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Iron removal from aqueous solution by oxidation, precipitation and ultrafiltration

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ABSTRACT

In the present work, the kinetics of the oxidation and precipitation of iron in presence of sulphate and ethylenediamine tetraacetic acid (EDTA) ions during ultrafiltration process was studied. The presence of these ions delayed significantly the kinetics of oxidation—precipitation by the formation of iron-sulphate or more stable iron-EDTA complexes. This increased the solubility of iron during ultrafiltration process. A mechanism was elaborated to explain the complexation of these ions with iron. The ultrafiltration permitted to separate the iron colloids but not the iron complexes with sizes lower than the diameter of the membrane pores. The ultrafiltration of solutions containing iron requires a regular and efficient cleaning process to avoid the membrane plugging.

Keywords: Iron; Oxidation; Ultrafiltration; Sulphate; EDTA

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1. Introduction

The availability of resources in mediocre quality water, as the saline underground waters, and the waters of drainage, represents an important stake henceforth, notably in the arid and semi-arid zones of the countries having few resources in water. The water desalination is a very established technology for cities water provision. The most current desalination techniques are the thermal distillation for the treatment of increased water quantity (55 000 $m^3 h^{-1}$) and the membranes technology, i.e. the inverse electrodialyse [1], the reverse osmosis [2], ultrafiltration [3] and nanofiltration [4]. The membranes technology processes are used for the desalination of brackish waters with salt concentrations inferior to 10 $g L^{-1}$, while the processes of inverse osmosis and thermal distillation are generally applied to desalinate the sea water of which the salt concentration is superior to 30 $g L^{-1}$.

The thermal distillation permits to transform salted water in steam that is condensed to get the desalinated water. With the inverse electrodialyse process, salts separated from water under the action of an electric load. The inverse osmosis consists in the application of a pressure on water introduced in the system that is forced through a semi-permeable membrane keeping most salts. The experienced pressure should be especially high as the salt concentration in water is raised. Ultrafiltration is not fundamentally different from reverse osmosis, microfiltration or nanofiltration, except in terms of the size of the molecules it retains. In fact, ultrafiltration is a variety of membrane filtration in which hydrostatic pressure forces a liquid against a semi-permeable membrane. Suspended solids and solutes of high molecular weight are retained, while water and low molecular weight solutes pass through the membrane.

Different techniques for iron removal are used in water purification processes, i.e. limestone filter [5], ion exchange on cationic exchange resins [6] and the oxidation—precipitation of iron (II) into iron hydroxides, especially the iron oxyhydroxide FeOOH. The iron hydroxides colloids can be removed by membrane processes based on reverse osmosis [7], nanofiltration [7, 8] and ultrafiltration [9]. Ultrafiltration process was used as a pre-treatment process prior to desalination on reverse

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osmosis membranes to separate colloidal suspension of ferrous iron [10]. However, these membranes water treatment techniques are confronted to scale formation which affected their performance. Therefore, the ultrafiltration of solutions containing colloidal suspension of iron precipitates requires establishing procedures of plugging control and cleaning because these species have strong plugging properties vis-a-vis the membrane. In order to avoid the membrane plugging, iron has to be removed from the raw waters using a pre-treatment process that includes certain operations such as oxidation and separation. These operations are affected by different parameters such as temperature, pH [11], oxygen flow [12] and complexant ions [13, 14], i.e. humic acids [15].

The present work aims to investigate the effects of complexant ions, i.e. sulfate and ethylenediamine tetraacetic acid (EDTA) on iron removal from aqueous solutions. Iron colloids formation was provoked by oxidation and precipitation. It aims also to study the performance of the ultrafiltration process to remove iron from solutions containing complexant ions when this membrane process is used in combination with oxidation and precipitation.

