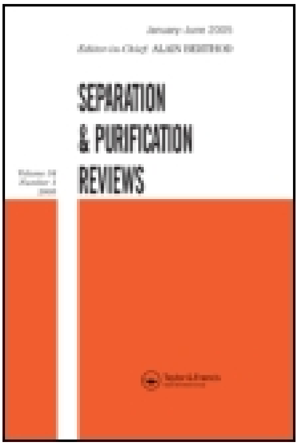

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Physicochemical Aspects of Electrocoagulation

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Electrocoagulation is an electrochemical technique which is being applied to the removal of a number of water pollutants: metals, organic contaminants, dyes and pigments, colloidal solids and particles, soluble inorganic pollutants, and others. Both the electrochemical reactions that take place at the electrode and the effect on the bulk solution are explained. The influence of the metal cation concentration (iron or aluminum) as well as the pH of the aqueous solution is shown. The advantages and disadvantages of electrocoagulation compared to traditional coagulation methods are reviewed. Some considerations about the mathematical modeling of the process and actual reactor design are described. Some techniques that are derived from electrocoagulation—electro-Fenton and peroxi-coagulatio—are explained. Finally, the efficiency of removal for a number of pollutants from wastewater is presented.

KEYWORDS Electrochemical treatment, wastewater, electrode, electrocoagulation

INTRODUCTION

Electrochemistry is the branch of chemistry concerned with the interrelation of electrical and chemical effects. A large part of this field deals with

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the study of chemical changes caused by the passage of an electric current and the production of electrical energy by chemical reactions. In fact, the field of electrochemistry encompasses a huge array of different phenomena (e.g., electrophoresis and corrosion), devices (electronic displays, batteries), and technologies (electroplating of metals, aluminum and chloride production) (1).

Electrochemical technology is a broad field that has many environmental applications. During the last two decades, a special research field: environmental electrochemistry has been developed. Environmental electrochemistry involves electrochemical techniques or methods to remove environmental pollutants from gases, liquids and soil (2,3).

Electrochemical techniques to treat wastewater can be divided in two types depending mainly on where the reactions take place: directly at the anode or indirectly in the solution by ions supplied from the electrode. In the direct anodic oxidation process the pollutants are first adsorbed on the anode surface and then attacked by the anodic electron-transfer reaction. Organic compounds are destroyed by the application of the required potential (4,5). The electrochemical conversion/combustion of organics on oxide anode (MO_x), takes places in 3 steps, the first one is the anodic production of adsorbed hydroxyl radicals as shown in eq. [1]:

$$MOx + H_2O \rightarrow MOx(^{\bullet}OH) + H^+ + e^- \qquad [1]$$

Then, the adsorbed $OH^{\bullet}$ interacts with oxygen present in the anode forming a higher metal oxide MO_{x+1} eq. [2]:

$$MO_x(^{\bullet}OH) \rightarrow MO_{x+1} + H^+ + e^- \qquad [2]$$

On the anode surface the active oxygen could be from adsorbed hydroxyl radicals or from oxygen in the metal oxide (MO_{x+1}), and will in either case react with oxidizable organics forming selective products or causing complete mineralization (6–9).

In an indirect process there are two possible electrochemical products: strong oxidants such as hypochlorite/chlorine and hydrogen peroxide (10–12). The chlorine/hypochlorite oxidizes the pollutants, by reducing to chloride ions as shown in eq. [3–5]:
At the anode

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \qquad [3]$$

At the cathode

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \qquad [4]$$

In solution

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- HOCl \rightarrow H^+ + OCl^- \qquad [5]$$

This process is described much more in depth in a previous review paper (13).

The objective of this process is to produce coagulants from the anodic dissolution of aluminum or iron electrodes. Thus, the main purpose of this paper is to explain the mechanisms involved and the use of iron and aluminum electrodes to produce coagulants to destabilize colloidal pollutants and to remove them from wastewater.

Electrocoagulation has been proposed in recent years as an effective method to treat various wastewaters such as restaurant (14) and urban wastewater (15), as well as nitrate, arsenic and chromium bearing industrial wastewater (16–18) and others. Electrocoagulation involves the anodic dissolution of aluminum or iron followed by hydrolysis, producing flocculates which destabilize and aggregate the suspended particles and absorb dissolved contaminants. This method has several advantages: simple equipment which is easy to operate and automate, short retention time, high sedimentation velocity and a reduced amount of sludge (19).

The purpose of this paper is to show different techniques that can be applied using different anodic materials, modifying aqueous solution pH, adding chemical reagents during the process, among others, and to present a comparative analysis in terms of pollutant removal efficiency. It is also presents new approaches to optimize the use of the ionic species of iron and aluminum to remove pollutants with electro-fenton, peroxicoagulation, and other techniques.

COAGULATION VS. ELECTROCOAGULATION

To understand electrocoagulation a quick review on the phenomena that takes place in coagulation is necessary. In general, colloidal systems contains particles in the range from 0.1 μm to 1 nm (10^{-9} m), which makes the settling velocity from 0.3 to 3 m/year, in other words it is impractical to use physical separation techniques. Colloidal suspensions that do not agglomerate are called stable. These particles have a characteristic electric charge which makes ions that surround them create a double electric layer, so colloidal particles will repel, preventing contact (20).

