

## Recovery of iron (III) from aqueous streams by ultrafiltration

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### Abstract

Biological wastewater treatment plants (BWWTP) are widely used to treat effluents from chemical process industry. However, there exist refractory substances, such as phenolic compounds, which require previous treatments. Advanced oxidation processes (AOP) are thoroughly being studied as pre-treatment to deal with such phenolic compounds before a BWWTP. Metal salts are widely used as homogeneous catalysts in AOP because they present higher activity than those heterogeneous. Unfortunately, to prevent subsequent environmental damage, they have to be recovered (and/or recycled) from the reactor effluent, which increases the treatment cost. Iron is often added as effective catalyst in the abovementioned AOP. In this study, a 5 kDa molecular weight cut-off (MWCO) ultrafiltration ceramic membrane (TAMI Industries, France) is tested to directly retain iron species from water. The influence of transmembrane pressure, solution pH, iron concentration and iron valence ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) over iron retention at room temperature is investigated. The results indicate that there is a strong connection between iron speciation and recovery efficiency. When soluble charged iron hydroxide species are present in solution, high retention is attained, up to 99.9%. Thus, the retention mechanism involved could be the interaction between these metal hydroxides in solution and the membrane surface, forming a dynamic membrane.

**Keywords:** Ceramic membrane; Iron; Ultrafiltration; Heavy metal recovery; Wastewater treatment

### 1. Introduction

Industrial wastewater containing refractory compounds have to be partially mineralised in order to allow their subsequent treatment in

BWWTP [1,2]. Among all existing processes able to amend such effluents, advanced oxidation processes (AOPs) are being widely used. Specifically, Fenton-based processes employ iron salts to catalyse the oxidation of refractory compounds at soft conditions with hydrogen peroxide as oxidant [3]. The main problem of Fenton

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process is that a mixture of iron (II) and iron (III) species exits the reactor together with the partially-mineralised organic compounds. Thus, a further treatment is required to remove iron species from the effluent in order to accomplish environmental legislation and to reuse them, if possible, in the reaction step. There are some processes that can deal with metal recovery such as precipitation, adsorption, extraction, and so on. Nevertheless, these processes require expensive reagents or need an important addition of energy. Moreover, they may be somewhat ineffective to metal recovery. Membrane processes such as reverse osmosis and nanofiltration can recover metallic ions [4,5], but they are still expensive due to the energy needs because of the high transmembrane pressure required. Ultrafiltration membranes work at lower transmembrane pressure than reverse osmosis and nanofiltration. However, ultrafiltration membranes are usually employed to recover macromolecular species or metallic species with previous addition of soluble polymers [6] or surfactants [7]. Obviously, ultrafiltration assisted with soluble polymers and surfactants need a supplementary step which ensures the recovery and reuse of the added polymers or surfactants [8]. However, according to the classical theory of filtration, there is no chance to use ultrafiltration to directly recover metal salts.

In this study, iron recovery is attained using a commercial ceramic ultrafiltration membrane (5 kDa MWCO) without any incorporation of chemical additives. The effect of transmembrane pressure, solution pH, iron concentration and iron nature on permeate flux decrease and iron retention is shown.

## 2. Materials and methods

### 2.1. Membrane

The tested membrane was a 5 kDa MWCO trichannel commercial membrane supplied by Tami Industries (France). Its active layer was formed by a mixture of zirconium and titanium

oxides and its support by a mixture of aluminium, titanium and zirconium oxides. Its external diameter was 10 mm, being the total length 250 mm. The hydraulic diameter of each channel was 3.6 mm and the total available filtration area was 94 cm<sup>2</sup>.

### 2.2. 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. 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 iron solutions.

### 2.3. Apparatus, experimental methods and analysis

The ultrafiltration apparatus was a home-made tangential flow laboratory pilot plant. It consisted of a 5 L reservoir tank, a pump, a pressure dampener, pressure gauges to control pressure along the experiment and an ultrafiltration module. During filtration tests, both permeate and retentate were recycled to the feed tank in order to operate in continuous mode at room temperature. The transmembrane pressure was fixed by fitting a backpressure valve located in the retentate stream. Permeate was kept at atmospheric pressure. Fig. 1 shows the described experimental set-up.

