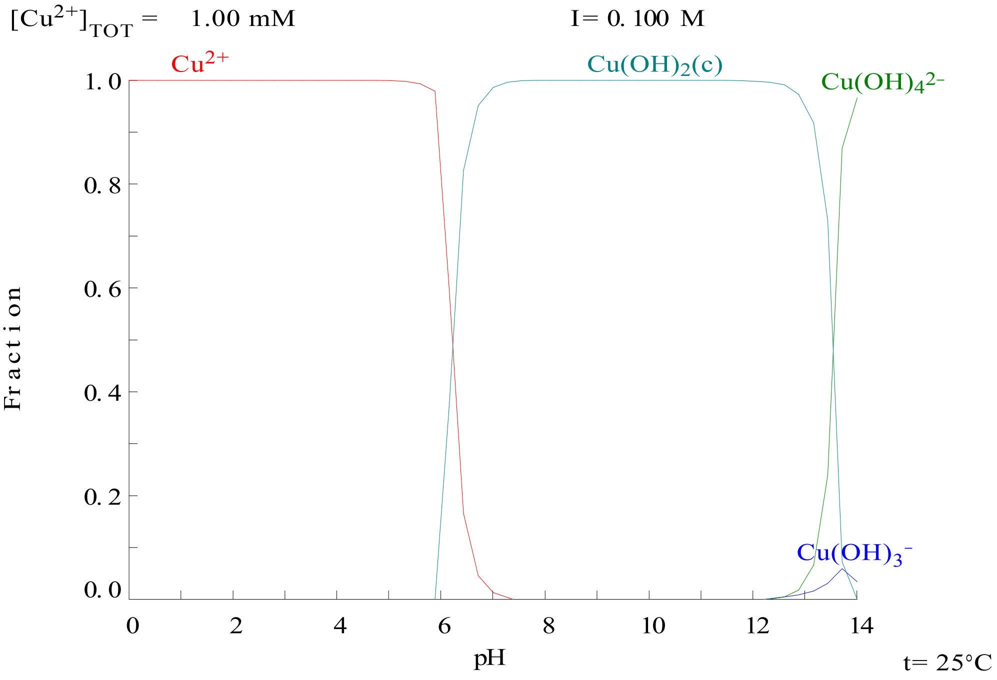

Figure 5. Chemical speciation diagram of a 1.0 mM Cu (II) solution at 25ºC

3.3. Chromium (III) filtration

Several solutions containing chromium (III) were filtered at pH ranging from 1 to 6. The filtration results are shown in Figures 6 and 7. As it can be seen in Figure 6, the TMP plays an important role on the permeate flux decrease occurred during the operation.

On the one hand, as in the cases of iron mixtures and copper solution filtration, the higher the TMP, the larger the permeate flux decline. On the other hand, as the pH of the solution to be filtered increases, the permeate flux decrease becomes higher. This trend agrees with the results showing the chromium retentions of the same solutions.

As it can be seen in Figure 7, when the TMP increases, the iron retention falls. Furthermore, as the pH of the solution increases, the chromium retention is better. This result can be explained as in the iron (III) case and attributed to the presence of soluble chromium hydroxide species. The speciation diagram shown in Figure 8 illustrates that, the higher the pH of the solution, the higher the fraction of chromium charged hydroxides present in solution. Thus, these results seem to indicate that when filtering other heavy metals different than iron, the main mechanism allowing the metal retention is the same, the presence of soluble charged hydroxides which can interact with the ceramic material of the membrane surface, forming an active filtering layer that performs as the actual membrane.