2. Materials and methods

2.1. Chemicals and materials

Firstly, experiments were carried out to investigate the kinetics of iron precipitation in a 6 g L^{-1} NaCl (CAS n° 7647-14-5) solution and in a solution containing 4.9 mg L^{-1} of Na_2SO_4 (CAS n° 7757-82-6). The initial iron concentration was fixed at 2.8 mg L^{-1}. Thereafter, the effect of the complexant EDTA (CAS n° 2001-94-7) was studied. A constant Na_2SO_4 concentration of 4.9 g L^{-1} was added to solutions with molar EDTA/iron ratios, R = [EDTA]/[Fe] equal to 0.5 and 1. For all these experiments, the iron precipitation was provoked by air bubbling and stirring. Finally, experiments on iron removal by a hybrid system (oxidation—precipitation—ultrafiltration) from solutions containing NaCl, Na_2SO_4 and both Na_2SO_4 and EDTA were investigated. The chemicals concentrations are comparable to those of the oxidation—precipitation study. For all experiments, the ionic strength of the prepared solutions was 0.1 M. The initial pH was fixed at 7.3. Iron was added in the form of $FeCl_2{\cdot}7H_2O$ (CAS n° 13478-10-9). The used salts were of p.a., grade from Fluka. The utilized water was deionized using Millipore Elix3.

2.2. Experimental set-up

All experiments were carried out at room temperature in a 6 L reactor in which a volume of 4 L of the studied solution was placed. The membrane system is a submerged membrane one. An aspiration pump immersed in the reactor permitted to collect the samples to be analysed. An airflow meter controlled the injected air flow and a manometer indicated the transmembrane pressure (TMP) (Fig. 1). The reactor was maintained perfectly agitated by a propeller-driven stirrer operating at 500 rpm with airflow rate of 150 L h^{-1}. The air has been injected in the bottom of the submerged membrane module to avoid the deposition of iron precipitates on the membrane. A rigid breakthrough envelope permitted to maintain and to protect the hollow fibres. The characteristics of the membrane module submerged in the reactor are given in Table 1.

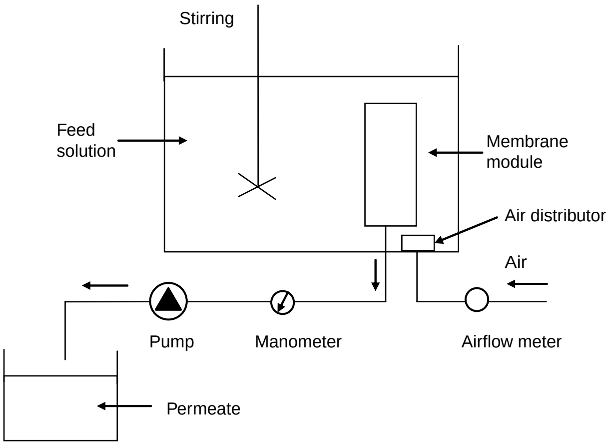

Fig. 1. Schematic illustration of the hybrid system (oxidation—precipitation—ultrafiltration) set-up.

2.3. Analysis procedures

Ultrafiltration experiments of two solutions of 4.9 g L^{-1} Na_2SO_4 with or without EDTA (2.5 10^{-5} M) and a solution of 6 g L^{-1} NaCl have been achieved. The membrane permeability to these solutions which did not contain iron has been determined from the slope of the curves of the permeate flow as a function of the TMP. This value was considered as a reference and permits to determine if the cleaning of the membrane was efficient or not. It permits, also, to calculate the membrane resistance. The permeate flow was determined by measuring the permeate solution weight with a 'Sartorius' balance. According to these experiments, the TMP was fixed at 100 mbar. Thereafter, 2.8 mg L^{-1} of iron was added to solutions with comparable compositions as those without iron. Then, ultrafiltration experiments were investigated.

A periodic samples of 20 mL were taken from the reactor when ultrafilitration was not applied or from the permeate solution during ultrafiltration experiments, then acidified by the sulphuric acid (1.77 M) to a pH = 1 and filtered through a 0.45 µm filter. Then, the total iron

Table 1
Ultrafiltration membrane module characteristics.

Type	Fibre number	Length (mm)	External diameter (mm)	Surface of filtration (m^3)	Specific surface (m^2/m^3)	Pores diameter (μm)	Resistance, Rm (m^{-1})
GUFS-2	18	250	0.72	0.01	127.3	0.01	$2.5(\pm0.5)10^{12}$

concentration has been determined by atomic absorption spectrophotometer 'Varian AA 120'. To determine the iron (II) concentration, the orthophenanthroline was added to the samples and then analysed using a spectrophotometer (UV/VIS, V-530 JASCO). The orthophenanthroline forms red coloured complex with only iron (II). The sizes of iron precipitates from the different solutions were determined using a Laser granulometer 'Malvern Master Size/E'.

