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Production of coagulant reagents for electro-coagulation processes at low current densities

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ABSTRACT

In this work, the electrochemical production with low current densities of iron and aluminium reagents for electro-coagulation processes has been studied. It has been found that pH is a very important parameter, being strongly related to the speciation of iron in terms of iron (II) or iron (III) species, and also to the efficiency of the electrochemical reagent-dosing process. Iron (II) species are only significant under acidic conditions because in neutral and alkaline conditions iron (II) is rapidly transformed into iron (III). Efficiencies in the dissolution of the metals are very high and, in some cases, over the value expected for a 100% – efficiency (super-faradaic efficiencies), due to the non-electrolytic dissolution of the electrodes, which is very important for iron under acidic conditions, and even more important for aluminium at alkaline pHs. This significant non-electrolytic contribution explains the different trends observed in the efficiency changes with current density.

Keywords: Electro-coagulation; Iron; Super-faradaic efficiencies; Electro-dissolution; Aluminium; Coagulants

1. Introduction

In the recent years, many works have been published related to the application of electro-coagulation in the treatment of many types of wastewaters including O/W emulsions [1,2], dye and textile wastewater [3–6], other industrial wastewaters containing hazardous species, and municipal wastewaters [7–14]. Applications to the treatment of potable water [15,16], and even to the removal of inorganic ions, such as nitrogen compounds or fluoride, have also been described [17]. In addition, some others works have been focused on the comparison of this promising electrochemical technology with conventional coagulation processes [18–20].

Primarily, both technologies merely differ in the way of dosing coagulant reagents: in the coagulation process, the addition of hydrolyzing metal salts (of iron or aluminium) as coagulant reagents is carried out by salt-solution dosing, while the electrochemical method involves the in-situ production of coagulants by electrolytic oxidation of an appropriate anode material (carbon steel or aluminium sheets).

However, in literature many advantages are proposed for the electrochemical technology such as the simplicity of the equipment required, versatility, safety and easy automation of the process [21]. Some of these advantages have been confirmed by many studies [20,22,23], other not [19], although they have been widely repeated in specialized literature. At the present moment, it is difficult to make a complete comparative analysis of both technologies, different of the very interesting works focussed on

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particular cases, but there are some recent figures which demonstrate the interest of electro-coagulation technologies for full scale applications:

- It leads to a treated water with less conductivity that a coagulation treatment because the net coagulant reagent dosed by electro-coagulation is insoluble aluminium or iron hydroxide instead of the huge amount of salts that should be added in a conventional physicochemical treatment [24], and because it often has a buffering effect on the pH [18,20] that makes not necessary neutralization after the coagulation treatment. This means fewer salts and, consequently, a higher quality effluent.
- It requires low energy and this makes possible to be powered by green energy sources, such as solar power, wind mills and fuel cells [25].

The second point is particularly interesting, because it opens the possibility of very attractive integrated processes. However, to apply this, it is convenient to use low current densities, because they also lead to low cell potentials and, consequently, to low energy consumptions. In addition, low current densities also helps to overcome problems related to the coexistence of oxygen and hydrogen in a non-divided reactor, and which may have significance in full scale applications. Moreover, it has been reported the super-faradaic efficiencies in the production of reagents (that frequently are reported for these processes) are more significant for low current densities [26,27].

Taking into account this background, the goal of this work has been to clarify the production of coagulant reagents during electro-coagulation processes carried out at low current densities in order to try to find the way to obtain good efficiencies in the production of reagents and low energy consumptions. Another point that it is aimed to clarify, it is the occurrence of iron(II) species during the treatment with iron, and at what time this occurrence is significant from the viewpoint of the treatment results.

