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Review

Enhanced electrocoagulation: New approaches to improve the electrochemical process

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Abstract

Electrocoagulation is a promising technology for the removal of colloids from different types of wastewater and it has also demonstrated good efficiencies for the breaking-up of emulsions. It consists of the dissolution of aluminum or iron anodes, promoting the formation of coagulant reagents in wastewater that helps to coagulate pollutants and the formation of bubbles that favors the mixing (electroflocculation) and the removal of suspended solids by flotation (electroflotation). During the recent years, the combination of this technology with other treatment technologies has become a hot topic looking for a synergistic improvement in the efficiencies. This work aims to review some of the more recent works regarding this topic, in particular the combination of electrocoagulation with ozonation, adsorption and ultrasound irradiation.

Keywords

Electrocoagulation; ozonation; adsorption; ultrasound irradiation; pulse application

Introduction

Electrochemical treatment techniques have attracted a great deal of attention because of their versatility and environmental compatibility. Electrochemical reactions take place at the anode and the cathode of an electrolytic cell when an external direct current voltage is applied. In fact, the main reagent is the electron, which is a “clean reagent”[1,2] and this fact helps to explain the lower production of wastes associated to these technologies. Applications studied in the recent years range from the oxidation of organic pollutants contained in wastewater to the electroremediation of soils.

Electrochemical methods have also been used as coagulation processes to remove color and cloudiness from turbid industrial wastewater. In this application, the electrochemical process generated numerous flocculates, achieving high efficiency in clearing the wastewater[3,4]. The term electrocoagulation involves the in situ generation of coagulants by electrolytic oxidation of an appropriate sacrificial anode (iron or aluminum), which causes the dissolution of electrode plates into the effluent. Metal ions, at an appropriate pH, can form wide range of coagulated species and metal hydroxides that destabilize and aggregate particles or precipitate and adsorb the dissolved contaminants. Main stages involved in the electrocoagulation process using aluminum anodes have been previously identified [5,6]. The anodic process involves the oxidative dissolution of aluminum into aqueous solution as reaction (1) indicates as well as the oxidative dissociation of water as reaction (2) shows.

$$Al \rightarrow Al^{3+} + 3e^{-} \quad (1)$$

$$2H_2O \rightarrow O_{2(g)} + 4H^{+} + 4e^{-} \quad (2)$$

In the case of iron or steel anodes, it is not iron (III) but iron (II) the main product of the electrochemical process (Eq.3) [7]. Then, oxygen is known to be involved for further Fe^{2+} oxidation into Fe^{3+} (Eq. 4)

$$Fe_{(s)} \rightarrow Fe^{2+} + 2e^{-} \quad (3)$$

$$4\ Fe^{2+} + 4H^{+} + O_{2(g)} \rightarrow 4Fe^{3+} + 2H_2O \quad (4)$$

Once dissolved iron and aluminum, can participate in many chemical reactions (Eqs. 5-10). In fact, speciation of iron and aluminum during electrocoagulation is very complex [8,9] and the description of the interactions between pollutants and the coagulant species is one of the most relevant topics nowadays in this field [10-13].

$$M(OH)_4^{-} + H^{+} \leftrightarrows M(OH)_3 + H_2O \quad (5)$$

$$M(OH)_3 + H^{+} \leftrightarrows M(OH)_2^{+} + H_2O \quad (6)$$

$$M(OH)_2^{+} + H^{+} \leftrightarrows M(OH)^{+2} + H_2O \quad (7)$$

$$M(OH)^{+2} + H^{+} \leftrightarrows M^{+3} + H_2O \quad (8)$$

$$M(OH)_3(s) \leftrightarrows M^{3+} + 3OH^{-} \quad (9)$$

It is interesting that in electrocoagulation papers little attention has been paid on cathodic reactions. Regardless of whether iron or aluminum is used, the main reaction that is reported is water reduction (Eq. 10).

$$2H_2O + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)} \quad (10)$$

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 and other coagulants (Eqs. 5 to 9);
b. hydrogen gas is produced increasing turbulence. This process contributes in the destabilization of colloidal particles leading to flocculation (so-called electro-flocculation process), and
c. contribution to electroflocculation which is a simple process that floats pollutants (or other substances) by their adhesion onto tiny the bubbles formed by the hydrogen evolution [14] (so-called electroflotation process)

As a consequence of this complex interaction, the electrochemical cell combines several processes at the same time in the same reactor and this becomes a significant advantage of this type of processes as compared with conventional coagulation treatments. In particular, from the economical point of view they compare favorably with coagulation processes [15-17] in many applications.