3. Experimental results

3.1. Iron colloids formation by oxidation and precipitation

For all experiments, the iron colloids formation was provoked by oxidation and precipitation. Ultrafiltration was not applied. Fig. 2 shows the iron concentration evolution with time in solutions containing an initial iron concentration of 2.8 mg L^{-1} and NaCl or Na_2SO_4 with or without EDTA. After the first minute, a significant iron concentration decrease was observed in the different solutions. In presence of sulphate ions, the iron solubility was greater than that in NaCl solution during the first 20 min. This indicates that the sulphate ions delayed the iron precipitation. At the end of the experiments, the precipitates were identified by X-ray diffraction (XRD). The XRD pattern showed mainly four large peaks at d-spacings of 3.31, 2.49, 1.93 and 1.53 Å characteristics of iron oxide hydroxide, FeOOH and indicated a poorly crystalline phase [16]. The increase of the iron solubility was remarkably improved when the EDTA was added to the sulphate solution. In fact, for a molar ratio [EDTA]/[Fe] of 0.5, the iron concentration evolution observed during the 20 first minutes is close to the one obtained in the absence of EDTA. Thereafter, the iron concentration remained practically constant and reached 0.3 mg L^{-1}. However, in presence of only sulphate ions, all the iron precipitated in the solution. For a molar ratio [EDTA]/[Fe] of 1, the iron concentration remained practically constant (~0.6 mg L^{-1}). It is worth noticeable that the iron solubility became twice higher when the molar ratio [EDTA]/[Fe] was multiplied by 2. The iron solubility increase in presence of sulphate ions was explained by the formation of intermediate iron sulphate complexes [16, 17]. These complexes are less stable than iron oxide hydroxide. The constant solubility of iron in presence of EDTA ions could be explained by the formation of more stable iron-EDTA complexes.

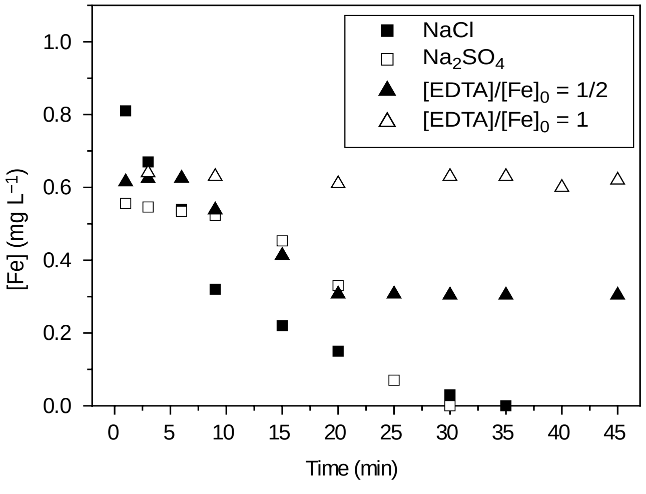

Fig. 2. Iron concentration evolution with time in feed solutions containing an initial iron concentration of 2.8 mg L^{-1} and respectively, 6 g L^{-1} NaCl, 4.9 g L^{-1} Na_2SO_4 with or without EDTA at a stirring of 500 rpm and an airflow rate of 150 L h^{-1}.

3.2. Ultrafiltration study

The application of the ultrafiltration as a process of separation is possible if the size of the particles is sufficient so that they do not cross the membrane pores. The size distributions of the iron precipitates, obtained from NaCl, Na_2SO_4 and both Na_2SO_4 and EDTA solutions containing an initial iron concentration of 2.8 mg L^{-1}, at times slightly greater than 5 min, are given in Fig. 3. The mean colloids sizes were 300, 28 and 15 μm for NaCl, Na_2SO_4 and both Na_2SO_4 and EDTA solutions, respectively.