The zeta potential is used as an experimental measure of the effective charge of the particle as it moves through the solution, thus providing a direct indicator of solution stability. The zeta potential can be measured by a zeta meter; typical values are around −40 to −20 mV. Suspensions that are well destabilized by the charge neutralization mechanisms have zeta potentials close to zero (21).

Coagulation is a phenomenon in which the charged particles in colloidal suspension are neutralized by mutual collision with counter ions and agglomerated, followed by sedimentation. Therefore, the main goal is to destabilize the particles so that they can aggregate forming "flocs," which will precipitate from aqueous the solution. Aluminum and iron salts can be added to the aqueous solution to neutralize the charge of the colloidal particles. However, it is generally accepted that coagulation by aluminum and iron salts is through the hydrolyzed species rather than the aqueous ions themselves. Two main mechanisms can be distinguished as adsorptive charge neutralization and bridging enmeshment involving precipitation of amorphous hydroxides (22,23).

Over the last 20 years new coagulants, both inorganic and organic, have been investigated in an attempt to improve the elimination of organic matter and the total suspended solids during the treatment of wastewater. When anionic polyelectrolytes are used as coagulant aids in conjunction with metal salts, they are usually added after the coagulant due to the negative charge of the particles in wastewaters, thus ensuring greater efficiencies. Nowadays, the use of polyaluminum chloride (PACl) has demonstrated superior performance to traditional Al coagulants ($AlCl_3$ and alum) generating less sludge and less pH dependence (24–28).

On the other hand, electrocoagulation is an electrochemical technique in which aluminum and iron "sacrificial" electrodes are dissolved, generating in situ coagulant agents, which will destabilize the colloidal particles. The main difference from chemical coagulation is the addition of metal cations in situ rather than via external dosing. Simultaneously electrolytic gases (typically hydrogen) are generated at the cathode. Depending on the reactor operating conditions and the pollutant, these bubbles (gases) may float some portion of the coagulated pollutant to surface (29–31).

Electrocoagulation has a dual role in both coagulant addition and bubble generation. Coagulant addition results in aggregation with an increase in size. At low currents particle aggregation occurs but the bubble concentration is low so sedimentation is the dominant removal mechanism. Under this condition the electrocoagulation reactor is primarily operating as an electrochemical dosing reactor. However, at higher currents the bubble concentration increases. The combination of increased aggregation and bubble production makes flotation the primary removal mechanism. The mathematical analysis of an electrocoagulator reactor working as a flotation unit is described elsewhere (32–36). In this paper the electrocoagulation process will be described as a coagulator reactor.

The main advantages of electrocoagulation over chemical coagulation are: less chemicals are needed, sludge is reduced and settles faster, and equipment is simple and easy to operate and automate. However, some of the disadvantages are: the sacrificial anodes need to be replaced when exhausted, the oxide film can passivate the electrodes and the aqueous media needs to be conductive (37).

ELECTRODE REACTIONS

Electrode reactions are heterogeneous and take place in the interfacial region between electrode and solution, the region where charge distribution differs from that of the bulk phases. The electrode process is affected by the properties of this region. The electrode can act as a source (for reduction) or a sink (for oxidation) of electrons transferred to or from species in solution, as in eq. [6]:

$$O + ne^- \rightarrow R \qquad [6]$$

where O and R are the oxidized and reduced species, respectively.

The electrode can also take part in the reaction, as in dissolution of the electrode metal, as shown in eq. [7] (38–40);

$$M \rightarrow M^{n+} + ne^- \qquad [7]$$

In electrochemical processes there are always anodic and cathodic reactions, and depending on the chemical species and their interactions with the electrodes, then in the bulk of the solution redox reactions will takes places as described below.

Anodic and Cathodic Reactions

Electrochemical reactions take place at the anode and the cathode of an electrolytic cell when an external direct current voltage is applied. The term electrocoagulation involves the in situ generation of coagulants by electrolytic oxidation of an appropriate sacrificial anode (iron or aluminum). The main stages involved in the electrocoagulation process using aluminum anodes have been previously identified (41,42). The anodic process involves the oxidative dissolution of aluminum into aqueous solution as reaction [8] indicates as well as the reductive dissociation of water as reaction [9] shows:

$$Al \rightarrow Al^{3+} + 3e^- \qquad [8]$$

$$2H_2O \rightarrow O_{2(g)} + 4H^+ + 4e^- \qquad [9]$$

In the case of iron or steel anodes, two mechanisms for the production of the metal hydroxide have been proposed (43). In Mechanism 1, common in high pH media where oxygen can be involved for further Fe^{2+} oxidation in Fe^{3+}:

$$4\, Fe_{(s)} \rightarrow 4\, Fe^{2+}_{(aq)} + 8e^{-} \qquad [10]$$

In Mechanism 2, in lower pH media, there is no further oxidation:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-} \qquad [11]$$

It is interesting that in electrocoagulation papers little attention has been paid on anodic reactions. Regardless of whether iron or aluminum is used, the main reaction that is reported is:

$$2H_2O + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)} \qquad [12]$$

However, this reaction has three important implications on the electrocoagulation technology: (a) provides hydroxyl ions which then react in bulk solution with iron or aluminum cations to form insoluble species; (b) hydrogen gas is produced which contributes in the destabilization of colloidal particles leading to flocculation, and (c) contribution to electroflotation which is a simple process that floats pollutants (or other substances) by their adhesion onto tiny the bubbles formed by the hydrogen evolution (44–46). This paper describes how cathodic reactions can be used to modify the electrocoagulation technology to increase the pollutant removal efficiency.