2. Materials and methods

2.1. Experimental procedure

Bench-scale electro-coagulation studies were used to characterize the electro-dissolution of iron and aluminum sheets at low current densities. Electro-coagulation experiments were carried out in batch operation mode. Experimental setups and procedures have been widely described elsewhere [28,29]. In these experiments, the coagulant reagent came from the dissolution of iron or aluminum electrodes placed in a single compartment electrochemical flow cell. Both electrodes (anode and cathode) were square in shape (100 cm^2) and the electrode gap was 9 mm. It is worth to state that in every case the anodic and cathodic materials were the same. This is a normal practice in industrial electro-coagulation processes, because this allows the inversion of the polarity as a response to avoid operation problems, which can be caused by the formation of films of carbonates on the surface of the cathodes, or by the passivation of the anodes. The electrical current was applied using a DC Power Supply FA-376 PROMAX. The synthetic water containing 1000 mg NaCl dm^{-3} was stored in a glass tank (5 dm^3), and recirculated through the electrolytic cell by a peristaltic pump.

2.2. Analysis procedure

The total aluminum or iron concentration was measured off-line using an Inductively Coupled Plasma LIBERTY SEQUENTIAL VARIAN according to a standard method [30] (Atomic Emission Spectroscopy). To determine the total metal concentration, samples were diluted 50:50 v/v with 4 N HNO_3 to ensure the total solubility of metal.

The ferrous iron concentration was determined by the 1,10 phenanthroline method [30]. The samples were analyzed as soon as possible to prevent air oxidation of ferrous iron to ferric iron, which is not determined.

The pH in the aqueous phase was measured using a pH 25 pH-meter (Crison Instruments, Spain). This equipment uses the 50 50 universal pH electrode and it needs to be calibrated regularly with buffer solutions.

3. Results and discussion

Fig. 1 shows the dissolution of iron and aluminum during electrolyses of sodium chloride solutions at a current density of 1.75 mA cm^{-2} and within a pH range close to neutrality. During the experiments pH was monitored (data not shown), and in every case it remained almost constant during the whole process.

It can be observed a linear trend in both cases, with an efficiency that differs significantly from that expected from a purely electrochemical process, in which it is modeled a 100%-efficiency (according to Faraday's law).

In the case of iron, efficiency is slightly under the theoretical 100%-efficiency value, which indicates that iron dissolution competes with water oxidation on the anodic surface very efficiently, but, in spite of that, some water oxidation is still produced as a side reaction. In this point, it is worth to say that iron (III) is the lone specie observed during the electrolyses of iron electrodes, in spite iron (II) analyses were performed immediately after sample collection. This is important because, according to literature, iron (III) is assumed to be

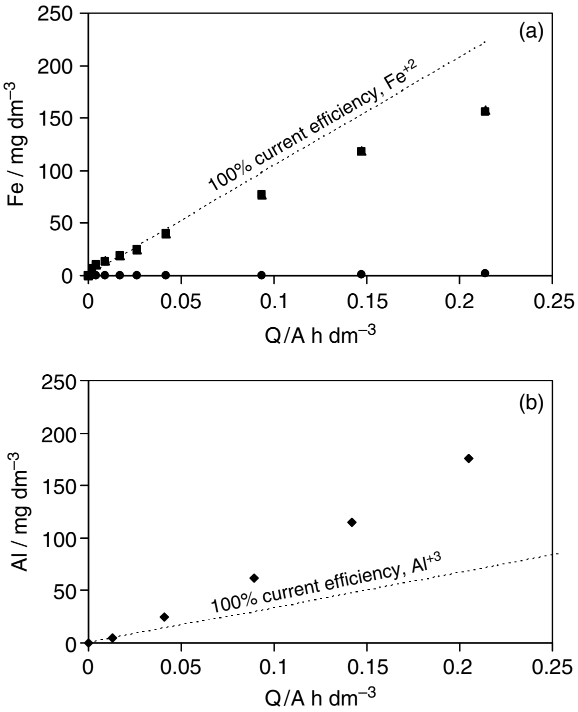

Fig. 1. Electro-dissolution of iron (a) and aluminum (b) during the electrolysis of a neutral solution containing 1000 ppm NaCl at a current density of 1.75 mA cm^{-2} (■ Fe^{+3}, ● Fe^{+2}, ▲ Fe_{total}, ◆ Al_{total}).

produced by oxidation of iron (II) with dissolved oxygen [10,26,31,32] and thus, this side process can enhance the oxidation of iron (II) providing the limiting reagent. This also means that from the practical point of view, electro-coagulation processes behave as if iron (III) is directly dosed to the treated wastewater, at least inside a pH range close to neutrality, which is the most common for electro-coagulation applications.

