ASPECTS REGARDING THE ELECTROCOAGULATION APPLICATIONS IN THE WATER AND WASTEWATER TREATMENT

AIDA DERMOUCHI1*, MOSSAAB BENCHEIKH-LEHOCINE1, SIHEM ARRIS1, VALENTIN NEDEFF2, NARCIS BARSAN2

1Faculty of Pharmaceutical Engineering Process, University of Constantine 3, Constantine, Algeria.
2“Vasile Alecsandri” University of Bacau, Calea Marasesti 156, Bacau, 600115, Romania

Abstract: Electrocoagulation (EC) has been known for over a century. Applications in industry as water and wastewater treatment processes were adapted for the removal of suspended solids, organic compounds, COD (Chemical oxygen demand), BOD (biochemical oxygen demand), metallic and non-metallic pollution. The main advantage in EC technology is the fact that it works without the addition of chemical products. The DC current between metallic electrodes immersed in the effluent is used as an energy source for this technique, which causes their dissolution. The effect of the main parameters, current density, treatment time, initial pH, temperature, electrode materials, conductivity and distance between the electrodes were investigated. According to the conclusion of the works published in recent years, the removal efficiencies of pollutants materials by EC process are very important.

Keywords: electrocoagulation, water and wastewater treatment, electrodes, pollutants

1. INTRODUCTION

In many applications for water, wastewater and sludge treatment are used, with high performance, the coagulation, flocculation and electrocoagulation processes [1-6].

The electrochemical technique contributes in many ways to a cleaner environment and covers a very wide range of technologies. The use of this method in the water treatment was firstly reported in Great Britain in 1889 [4]. In recent years, a special field of research known as environmental electrochemistry was developed.

Electrocoagulation in recent years has become a very important electrochemical method through several successes that have been acquired in water and wastewater treatment such as used water containing heavy metals, emulsions, suspensions and also in potable water treatment. This process presents an alternative to conventional coagulation with several advantages such as ease of use, low quantities of produced sludge, avoidance in chemical usage, consequently, there is no need to neutralize excess chemicals and no secondary pollution problems [5].

Electrocoagulation (EC) generally refers to a group of technologies that use an electrical current that coagulates organic constituents and suspended solids in water. The coagulated organics have the ability to adsorb certain ionic constituents, making it possible to separate a flocculent with a majority of the suspended organics and

* Corresponding author, email: dermouchi_ad@hotmail.fr
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some of the ionic constituents removed. Another variant of this system oxidizes an iron or aluminum anode to form an iron or aluminum hydroxide flocculent that can co-adsorb/co-precipitate some ions.

2. THEORY OF ELECTROCOAGULATION

Electrocoagulation (EC) is a process containing a complex of physicochemical phenomena. The synergy between these mechanisms depends on the metal cations generated in situ, resulting metal hydroxides forms, the ionic species present in the aqueous medium and electrolyte gas micro-bubbles generated. Generally EC process has three successive stages:
(a) Formation of coagulants, by electrolytic oxidation of the sacrificial electrode;
(b) Particle destabilization of the suspension;
(c) Aggregation phases destabilized to form flocs.

The particle suspension destabilization mechanisms and breaking emulsions have been described in large steps and can be summarized as follows [5, 7]:
- Compression of the diffuse double layer around the charged species, which is achieved by the interactions of ions generated by dissolution of the sacrificial electrode, due to current passage through the solution.
- Charge neutralization of the ionic species present in wastewater by counter ions produced by the electrochemical dissolution of the sacrificial anode. These counter ions reduce the electrostatic antiparticle repulsion to the extent that the van der Waals attraction predominates, thus causing coagulation. A zero net charge results in the process.
- Adsorption of colloidal particles neutralized to metal hydroxides (M(OH)\(_3\)) that led to the formation of flocs.

The application of all these phenomena provides the overall principle of flocculation coagulation. This technique is the combination of three main interrelated processes, working synergistically to remove pollutants: electrochemistry, coagulation and flotation [8]. Highlight the complexity and interdependence of the relevant phenomena with the intrinsic electrocoagulation process.

3. REACTIONS AT THE ELECTRODES

The step of electron transfer that occurs at each electrode during electrical current passage is an inevitable oxidation of the anode that leads to the loss of electrons and a reduction at the cathode resulting in an electron gain [8]. Generally the two most used metals in the process of EC are aluminum and iron, by their importance within the coagulation and precipitation processes. The chemical reactions of iron and aluminum that take place at the electrodes are shown as follows [9]:
- Anodes. The metal electrode is oxidized and changes from solid to ionic state in solution:

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \]  \hspace{1cm} (1)

- In alkaline conditions:

\[ \text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \]  \hspace{1cm} (2)

- In acidic conditions:

\[ \text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ \]  \hspace{1cm} (3)
- Iron anode:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (4) \]

- In alkaline conditions:

\[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \quad (5) \]

- In acidic conditions:

\[ 4\text{Fe}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}^{3+} + 4\text{OH}^- \quad (6) \]

- The cathode:

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (7) \]

The metal cations generated in the solution create complexes with the hydroxide ions. Figure 1 summarizes the most important reactions during water treatment using EC process.