Bulk Solution Reactions

Once the aluminum has been dissolved it acts as a coagulant reagent. Aluminum ions hydrolyze and mononuclear complexes are formed as indicated in reactions [13–16]:

$$Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^{+} \qquad [13]$$

$$AlOH^{2+} + H_2O \rightarrow Al(OH)_2^{+} + H^{+} \qquad [14]$$

$$Al(OH)_2^{+} + H_2O \rightarrow Al(OH)_3 + H^{+} \qquad [15]$$

$$Al(OH)_3 + H_2O \rightarrow Al(OH)_4^{-} + H^{+} \qquad [16]$$

As the Al concentration increases and/or the solution "ages," polynuclear aluminum complexes are formed and aluminum hydroxide precipitates as shown here:

$$Al^{3+} \rightarrow Al(OH)_n^{(3-n)} \rightarrow Al_2(OH)_2^{4+} \rightarrow Al_{13}\,complex \rightarrow Al(OH)_3 \quad [17]$$

The presence of aluminum ions and aluminum complexes destabilize the colloidal particles breaking the emulsion. This process leads to flocculation that generates bigger particles. Then, the flocs settle and form sludge at the bottom of the reactor. In the case of iron or steel anodes, two mechanisms for the production of the metal hydroxide have been proposed (47).
In Mechanism 1 (basic medium): Reaction in solution

$$4Fe^{2+}_{(aq)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe\,(OH)_{3(s)} + 8H^{+}_{(aq)} \quad [18]$$

Overall

$$4\,Fe_{(s)} + 10H_2O + O_{2(g)} \rightarrow 4\,Fe(OH)_{3(s)} + 4H_{2(g)} \quad [19]$$

In Mechanism 2 (neutral or acidic media): in solution

$$Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow Fe\,(OH)_{2(s)} \quad [20]$$

Overall

$$Fe_{(s)} + 2H_2O \rightarrow Fe(OH)_{2(s)} + H_{2(g)} \quad [21]$$

The $Fe(OH)_{n(s)}$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation.

ALUMINUM AND IRON CONCENTRATION IN AQUEOUS SOLUTION

The aluminum and iron concentration in wastewater plays an important role since the metal concentration and pH define possible chemical species present in aqueous solution. It is possible to calculate the maximum amount of aluminum and iron electrochemically produced using Faraday's law as shown in eq. [22]:

$$n = \frac{it}{zF} \quad [22]$$

where i is the current in amperes, t is the electrolysis time in seconds, F is the Faraday constant ($F = 96500 \text{ C mol}^{-1}$), and z is the charge of the cation ($z = +3$ for Al or 2+ for Fe) (48–50). Then, to obtain the concentration in solution in mol/L, eq. [22] can be used:

$$[M] = \frac{n}{V} \qquad [22]$$

where n is the number of moles and V the volume of the reactor.

Current Density

The current density is the relation between the current applied by the external direct current into the electrochemical cell, specifically in the anode area, as eq. [23] shows:

$$i = \frac{I}{A} \qquad [23]$$

where I is the current (A) and A corresponds to the total anodic area (m^2).

The operating current density in batch electrocoagulation is the only operational parameter that can be controlled directly. It determines the coagulant dose and the bubble generation. However, running a reactor at the highest allowable current density may not be the most efficient mode of operation. For any specific application some experimental test should be done in order to know the "optimal" current density value. If there is no information regarding the current density a good initial approach will be to try between 20–25 A m^{-2} (51).

Superfaradic Efficiencies

The current efficiency (Φ) for the production of dissolved aluminum by the passage of electrical charge Q (C) per unitary volume V (m^3) is:

$$\Phi = \frac{3FV[Al(III)]}{Q} \qquad [24]$$

If the aluminum or iron concentration in aqueous solution corresponds to the maximum theoretical quantity of electrochemical Al or Fe produced then the current efficiency should be 100%. However, in recent research it has been found that Faradaic efficiencies are larger than 100%. For example using oil suspension, latex emulsion and colloidal dispersion of silica, the efficiencies were 140–190% for oil and silica dispersion and 100–160% for latex (52), in tap water 114–137% (53) and synthetic colloid-polluted wastes around 388%. These strange efficiencies have been called "superfaradiac efficiencies." This term describes the difference between the maximum theoretical amount of aluminum in aqueous solution and the actual Al detected.