In the case of aluminum, experimental results are significantly over the expected values for a 100%-efficiency process according to Faraday's law. This super-faradaic efficiency is explained in terms of a chemical dissolution process, which corresponds to the oxidation of the aluminum sheets with the simultaneous reduction of water to form hydrogen, according to Eq. (1) [8]:

$$2Al + 6H_2O \rightarrow 2\ Al^{3+} + 3H_2 + 6OH^- \qquad (1)$$

Thus, in a previous work of our group [27], it was confirmed that the chemical dissolution rate of aluminium sheets is several orders of magnitude higher at alkaline pHs than at neutral or acidic pHs. It was also obtained that to model the electro-dissolution process, it was very important to consider the pH profiles between the anode and the cathode, because the electrochemical oxidation and reduction of water can modify importantly the pH on the anode and on the cathode surfaces respect to the bulk pH, and this affects significantly to the chemical dissolution process. This is especially important on the cathode surface, where the pH can become strongly alkaline, even in case of acidic pHs in the bulk electrolyte, helping to explain the observed results.

At this respect, Fig. 2 shows the effect of the pH on the chemical dissolution of iron and aluminum. To obtain these values, pieces of metal were submerged into a sodium chloride solution, and the pH was adjusted with hydrochloric acid or sodium hydroxide. As it can be observed, alkaline pH favors the chemical dissolution of aluminum, while acidic pHs favor iron dissolution, being in both cases the production of coagulants very significant, and allowing to explain the super-faradaic efficiencies obtained in the case of aluminum for the experiments shown in Fig. 1. In addition, it can be observed that the chemical dissolution of aluminum at alkaline conditions (best conditions for aluminum dissolution) is more significant (up to seven times) than that obtained with iron at the acidic conditions (best conditions for iron). In every case hydrogen bubbles evolving from the sheets surfaces were clearly observed, especially in the conditions in which the dissolution rates are higher. This confirms Eq. (1) as the probable cause of the non-electrolytic release of aluminum and allows proposing Eq. (2) in order to explain iron dissolution:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad (2)$$

Once iron (II) is formed it is known to be oxidized with oxygen according to Eqs. (3)–(6) [33]:

$$Fe^{2+}(ac) + 2OH^-(ac) \rightarrow Fe(OH)_2(s) \qquad (3)$$

$$4Fe^{2+}(ac) + O_2(g) + 2H_2O(l) \rightarrow 4Fe^{3+}(ac) + 4OH^-(ac) \qquad (4)$$

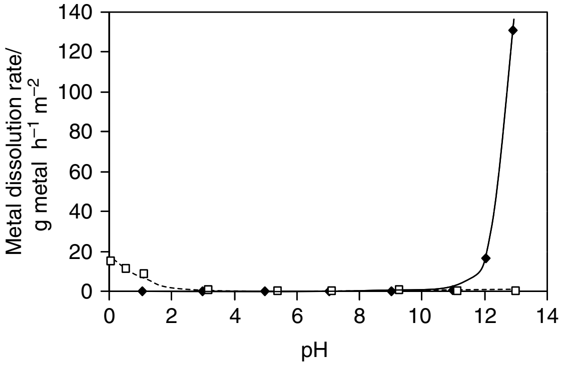

Fig. 2. Effect of the pH on the chemical dissolution of iron and aluminum sheets in contact with a solution containing 1000 ppm NaCl (□ iron, ◆ aluminum).