The solutions compositions and the permeate flow J at fixed TMP of 100 mbar are given in Table 2. The permeate flow (J) is compared to that of the same

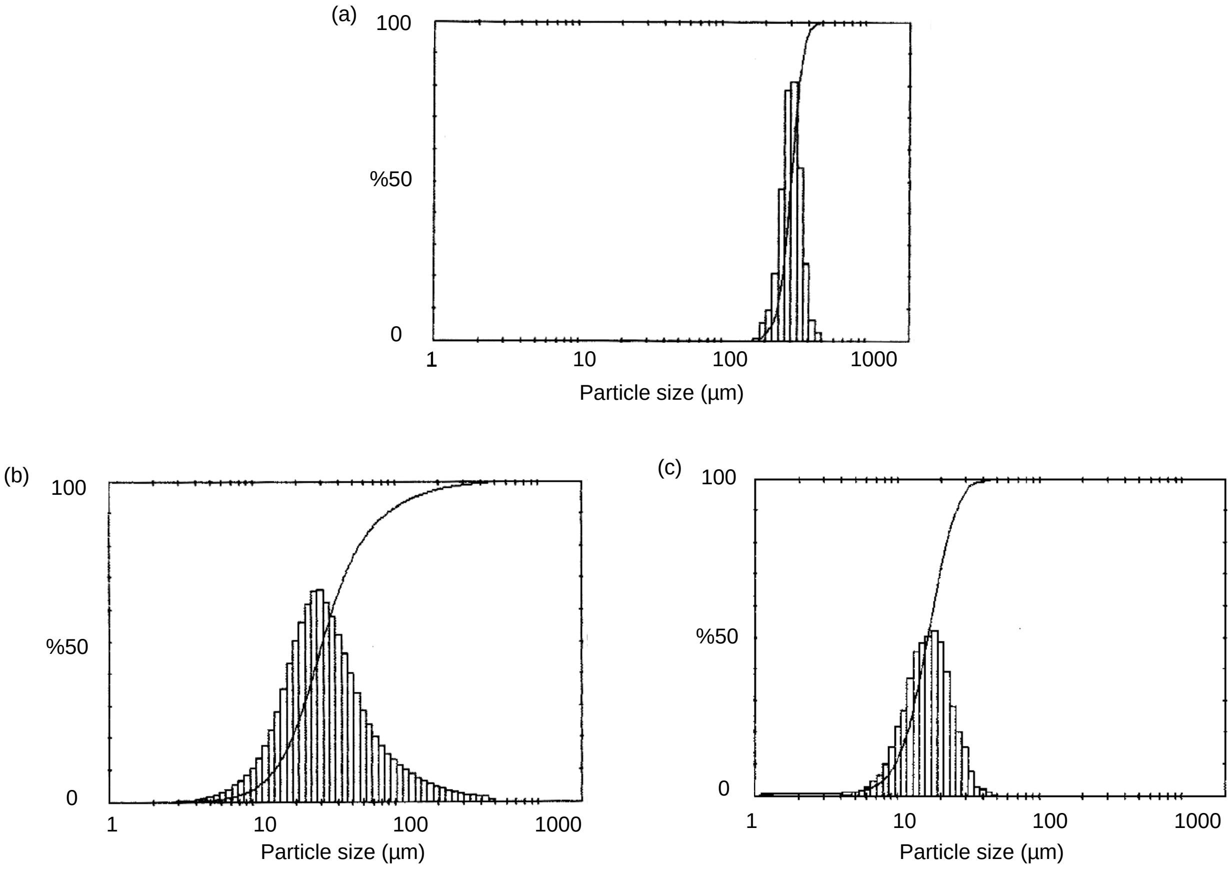

Fig. 3. Size distributions of iron colloids in feed solutions containing an initial iron concentration of 2.8 mg L^{-1} and (a) 6 g L^{-1} NaCl (b) 4.9 g L^{-1} Na_2SO_4 and (d) 4.9 g L^{-1} Na_2SO_4 and 2.5 10^{-5} M EDTA at a stirring of 500 rpm and an airflow rate of 150 L h^{-1}.

Table 2
The solutions compositions and the permeate flow J at a fixed transmembrane pressure of 100 mbar.