As for coagulation processes, electrocoagulation highly depends on the wastewater pH and it becomes a critical parameter in the performance of this technology. This parameter determines the speciation of aluminum and iron and hence the primary coagulation mechanisms occurring in the electrocoagulation cell. In fact, pH is one of the key differences between coagulation and electrocoagulation as conventional coagulation acidifies the treated wastewater due to the acidic properties of the typical coagulants dosed (iron chloride, aluminum sulfate, etc.), which are known to behave as Lewis acid. These properties make necessary the neutralization of wastewater after the coagulation treatment and this process implies an undesired increase in the salinity of the effluent. On the other hand, electrocoagulation typically buffers the pH during the treatment in values within the range 8-9, which should be a proper value even for direct discharge and no further neutralization is required [18].

Recent studies shows many promising applications of electrocoagulation in the treatment of lowland surface water [19], water [6,20,21], metal plating wastes [22], other types of industrial wastewater [5,23-30], urban wastewater [31-33] and even in disinfection [34,35]. In fact, it is one of the most promising environmental technologies based on electrochemical engineering [36,37]. Electrochemical methods offer two main advantages over traditional chemical treatment: less coagulant ion is required and less sludge is formed [19,22,31]. In the recent years, the potential of this technology is tried to be even further increased by the synergistic combination with other treatment technologies. The objective of the present manuscript is to review the potential of electrocoagulation for the treatment of industrial effluents coupling it with four types of processes:

- Electrocoagulation-ozone processes
- Electrocoagulation- adsorption processes
- Electrocoagulation-ultrasound processes
- Electrocoagulation-pulses processes

2. Electrocoagulation-ozone processes

Ozonation implies the use of ozone in the treatment of wastewater. Ozone is a strong oxidant that oxidizes organic pollutants via two pathways: direct oxidation with ozone molecules and/or the generation of free-radical intermediates, such as the •OH radical, which is a powerful, effective, and non-selective oxidizing agent [38]. The ozonation process has the advantage of being able to be applied when the flow rate and/or composition of the effluents are fluctuating. However, the high cost of equipment and maintenance, as well as energy required to supply the process, constitutes some of the disadvantages. Moreover, ozonation process requires the transfer of ozone molecules from gas phase to liquid phase, where the attack on the organic molecules occurs. Therefore, mass transfer limitations are also a relevant factor to be considered in the oxidation process involving ozone. In many cases, the ozone consumption rate per unit of volume can be so high that mass transfer is the limiting step, reducing the process efficiency and increasing the operating costs [39]. In addition, the ozonation performance is affected by the presence of organic matter, suspended solids, carbonate, bicarbonate and chlorine ions and also

by pH and temperature [40]. Some studies using real industrial wastewater have pointed out that ozone by itself does not achieve high levels of pollutant removal [41]. In particular, the oxidation of wastewater from molasses fermentation with ozone results in an effective color removal but is less effective in removing organic matter [42]. Similar results were obtained when ozone was used to treat textile wastewater, where ozone treatment proves to be very effective for complete color removal but provides only partial reduction of the chemical oxygen demand (COD) [43]. Also, previous research on ozone-coupled methods indicates that the ozonation of anaerobically pretreated wastes enhances significantly the organic removal in comparison to the ozonation of unpretreated wastes, and substrate conversions in the range of 40–67 % are obtained [44].