$$4\,\mathrm{Fe}(\mathrm{OH})_2(\mathrm{s}) + \mathrm{O}_2(\mathrm{g}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{l}) \rightarrow 4\mathrm{Fe}(\mathrm{OH})_3 \quad (5)$$

$$4\,\mathrm{Fe}^{2+}(\mathrm{ac}) + 4\mathrm{H}^{+}(\mathrm{ac}) + \mathrm{O}_2(\mathrm{g}) \rightarrow 4\mathrm{Fe}^{3+}(\mathrm{ac}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{l}) \quad (6)$$

Fig. 3 shows the electrochemical dissolution of iron at acidic pHs (close to 3.0). A very different behavior can be noticed if results are compared to that shown in Fig. 1 for neutral conditions. The pH still remains constant during the whole electrolyses (data not shown). However, iron (II) is a very important fraction of the total iron released as coagulant, and the current efficiency of the process is clearly over the 100%-efficiency line. A key point in the interpretation of results, it is the fact that iron (II) determinations were immediately done after sampling collection. This allows to minimize iron (II) transformation into iron (III) by reaction with dissolved oxygen produced during the electrochemical process. Then, for electrochemically assisted coagulation, iron (II) species are very important under acidic conditions, and they should be considered in order to explain results of electro-coagulation processes. In addition, and according to Fig. 2, super-faradaic efficiencies can be explained by the non-electrolytic contribution, which is favored at acidic pHs for iron. In this way, super-faradaic efficiencies for iron are lower than those observed in Fig. 1 for aluminum. This can be explained in terms of the smaller non-electrolytic dissolution of iron as compared with aluminum in the proper conditions for both materials (different pH in both cases). As it was previously explained, the acidic conditions on the anode surface are even more intense than in the bulk, as a consequence of the production of oxygen by water oxidation. Thus, this should have a positive effect on the results of the process because it should promote the non-electrolytic dissolution of iron.

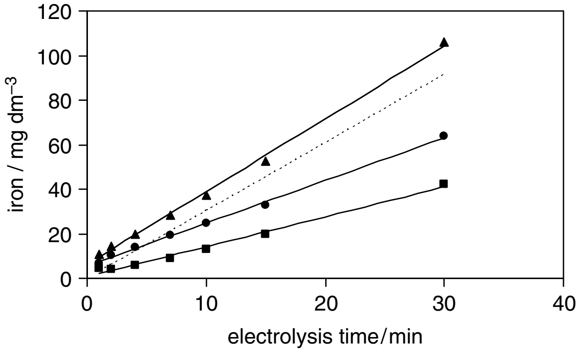

Fig. 3. Electro-dissolution of iron during the electrolysis of a pH 3 solution containing 1000 ppm NaCl at a current density of 1.75 mA cm^{-2} (■ Fe^{+3}, ● Fe^{+2}, ▲ Fe$_{\mathrm{total}}$). Discontinuous line stands for the faradaic-expected dissolution of iron (100% electric current efficiency).

Fig. 4 shows the effect of the pH and the current density (in the low range of current densities studied in this work) on the production of iron (II), and on the efficiency of the electrochemical process. The system behaves as at neutral conditions principally iron (III) ions escape from the anode and achieve the bulk of the solution while at acid conditions both iron (II) and iron (III) escape from the anode and achieve the bulk of the solution. Two limit behaviors are found to explain the effect of the current density on the efficiency. At acidic pHs, iron (II) is formed in significant percentages over the total iron released, being even more than 80% of the total iron dissolved. This ratio decreases with current density, maybe because of the higher production of oxygen by water oxidation, which favors the oxidation of iron (II) into iron (III). Efficiency is clearly super-faradaic at lower current densities and under acidic pH, and it decreases with current density almost linearly, being for the larger current density studied below 100% value. On the contrary, at neutral and alkaline pHs, efficiency in the production of iron is clearly below the faradaic value, within the whole range of current densities studied. In addition, no iron (II) is observed at these conditions which means that it should be rapidly oxidized once formed. At described previously for the effect of current density, this observation may be explained by an enhanced oxidation of iron