A typical test started by filling up the feed tank with 3 L of solution to be tested. Then, the pump was switched on, fixing the feed flow at 31.4 L/h. This flow corresponds to 0.27 m/s of tangential velocity. Subsequently, transmembrane pressure was set to 2 bar and the filtration

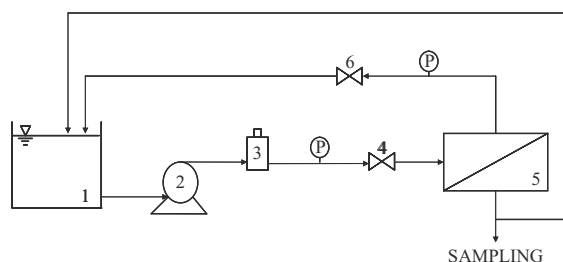


Fig. 1. Filtration experimental set-up. (1) Feed tank, (2) pump, (3) pulse dampener, (4) valve, (5) membrane cell, (6) backpressure valve.

was started. About 10 mL samples of permeate were taken and the permeate fluxes were periodically measured during filtration runs. Once the steady state achieved, the transmembrane pressure was changed to a higher pressure. The aforementioned procedure was repeated for transmembrane pressures of 4, 6 and 8 bar. Before and after filtration runs, pure water flux was measured at 2, 4, 6 and 8 bar using deionised water in order to know the permeate flux decrease and membrane fouling due to filtration. After that, membrane was cleaned with 10 g/L oxalic acid solution at 50°C for 1 h. Later, the membrane was rinsed with deionised water until assuring a neutral pH in both permeate and retentate. Then, the deionised water flux was measured in order to assure a complete removal of all species deposited over the membrane. Once completely cleaned, the membrane was submerged in deionised water in order to maintain its hydration state.

Iron in the feed and permeate samples was analysed by atomic absorption (Perkin Elmer spectrophotometer, model 3110) in order to determine iron content and, subsequently iron retention. Metal retentions ( $R$ ) were evaluated from initial feed concentration ( $C_f$ ) and permeate concentration ( $C_p$ ) as follows:

$$R (\%) = 1 - \frac{C_p}{C_f} \quad (1)$$

The permeate flow was directly measured with a balance (A&D Instruments, GF-1200) in

order to determine the change of permeate flux during the filtration runs.

### 3. Results and discussion

#### 3.1. Water permeability

As abovementioned, the water flux ( $J_w$ ) was always measured before starting a filtration run. As expected, Fig. 2 shows that the permeate flux of water is proportional to the transmembrane pressure (TMP). The average membrane pure water permeability is 23.8 L/h m<sup>2</sup> bar.

#### 3.2. Ultrafiltration of iron (III). Effect of the pH

The results from ultrafiltration of 0.90 mM iron (III) solutions are shown in this section. In particular, transmembrane pressure and pH effect on flux decrease and iron (III) retention are shown in Figs. 3 and 4, respectively. Permeate flux decrease is expressed by the ratio between the actual permeate flux ( $J_p$ ) at steady state and the initial water permeate flux, i.e. evaluated before starting the filtration run ( $J_w$ ). For instance, a ratio  $J_p/J_w$  equal to 0.90 means that, during filtration, the permeate flux is 10% lower than the initial pure water flux.

As it can be seen in Fig. 3, the permeate flux decreases due to the ultrafiltration of the 0.90 mM

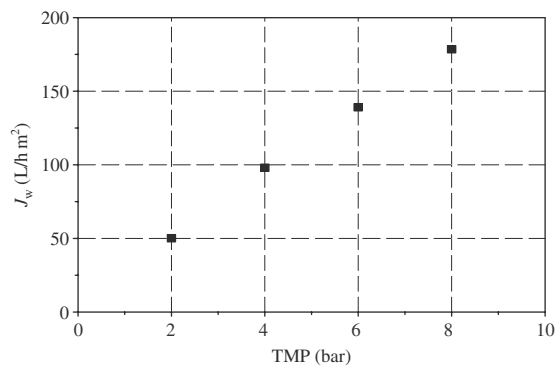


Fig. 2. Water flux at different TMP.