This behavior in the reduction of COD can be ascribed to the initial pH value of wastewater, where the decomposition of ozone in water to form hydroxyl radicals occurs through the following mechanism [45], where hydroxide ions initiate the reaction (Eqs. 11-16):

$$O_3 + OH^- \rightarrow O_2 + HO_2^- \quad (11)$$

$$O_3 + HO_2^- \rightarrow HO_2^{\cdot} + O_3^{\cdot -} \quad (12)$$

$$HO_2^{\cdot} \rightarrow H^+ + O_2^{\cdot -} \quad (13)$$

$$O_2^{\cdot -} + O_3 \rightarrow O_2 + O_3^{\cdot -} \quad (14)$$

$$O_3^{\cdot -} + H^+ \rightarrow HO_3^{\cdot} \quad (15)$$

$$HO_3^{\cdot} \rightarrow OH^{\cdot} + O_2 \quad (16)$$

According to reactions (11) and (12) the initiation of ozone decomposition can be artificially accelerated by increasing the pH value. Side reaction (Eq. 17) is a fast process and plays an important role in waters with low dissolved organic carbon and alkalinity [46] since it can reduce the oxidative capacity of the system:

$$OH^{\cdot} + O_3 \rightarrow HO_2^{\cdot} + O_2 \quad (17)$$

Regarding the combined process, Table 1 summarizes the main papers found in the literature. Typically, the iron provided by the electrochemical reactor is not enough to remove all the pollutants present in aqueous solution. Thus, the ozone contributes importantly to improve the pollutant removal. Initially, the ozone contribution in the integrated process increases the oxidation of pollutants that are dissolved in the solution and that cannot be eliminated via electrocoagulation. An advantage of supplying ozone into the reactor is that it promotes the mixing between the reactants and also maximizes the organics oxidation, that results in the decreasing of COD and color [28,47,48]. Furthermore, the ozone provides good mixing thought the reactor which improves the mass transfer. The ozone action also contributes to reduce the amount of sludge produced.

In addition to processes coming from the combination of the effects of the single treatment technologies, the combined process involves an increased hydroxide radical production because Fe^{2+} catalyzes ozone decomposition to generate hydroxyl radicals (Eqs. 18-20) in the well-known Fenton process. This process helps to explain the synergistic effect of the combination of both technologies and the resulting high efficiencies.

$$Fe^{2+} + O_3 \rightarrow (FeO)^{2+} + O_2 \quad (18)$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + HO^{\cdot} + OH^- \quad (19)$$

$$FeO^{2+} + Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2O \quad (20)$$

Table 1. *Pollutant removal using coupled electrocoagulation - ozone processes*

Wastewater	Process Conditions	Poll. Removal	Ref.
C.I. Reactive Yellow 84	Ozone flow rate 20 mL min^{-1}, Iron electrodes; current density 15 mA cm^{-2}	85 % TOC 100 % color	[49]
Reactive Blue 19	Ozone flow rate 20 mL min^{-1}, Iron electrodes; current density 10 mA cm^{-2}	80 % TOC 96 % Color	[50]
Reactive Black 5	Ozone flow rate 20 mL min^{-1}, Iron electrodes; current density 10 mA cm^{-2}	60 % COD 94 % Color	[51]
Distillery effluent	Ozone flow rate 15 L min^{-1}; initial pH 6 Iron electrodes; current density 3 Adm^{-2}	83 % COD 100 % Color	[52]
Industrial wastewater	Ozone flow rate 23 L min^{-1}; initial pH 7 Iron electrodes; current density 26 mA cm^{-2}	63 % COD 90 % Turbidity	[42]
Red MX-5B	Ozone flow rate 0.5 L min^{-1}; initial pH 6.1 Iron electrodes current density of 1.5 mA cm^{-2}	100 % Color	[53]
Boat pressure washing wastewater	Iron and aluminium electrodes current density 17 mA cm^{-2}	88.46 %,TOC 76.28 % COD	[54]
Acid Orange 6 azo Dye	Ozone concentration 36 mg L^{-1}; initial pH 4.5 Iron electrodes current density 88.6 mA cm^{-2}	50 % TOC 80 % Color	[55]