A possible explanation of this difference is that an electrochemical process takes place at the cathode promoting aluminum dissolution. The electrochemical oxidation and reduction of water can modify the pH on the anode and cathode surfaces with respect to the bulk pH. This is especially important on the cathode, where the pH can become strongly alkaline. On the anode aluminum dissolution competes favorably with oxygen evolution. This can justify the important contribution of the chemical dissolution to the total dissolution rate (54).

Chemical Species in Aqueous Solution

At a given aluminum or iron concentration, and calculating the total ionic strength, the thermodynamic data available in the literature can be used to obtain the possible predominance zone diagrams, that can illustrate how the aluminum and the iron can be present as cations, or as hydroxycomplexes depending on the aqueous solution pH. These diagrams provide a deeper understanding of aqueous solution chemistry.

The theoretical distribution is presented as a function of both: pH and cation concentration. The use of these diagrams and the thermodynamic data available can be found in the literature (55–59). Figure 1 shows the iron diagram using a concentration in aqueous solution of 0.1 μM. Note that the iron will be as Fe^{2+} in a wide pH range. At pH of 10 the aqueous species

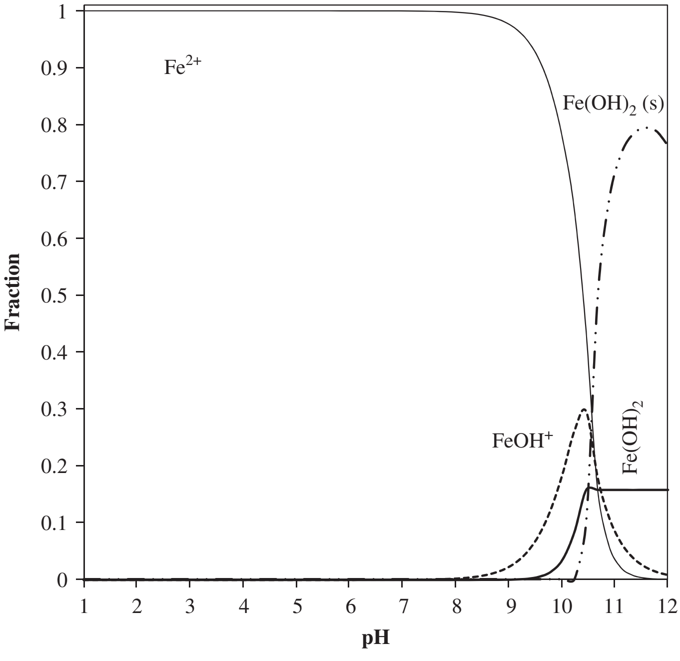

FIGURE 1 Fe(II) species distribution as a function of pH, at a dilute concentration of 0.1 μM.

$Fe(OH)^+$, $Fe(OH)_2$, $Fe\,(OH)_3^-$, $Fe\,(OH)_4^{2-}$ appear. However the insoluble species $Fe(OH)_2$ (s), start from 10.5 and increases as pH rises.

When the amount of iron in the aqueous media increases to 60 mM (Figure 2a), due to the electrodissolution of the anode, note that only two iron species will be present in the system, namely Fe^{2+} and $Fe(OH)_2$ (s). Furthermore, sometimes the presence of support electrolytes, introduces

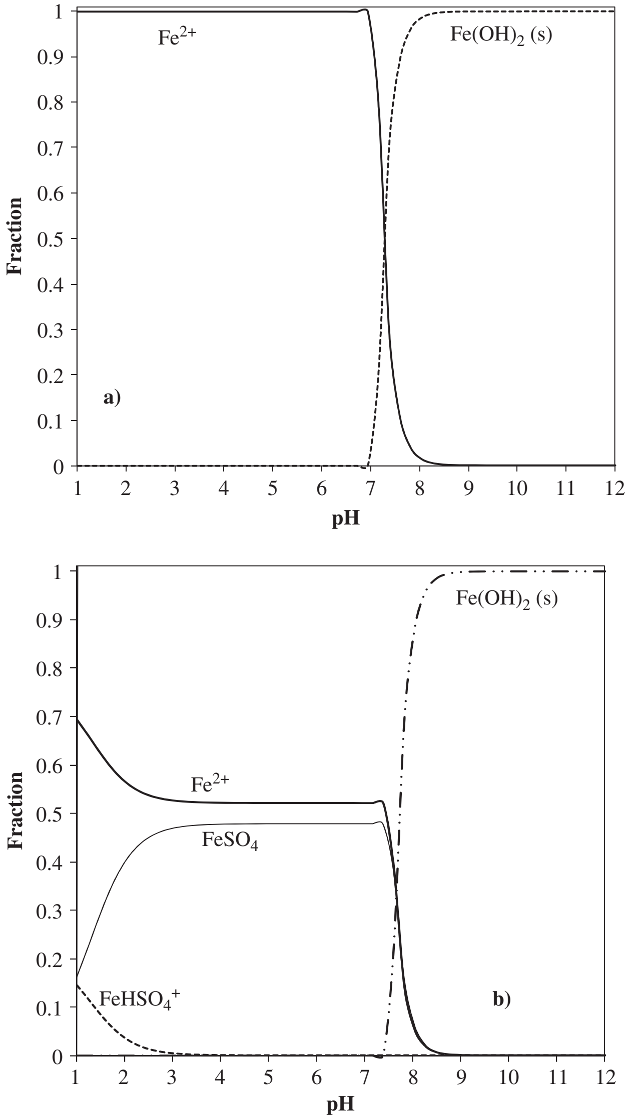

FIGURE 2 Fe(II) species distribution as a function of pH, at a concentration of 60 mM; a) without support electrolyte and b) with support electrolyte 0.1 M Na_2SO_4.

new species into aqueous media, in this case Figure 2b shows the chemical species formed.

