

Electrocoagulation treatment of industrial wastewater including textile dyeing effluent – a review

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ABSTRACT

Electrocoagulation (EC) treatment can be used as an effective alternative to the existing treatment methods. It is a distinct, economical and an environmental friendly choice for meeting water treatment discharge standards and compliance requirements. Due to improved material of construction and process design, the EC process is widely accepted. Presently, this process has gained attention due to its ability to treat large volume of effluent with low cost. The EC process includes the in-situ generation of coagulants via the electro-dissolution of a sacrificial anode, which is usually made up of iron or aluminum. This paper presents a review of the research works available in the open literature on the electrochemical treatment of industrial effluent such as textile, pulp and paper, paint, food, electroplating, distillery, etc. The mechanism and design consideration for electrochemical treatment of wastewater is also presented.

Keywords: Industrial effluent; Organic removal; Heavy metal removal; Electrocoagulation; Operating parameter

1. Introduction

In last few decades industrial sector have grown rapidly. Water is the most essential part for many industrial productions. Industries mostly use fresh water and ultimately discharge in the form of polluted water. Consequently, environmental degradation has emerged as a major challenge all over the world in the recent years. Chemical industries use water for several purposes such as a process raw material, as a solvent, a scrubbing medium, a heat transfer agent, a cleaning agent, etc. Wastewater generated during most of the processes may contain several organic and inorganic chemicals, which cannot be discharged directly into water bodies or on land or into sewers. Due to such

serious environmental concerns various countries regulate the amount and quality of the effluents. Therefore, pollution abatement and environmental protection are now the policy statements of large enterprises. These policies encourage the minimization of fresh water use.

Various processes such as wet oxidation [1], thermolysis [2], coagulation [3], absorption [4] and membrane separation [5] have been reported to treat various industrial effluents. All these processes have their own limitations. Electrocoagulation (EC) is one of the better options for the treatment of various industrial effluents [6].

The current challenge is the financially realistic implementation of new and highly effective but cost and energy intensive, treatment technologies. Advanced wastewater

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treatment goes beyond the level of conventional secondary treatment to remove significant amounts of nitrogen, phosphorus, heavy metals, biodegradable organics, bacteria and viruses [7]. Electrocoagulation is a technique used for wastewater treatment, industrial processed water [8] and medical treatment [9]. Electrocoagulation process removes contaminants that are generally more difficult to remove by filtration or for chemical treatment systems such as emulsified oil [10], petroleum hydrocarbons [11], refractory organics [12], suspended solids [13] and heavy metals [14]. Electrocoagulation has been used primarily to treat wastewater from pulp and paper industry [15], mining [16] and metal processing industries [17]. In addition, Electrocoagulation has been applied to treat water containing foodstuff waste [18], oil waste [19], dyes [20], public transit [21], organic matter from landfill leachates [22], defluoridation of water [23], synthetic detergent effluents [24], etc.

During last few decades, the environmental sector has shown a very high interest in the treatment of different types of water and wastewater by electrocoagulation process. The aim of this work is to review previous studies on the wide range applications of electrocoagulation employed in the treatment of wastewater emanating from different industries such as textile, paint, pulp and paper, food, tannery and electroplating industries.

2. Electrocoagulation treatment

Electrocoagulation is well known as radio frequency diathermy or short wave electrolysis. The basic principle of the electrocoagulation is based on the production of cations electrolytically from different electrodes which are

responsible for the increase of the coagulation of contaminants present in wastewater [6]. Electrophoretic motion tends to concentrate negatively charged particles toward anode and positively charged particles toward cathode [7,8] as presented in Fig. 1. The consumable metal electrodes used continuously to produce polyvalent metal cation in the region of anode. These cations neutralize the negative charge of the particles moved toward the anode by production of polyvalent cations from the oxidation of the sacrificial anode (Fe and Al) [6–8].

3. Mechanism of electrocoagulation treatment

In electrocoagulation process, the dissolution of the electrode takes place at anode which is called sacrificial anode producing metal ions that acts as coagulant in the aqueous solution [25].

Generally, electrocoagulation system consists of metal plates submerged in the aqueous solution as presented in Fig. 2. The electrodes are usually made up of aluminum, iron or stainless steel because these metals are cheap, readily available, non-toxic and proven effective [7,26]. Electrochemical unit may be one or multiple anode–cathode pairs which is connected in either a monopolar or bipolar mode [27,28]. During the process of electrocoagulation, following reactions takes place at the respective electrodes [28]. Anodic reactions:

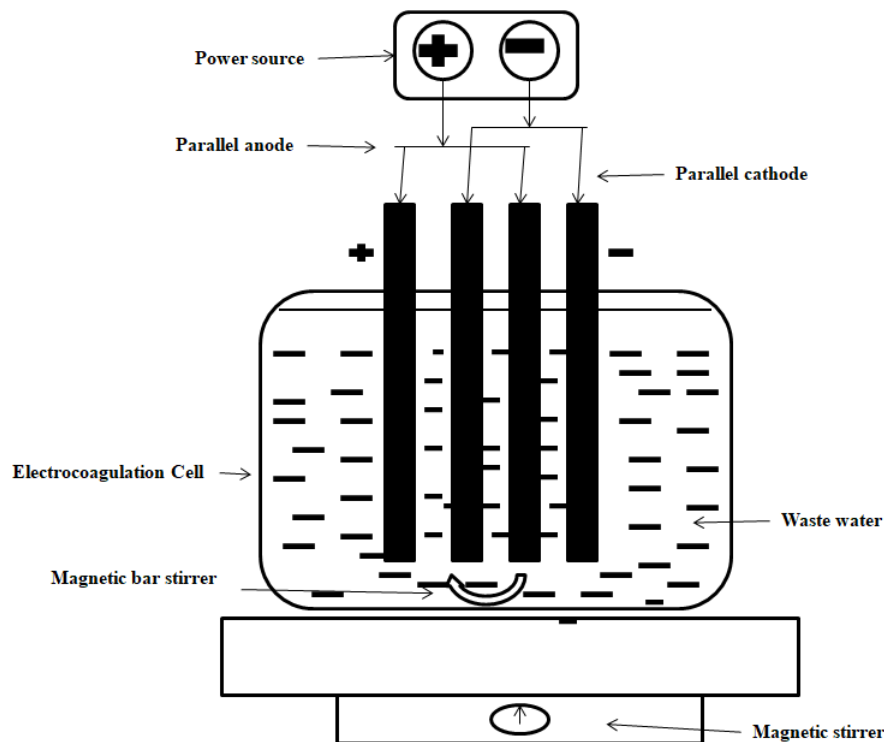
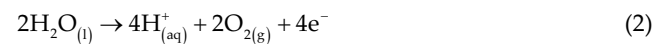
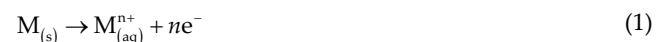


Fig. 1. Schematic diagram of the experimental setup used for the electrocoagulation study.

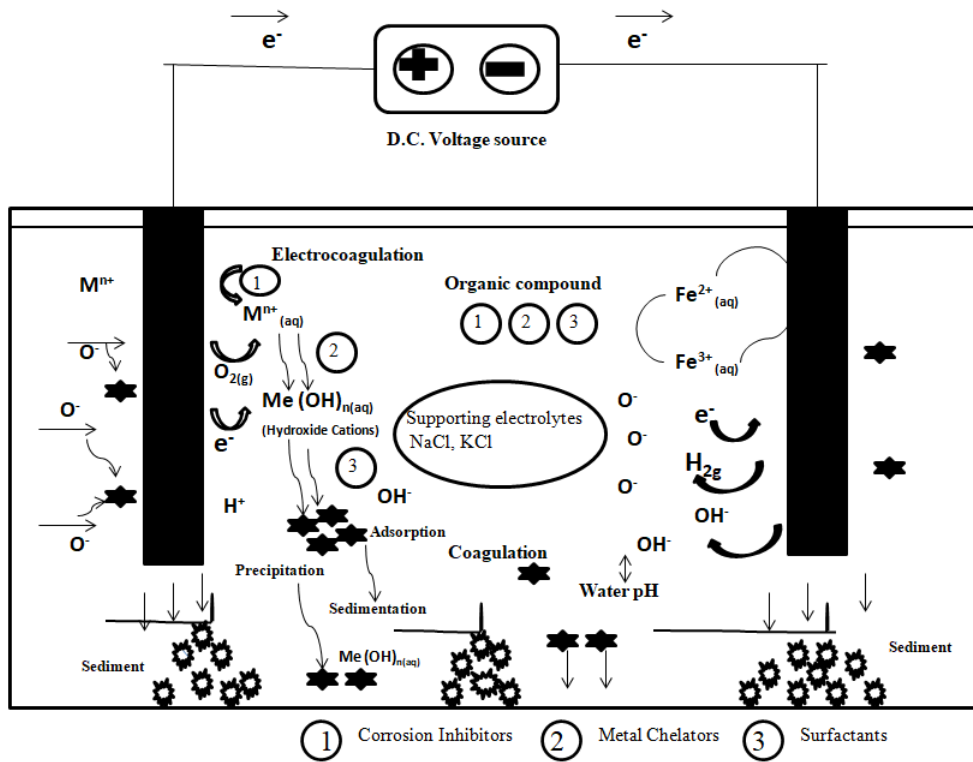
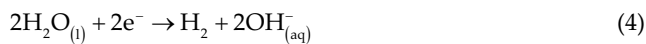


Fig. 2. Diagram showing complexities and interactions in an electrochemical reactor.

Cathodic reactions:



where M is the metal ions. Some side reactions also takes place in electrocoagulation process such as increase of pH due to the formation of hydroxyl ions or the consumption of hydronium ions/protons and reduction of metal ions on the cathodes. Generated metal cations reacts spontaneously forming various monomeric and polymeric species which finally transform into metal hydroxide [29]. Formation of these complex reactions strongly depends upon the pH of the aqueous solution. Destabilization of pollutants present in the solution allowing coagulation, further separation of contaminants from the solution takes place by settling or flotation [30]. Destabilization of the contaminants is achieved by two different mechanisms.

(a) Charge neutralization of the ionic species present in the wastewater and (b) sweep flocculation where the impurities are trapped and removed [31].

Flocs formed in electrochemical process are similar to that of chemical flocs except that electrochemical flocs are large in size; contain less bound water, acid resistant and more stable. Hence, flocs are easily separated by filtration. Gas bubbles are produced during the process which carries the pollutants to the top of the solution where these contaminants are easily collected and removed [31].

4. Operational parameters during electrochemical treatment

Operational parameters responsible for influencing the efficiency of electrocoagulation process are applied current density, electrode material used, treatment time, initial pH of the wastewater, composition of the wastewater, electrode gap, passivation of anode and water flow rate. As reported by Prajapati and Chaudhari [6–8], Henriques et al. [9] and Yang et al. [10], efficiency of electrocoagulation process depends strongly on different operational parameters.