Main challenge for this technology is the scale-up. Most of the studies are at the lab-scale or the bench-scale and typically efficiencies can be greatly improved if a proper scale up is carried out. The design of the reactor seems to be a critical point because it fixes the flow patterns and hence the interaction of the species formed by electrocoagulation with ozone. Another challenge for this technology is the production of ozone by simultaneous anodic oxidation, taking advantage of the possibilities of electrochemical technology to produce oxidants[56]. A good possibility could be the use of cells equipped with bipolar cells such as the recently proposed by Llanos *et al.* [35]

3. Combined electrocoagulation- adsorption processes

Adsorption is a very well-known water and wastewater treatment process, which is gaining prominence as a means of reducing metal ion and organic concentrations in industrial effluxents [57]. The biosorbents derived from dead biomass, are considered the cheapest and most abundant environmentally friendly option [58,59]. Nowadays, the development of inexpensive adsorbents for the treatment of wastewater is an important area in the environmental sciences [60,61].

The use of an electrochemical treatment in combination with adsorption as a pre-treatment step to enhance adsorption capability of biosorbents has been assessed in many cases. However, the applications must be carefully evaluated, because technical incompatibilities may arise. This combined technology demonstrates a very good efficiency in the removal of many different pollutants as it is shown in Table 2. The filtering capacity of the sorbent bed is an efficient treatment to remove the suspended solids produced by the electrocoagulation process while simultaneously it helps to remove all soluble pollutants that were not effectively trapped by the flocs. Most of the studies select aluminum instead of iron as anode because aluminum coagulants promotes neutralization coagulation processes instead of enmeshment into growing precipitates which helps avoiding operational problems in the filtering system.

Table 2. *Pollutant removal using coupled electrocoagulation-adsorption processes*

Wastewater	Process Conditions	Pollutant Removal	Ref.
Cr(VI)	Al electrodes, sorbent red onion skin, pH 3-6	97 % Cr	[62]
Cardboard paper mill effluents	Al electrodes, current density 4.41 mA cm^{-2} sorbent granular activated carbon, pH 5.3	99 % COD	[63]
Marine Blue Erionyl MR	Al electrodes, sorbent granular activated carbon, pH 6.0	100 % dye	[64]
Reactive Black 5	current density 277 A m^{-2} sorbent granular activated carbon, pH 7	100 % dye, 100 % COD, 100% Toxicity	[65]
Cr(VI)	Al-Fe, current density 26.7 mA cm^{-2} Sorbent granular activated carbon	99 % Cr(VI)	[66]
Indigo carmine	Al electrodes Sorbent granular activated carbon	99 % Colorant	[67]
Nakdong River	Al electrodes, Al-fiber filter	65 % TOC	[20]
Industrial Wastewater	Al electrodes, current density 45.45 A m^{-2} Sorbent Ectodermis of Opuntia, pH 8	84 % COD, 78 %, BOD5, 97 % color, 98 % turbidity, 99 % fecal coliforms	[68]

Thus, the coupling of electrochemical and adsorption processes might prove a judicious choice for treating industrial wastewater with mixtures of different types of pollutants including both organic and inorganic pollutants. This technology has also been studied in systems in which an adsorbent bed used for the fast removal of pollution from wastewater is continuously regenerated using electrolysis [69,70]. Efficiencies obtained are high enough to consider this technology as a promising choice in the treatment of many effluents polluted with organic species. Most studied found in the literature are carried out at the lab or bench-scale. As for the combination of electrocoagulation with ozone, it is expected that with a proper scale-up, which develop an efficient cell from the view point of the filtering, adsorption and electrochemical processes, efficiencies obtained would be even higher.