If one observes these diagrams, one could conclude that at low iron concentration in aqueous solution there are a number of soluble chemical species, on the contrary at a more concentrated solution the solubility interval is modified and there is a greater presence of the insoluble iron species. If there is dissolved oxygen in the aqueous media ferrous ion will oxidize to ferric ion. Then the chemical species in the system will be Fe^{3+}, $Fe\,(OH)_2^+$, $Fe(OH)^{2+}$ and $Fe_2O_3(s)$ as shown in Figure 3.

The insoluble species appears from 2.5 and increases as pH rise. This fact is desirable if the removal of pollutants is the objective. Again, when the Fe(III) concentration is increased to 60 mM and there is the presence of electrolyte in the system, new species appears as shown in Figure 4 (a and b). In the case of Aluminum, Figure 5 presents the chemical species at low concentrations, whereas Figure 6 (a and b) shows the species at 60 mM without and with the presence of support.

At low Al concentration the insolubility will be from pH 5 to 7.5. At a more concentrated Al concentration the insolubility begins from pH 3.5 to 12. However, the presence of the support electrolyte promotes the formation of new insoluble species from pH 2.5. As can be observed (Figures 1–6) the cation concentration in aqueous solution influences the presence of soluble and insoluble chemical species. These species are affected by the aqueous pH. There is a strong influence in the chemical species if there

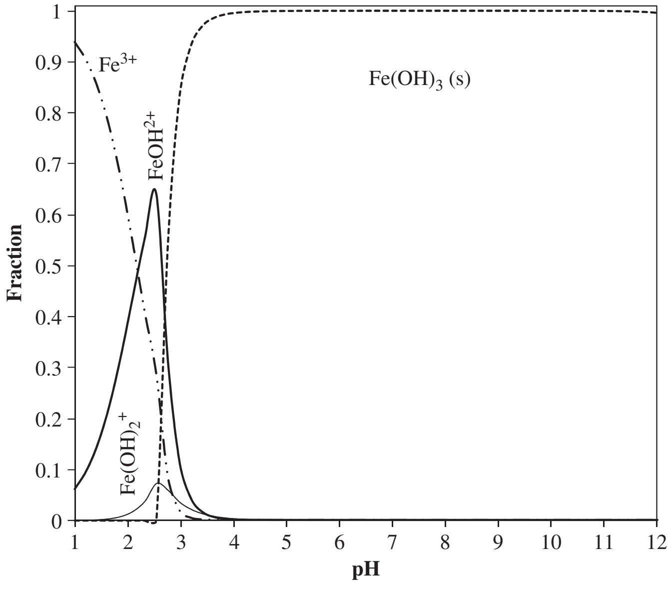

FIGURE 3 Fe(III) species distribution as a function of pH, at a dilute concentration of 0.1 μM.