Water electrolysis leads to oxygen small bubbles production at the anode and hydrogen production at the cathode. These bubbles attract flocculated particles and by natural buoyancy they will be floating on water surface [10]. The variation of the bubble diameter depends on the experimental conditions, the latter varying in the range of 20–70 μm [11]. In typical aqueous environments and conditions of EC processes, iron can dissolve in divalent and trivalent forms as Fe(II) and Fe(III) respectively, whereas aluminum dissolves only in trivalent form as Al(III) [12]. Generally the pollutants are adsorbed and/or trapped on the surface of the flocs generated by electrocoagulation. Critical analysis of electrocoagulation of organic pollutants shows the existence of two separate processes [13]:

- Electrochemical process through which the metal flocs are generated;
- Physico-chemical process through which the effluents are adsorbed on the surface of the flocs.

![Fig. 1. Schematic diagram of typical reactions during the EC treatment with two electrodes [12].](image)
4. FACTORS AFFECTING ELECTROCOAGULATION

4.1. Current density and treatment time
Current density is a very important parameter in EC processes because it is the only parameter that can be directly controlled. The coagulant dosage and bubble generation rates are influenced directly by electrical current density that strongly influences solution mixing and mass transfer at the electrodes [14]. A simple relationship to determine the amount of electrode material that can be dissolved is derived from Faraday’s law when electrical current and treatment time are known as:

\[ W = \frac{itM}{eF} \]

where \( W \) is the quantity of electrode material dissolved (in grams of M per square centimeter), \( i \) is the current density (A·cm\(^{-2}\)), \( t \) is time (in seconds), \( e \) is the number of electrons in oxidation/reduction reaction, \( F \) is Faraday’s constant 96,500 C·mol\(^{-1}\), \( M \) is molecular weight of the electrode material (g·mol\(^{-1}\)).

According to this equation, the quantity of aluminum produced at the cathode depends more on treatment duration and on the added electrical charge by unit volume. The efficiency of the procedure of electrochemical treatment is linked to electrolysis time because it can change with the electrical current density or sample pH [15]. The electrical current supply system in EC processes determine the quantity of Al\(^{3+}\) or Fe\(^{2+}\) ions released from the electrodes. For aluminum the electrochemical equivalent mass is 335.6 mg/(A·h), and for iron its value is 1,041.0 mg/(A·h) [16]. Moreover, it appears that the produced bubbles sizes are reduced when electrical current density increases, which is advantageous for the separation process [17]. The electrical current efficiency is defined as the ratio of the electrical current consumed in producing a target product to that of the total electrical current consumed [16].

4.2. pH effect
It has been shown that the initial pH greatly influences the performance of the electrocoagulation process [18-20]. Generally, the pH of the solution changes during this process, as also observed by others investigators [21, 22]. During the electro-coagulation, the hydrogen gas formation at the cathode, this leads to an increase in pH. After electrocoagulation, effluent pH will increase, as opposed to alkaline influence that will be decreased, achieving one of the key benefits of this process [9]. In addition, it has an effect on the conductivity of the solution, the dissolution of the electrodes, speciation hydroxides and also on the potential zeta colloidal particles.

4.3. Conductivity effect
The electrical current efficiency is dependent on electrical conductivity, when it is low the electrical current efficiency will decrease. Therefore, a strong applied potential is required which will lead to the passivation of the electrode and an increase in the processing cost. Solution conductivity is dependent on the concentration and the type of electrolyte (NaCl, KCl, Na\(_2\)SO\(_4\), and KI) present. Generally NaCl is added to increase the electrolytic conductivity [23, 24]. The negative effect of CO\(_3^{2-}\) and SO\(_4^{2-}\) decreases with Cl\(^{-}\) addition. Electrical Current efficiency decreases rapidly with the deposition Ca\(^{2+}\) and Mg\(^{2+}\) and the formation of oxides layer due to the presence of Ca\(^{2+}\) and Mg\(^{2+}\) [10]. A presence of Cl\(^{-}\) at a level of 20% of the total anions concentration is recommended to ensure a normal operation of electro-coagulation in water treatment [9].