Solution composition	Without iron	With 2.8 mg L^{-1} of iron	$\Delta J/J_0 \times 100$
	Permeate flow, J_0 ($L\ h^{-1}m^{-2}$)	Permeate flow, J ($L\ h^{-1}m^{-2}$)	
6 g L^{-1} NaCl	40.44	39.96	1.1
4.9 g L^{-1} Na_2SO_4	41.1	37.5	8.7
4.9 g L^{-1} Na_2SO_4+ 2.5 10^{-5} M EDTA	43.8	42.32	3.3

solution (J_0) without iron addition. The flux decline ratio $\Delta J/J_0$ indicates if the membrane plugging occurs during iron removal experiments. For NaCl solution, the addition of iron did not affect the permeate flow, i.e. $\Delta J/J_0 = 1.1$ %, what is not surprising considering the size of the colloids (~300 µm). For the EDTA and Na_2SO_4 solutions, the permeate flow decreased when iron was added. However, the decrease was more pronounced for Na_2SO_4 solution. This is related to the small size of the iron oxide hydroxide colloids which partially penetrated in the pores of the membrane. The addition of EDTA ions to the sulphate solution favoured the iron transfer through the membrane. This is indicated by the decrease of $\Delta J/J_0$ when EDTA ions were added to the sulphate solution.

The ultrafiltration of the 6 g L^{-1} NaCl solution, containing an initial iron concentration of 2.8 mg L^{-1}, showed the presence of 0.4 mg L^{-1} of iron after 36 min. However, after the same period, iron was not detected during the iron oxidation in the same solution without ultrafiltration. This was related to a partial dissolution of the iron precipitates formed in the membrane or in the hoses during previous experiments. This was confirmed by the presence of iron during ultrafiltration of distilled water. Therefore, intensive cleaning of the pilot and systematic control of the iron concentration of the permeate solution was elaborated after every test. So, after each experiment, the membrane module has been cleaned by citric acid solution (3 g L^{-1}) during 2 h, then by distilled water. This allowed eliminating the iron deposits on the membrane.

The iron concentration evolution during ultrafiltration of Na_2SO_4 solution containing an initial iron concentration of 2.8 mg L^{-1} are given in Table 3. The iron appeared in the permeate solution after 7 min. Thereafter, the values determined were two times weaker than those determined during iron removal by oxidation—precipitation without ultrafiltration. This was related to the catalytic action of the iron oxide hydroxide that deposited on the membrane which improved the iron precipitation. The iron concentration decreased during time to reach the value of 0.18 mg L^{-1} after 33 min. In addition, a concentration of 0.1 mg L^{-1} of Fe (II) was determined after 14 min of experiment. Then, only Fe(III) was detected.

Ultrafiltration of Na_2SO_4 solution containing an initial iron concentration of 2.8 mg L^{-1} has been achieved in presence of EDTA (2.5×10^{-5} M). The solubility of iron increased then remained practically constant and equal to 0.3 mg L^{-1} after ~60 min of ultrafiltration. These results are comparable to those obtained for iron removal by oxidation—precipitation without ultrafiltration.

Table 3
The iron concentration evolution in the permeate solution during ultrafiltration of Na_2SO_4 solution containing an initial iron concentration of 2.8 mg.L^{-1}.

Time (min)	$[Fe]_{total}$ (mg L^{-1})	[Fe (II)] (mg L^{-1})	[Fe (III)] (mg L^{-1})
1	< 0.1	< 0.1	< 0.1
5	< 0.1	< 0.1	< 0.1
7	0.25	0.1	0.15
14	0.25	0.1	0.15
33	0.18	< 0.1	0.18

4. Discussion

The iron removal from NaCl solution was possible by iron oxidation which enables Fe^{2+} to transform into Fe^{3+}, then the formation of iron oxide hydroxide, FeOOH. At pH = 7.3, the iron precipitation kinetic was high since the concentration of iron measured after 30 min was lower than the detection limit (0.1 mg L^{-1}) of the analysis technique used in the present work.