4. Combined electrocoagulation-ultrasound processes

The treatment of wastewater in an electrolytic cell by ultrasound irradiation is expected to improve significantly the kinetics and the effectiveness of the electrode processes taking place in the cell [71-73]. A number of favorable impacts of using ultrasound in electrocoagulation are the following:

- Destruction of the compact layer formed at the electrode surfaces by the products of electrode reactions.
- Decrease in the thickness of the diffuse part of the electrical double layer created at the electrode surface.
- Direct activation of the ions in the reaction zone at the electrodes by ultra-sound waves.
- Activation of the electrode surfaces by means of generation of defects in the crystal lattices of the electrodes.
- Local augmentation of the temperature at the electrode surfaces as a result of friction between the liquid and the surfaces.

However, the ultrasound used may cause a few negative effects directly related to the purification process, such as the following:

- Destruction of a part of the obtained colloidal hydroxides by the action of the acoustic waves. This means a diminution of the solid phase that takes part in the adsorption process and a diminution of the removed contaminations respectively.

- Destruction of a part of the formed adsorption layer at the surface of the colloidal particles and possible return of the adsorbed ions to the liquid phase.
- Disorganization of the migration processes in the medium by the ultra-sonic waves.

Main studies found in the literature regarding this combined technology are shown in Table 3.

Table 3. *Pollutant removal using coupled electrocoagulation- US irradiation processes*

Pollutant	Process Conditions	Pollutant Removal, %	Ref.
Cl - SO_4^{-2}	treatment time 60 min; Ultrasonic low-frequency Electrocoagulation Fe, current density 40 mA cm^{-2} Media Cl- 500 ppm pH 3.8; Media SO_4^{-2} 500 ppm pH 2.8; Mine water	Very important removals with an increase in the amount of sludge at 25Hz.	[71]
Cr(VI)	Ultrasonic and sludge obtained for Electrocoagulation Fe of pharmaceutical wastewater ; EC: Conditions: rpm = 150, pH = 7.0 and sludge = 10 g L^{-1}.; Sono-EC Conditions: frequency 30 kHz, pH = 7.0 and time = 100 min.	100 % of removal at 275 min when used 200 mg L^{-1} of Cr(VI); 100 % of removal at 190 min when used 200 mg L^{-1} of Cr(VI)	[72]
Cu(II)	Current 1.0 A. Electrolysis 8 h In the sonicated field, voltage and temperature were constantly increased, in order to maintain the same thermal conditions for non-sonicated solutions. Temperature was adjusted to match those during the sonicated process.	Electrolysis 100 and 200 mg L^{-1} removed 55 an 63 % of Cu(II) increasing concentration of Cu the removal was of 93 %; Sono-Electrolysis 100 and 200 mg L^{-1} removed 94.6 an 95.5 % of Cu(II) increaseing concentration of Cu the removal	[73]
Non-ionic surfactants (SA)	Current density 0.5–2.5 A dm^{-2}, treatment time 5–40 min, ultrasonic power density 0.5–3.0 W cm^{-2}. Frequency 22 ± 1 kHz. Treatment time: 10 min	68 % of AS only CE EC with US 90 %	[74]
car-washing wastewater	I=1.2 A pH= 6 treatment time 20 min	COD 68.77 % and turbidity 96.27 %	[75]

Main results of these studies show that the combined process promotes the flocculation through vigorous mixing and the oxidation through the formation of radicals that contribute to the enhancement of the efficiency of electrocoagulation processes by chemical polishing of the surface of the flocs and by the oxidation of soluble pollutants in the bulk. This fact helps to explain the high efficiencies reached. In this case, performance of iron electrodes is better than that of aluminum electrodes. This fact can be explained in terms of the enhanced performance of the enmeshment of the pollutant into growing metal hydroxide flocs which is much more important for iron than for aluminum coagulants.

Hence, sono-electrocoagulation treatment has demonstrated superior performances in treatment of industrial effluents than single electrocoagulation. However, and as it was described for the other two previous technologies, scale-up should be considered as a major challenge.

5. Electrocoagulation-pulsed processes

Pulsed electrocoagulation technology is a novel method for wastewater treatment. It uses the interactions of electrochemical technology and polarity reversal in an electrical field to induce dipole formation in nonpolar particles in the wastewater, thus enabling the formation of micro-aggregates of insoluble substances.