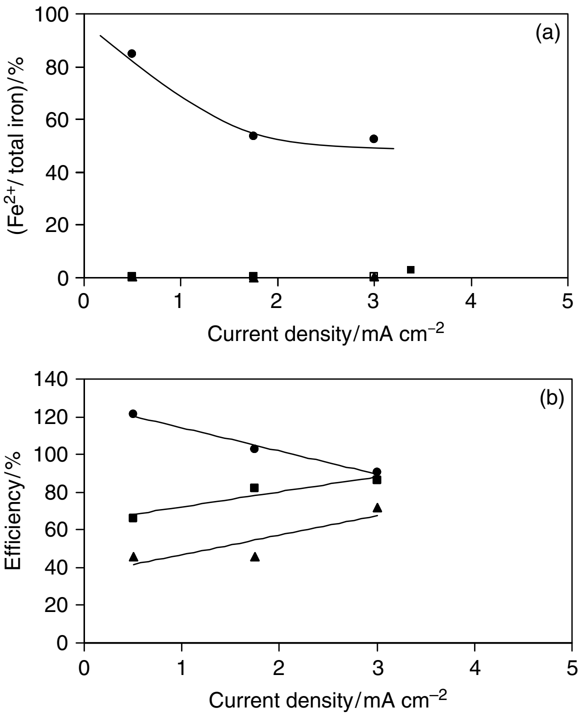

Fig. 4. Effect of the pH on (a) the production of iron (II) and on (b) the efficiency of the dissolution process during the electrolysis of 1000 mg dm^{-3} NaCl solution (● pH 3, ■ pH 7, ▲ pH 11).

(II) favored by the larger anodic production of oxygen (the main side reaction in the process) as a consequence of a less effective iron dissolution.

It is significant the different trend observed for the effect of current density on the efficiency in the production of iron species. At acidic pHs, an increase in the current density has a negative effect on the efficiency while at neutral and alkaline pHs, the trend of efficiency reverses and the effect becomes positive. The enhanced chemical dissolution of iron at strongly acidic conditions, described in Fig. 2, may help to explain this observation. At this point, Fig. 5 shows the efficiency in the iron and aluminum dissolution with respect to the current density at neutral pH values. Thus, the effect of the current density on the aluminum dissolution at neutral pH is the same than reported for iron dissolution at acidic pH. This trend can only be explained in terms of the very significant non-electrolytic release of iron and aluminum shown in Fig. 2, which does not depend on the current density, because it is a chemical process. Likewise, the amount of reagent released electrolytically is more significant at higher current densities and for that reason, the non-electrolytic reagent becomes less significant in percentage (constant in amount), giving way to the observed trends.

These observations are of a great significance for electro-coagulation processes because they clearly show that at near neutral pHs only iron (III) species have to be considered to explain the electro-coagulation process, and iron (II) species do not play a significant role from the practical viewpoint. In addition, it is also important to know that at these pH conditions the effect of the non-electrolytic dissolution of aluminum is more significant than that of iron. At this point, one of the major advantages of electro-coagulation as compared with coagulation is the reduction in the conductivity, just the opposite trend that it can be found in a conventional coagulation-flocculation treatment. This can be easily understood if it is taken into account that the net coagulant reagent dosed by electro-coagulation is insoluble metal hydroxide instead of the huge amount of salts that should be added in a conventional physicochemical treatment. This is also important because electro-coagulation avoid the neutralization operations that should be done in conventional coagulation processes, which increase significantly the conductivity of the treated water, affecting negatively to its quality.