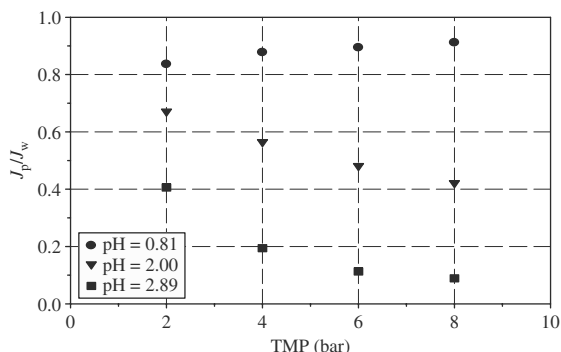


Fig. 3. Permeate flux decrease at different TMP. Effect of the pH.

iron (III) solution, at any pH. This could be due to the concentration polarization but probably the formation of a stable layer of soluble iron species over the membrane surface could better explain this high flux reduction. More significant flux decrease is obtained at pH = 2.89 and pH = 2.00. This common trend could be due to the deposition of iron (III) species on membrane material, which causes a decrease of effective membrane pore size even giving a stable layer that acts like a new membrane. As it is well known, metallic species easily interact with ceramic materials that compose the ceramic membrane tested in this work. Instead, no significant effect of transmembrane pressure on permeate flux is observed at pH = 0.81. This is in agreement with iron (III) retentions obtained and will be explained later.

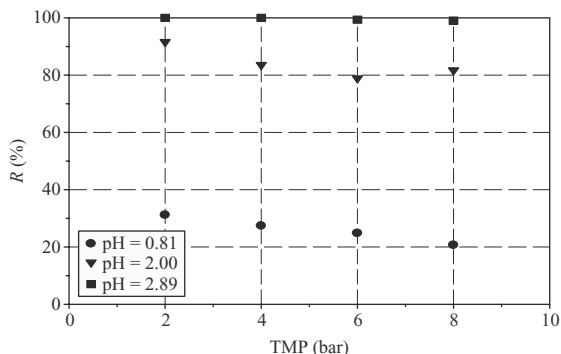


Fig. 4. Iron (III) retention at different TMP. Effect of the pH.

Fig. 4 illustrates the effect of TMP over the retention at different pH. As it can be seen, the retention slowly decreases as TMP increases. On the other hand, pH has a major influence on the retention. At high pH, the retention increases, being practically 100% at pH = 2.89. The chemical forms of iron (III) in solution probably play a key role on the iron (III) retention. The chemical speciation diagram of the iron (III) at a concentration of 0.90 mM and room temperature is shown in Fig. 5. These chemical speciation diagrams were generated by using a freely available metal speciation diagram software [9].

Iron (III) exists in a wide variety of chemical forms as a function of the solution pH. Therefore, all iron forms may be retained in a different way. Comparing Figs. 4 and 5, it can be hypothesized that the higher the soluble hydroxides concentration in solution, i.e. the higher the pH, the greater the iron (III) retention and the lower the permeate flux. It must be noted that, at pH = 0.81, almost no hydroxylated iron species exist in solution and, subsequently, the iron retention was poor and the permeate fluxes were approximately 85% of the initial water flux. Some evidence of the importance of pH over metal retention, in connection to the chemical forms of species, was