4.4. Temperature effect
The study of temperature effects on the removal of pollutants by EC has been considered in a few papers. The study of solution temperature effects on boron removal when ranging from 293–333 °K was considered [25], have shown that temperature increase results in a better boron removal efficiency that increased from 84 to 96 %. The inverse effect was observed, however, during temperature increase between 293 and 333 °K when paper mill wastewater is considered [26]. EC process studied the temperature effects on phosphate removal from wastewater in the extent of 293 to 333 °K [27, 28]. The removal efficacy was 29% less at 293 °K than at higher temperatures. The temperature in the reactor tends to increase during the study as a result of reactions. This increase in temperature is a result of electrolytic reactions depending on contact time, electrode type and applied electrical power [29]. Increasing temperature also enhances the solubility of aluminum. However, it seems that increasing temperature can have positive and negative effects on the removal efficiency.
4.5. Distance between the electrodes
Reactions in electrolysis reactor are affected by the space between the two electrodes. The IR drop is related to
the distance between the electrodes, the surface area of the cathode, the specific conductivity of the solution and
the current. It can be easily minimized by decreasing the distance between the electrodes and increasing the area
of cross section of the electrodes and the specific conductivity of the solution [16].

4.6. Electrode materials effect
According to studies reported in the scientific literature, the aluminum electrodes (Al) and iron (Fe) are the most
commonly used electrode materials in most studies, due to easy availability, low cost, and better dissolution [29].
Also compared the performance of iron and aluminum electrodes for phosphate removal from aqueous solutions.
[30] Compared the performance of iron, aluminum electrodes and stainless steel for the treatment of textile
industry wastewater. Their conclusion was that the optimal operating conditions of electrocoagulation vary with
the electrodes materials [31]. Fe-Al pair has been the most effective in removing indium from water. In addition
to these traditional materials, dimensionally stable anodes, such as SnO2, PbO2, graphite, nickel, etc., and boron-
doped diamond (BDD) electrodes have the advantage of greater chemical resistance and higher efficiency in the
treatment of cyanide-bearing wastewaters. A comparison of data between Fe and Al electrodes for different
types of pollutants has been illustrated in Figure 2. Results showed that phenols and hydrocarbons are better
removed when using Al electrodes whereas for turbidity and fat they are less efficient than Fe electrodes. There
is no significant difference between Al and Fe electrodes for COD elimination.

![Fig. 2. EC performance for removal pollutants in different current densities and various electrolysis times: (a) Fe
electrode, (b) Al electrode [32].](image-url)
5. APPLICATIONS OF ELECTROCOAGULATION PROCESS

The efficiency of electrocoagulation has been proven in the removal of suspended solids, oil and grease. In fact, it can treat water for a small or medium community water supply, for boiler water needs for industrial processes where a large water treatment plant is not economical or necessary.

Cutting oil emulsion is an aqueous solution generally occurring in a wide variety of industrial applications. These emulsions are very stable, due to the presence of surfactants and co-surfactants. A few literature studies are available considering the treatment of metal cutting oil emulsion and oily wastewaters by EC [24]. Reported that turbidity and COD removal efficiency are respectively of 98 % and 72 % [33]. Found an elimination percentage of 90 % for COD and 99 % for Turbidity. According to [34] an elimination efficiency of about 92%, 82% and 100% was observed respectively for COD, COT and turbidity.

![Cutting oil emulsion: (a) before and (b) after treatment by electrocoagulation technique.](image)

The tannery and textile industries represent a very important economic sector in many countries. A study has been conducted on the treatment of wastewater from a tannery plant using the EC technique [35]. Studied the paper mill wastewater (gravitationally and biologically pre-treated). They reported that removal efficiency of COD and turbidity, in the EC process, attained respectively 68 % and 100 % [36] studied the treatment of tissue paper wastewater by EC, was found a removal efficiency for COD, Turbidity and BOD respectively of 50%, 97 % and 60 % [37] reported that, after optimization, the EC treatment was found very effective with removals efficiencies for COD and BOD of 95 % and 96 % respectively and produced clear water (Figure 3 and 4).

![Tannery wastewater: (a) before and (b) after treatment by electrocoagulation technique.](image)

Electrocoagulation has been widely used for other types of industrial wastewater such as treatment of drinking water and urban wastewater, suspended particles, chemical and mechanical polishing wastewater containing fluoride, and solutions containing heavy metals, pulp and paper industry wastewater.
6. CONCLUSION

Electrocoagulation is an electrochemical technique with many applications used successfully in the treatment of water or wastewater, and yet its potential is not fully realized.

This literature review to the process electrocoagulation shows us the importance of the work done in recent years to develop this process. These research efforts have led to the design of industrial electrochemical reactors successfully treating effluent with high pollution load in various types of waters.

This method became more advantageous over other methods by its ease of installation, lower cost, and possibility of automatic control and elimination of handling problems of reagents.

REFERENCES