In Na_2SO_4 solution, the solubility of iron was higher than in NaCl solution. This was related undoubtedly to the formation of complexes between the sulphate ions and the ferrous and ferric ions. These complexes were less stable than iron oxide hydroxide so they lead only to a delay of the precipitation. Also, the atomic force microscopy (AFM) analysis (Fig. 4) showed that the surface roughness of the FeOOH precipitates increased

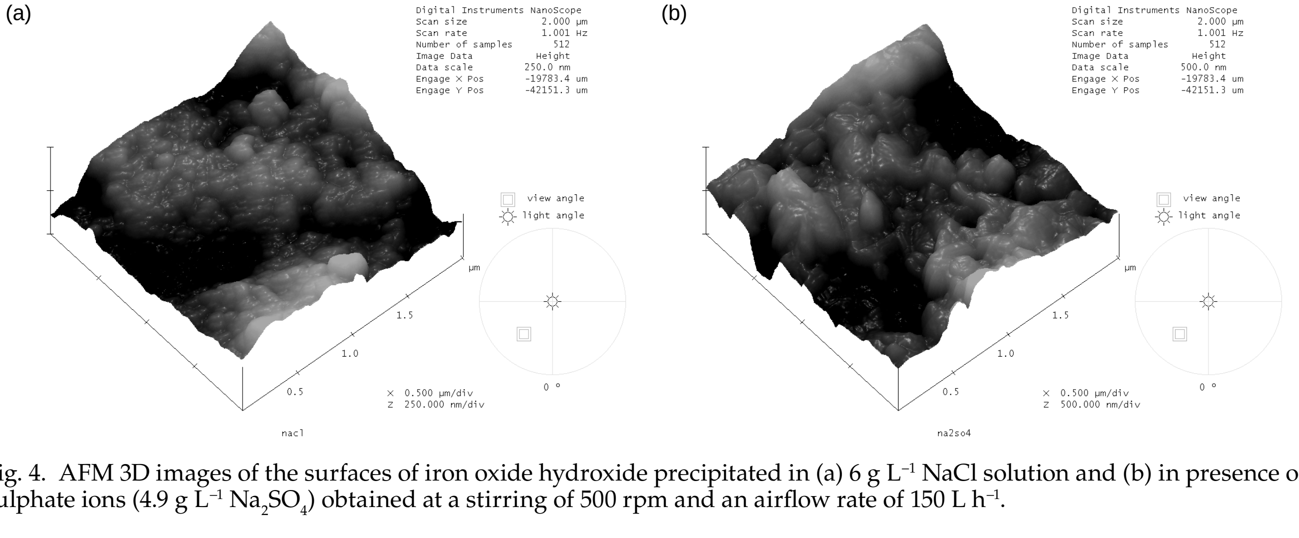

Fig. 4. AFM 3D images of the surfaces of iron oxide hydroxide precipitated in (a) 6 g L^{-1} NaCl solution and (b) in presence of sulphate ions (4.9 g L^{-1} Na_2SO_4) obtained at a stirring of 500 rpm and an airflow rate of 150 L h^{-1}.

from 46.5 nm in NaCl solution to 116.8 nm in presence of sulphate ions. This is due to sulphate adsorption on the FeOOH precipitates surfaces. This was supported by scanning electron microscopy (SEM) investigation [16].

In presence of sulphate ions and very low concentrations of EDTA, the iron solubility increased. It reached 0.3 and 0.6 mg L^{-1} for an [EDTA]/[Fe] molar ratios of 0.5 and 1, respectively (Fig. 2). This is coherent with the solubility diagram of Fe(III) with the pH calculated in absence and in presence of EDTA ions (Fig. 5). The complex Fe(III)-EDTA was very stable. This diagram permitted to explain the increase of the Fe(III) solubility in presence of increased EDTA concentration observed in the present work. The existence or not of the Fe(II)-EDTA complex that could be responsible for the increase of the solubility could not be verified. Indeed, the spectrophotometric method of Fe(II) analysis is not applicable in presence of EDTA ions, because the complex Fe(II)-orthophenanthroline is less stable than the complex Fe(II)-EDTA.

The first landing observed in the temporal evolution of the iron concentration for a molar ratio [EDTA]/[Fe] of 0.5 and in presence of sulphate ions (Fig. 2), showed that there is a competition between the sulphate and EDTA ions to complex iron. This is foreseeable because, in spite of the strong affinity of the EDTA ions for the ferrous or ferric ions, the EDTA ions concentration (2.5×10^{-5} M) was 2000 times lower than the sulphates concentration (0.05 M).