4.1. Current density

Current density is the electric current per unit cross sectional area of electrode. Current density is important parameter for electrocoagulation [32–35]. The removal of pollutant from wastewater strongly depends on amount of metal ions released during the process. Amount of metal ions released during the process is dependent on the current density [36–38]. A simple relationship for an amount of electrode material dissolved can be derived from Faraday's law [39] as follows:

$$m = \frac{It_s M}{ZF} \quad (5)$$

where m = metal ions; F = Faraday's constant; Z = valency of the ions m ; I = applied current in ampere; t_s = treatment time in minutes; M = molar mass of electrode material.

It determines the bubble production rate, size and growth of the flocs in the process. If current density increases, bubble generation rate also increases with increase in the separation effect. With an increase in the current density, the amount of ion production on anode and cathode increases which further increases the removal efficiency [40]. If current density increases above its optimum limit, it does not result in the increase of removal efficiency [40]. Applied current densities can be varied from 100 to 250 A m⁻². Minimum 100 A m⁻² is required for good decolourization efficiency [41]. Several researchers reported that current density between 80 and 100 A m⁻² as an optimal value for the wastewater depending upon the characteristics of wastewater [41,42]. In general the cost of the electrocoagulation lies between 1 and 3 \$ m⁻³ [7].

4.2. pH

Initial pH of the wastewater is one of the most important parameter in electrocoagulation [40,42]. The maximum efficiency is obtained at optimum pH for the particular pollutant. If the wastewater has high electrical conductivity, the pH effect gets reduced [43]. The optimum pH of the solution depends upon the type of effluent which is used for treatment. For example in most of the cases textile effluent get optimized in pH 3–5, distillery industries effluent get optimized at pH 4.5 to 5.5, etc. It was established that at low pH, the chemical dissolution of metal ions such as iron could be significant and total iron concentration can be higher than would be theoretically expected.

In the case of aluminum, dissolution of aluminum at cathode occurs because pH increases to a level where aluminum is formed [44]. Also it may be observed that the acidic bulk solution inhibits this reaction because of hydroxyl ions that are produced and consumed by the acid in the solution. At acidic pH, the dissolution of the iron electrode is found to be significant even without electricity, whereas oxidation of Fe(II) to Fe(III) occurs only at pH above 5 [45]. The dissolution rate decreases at high pH due to the decrease in corrosion rate of iron at alkaline pH [46]. It was reported in the study by Mahmoodi and Dalvand [46] that in the presence of oxygen, a passive layer forms on the surface which decreases corrosion rate. Electrocoagulation is more suitable when higher pH is desired, whereas chemical coagulation is preferred when low pH is essential before discharge [47]. Verma et al. [48] studied the removal of hexavalent chromium from synthetic solution using electrocoagulation and found that the pH of the solution has a significant effect on the Cr(VI) removal efficiency.

4.3. Electrode gap

The inter electrode gap in the electrocoagulation process is again one of the most important factor as the electrostatic field depends on the gap between the electrodes. When the electrode gap (g) between the anode and cathode is larger, resistance (R) offered by the cell increases [49] and governed by following relation:

$$R = \frac{g}{KA} \quad (6)$$

K (S m⁻¹) is the cell specific conductance; A (m²) is the electrode surface area. If A is higher, g (m) value between anode and cathode increases R (ohm). From Faraday's law, the amount of oxidized metal decreases with higher g and consequently the pollutant removal efficiency decreases. Xueming et al. [50] reported that ohmic potential drop is proportional to the inter electrode spacing. Reducing this spacing is one of the great importances for reducing the electrolysis energy consumption. But at the minimum electrode gap, the removal efficiency also decreases. This happened because the generated metal hydroxides acts as the flocs and remove the contaminants present in wastewater by sedimentation and get degraded by collision with each other due to high electrostatic attraction [51].

During electrolysis, the solution close to the cathode becomes more concentrated because of the different mobilities of the ions present, and this effect can also be reduced by agitation of the bulk solution [52]. The inter electrode gap gets partially filled with gases during electrolysis, which increases its electrical resistance [53].

The planned electrode gap depends on the field conditions. A minimum electrode spacing of 3 and 8 mm is possible when handling synthetic wastewater and real wastewaters [54]. When working with low cell voltage which favours the formation of well settleable flocs, it is appropriate to restrict the inter-electrode spacing to not less than 10 mm; else the electrocoagulation reactor may require frequent polarity reversal because of the frequent flocs deposits; induced by the lowering of turbulence in between the electrodes [55]. A narrow spacing of less than 10 mm is accompanied with low energy consumption. At increased inter-electrode spacing, an increase in cell voltage occurs, causing an increase in the power consumption [56]. When planning for highly active electrode surface area to volume of the reactor, the inter electrode gap should be just sufficient enough to provide sufficient turbulence in between the electrodes which initiates mass transfer within the electrocoagulation reactor.

4.4. Electrolysis time

The removal efficiency of pollutants also depends on the electrolysis time. Efficiency increases with an increase in time. As the time increases, concentration of hydroxides ions also increases, but further increase in electrolysis time, the pollutant removal efficiency becomes constant and does not increase with increase in time. This may be due to excess amount of ions which promotes destabilization of particle [44].