Fig. 6 informs about the influence of the current density on the parameters that are necessary for the sizing of electro-coagulation processes at neutral conditions and in chloride media. As it can be observed, inside the range of current densities studied, iron and aluminum behaves in a very different way. The influence of current density is stronger for aluminum than for iron due to the stronger influence of the cell potential in the case of aluminum. This means that energy cost is almost not influenced by current density in the case of iron while its dependence in the case of aluminum is very significant. In addition, production rate of reagent is greater in the case of aluminum due to the huge contribution of the non-electrolytic dissolution of aluminum giving way to more efficient processes from the viewpoint of reagent dose.

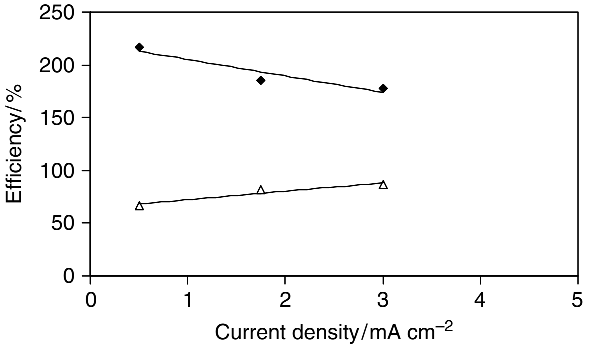

Fig. 5. Effect of the anodic material on the efficiency of dissolution of iron (Δ) and aluminium (◆) during the electrolysis of 1000 ppm NaCl neutral solution.

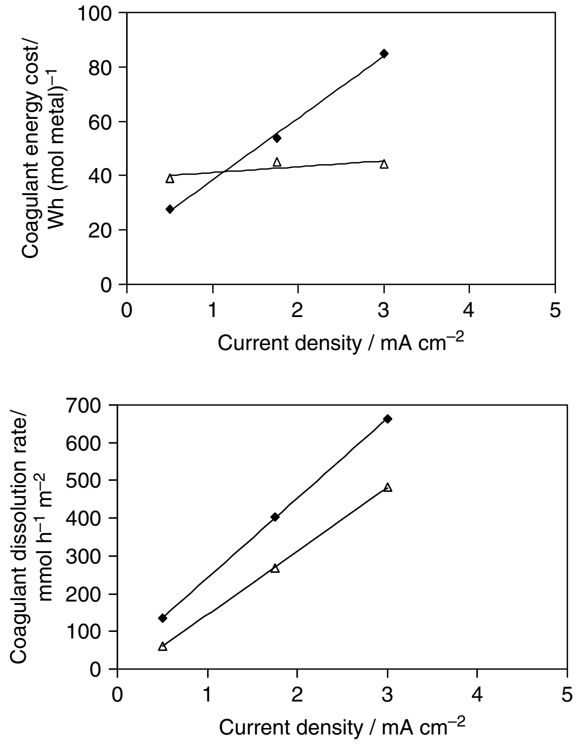

Fig. 6. Influence of the current density on the coagulant dissolution rate and cost of the coagulant dose, during the electrolysis of 1000 ppm NaCl neutral solution (◆ aluminium, Δ iron).

4. Conclusions

From this work, it was obtained that the production of iron and aluminum as coagulant reagents for electrocoagulation processes is greatly influenced by the pH, as a consequence of a non-electrolytic contribution which is greater at acidic pHs for iron and at alkaline pHs for aluminum. This explains the super-faradaic efficiencies observed for the production of aluminum and iron reagents and also it justifies the higher values observed for these super-faradic efficiencies in the case of aluminum, because the non-electrolytic contribution is more than seven times higher in this case. As the non-electrolytic contribution does not depend on the applied current density, trends in the efficiency of the dissolution of metals with the current efficiency are influenced by the pH. In the case of aluminum and in the case of iron at acidic pHs, current density affects negatively to the efficiency. In the case of iron at acidic and neutral pHs, current density improves the efficiency. Iron (II) species are only significant in the electrolytic dosing of iron at acidic pHs. Under neutral or alkaline pHs, iron (III) species are the only species that should be consider because iron (II) is rapidly transformed into iron (III).

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