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A review of electrocoagulation technology for the treatment of textile wastewater

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Abstract: The conventional coagulation technique of textile wastewater treatments is plagued with the issue of low removal rate of pollutants and generation of a large quantity of sludge. Recently, electrocoagulation (EC) technique gained immense attention due to its efficiency. The technique involves dissolution of the sacrificial anodes to provide an active metal hydroxide as a strong coagulant that destabilizes and amasses particles and then removes them by precipitation or adsorption. EC process is influenced by operating parameters such as applied current density, electrodes material and configuration, type of electrical connection, pH and conductivity of the solution, and mixing state. Consequently, this work reviewed the major and minor reactions of EC process with operational parameters, design of EC cell, mass transfer studies and modeling, and industrial wastewater applications. The work also includes comparison of EC technique with conventional coagulation and combinations with other techniques. Special emphasis is on removal of pollutants from textile wastewater. Further, the electrical energy supplies and cost analysis are also discussed. Even though several publications have covered EC process recently, no review work has treated the systematic process design and how to minimize the effect of passivation layer deposited

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on the surface of the electrodes. EC process with rotating electrodes has been recommended to reduce this phenomenon. The effect of electrodes geometry is considered to enhance the conductivity of the cell and reduce energy consumption. The studies of ionic mass transfer were not implemented before special by limiting current method during the EC process. Moreover, no aforementioned studies used computational fluid dynamics modeling to present the mass transfer inside the EC reactor.

Keywords: efficiency; electrocoagulation; operating parameters; pollutant removal; textile wastewater.

1 Introduction

Many industrial processes are piloted using a large amount of fresh water, which is exhausted as wastewater. The wastewater needs to be treated properly to decrease or eradicate the pollutants and attain the purity level for its exploitation in the industrial process to promote sustainability (Barrera-Díaz et al. 2012). The textile industry is one of the important pollutant sources, which involves a wide range of machinery and processes to produce the required shape and properties of the product. A huge amount of effluent is generated in the various processes such as sizing, scouring, bleaching, mercerizing, dyeing, printing, and finishing as shown in Figure 1 (Verma et al. 2012). The contaminants in the effluent are colloidal elements and dissolved organic matters, which contain mainly by-products, residual dye, salts, acid/alkali, auxiliary chemicals, and cleaning solvents. Coloring matter is the major contaminant in the textile effluent and has to be removed before discharging the effluent into the aqueous ecosystem (Khandegar and Saroha 2013a,b,c).

Coagulation is a chemical treatment used prior to sedimentation in textile wastewater treatment. It is a process for combining small particles into larger aggregates. The main drawbacks of this treatment method are low removal efficiency, long detention time, and large quantity of sludge. Moreover, coagulation requires large quantity of chemicals for coagulation, flocculation, pH, and conductivity adjustment, which makes the process uneconomical

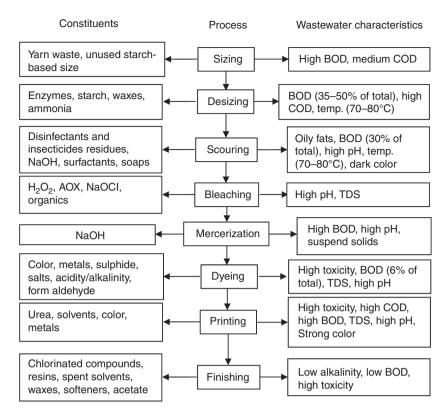


Figure 1: Component of major pollutants involved at various stages of a textile manufacturing industry adopted from Verma et al. (2012).

(Yildiz et al. 2008, Moreno et al. 2009, Un et al. 2009, Ali and Yaakob 2012, Barrera-Díaz et al. 2012).

Many technologies like biological oxidation, chemical oxidation, advanced oxidation, nanofiltration, and adsorption have been investigated. In addition to that, electrochemical technologies, such as electrodeposition, electrocoagulation (EC), electroflotation (EF), electrooxidation (EO), and electrokinetic remediation, have received significant attention over the years. Their popularity is due to the ease of distribution and moderate required amount of chemicals (Barrera-Díaz et al. 2012). However, most of the aforementioned methods have some major drawbacks. For example, biological oxidation is undoubtedly an inexpensive process, but the existence of toxic or biorefractory molecules may hinder this approach due to effluents' contamination with organic compounds (Panizza and Cerisola 2009, Barrera-Díaz et al. 2012). Chemical oxidation has low capacity rates and needs transportation and storage of dangerous reactants (Panizza and Cerisola 2009); advanced oxidation processes require high investment costs (Martinez-Huitle and Ferro 2006, Panizza and Cerisola 2009); nanofiltration and adsorption processes are not always sufficient to achieve the discharge limits (Bousher et al. 1997, Wachinski 2012); and EO and electrodeposition processes need long reaction times to achieve the treatment (Chen 2004, Martinez-Huitle and Ferro 2006).