The mean colloids sizes were 300, 28 for NaCl and Na_2SO_4 solutions, respectively and 15 µm for a solution containing both Na_2SO_4 and EDTA. The mean size of colloids depended on the nature of the salts present in the aqueous solution since the ionic strength was the same for all the investigated solutions. The size differences are probably related to the interactions between the formed iron oxide hydroxide precipitates. For NaCl solution, the colloids agglomerated under the action of the electrostatic interactions. Fukushi and Sverjensky [18] showed that the sulphate ions could be adsorbed on the FeOOH precipitates since the ferric hydroxide colloids are charged positively [19]. The adsorption of the sulphate and EDTA anions on the surfaces of the colloids modified their valence and contributed to the decrease of their agglomerations by repulsion. Consequently, the ultrafiltration process permitted to separate the iron colloids but not the iron complexes with sizes lower than the diameter of the membrane pores. In practice, the oxidation—precipitation method in combination with ultrafiltration process could successfully remove iron from waters. However, in presence of high concentration of complexant ions such as humic acids, the hybrid system (oxidation—precipitation—ultrafiltration) for iron removal could be used as a pre-treatment process to reverse osmosis. In fact, limited soluble iron amount was transferred through the ultrafiltration membrane due to the increased iron solubility and the reduced sizes of the complexes formed. Also, the addition of the EDTA and sulphate ions reduced the iron colloids sizes which partially penetrated in the ultrafiltration membrane pores. This leads to the membrane plugging. So, it is necessary to establish procedures of plugging control and membrane cleaning. Even thought, ultrafiltration tests by using different membranes should be realized to check membrane performance like flux and rejection. For example, it was shown that ceramic ultrafiltration membranes can be successfully employed to separate iron (III) from aqueous solutions [20].

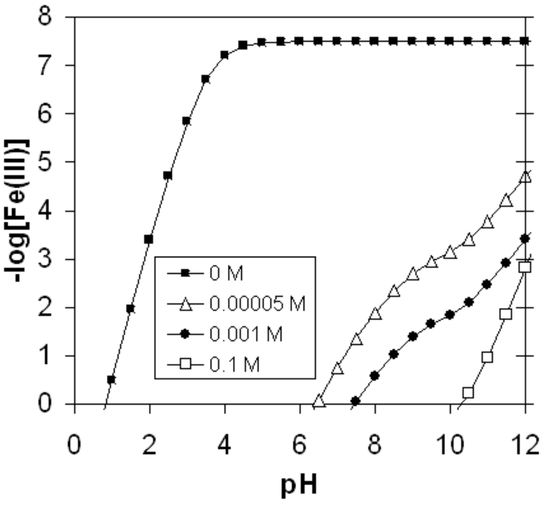

Fig. 5. Iron (III) solubility with pH in presence of different EDTA concentrations.

A schematic mechanism was elaborated from these results explaining the complexation of EDTA and sulphate ions with iron (Fig. 6).

5. Conclusion

The iron removal from solutions containing NaCl, Na_2SO_4 and EDTA ions by oxidation, precipitation in combination with ultrafiltartion process was studied. It was shown that the presence of sulphate ions in the solution delayed significantly the kinetics of oxidation and precipitation of iron by the formation of iron-sulphate complexes. This increased the solubility of iron during ultrafiltration process. The adsorption of the sulphate ions on the iron precipitates could also limited their growth. In the presence of EDTA ions, an increase of the iron solubility has been observed depending on the added EDTA ions concentration. This was due to the stability of the iron-EDTA complexes