The aggregates formed are further assisted in forming macro-aggregates. Charge neutralization of ions or charged materials also takes place in the electrochemical reactor, turning them into insoluble, suspended substances in the wastewater. The neutralization process enhances the efficiency of removing electrical conductivity [76]. In Table 4, there are some examples of using

electrocoagulation pulsed treatments, which show that has been done with wastewater of different origins. As it can be observed, it has proven effective in the treatment of urban wastewater and different types of industrial wastes.

Table 4. *Pollutant removal using coupled electrocoagulation-pulsed processes*

Wastewater	Process Conditions	Pollutant Removal	Ref.
Higher Cr(VI) concentrations	Cr(VI) initial concentrations (50- 1000 mg L^{-1}) Electrical energy consumption (EEC) range: 4-58 kWh m^{-3} wastewater, current density (CD): 56–222 A m^{-2}, operating time: 20–110 min, pH 3–9 ($pH_{optimum}$ 5), voltage: 15–25 V.	99 %	[47]
Synthetic solutions containing mercury(II)	Hg (II) 2×10^{-5} M,distance between the electrodes was 3 cm, current density ranging from 2.5 to 3.1 A dm^{-2}; charge loading 9.33- 15.55 F m^{-3} , iron and aluminum electrodes, 3 - 7.	99.9 %. With iron, 15 min of electrolysis was sufficient to reach the highest removal; aluminum required 25 min for the same result.	[77]
Solutions of a dye Dianix Yellow CC (DY) and Procion Yellow (PY)	Range pH (4-8), Current density (40-120 A m^{-2}) Frequency (200-900 Hz^{-1}), Operation time (100 min)	99 %	[78]
Industrial and municipal wastewater	Pilot plant of electrochemical treatment system (0.3 m^3h^{-1}). Ti/RuO_2–TiO_2 anode was larger than with a platinum anode	The removal of T-N, T-P, NH_4–N and COD was approximately 90 %	[79]
Berberine hydrochloride (BH) wastewater	Fe electrodes and Al electrodes. The optimal conditions of reaction time of 3.5 h, pulse duty cycle of 0.3, pulse frequency of 1.0 kHz, current density of 19.44 mA cm^{-2}, and electrode distance of 2.0 cm	90.1 % BH and 62.6 % COD	[80]
Dye wastewater	Fe electrodes and 1000 mg L^{-1} Dye solution in a 15 mins electrolyzing time	99.62% of color removal and 91.15% of COD	[81]
Old corrugated containerboard (OCC)-based Paper Mill Wastewater	Current density of 0 to 240 A m^{-1} , a hydraulic retention time of 8 to 16 min and a coagulant (anionic polyacrylamide) dosage of 0 to 30 mg L^{-1}	Electrical conductivity: 47.7 %; Suspended. Solids: 99.3 %;COD: 75 %	[76]
Cooking oil (1800 mg/L, scour (1000 mg/L) and sodium sulfate (1g/L)	Al electrodes, dimensions of 50×110×2 mm; AC power (SMD 30)	Passivation of Al electrodes is not observed	[82]
Electroplating wastewater	Having a pH of 4, voltage 2.5 V, hydraulic retention time of 15 minutes, current density of 25 A m^{-2}	99.5 %	[83]
Oil wastewater	Electrode distance of 3.3 cm, pH of 4, current density of 49.38 $mAcm^{-2}$, reaction time of 15 min and pole switching time of 10 s.	96.21%	[84]

Conclusions

Electrocoagulation has demonstrated to be a promising technology in the removal of pollutants from different types of wastewater. However its combination with other technologies can help to increase efficiency due to synergistic effects such as those derived from the formation of radicals in the ozonation (by interaction of ozone with iron (II)) or in the US irradiation. Results depend on the particular application (technology combined and type of wastewater) and should be evaluated carefully. Scale-up is the major challenge of this technology for the next years, although the very positive results obtained at the lab and bench scales make these studies very promising.

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