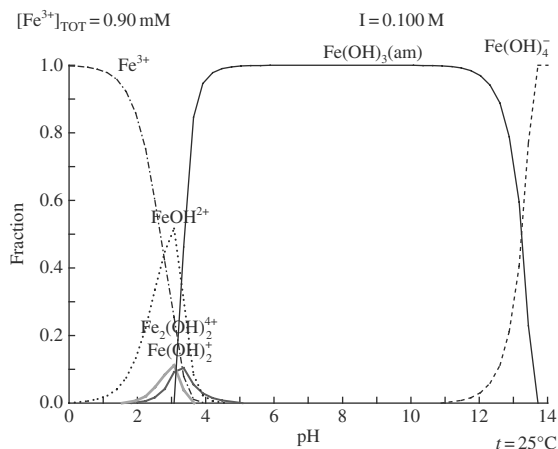


Fig. 5. Speciation diagram of 0.90 mM iron (III) solution.

also shown in a previous study focused on nano-filtration of cobalt species [10].

### 3.3. Ultrafiltration of iron (III) solutions. Effect of the initial concentration

Initial concentration of metal can have an important effect on permeate flux decrease and iron (III) retention. Moreover, it is important to know the effect of initial concentration in order to know the limitations of the process and their optimal operating conditions. Thus, 4.5 mM and 9.4 mM iron solutions were filtered and compared with results from 0.90 mM solution. The pH of both solutions was fixed to 2.00 because it was the best pH to obtain satisfactory iron (III) retentions at 0.90 mM, as previously stated. Fig. 6 shows the initial concentration effect on the permeate flux.

The permeate flux reduction is higher as the initial concentration increases. Higher interaction between iron (III) and the membrane material probably occurs when solute concentration is higher because the concentration over the membrane surface increases. The iron (III) speciation diagram at higher iron concentration demonstrates that the fraction of hydroxylated species is almost constant although the absolute concentration obviously increases. Thus, these results can be

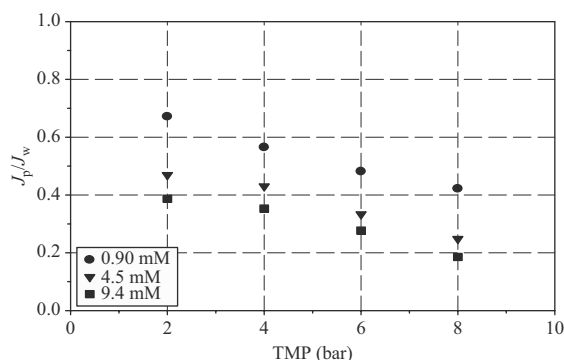


Fig. 6. Permeate flux decrease at different TMP. Effect of the initial concentration.

explained by the better interaction between iron soluble hydroxides and the membrane material, which enhances the adsorption and/or formation of a stable layer. The effect of the feed iron concentration over the retention is shown in Fig. 7.

Regardless the TMP, the iron (III) retention ranges from 70 to 95%. Between 2 and 4 bar, the iron (III) retention slowly decreases to increase again between 4 and 8. The different retention could be related to the thickness and stability of the dynamic layer, which in turn depends on the TMP pressure, i.e. the permeate flux, and the iron concentration in the bulk solution. Thus at high TMP and iron concentration, the formed layer is expected to be more stable and steady so the retention shows similar trends. In addition, the TMP can also affect the thickness of the layer by compacting it.

### 3.4. Ultrafiltration of iron (II) solutions

Different solutions containing iron (II) sulfate at different pH values ranging from 1 to 6 were filtered at different transmembrane pressures (2, 4, 6 and 8 bar). In all cases, no iron (II) retention was attained. Fig. 8 shows the chemical speciation diagram of a 0.90 mM iron (II) solution. As it can be seen, there are no soluble charged hydroxide species, which is a major difference with respect iron (III). Therefore, these experiments

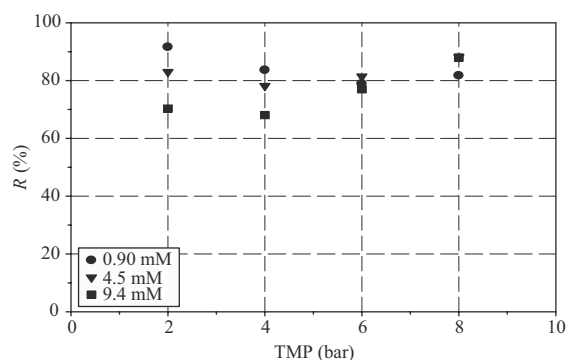


Fig. 7. Iron (III) retention at different TMP. Effect of the initial concentration.