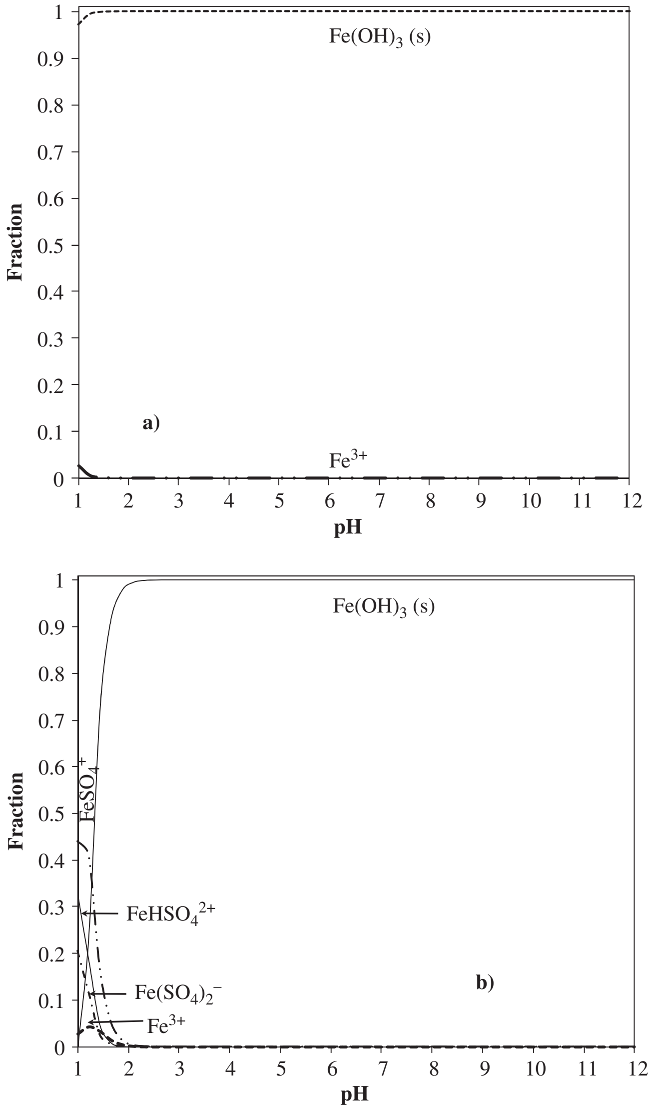

FIGURE 4 Fe(III) species distribution as a function of pH, at a concentration of 60 mM; a) without support electrolyte and b) with support electrolyte 0.1 M Na_2SO_4.

is added a supported electrolyte. Fe(III) and Al(III) in high concentrations forms insoluble species that affect the removal of pollutants.

COMPARATIVE ANODIC ELECTRODE EFFICIENCIES IN WASTEWATER TREATMENT

Some studies have been carried out using different quality of wastewater and anodic materials Fe and Al. Table 1 shows the removal efficiencies obtained

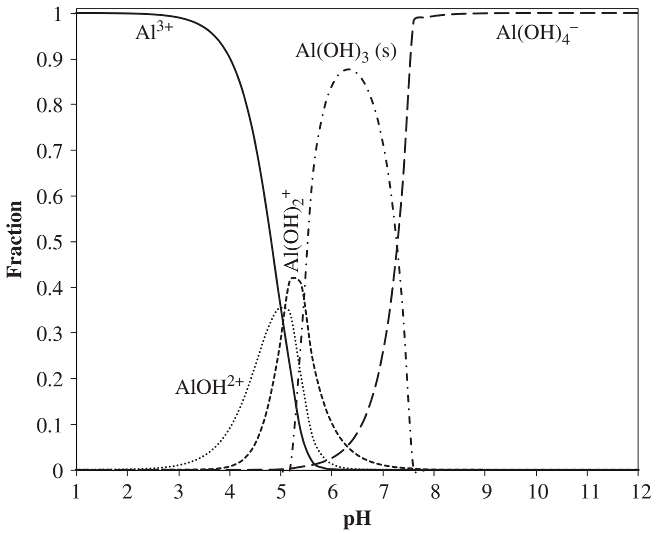

FIGURE 5 Fe(III) species distribution as a function of pH, at a dilute concentration of 0.1 μM.

when different anode material have been used. As can be observed from Table 1, using Fe electrodes introduce a green color into treated waster which then turned yellow and turbid. The explanation of this phenomena is due to the presence of Fe^{2+} ions, which in acidic or neutral conditions oxidizes to Fe^{3+}. When Fe^{3+} combines with hydroxyl radicals it forms $Fe(OH)_3$ which gives turbidity and colored the water with a yellow color. This is the reason why in most cases Al electrodes are chosen for electrocoagulation processes. However, in the case of As removal Fe electrodes removes much better this pollutant than the Al does. The reason for this is that the adsorption capacity of hydrous aluminum oxide for As(III) is much lower in comparison with ferric oxides (60).

ELECTROCHEMICAL TECHNOLOGIES DERIVATE FROM ELECTROCOAGULATION

Iron Electrocoagulation Enhanced Methods

In most of the previously described methods the anode and cathode materials are the same, this is, when iron is used as an anode the cathode employed is iron and when aluminum is the anode the counterelectrode is also aluminum. Wastewater treatment using electrocoagulation can be enhanced obtaining higher depollution rates when small modifications are made in both: the cathode materials and the aqueous solution media.