4.5. Temperature

Temperature of the solution is one of the basic parameter on which process efficiency depends. Effect of solution temperature on the electrocoagulation reaction performance has been studied by many researchers [57–60]. Test results shown that removal of phosphate ion increases by increasing solution temperature up to 60°C. A further increase in the solution temperature is found to decrease the removal efficiency of phosphate ions [61]. These findings can be explained by the fact that increasing solution temperature

can improve ions transfer from the anode or cathode surface to the solution bulk resulting from the decrease in solution viscosity and the consequent increase in the ions diffusivity according to Stokes equation [62].

$$\frac{D\mu}{T} = \text{Constant} \quad (7)$$

where D , μ and T are ions diffusivity ($\text{m}^2 \text{s}^{-1}$), solution viscosity (kg ms^{-1}) and solution temperature ($^{\circ}\text{C}$), respectively. The decrease in phosphate removal efficiency occurring at solution temperature above 60°C is explained by the fact that higher solution temperature enhances the metal anode and cathode passivation by the formation of protective metal oxide layers, which decreases M^{n+} ions dissolution and ultimately the electrocoagulation reactor performance [63,64].

It has been reported that when temperature is too high, there is shrinkage of large pores of the metal hydroxide gel, which causes the formation of dense flocs that are more likely to deposit on the electrode surface. Increasing temperature also enhances the solubility at aluminum. However, it seems that increasing temperature can have positive and negative effects on the removal efficiency depending on the removal mechanism of pollutants [65]. Furthermore, removal efficiencies of pollutant in the temperature range of 10°C – 30°C were also experiential. It was observed that removal efficiency decreases above the 30°C temperature. The efficiency of boron removal was increased to 84%–96% as the temperature was increased from 20°C to 60°C [66].

4.6. Conductivity

Conductivity of sample is an influential parameter in electrocoagulation. Concentration of residual metal coagulant and final pH of solution mainly depends on the conductivity of the sample. Conductivity is naturally higher in neutral pH because more ions were added into the solution [66]. The sample must have some optimum conductivity for the flow of current. There is an increase in the current density with an increase in the conductivity of the solution at constant cell voltage or reduction in the cell voltage at the constant density [67,68].

The conductivity of the suspension can be adjusted to the desired value by varying the salinity of the wastewater to be treated. Addition of salt to the solution reduces the voltage and alters the voltage distribution between the electrodes [15]. Mahesh et al. [15] have performed the studies in the conductivity range of 0.7 – $1.1 \text{ mmhos cm}^{-1}$ for the treatment of pulp and paper mill effluent. However, a too high conductivity may lead to secondary parasite reactions, diminishing the main reaction of the electrolytic decomposition. Several electrolytes have been employed to elucidate their influence on the electrochemical treatment of wastewaters. They can be classified as inert (NaNO_3 , Na_2SO_4 and MnSO_4), halide salts (NaCl , KBr , KI and CaCl_2) and a reducing agent ($\text{Na}_2\text{S}_2\text{O}_5$).

4.7. Electrode material

Electrode material defines which electrochemical reactions will take place in the electrocoagulation system.

As reported by Prajapati and Chaudhari [6–8], aluminum and iron electrodes both have been used successfully in electrocoagulation system. Aluminum dissolves in all cases as Al^{3+} whereas there is some controversy, whether iron dissolves as Fe(II) or Fe(III) . Most results indicate that iron dissolves as Fe(II) and is oxidized in bulk solution to Fe(III) , if there are oxidants, such as oxygen present in sufficient concentration and pH is alkaline [44]. Fe(II) is a poor coagulant compared with Fe(III) due to higher solubility of hydroxides and lower positive charge which explains some poor results obtained with iron electrodes [69].

Optimal material selection depends on the pollutants to be removed and the chemical property of the electrolytes. In general, aluminum seems to be superior compared with iron in most of the cases when only the efficiency of the treatment is considered. Inert electrodes such as metal oxide coated titanium are used as cathode in some cases. Linares-Hernandez et al. [70] obtained high removal of colour with aluminum electrodes, while iron is more effective than aluminum in reducing organic load from industrial wastewater. A combination of iron and aluminum removes both colour and COD with high efficiency [58]. Aluminum electrodes are most effective in removing colour from wastewater, whereas iron electrodes removed COD and phenol from the wastewater more effectively than aluminum electrodes [71]. A combination of aluminum and iron electrodes removed colour, COD and phenol with high efficiency. Combination of electrodes have been studied for arsenic removal from groundwater [72]. Similar results are obtained for copper, chromium and nickel removal from metal plating wastewater [73–75].

4.8. Electrode passivation

One of the greatest operational issues with electrocoagulation is electrode passivation. The passivation of electrodes is the concern for the longevity of the process. Passivation of aluminium electrodes has been widely observed in the literature [76,77]. The latter also observed that during electrocoagulation with iron electrodes, deposits of calcium carbonate and magnesium hydroxide are formed at the cathode and an oxide layer is formed at the anode.

Nikolaev et al. [76] investigated various methods of preventing and controlling electrode passivation including changing polarity of the electrode, hydro mechanical cleaning, introducing inhibiting agents, mechanical cleaning of the electrodes. According to Nansou-Njiki et al. [78] and Zodi et al. [79], the most efficient and reliable method of electrode maintenance is the periodic mechanical cleaning of electrodes; which were a nontrivial issue for large-scale, continuous processes.

5. Approaches to electrocoagulation reactor designs

The approach to electrocoagulation reactor design is to handle a variety of wastewater. The key focus of the studies by Dubrawski and Mohseni [80] and Drouiche et al. [81] is on the removal of a particular pollutant from simulated wastewater rather than from the real streams emanating from industries or polluting sources. Such approach will lead to a long term disadvantage in the sense that the knowledge gets limited to a specific operating condition quite far away from

reality. Therefore, it is necessary to have a critical look at the key aspects of reactor design (physical and chemical parameter) with an emphasis on its application to the process.