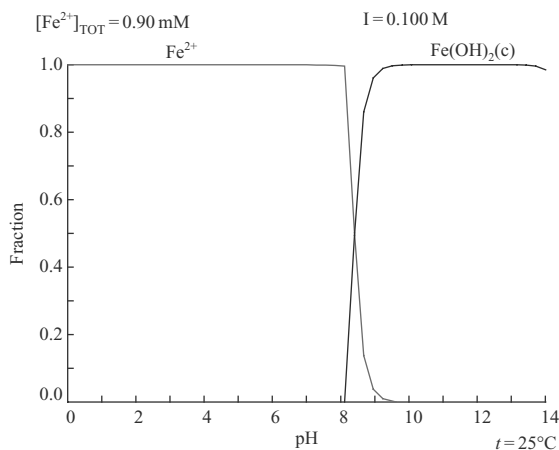


Fig. 8. Speciation diagram of 0.90 mM iron (II) solution.

reinforce the assumption that the mechanism allowing the retention of iron (III) is the presence of soluble charged iron hydroxide species, which are responsible of the iron (III) retention due to their interaction with the membrane material.

#### 4. Conclusions

Ultrafiltration of iron (III) and iron (II) was studied. A 5-kDa ceramic membrane is able to retain iron (III) species at transmembrane pressures between 2 and 8 bar without adding any enhancing filtration substance. Nevertheless, the pH of the feed solution is especially important due to its significant effect on iron (III) retention. It is suggested that the presence of soluble iron (III) hydroxides has an important role over the filtration efficiency. Additionally, when the iron (III) concentration in the feed solution increases, iron (III) retention slightly decreases at 2 and 4 bar but it remains almost constant at higher pressures.

On the contrary, when solutions of iron (II) are filtered, negligible iron (II) retention was achieved. Inspecting the chemical speciation diagram of the iron (II) and the iron (III), the results are in agreement with the assumption that soluble iron hydroxides are the species responsible of the

retention. The absence of these species for iron (II) gives negligible retention and almost invariable flux. Thus, the occurrence of a dynamic layer formed by hydroxylated iron (III) species can be hypothesized as probable rejection mechanism. Thus, effective ultrafiltration of iron (III) can be accomplished without adding complexing agents or macromolecules to enlarge the size of the targeted species.

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#### Symbols

$C_f$	feed iron concentration (mM)
$C_p$	permeate iron concentration (mM)
$R$	metal retention (%)

#### References

- [1] A. Pintar, Catal. Today, 77 (2003) 451–465.
- [2] M. Santiago, F. Stüber, A. Fortuny, A. Fabregat and J. Font, Carbon, 43 (2005) 2134–2145.
- [3] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez and S. Espulgas, Appl. Catal. B: Environ., 47 (2004) 219–256.
- [4] H.A. Qdais and H. Moussa, Desalination, 164 (2004) 105–110.
- [5] J. Tanninen, M. Mänttari and M. Nyström, Desalination, 189 (2006) 92–96.
- [6] R. Molinari, P. Argurio and T. Poerio, Desalination, 162 (2004) 217–228.
- [7] F. Beolchini, F. Pagnanelli, I. De Michelis and F. Vegliò, Environ. Sci. Technol., 40 (2006) 2746–2752.
- [8] H. Kim, K. Baek, J. Lee, J. Iqbal and J.-W. Yang, Desalination, 191 (2006) 186–192.
- [9] I. Puigdomenech, Medusa Software, 2004, www.kemi.kth.se/medusa.
- [10] K.-W. Choo, D.-J. Kwon, K.-W. Lee and S.-J. Choi, Environ. Sci. Technol., 36 (2002) 1330–1336.