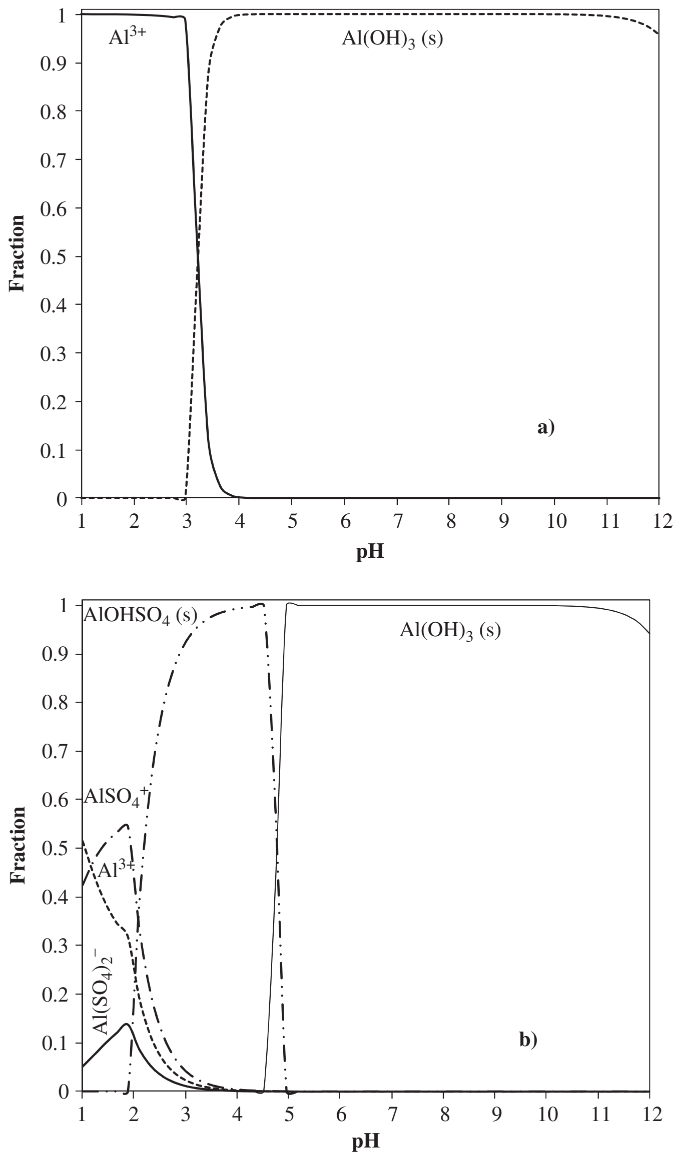

FIGURE 6 Al(III) species distribution as a function of pH, at a concentration of 60 mM; a) without support electrolyte and b) with support electrolyte 0.1 M Na_2SO_4.

Electro-Fenton

Electro-Fenton is an indirect electrochemical method as well as electrocoagulation. Although one could establish that this method does not involve the coagulants agent is situ as in electrocoagulation occurs, this method is quite powerful in destroying organic pollutants in solution, and it requires the addition of iron salts into solution. This method is also the basis for the

TABLE 1 A Comparison in the Pollutant Removal Efficiency Using Different Anode Materials

Wastewater	Aluminum anode (% Removal)	Iron anode (% Removal)	Comments	Ref.
Restaurant wastewater	90% of chemical oxygen demand (COD)	90% of COD	The effluent with Al electrodes was clear and stable, whereas the effluent with Fe appeared greenish first and then turned yellow and turbid.	(14)
Potato chips manufacturing wastewater	65% of COD 95% of turbidity	45% of COD 80% of turbidity	The effluent treated with Fe electrode appeared greenish first and then turned yellow and turbid.	(60)
Chemical mechanical polishing wastewater from semiconductor fabrication	99% of Cu 88% of COD	90% of Cu 85%n of COD	The Fe electrode treated wastewater presents turbidity (up to 60 nephelometric turbidity units (NTU))	(61)
Dye remazol red RB 133	100% of color removal	—	The optimal pH value is 3	(62)
Removal of fluoride	100% of F	___	The efficiency of deflourination by electrocoagulation exceeds that by coagulation because of the electrocondensation effect	(63–64)
Removal of arsenic from water	37% of As	99% of As	The initial As concentration was 2 mgL^{-1}.	(65)
Silica nanoparticles	_____	95% of residual turbidity	Electrocoagulation generates lesser amount of dry sludge as compared with chemical coagulation with polyaluminium chloride (PACl)	(66)
Oil suspensions	90% of total organic carbon (TOC)	___	Aluminun hydroxides showed a higher affinity for oil/kerosene suspensions.	(67)
Phenolic compounds from olive mill wastewater	76% of COD	___	The optimum pH was 4–6 and the current density 75 A m^{-2}	(68)

(*Continued*)

TABLE 1 (Continued)

Wastewater	Aluminum anode (% Removal)	Iron anode (% Removal)	Comments	Ref.
	91% of Polyphenols 95% of color			
Nonyphenol ethoxylates	75% of COD on NP4EO 58% of COD on NP16EO 44% of COD on NP40EO	63% of COD on NP4EO 44% of COD on NP16EO 37% of COD on NP40EO	The optimum pH for aluminum electrode was 8.8 while 9.5 for iron	(69)
Industrial sewage water	38% of chemical absorption of oxygen (CAO)	84% of CAO	The qualitative criterion of the presence of the organic substances was CAO.	(70)
Food-processing industrial wastewater	88% of COD 52% of biochemical oxygen demand (BOD)	—	The optimal conditions were achieved at pH 4 and 18.2 A m^{-2}	(48)

Chemical oxygen demand (COD), Biochemical oxygen demand (BOD), Nephelometric turbidity units (NTU), Chemical absorption of oxygen (CAO) and Total organic carbon (TOC).

next one: peroxi-coagulation. Thus, for a clear understanding in the electrochemical and chemical reactions and the differences between methods the Electro-Fenton is described first. In the Electro-Fenton process molecular oxygen and ferric ions are simultaneously reduced. Oxygen cathodic reduction in acidic media can be achieved using as electrode graphite causing oxygen reduction and producing H_2O_2 as eq. [25] shows (61):

$$O_{2(g)} + 2H^{+} + 2e^{-} \rightarrow H_2O_2 \qquad [25]$$

The ferric ion is also reduced to ferrous ions as shown in [26]:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \qquad [26]$$