Physical parameter

- Batch vs. continuous operation
- Reactor geometry
- SA/V ratio (m^2/m^3)
- Current density
- Specific energy consumption

Chemical parameter

- Electrode material
- Passivity and flake deposition
- Sludge separation

5.1. Physical parameters

5.1.1. Reactor operation

Studies by the researchers Makwana and Ahammed [82], Merzouk et al. [83], Zaroual et al. [84], Lai and Lin [85] have focused on laboratory/pilot scale or continuous mode of operation. Continuous electrochemical reactors (ECRs) are dynamic in operation. The stability and the performance of the ECRs at various flow rates and pollution load can be checked. Batch process on other hand show steady behaviour having a fixed volume, electrolysis time (t), pH, organic concentration (COD) with a varying amount of dissolution of electrode (with time) as per the requirement of the electrocoagulation. The sludge formed during batch treatment is sturdier than that formed in continuous ECRs [86,87].

Apart from this, the batch processes show steady-state behaviour due to fixed volume, electrolysis time (t), pH_v , organics concentration (COD), with a varying amount of dissolution of electrode (with time) as per the need of electrocoagulant generated in-situ, based upon the amount of residual organics in bulk solution. Batch reactors have tendency to show time-dependent behaviour with the electrocoagulant being fed continuously to the reactor; as the anode dissolves into a form capable of aggregating the pollutant, consequently pollutant, coagulant and pH concentrations vary with respect to time. Modelling of electrocoagulation reactor is very difficult because ECR shows inherent dynamic behaviour, coupled with the interplay between thermodynamic and kinetic considerations [15].

5.1.2. Reactor geometry

The successful treatment of wastewater depends highly on the geometry of the ECR because it affects the operational parameters such as anode dissolution, fluid flow regime, floc formation, flotation effectiveness, (electrolysis time in batch reactors), power consumption, mixing, filterability and settling characteristics. Number of researchers [61–64] suggested that the most common approach involves the use of circular cross-section reactors with either cylindrical electrodes or plate electrodes mostly focusing on ECRs on continuous mode. A simple downstream unit is often required

for the separation of the sludge/precipitate from the treated effluent while handling real wastewaters [63,64].

5.1.3. SA/V ratio (m^2/m^3)

One basic scale-up parameter would be the attempt to accommodate large electrode area in a small volume, which is referred to as the SA/V ratio. SA/V ratio is one of the important parameter for the reactor design. However, most of researchers so far did not focus on this issue when dealing with electrochemical treatment (ECT) of wastewaters. While comparing reactors, it is essential to compare the figures of merit under similar operating conditions. SA/V ratio is the measure of the potential to deliver coagulant and bubbles to the system. It is important to define the reactor volume, V precisely when using this figure of merit. It is often desirable to maximize this ratio to achieve a compact reactor design [64].

As the anode area increases, that is, as SA/V ratio increases, it induces a decrease in the necessary time required for a given current density. They showed the existence of an optimum current density for a fixed SA/V ratio. For a consistent anodic dissolution and hydrogen production rates, a constant optimal current density is essential [16]. Attempts to accommodate large electrode area in a small cell volume resulted in developments such as the multiple - cathode cell [63].

5.1.4. Current density

Current density is defined as the current per unit active electrode area (A m^{-2}). Current density has the most pronounced effect on the treatment as it is the most convenient control variable for the process [88]. The successful operation of ECR is highly dependent on optimal current density. For the available data such as influent composition and flow rate, current density is responsible for the rate of metal dissolution and the electrolytic bubble density production inducing mass transfer at the electrodes and in the bulk solution. When the current in the EC cell is increased, the gas bubble flux increases; this increases the separation effect. Apart from this when the concentration of gas bubbles is increased, the possibility that the two gas bubbles collide also increases. This reduces the separation effect since larger gas bubbles are less effective than smaller gas bubbles, because they have a smaller surface area/volume ratio. It is a well-known fact that when the rate of current transfer increases treatment rate also increases, therefore, less time is required for the treatment. The metal dissolution increases with an increase in the current. An increase in ionic strength will generally cause an increase in current density at the same cell voltage. In practical applications, it is necessary to limit the current density so as to reduce excessive evolution of oxygen [7] and other negative impacts such as heat generation. At high current density, only a fraction of the applied current, which is equal to the limiting current, is used for the combustion and the rest for the side reaction for oxygen evolution.

5.1.5. Energy consumption

ECT is an energy-intensive process and its effectiveness is assessed in terms of specific energy consumption

(SEC). It is the electrical energy necessary to form 1 kg of the desired product in a given ECR. As applied to wastewater treatment, the SEC is defined as the amount of energy consumed per unit mass of COD removed [89]. Treatment performance can also be expressed in terms of anode efficiency, that is, the mass of organic load removed divided by the electrode area, the applied current and the treatment time. In addition, power consumption is another important parameter which determines the efficiency of ECR. The power consumption of the electrochemical cells can be expressed as follows:

$$P = V.I = I.R^2 \quad (8)$$

where P is power consumption (W), V is the voltage (V), I is current (A), and R is the resistance (ohm). This equation shows that by reducing the resistance in the electrolyte, without changing the current, the specific power consumption can be reduced. As the conductivity of the electrolyte increases, the power required for any given degree of pollutants removal also decreases. Therefore, for wastewaters being discharged into sea/ocean, addition of a certain volume of seawater or salt (NaCl) to raise the conductivity of the wastewater to an optimal level may be desirable to reduce the resistance (increase the current) at a given voltage [90].