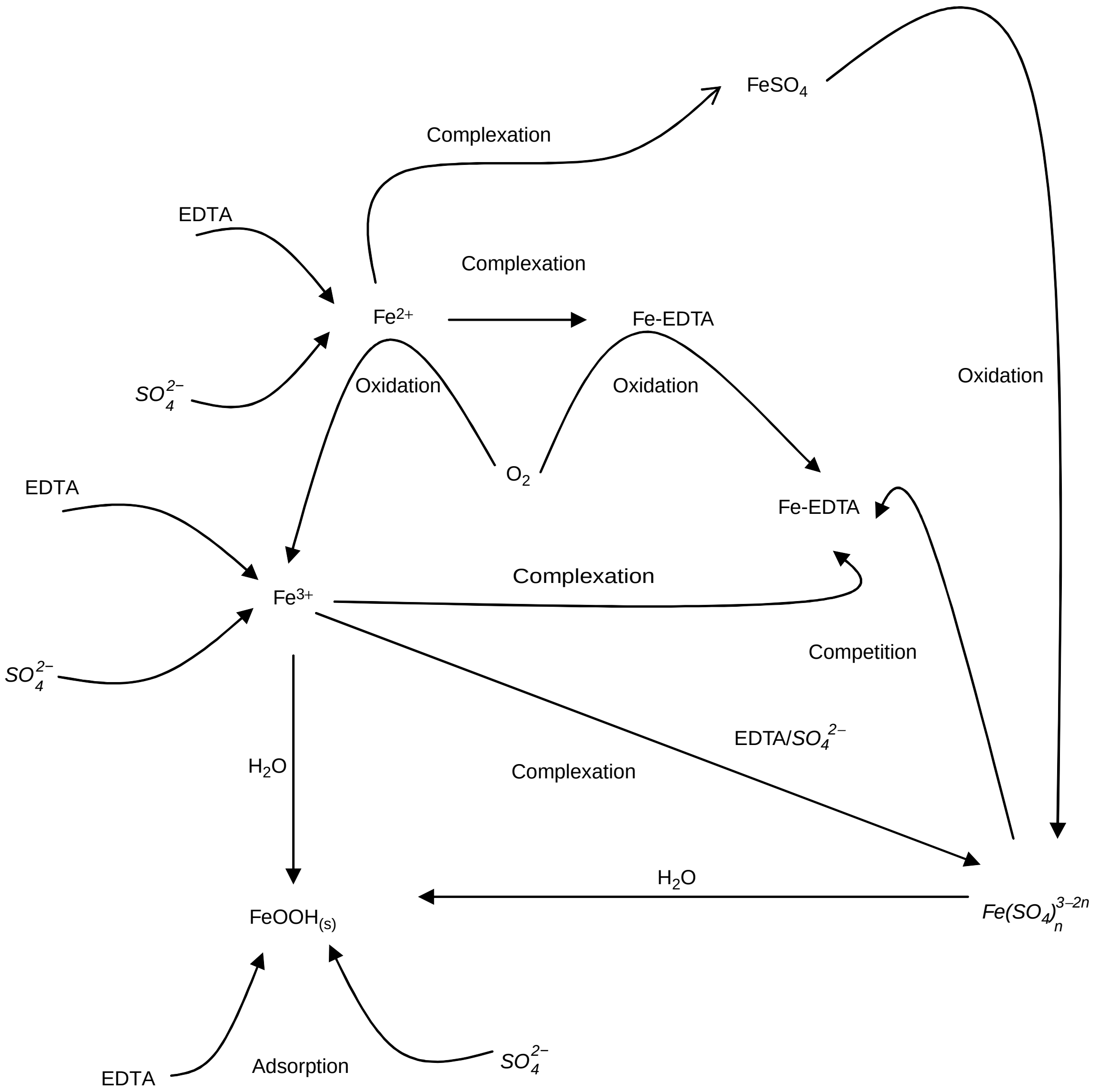

Fig. 6. A schematic mechanism explaining the effects of EDTA and sulphate ions on the iron precipitation from aqueous solution.

formed. The hybrid system (oxidation—precipitation—ultrafiltration) permitted to separate the iron colloids but not the iron complexes with sizes lower than the diameter of the membrane pores. So, in presence of high concentration of complexant ions such as humic acids, this hybrid system could be used as a pre-treatment process to reverse osmosis. On the other hand, the addition of the complexant ions reduced the iron colloids sizes which partially penetrated in the ultrafiltration membrane pores. This leads to the membrane plugging. So, the ultrafiltration of solutions containing iron requires a regular and efficient cleaning process to avoid an irreversible plugging of the membrane.

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