The Fenton's reaction occurs when ferrous ions react with hydrogen peroxide as [27] indicates:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+}\, OH^{-} + OH^{\bullet} \qquad [27]$$

Organics are destroyed by the action of $OH\bullet$ radicals produced in the aqueous media. The hydroxyl radical can react with organic matter as reaction [28] indicates:

$$\mathrm{RH} + \mathrm{OH}\bullet \rightarrow \mathrm{R}\bullet + \mathrm{H_2}O \qquad [28]$$

The hydroxyl radical has an oxidation potential of 2.8 V, just below fluorine 3.0; however, ozone has 2.1 and hydrogen peroxide only has 1.8 (62,63). Therefore, the main advantage of adding and electrogenerating H_2O_2 is to produce this hydroxyl radical which will react with the organic pollutants present in the wastewater. The organic radical can react with oxygen or with a hydroxyl radical to produce oxidation products, as shown in reaction [29] and [30].

$$\mathrm{R}\bullet + \mathrm{O_2} \rightarrow \text{products} \qquad [29]$$

$$\mathrm{R}\bullet + \mathrm{OH}\bullet \rightarrow \text{products} \qquad [30]$$

The Fenton's reagent (H_2O_2, Fe^{2+}) is generated in situ and electrochemically catalyzed, since the produced Fe^{3+} can be reduced again to Fe^{2+}. The Electro-Fenton process presents the following advantages: no addition of chemical reagent except a catalytic quantity of ferrous ions no pollution displacement to another medium and a complete degradation of organic pollutants (64–68).

PEROXI-COAGULATION

The peroxi-coagulation process uses a sacrificial iron anode to supply Fe^{2+} ions into aqueous solution and graphite is used as cathode, an oxidizing agent is produced in situ (reaction 20). These two species reacts in aqueous solution as eq. [31] shows:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + OH^{\bullet} + H_2O \qquad [31]$$

The main advantage in this process is based on the use of sacrificial Fe anode which is electrodissolved supplying stoichiometric amount of Fe^{2+}, which reacts with electrogenerated H_2O_2 so the contaminants are removed by their degradation with $OH^{\bullet}$ in aqueous solution and their coagulation with the formation of $Fe(OH)_{3(s)}$. The H_2O_2 produced in peroxi-coagulation is completely consumed due to its fast reaction with the high Fe^{2+} concentration present in the medium giving a high concentration of oxidizing $OH^{\bullet}$. It has been reported that efficient degradation of azo compounds can be achieved this method compared with electrocoagulation (69–74).

Aluminum Electrocoagulation Enhanced Methods

Electrocoagulation using aluminum electrodes can be enhanced when it is applied at a pH below 6. Further, adding an aluminum salt such as PAC or alum was found to be more appropriate. The initial presence of Al in the wastewater, induced and accelerated the formation of more sweep $Al(OH)_3$ flocs that adsorb particulate and soluble organic matter. In this way, both the performance and the rate of electrocoagulation were enhanced and the electrical energy consumption was also lowered with a significant decrease in the operating cost.

ENERGY COST

Chen et al. developed a simplified model for the estimation of the cell voltage and this involved the electrode potential of the anode and cathode, the activation overpotential, concentration potential and omhic potential drop. The unknown overpotential was estimated using the Tafel and Nerst equations. The formulae representing the electrolysis potential for non-passivated and passivated electrodes is:

$$U_0 = S + \frac{h}{k} i + K_1 \ln i + \frac{K_2 i^{m_1}}{k^m} \qquad [32]$$

where, U_0 is the electrolysis voltage between electrodes (V), h is the electrode gap (m), k is the conductivity of the water (mho m^{-1}), i is the current density, S, K_1, K_2, m_1 and m are constants that need to be calculated experimentally, and K_2 is 0 when the electrodes are non-passivated. If the electrode connection is monopolar U (total required cell voltages) equals U_0. One way to minimize the energy consumption is to reduce the net distance between electrodes (75–78).

Once that the required volts are obtained and from the experimental test the optimal current is know then is possible to estimate the amount of watts required as shown in eq. [33]:

$$Watt = V * A \qquad [33]$$

Then, this quantity should be converted in *k*Watt•h dividing by 1000 and multiplying for the process time. In this was it is obtained the total amount of energy required for the electrolysis. At this time the cost of 1 *k*Watt•h I USA is 8.39 cents per kilowatt hour (79).

CONCLUSIONS

This paper presents some of the fundamental aspects that take place in the electrocoagulation technique as used for treating wastewater. It is important to note the current density plays a major role since is the controlling parameter over the process, this defines the cation concentration in aqueous solution and the energy required for the process to occur. It has pointed out that once metallic ions are introduced in aqueous media new chemical process can take place and can be used to remove organic pollutants and therefore can make more attractive the use of this technique in the depollution of wastewater.

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