5.2. Chemical parameters

5.2.1. Electrode material

Electrode assembly is the heart of the ECT facility. The efficiency of any ECT process depends on the type of electrode used in the ECR. Therefore, selection of the anode material is of immense importance for an efficient ECT process. The selections of the anode for the removal of various pollutants/contaminants from wastewater are based on the nature of the pollutant. The treatment efficiency depends on the affinity of the pollutant toward the ions generated by electrode material.

Various types of electrode materials that have been used in ECT include aluminum, iron, cast iron, stainless steel (SS), carbon and platinum. In addition to these traditional materials, dimensionally stable anodes: SnO₂, PbO₂, graphite, nickel, etc., and BDD (boron-doped diamond) have also been used.

Aluminum and iron electrode are most suitable to treat distillery wastewater. Apart from this, other electrode material such as SnO₂, PbO₂, graphite, nickel, etc., and BDD (boron-doped diamond) electrodes have greater chemical resistance and ability to treat cyanide bearing wastewaters. Graphite and PbO₂ are the most common insoluble anodes generally used in electroflotation (EF) [63,64]. These anodes are cost effective and are easily available. However, PbO₂ anodes generate highly toxic Pb²⁺ leading to serious secondary pollution. IrOx, Ti/IrOx-Ta₂O₅ electrodes are expensive. It has been suggested that although similar average result can be obtained using Ti/PbO₂ or Ti/SiO₂ anodes, the latter is preferred because of its better ability to oxidize toxic compounds. If water contains Ca²⁺ and/or Mg²⁺ ions in significant amount, SS electrodes can be used [64].

5.2.2. Passivity and flake deposition

One of the important operational issues linked with ECT is flake deposition on anode electrode and electrode passivation. Passivation is recognized as a detrimental factor to the reactor performance as it increases the cell resistance between the electrodes and more energy gets wasted on heating the passivation layers. During the electrocoagulation, studies on chromium removal, Osipenko and Pogorelyi [77], observed the formation of calcium carbonate and magnesium hydroxide at the cathode and an oxide layer at the anode (an inhibiting layer), which reduces the system efficiency. With the continuation of the ECT process, these layers spread all over the electrode surface reducing the efficacy of the ECT process.

5.2.3. Sludge separation

A waste material is generated as a byproduct of any wastewater treatment plant is sludge. The sludge due to its putrescence, inherent moisture and variability in terms of its chemical and biological composition, poses problems in handling and disposal. Wastewater sludge might contain all the pollutants present in the raw wastewater. Handling, treatment and disposal of sludge has been a matter of great concern of its inevitability giving rise to pollution and has been the most vexing problems in the field of water pollution control [91]. The stability of the sludge generated by wastewater treatment processes depends strongly on its settling properties and filterability characteristics. Traditional biological wastewater treatment processes show poor settleability of the sludge due to the presence of microbial population which often causes serious bulking and foaming problems. Clarifiers and thickeners in wastewater treatment plants are essentially identical units; a clarifier produces clean water, while a thickener concentrates solids slurry as the desired product [92]. Gravity separators are required where flotation type ECRs are adopted for treating real wastewaters. The sludge obtained after the ECT may contain heavy metals which are persistent pollutants and may gain entry into water body and through food chain to the life systems. Therefore, the determination of sludge characteristics becomes very important in deciding the method of reuse/disposal (as fuel [6–8] in agriculture, as construction aggregates, as adsorbent, as flocculants aid into sewers, as composting material, or into landfills).

5.2.4. Electrochemical kinetics

Reactor kinetics must be quantified to assess the performance of any reactor [93]. In the case of an ECR, the rate of addition of the electrocoagulant is determined by the relevant electrode kinetics. Electrode reactions using real/synthetic wastewaters are heterogeneous and take place in the interfacial region between the electrode and the bulk solution. Both potential and concentration gradients exist between the electrode surface and the bulk solution. Thus, the chemical species to be oxidized must diffuse from the bulk phase to the electrode surface through a liquid film diffusion process before electron transfer can occur at the surface [85,93]. Thus, the electrochemical reactions are governed by the charge transfer and/or mass transfer.

Mayer and Klimpel [94] have proposed several kinetic models to represent the experimental electrokinetic data. These models are given below:

$$R = R^* (1 - e^{-kt}) \quad (9)$$

$$R = R^* \left(\frac{kt}{1 + kt} \right) \quad (10)$$

$$R = R^{*2} \left(\frac{kt}{1 + R^* kt} \right) \quad (11)$$

$$R = R^* \left(1 - \left(\frac{\ln(1 + kt)}{kt} \right) \right) \quad (12)$$

where R is recovery at time t and R^* is ultimate recovery and k is the rate constant

Limitations:

- This process is currently not used in industrial application
- There are relatively few “showcases” for this treatment technology
- Time to time replacement of sacrificial electrodes are required
- Bubble size distribution and density control is difficult
- Selection of electrode and overall maintenance of this process is not easy
- During the ECT process oxide film adhere to the surface of the electrode which affects the current carrying capacity of the electrode
- The minimum conductivity of the wastewater suspension may be required depending on the reactor design configuration
- Toxic chlorinated organic compounds may be formed in-situ, in the presence of chlorides

6. Overview of different types of wastewater treated by electrocoagulation

Electrocoagulation plays important role in removal of organic, inorganic and heavy metals from wastewater. It achieves maximum efficiency as compared with other physicochemical methods of wastewater treatment process. This process can be also used by coupling the ECR with low-cost renewable energy sources.