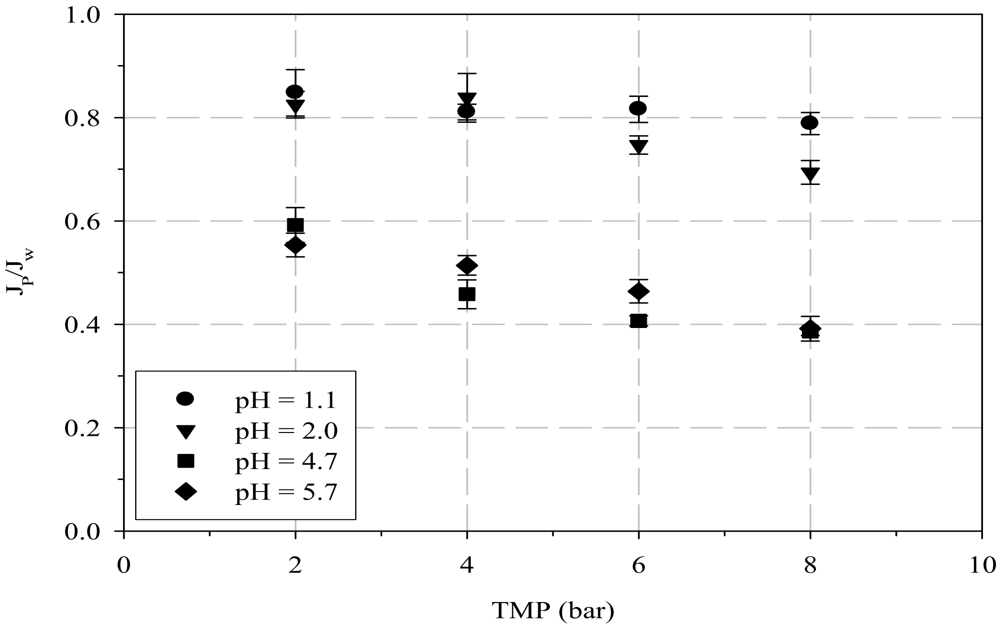

Figure 6. Effect of the TMP on the permeate flux decrease of a 1.0 mM Cr (III) solution at several pH

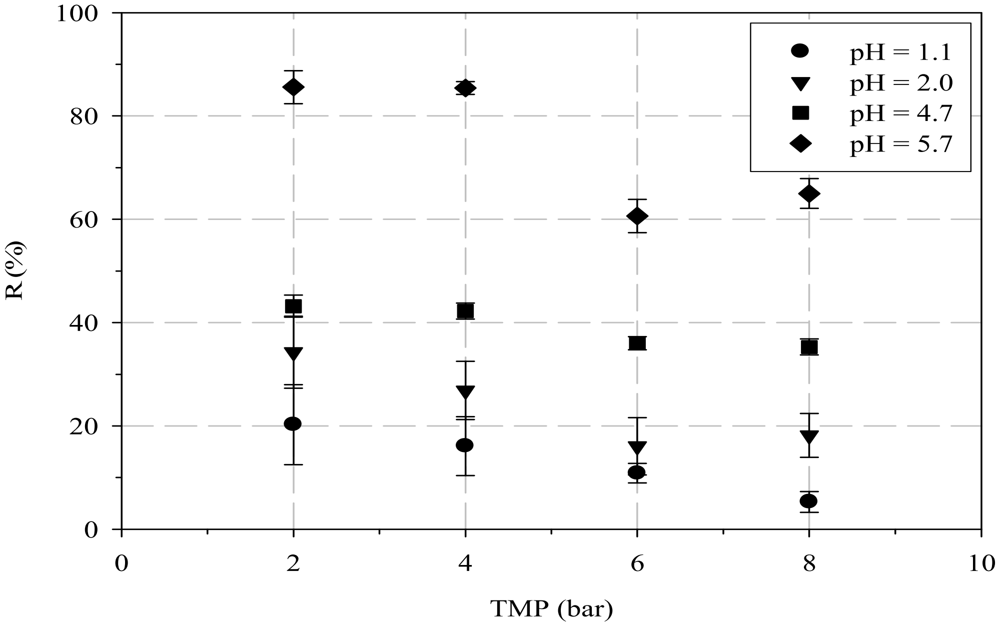

Figure 7. Effect of the TMP on the chromium retention of a 1.0 mM Cr (III) solution at several pH