Conversely, EC is an effective wastewater treatment technique for removal of pollutants. EC has been recognized to effectively treat wastewater from steam cleaners, pressure washers, textile manufacturing, metal platters, and meat and poultry processors. It is also effective for treating wastewater from commercial laundry, mining operations, municipal sewage, and palm oil effluents. This paper presents a review on the EC treatment of textile wastewater and highlighted the main drawbacks of this technique.

2 Coagulation concept

Pollutants in wastewaters are normally colloidal particles, which are not removable by flotation, typical filtration, or sedimentation due to their stability in water. Colloids are microscopic particles (in the range of 1 nm to 10 μm), which are dispersed throughout a substance solution. The stability of colloids in a solution depends on their surface charge. Stability (or destability) of colloids in water is a balance between the repulsive electrostatic force and

attractive van der Waals force. The van der Waals forces of attraction resulting from the permanent or induced dipoles are significant at very short distances. The repulsive force is due to the overlapping of the electrical double layers (EDL), Stern and diffused layers (Figure 2). The repulsion results in higher counterion concentration and repulsion of the particles to produce flocculants, which precipitate by gravity. It is difficult to measure the charge at the colloid surface, due to the charge concentrations in the Stern and diffuse layers. Consequently, zeta potential is used to measure the effective charge of the particle as it moves through the solution, providing a direct indication to particle stability (Vepsäläinen 2012).

In coagulation and flocculation technologies, particles are destabilized with the addition of inorganic or organic chemicals, which influence the EDL. Coagulants are chemicals that reduce the repulsive energy (energy barrier) between the particles. Therefore, the particles can agglomerate more easily by a weak bond (the secondary minimum of potential energy). Flocculation supports and enhances floc characteristics. Properties like settling ability and filterability can be improved by using flocculation aids. The pathway that undermines colloidal particles

in water includes compression of the EDL, adsorption destabilization (oppositely, charged ions or polymers are adsorbed on the surfaces of particles), inter-particle bridging, and precipitation.

There is a number of mixing stages in a representative coagulation process of wastewater treatment. For proper dispersion of chemicals in wastewater stream and collisions at the stage of coagulation, a fast agitation is required. However, the particle size growth takes place during the flocculation under a slow mixing phenomenon through induced velocity gradient. A detailed description of coagulation can be found in Verma et al. (2012).

Prominent coagulants used in wastewater treatment are aluminum and iron metal salts. Both metals can form multivalent ions, Al3+, Fe2+, and Fe3+, and various hydrolysis products. Fe(II) is a poor coagulant because it oxidizes to Fe(III) during the coagulation process to obtain higher efficiency. The most commonly used salts are simple aluminum and iron sulfates and chlorides. Metal cations go through a series of hydrolytic reactions depending on the pH of the solution, and mononuclear [Figure 3 and Eq. (1)] and polynuclear hydroxides form in the solution. Neutral amorphous metal hydroxides, Al(OH)₃ and Fe(OH)₃, are

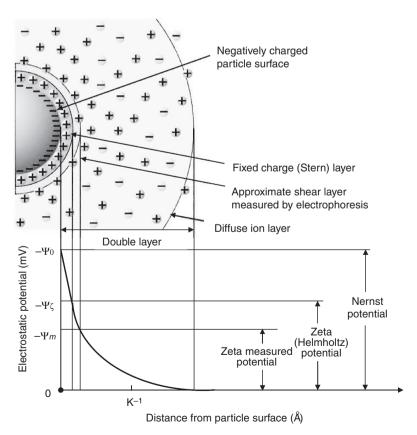


Figure 2: Conceptual representation of the electrical double layer adopted from Vepsäläinen (2012).