6.1. Pulp and paper industry

Pulp and paper industry is a large-scale consumer of water and generate significant quantities of toxic and non-biodegradable organic materials. Wastewater from textile contains high concentration of fatty acids, sulphur compounds, phenol and its derivatives, chlorinated lignin, etc. These toxic materials are not easily degraded by biological wastewater treatment. Therefore, development of efficient wastewater treatment technologies has become major concern prior to biological treatment. In recent years, electrocoagulation technique has got strong research interest because

it produces coagulants by dissolving electrodes in the cell, which helps the removal of the pollutants producing negligible secondary pollutants. Electrocoagulation cannot remove material that does not form precipitate such as sodium and potassium. If a contaminant cannot form flocs, the process will not work out. Therefore, the contaminants such as benzene, toluene or similar organic compounds cannot be removed. However, lignin, the macromolecule composed of three monomers namely *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol or its derivatives, can be removed by electrocoagulation. Table 1 presents studies on treatment of pulp and paper mill effluents by the EC process.

6.2. Textile wastewater

Textile industries are the most polluting industries. Wastewater of textile industry is found to contain a high degree of pollutants with very high total dissolve solid and suspended solids. The wastewater is highly coloured and viscous due to dyestuff and suspended solids. Sodium is the major cation due to high consumption of sodium salts. Chloride is a major anion found in the wastewater. Concentration of bicarbonates, sulphate and nitrate is also high. Heavy metals such as chromium, iron, zinc, lead, copper and manganese are also present. Treatment of dyeing wastewater can be done by many types of conventional and biological treatment, chemical coagulation, activated carbon adsorption, ultrafiltration and electrocoagulation. Each treatment method has its own advantages and disadvantages. Electrocoagulation is a very effective method for removal of contaminants from textile waste. Table 2 presents studies to treat textile effluents by the EC process.

6.3. Distillery industry

Distilleries have been generating huge quantities of highly toxic effluents greater in BOD, COD and TS (total solids) obtained from distillation column. Spent wash is the main effluent of distillery from analyzer column. Other wastewaters such as fermenter washing, fermenter cooling, floor washing, spillage and cooling. Among these spent wash generated for every liter of alcohol produced and is characterized by high percentage of dissolved organics (52,000–58,000 mg L⁻¹ BOD, 92,000–100,000 mg L⁻¹ COD) and inorganic material (1,660–2,200 mg L⁻¹ form of nitrogen, 225–3,038 mg L⁻¹ phosphorus and 9,600–17,475 mg L⁻¹ potassium, etc.), dark brown colour (238,000–252,000 Pt-Co unit), high temperature (70°C–100°C) and low pH (4–4.5) [123]. Spent wash is toxic to aquatic organisms. If disposed untreated on land, reduces alkalinity of soil and crops maybe destroyed. In some parts, the colour problem in groundwater is so acute that distilleries have to provide potable water to surrounding villages. It behaves much more hazardously when disposed into water bodies, since it may result in the complete depletion of dissolved oxygen and aquatic life will be destroyed. Various physical, chemical and biological techniques are used for the treatment of distillery spent wash. In biological treatment, anaerobic treatment is more effective than that of aerobic treatment due to high organic content of molasses in spent wash. But these methods are able to remove only 60%–80% COD from spent wash.

Table 1
Studies to treat pulp and paper mill effluents by the EC process

Reference	Current density	Time (min)	pH	Anode–cathode	% COD removal efficiency
Mahesh et al. [15]	55.6 A m ⁻²	40	7	Fe–Fe	80
Katal and Pahlavanzadeh [95]	70 mA cm ⁻²	30	7	Fe–Fe	88.4
Sridhar et al. [96]	15 mA cm ⁻²	20	8.4	Fe–Fe	77.2
Uğurlu et al. [97]	5 mA cm ⁻²	7.5	7.6	Al–Al Fe–Fe	75 55

Table 2
Studies to treat textile effluents by the EC process

Reference	Current density	Time (min)	pH	Anode–cathode	% COD removal efficiency
Zaroual et al. [98]	–	3	10.6	Fe–Fe	84
Muthukumar et al. [99]	5 mA ² cm ⁻²	–	12	(RuO ₂ –Ti)–Ti	85
Bayramoglu et al. [100]	200 A m ⁻²	10	11	Fe–Fe Al–Al	76 65
Lin and Peng [101]	92.5 A m ⁻²	240	10	Fe–Fe	51

Ultrafiltration/nanofiltration techniques provide colourless water from spent wash. The concentrated spent wash after reverse osmosis has very high BOD and COD. Hence, there is need to find out an economical technique for wastewater treatment. Electrocoagulation is found to be very effective for the destruction of recalcitrant organics from different synthetic wastewater as well as industrial wastewater as reported by central authority [124]. Table 3 presents studies to treat distillery effluents by the EC process.

6.4. Food industry

Wastewater generated by different types of food industries possesses high BOD and COD because of using variety of raw materials such as different types of fruits, vegetables, preservatives, colour, salt, oil, sugar, gelatin, etc. This adds high pollution loads into the wastewater. Wastewater from food industry is non-toxic in nature because it comprises less hazardous compounds. Among the food industries, the dairy industry is the most polluting

in terms of volume of effluent generated. Most of the water used in food industry is for washing and rinsing purpose. Wastewater treatment is done by aerobic and anaerobic biological techniques. But the aerobic treatment malfunctions due to fluctuating load and characteristics of wastewater. In recent years investigations have been focused on the treatment of wastewater using electrocoagulation due to increase in environmental restriction on effluent discharge. Electrocoagulation technique is successfully used for the treatment of soluble or colloidal pollutants such as slaughterhouse wastewater, vegetable oil refinery, and dairy industry wastewater. Table 4 presents studies on treatment of food industry effluents by the EC process.