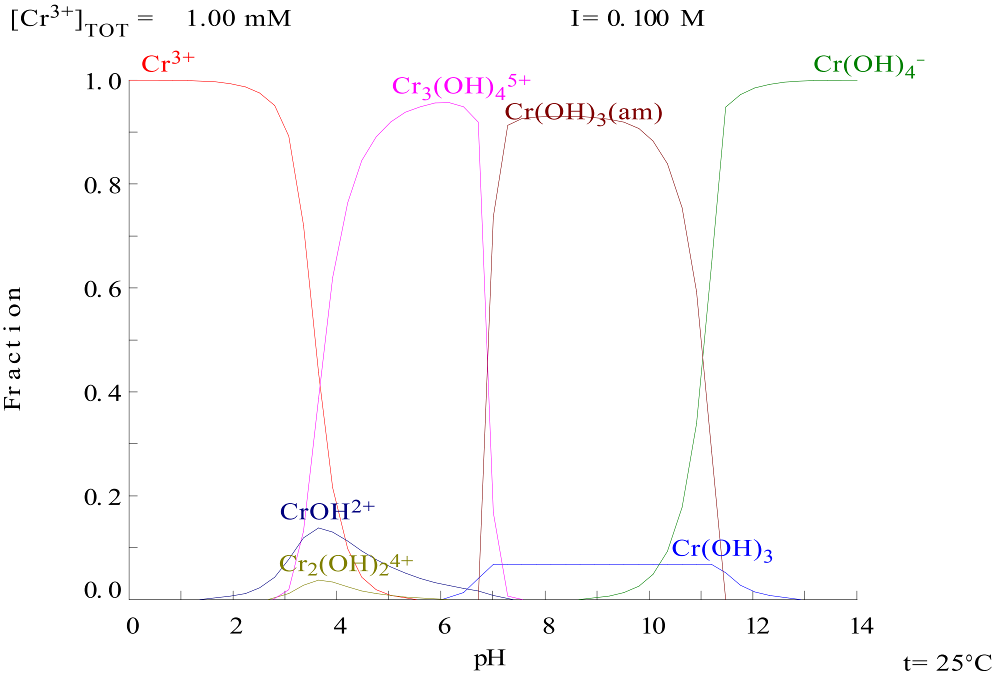

Figure 8. Chemical speciation diagram of a 1.0 mM Cr (III) solution at 25ºC

4. Conclusions

Iron present in form of iron (III) can be retained by a 5-kDa ceramic ultrafiltration membrane. However, when dealing with mixtures of iron (II) and iron (III), the retention depends on the iron (III)/iron (II) ratio. The results seem to indicate that iron (III) soluble charged hydroxides are the main responsible of the separation, while iron (II) is not able to form an active layer.

Copper (II) ions cannot be retained with the membrane selected in this work. As the chemical speciation diagram of copper shows, there are no soluble charged hydroxides in the solution at the pH tested, confirming the hypothesis that these soluble charged hydroxides are the main responsibles of the ion retention by forming an active stable layer over the membrane surface.

When dealing with 1.0 mM Cr (III) solutions, the pH is a key variable on the chromium retention. As the chromium speciation diagram shows, the fraction of soluble charged hydroxides increases with the pH of the solution. Thus, chromium retentions are larger when the pH of the solution is greater. In addition, as a result of the interaction between these hydroxides with the membrane material, the permeate flux noticeably decreases during the filtration process at high pH.

To sum up, the results presented in this contribution seem to indicate that a 5-kDa ceramic ultrafiltration membrane can be used in heavy metal recovery processes unless the nature of the ions gives no soluble charged hydroxides in solution. Thus, the behaviour of a conventional ceramic ultrafiltration membrane could be foreseen from a simple inspection of the expected speciation diagram.

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