6.5. Paint industry

Classification of paint industry is based on their primary solvent use. On this basis, paints can be classified as water based, organic solvent based or powder. A large variety of pigments and extenders of different grades are

Table 3
Studies to treat distillery effluents by the EC process

Reference	Current density	Time (min)	pH	Anode–cathode	% COD removal efficiency
Prajapati and Chaudhari [6]	44.5	120	8	Al–Al	93
Prajapati and Chaudhari [7]	99	120	8	Fe–Fe	93
Khandegar and Saroha [102]	0.817 A cm ⁻²	120	3	Al–Al, Al–Fe Fe–Fe	81.3, 71.8 52.4
Prasad and Srivastava [103]	45.45 A m ⁻²	60	8	Al–Fe	50.5
Thakur et al. [104]	146.75 A m ⁻²	130	6.75	SS–SS	63.1
Manisankar et al. [105]	6 A dm ⁻²	180	6.9–7.2	Graphite–Graphite	85.2

Table 4
Studies to treat Food industry effluents by the EC process

Reference	Current density	Time (min)	pH	Anode–cathode	% COD removal efficiency
Gengec et al. [106]	80 A m ⁻² , 12.5 A m ⁻²	30	4.5	Al–Al	48 49
Coskun et al. [107]	1 A	45	4.3	Al–Al Fe–Fe	53.4
Yavuz et al. [108]	15 mA cm ⁻²	20	7	Fe–Al	79.2
Hanafi et al. [109]	250 A m ⁻²	15	4.2	Al–Al	80
Un et al. [110]	35 mA cm ⁻²	90	7	Al–Al	93
Kobyas and Delipinar [111]	70 A m ⁻²	50	6.5, 7	Al–Al Fe–Fe	71 69
Murthy et al. [112]	–	30	7	Al–Al Fe–Fe	50 72
Barrera-Diaz et al. [113]	18.2 A m ⁻²	30	4	Al–Al	88
Kobyas et al. [114]	300 A m ⁻²	40	4, 6	Al–Al	60
Xu et al. [115]	–	16, 24	4.5	Al–Al Fe–Fe SS–SS	95 95 92

Table 5
Studies to treat paint industry effluents by the EC process

Reference	Current density	Time (min)	pH	Anode–cathode	% COD removal efficiency
Akyol [116]	35 A m ⁻²	15	6.95	Fe–Fe Al–Al	93 94
Lai and Lin [117]	0.06 A cm ⁻²	60	8.7	Al–Al	88.5
Chou et al. [118]	6.8 mA cm ⁻²	50	–	Fe–Al Fe–Fe Al–Al Al–Fe	96.3

Table 6
Studies to treat electroplating effluents by the EC process

Reference	Current density	Time (min)	pH	Anode–cathode	% Metal removal efficiency
Dermentzis et al. [119]	30 mA cm ⁻²	20	4–8	Al–Al	Near about 99% for Ni and Cu
Kobyas et al. [120]	60 A m ⁻²	30	8	Fe–Fe	99% removal for Cd and Ni both
Orescanin et al. [121]	60 A m ⁻²	40	–	Fe–Fe Al–Al	Cr(VI), Fe, Ni, Cu, Zn, and Pb removal efficiency were 99.94%, 100.00%, 95.86%, 98.66%, 99.97%, and 96.81%
Adhoum et al. [122]	4.8 A m ⁻²	20	4 and 8	Al–Al	Near about 80% for both Cu and Zn

used for different functional requirements and they vary widely from synthetic to natural minerals, organic, inorganic to metallic and depending on the source of raw materials. Paint is generally considered as a mixture of pigments, binder, solvent and additives. The components of paint also determine the characteristics of the waste generated in its

manufacture and use. In general, paint effluents are alkaline and have high BOD, COD, heavy metals, suspended solids and coloured materials. Electrocoagulation is an efficient method for removal of BOD, COD and colour from paint industry. Table 5 presents studies related to paint industry effluents by the EC process.

6.6. Electroplating industry

Electroplating is the technique of metal finishing through which deposition of a fine layer of one metal on another through electrolytic process is carried out. The wastewater discharged from electroplating contained acidic chromium, cadmium, lead, nickel, etc. The environmental load in electroplating industry mainly consists of process wastewater, sludge and sulphuric acid. The untreated rinsing water has a lot of waste such as iron – 150 mg L⁻¹, zinc – 240 mg L⁻¹, suspended material – 620 mg L⁻¹. Electrocoagulation is derived technique from conventional coagulation which can effectively adopted for the removal of COD, nickel, copper, chromium, cadmium from electroplating industry. Table 6 presents studies on treatment of electroplating effluents by the EC process.

7. Conclusion

In the present review, it is demonstrated that electrocoagulation has successfully been applied for the removal of harmful substance such as organics and heavy metal from wastewater. In addition, electrocoagulation has been applied to a wide range of industrial wastewaters. Mechanisms are expected to change through the process but the dominant mechanisms and their role are yet to be identified. Still, electrocoagulation method has been suffering the lack of a fundamental, methodical approach at a mechanistic level is reflected by the lack of similarities in reactor design and application. A logical, systematic approach to a fundamental understanding of electrocoagulation is still not available, and thus, needs further investigation. Number of key mechanisms is dependent on only few operational parameters such as pH and applied current, to maximize removal efficiencies. Therefore, a trade-off is required between various competing factors must be evaluated to provide a scientific basis for optimum operation conditions. In addition, the electrocoagulation process has only been empirically optimized, and hence, requires more fundamental understanding.

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