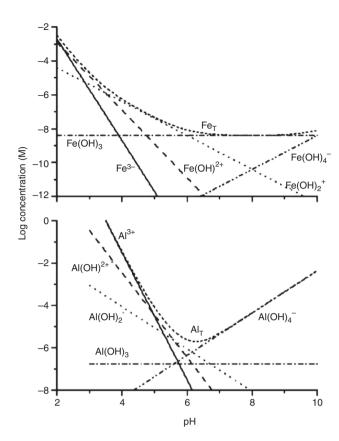


Figure 3: Concentrations of soluble monomeric hydrolysis products of Fe(III) and Al(III) in equilibrium with the amorphous hydroxides at zero ionic strength and 25°C adopted from Vepsäläinen (2012).

poorly soluble species. Distribution of mononuclear species of metals can be presented as solubility diagrams (Aoudj et al. 2010, Vepsäläinen 2012).

$$Me^{3+}(aq) + nH_2O \leftrightarrow Me(OH)_n^{3-n} + nH^+(aq)$$
 (1)

3 Theory of electrocoagulation

The need for alternative technologies for wastewater treatment has renewed scientific, economic, and environmental interests of the water treatment technologies (Ukiwe et al. 2014). Although EC seems similar to chemical coagulation, it has many differences like the side reactions that are described in this report. In the EC system, a number of reactions take place at the cathode and the anode. Figure 4 gives a detailed understanding of these reactions, showing the main mechanisms of destabilization of pollutants. The formation of coagulating ions takes place in situ through various stages:

(i) Formation of coagulants by electrolytic oxidation of the 'sacrificial electrode (anode)';

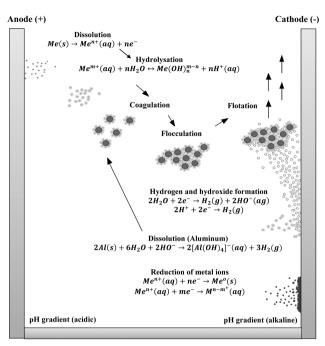


Figure 4: Typical reactions during the EC treatment adopted from Chaturvedi (2013).

- (ii) Weakening of the pollutants, particulate suspension, and breaking of emulsions; and
- (iii) Accumulation of the undermined phases to form flocs.

The summary of weakening mechanisms of the pollutants, particulate suspension, and breaking of emulsions is provided below (Jame 2012, Chaturvedi 2013):

- Compression of the diffused double layer near the charged particles through the interaction of the ions produced by oxidation of the sacrificial anode.
- Charge counterbalancing of the ionic species existing in wastewater by counterions twisted via the electrochemical dissolution of the sacrificial anode. These counterions decrease the electrostatic inter-particle repulsion to the extent that the van der Waals attraction prevails, hence resulting in coagulation.
- The floc formed through the coagulation produces a sludge blanket, which capitulates and bridges the colloidal species in the aqueous phase. The solid oxides, hydroxides, and oxyhydroxides generate the active surfaces for the adsorption of the contaminants.

3.1 Main reactions

Electrodes that produce coagulants into water are made from either iron or aluminum. In addition, there can be inert electrodes, typically cathodes, which are sometimes used as counterelectrodes in the system. Iron and aluminum cations dissolve from the anodes according to Eqs. (2) and (3) (Barrera-Díaz et al. 2012, Chaturvedi 2013):

$$Fe(s) \rightarrow Fe^{n+}(aq) + ne^{-}$$
 (2)

$$Al(s) \to Al^{3+}(aq) + 3e^{-}$$
 (3)

Iron can dissolve into divalent Fe(II), and trivalent Fe(III) forms in aqueous environment during the coagulation. Whereas aluminium dissolves only in trivalent form Al(III), Fe(II) can further oxidize to Fe(III) [Eq. (4)] under appropriate oxidation-reduction potential and pH conditions. To achieve a suitable rate of reaction, the presence of oxygen and neutral pH are necessary (Chaturvedi 2013).

$$4Fe^{2+}(aq) + 10H_2O + O_2(aq) \rightarrow 4Fe(OH)_3(s) + 8H^+$$
 (4)

Moreno et al. (2009) found that in an EC system, the potential of the iron anode is based on the region where Fe(III) iron is produced. Therefore, the potential of the cathode is suggested to be in the region where Fe(III) is reduced to Fe(II) (Gomes et al. 2007, Vepsäläinen 2012). The chemical dissolution of iron and its concentration are expected to be higher at low pH than theoretical expectations (Verma et al. 2013). For example, oxidation of produced Fe(II) is not noteworthy at pH 5, moderate at pH 6, and very rapid at pH 7-9 (Sasson et al. 2009, Al Aji et al. 2012, Barrera-Díaz et al. 2012).

Faraday's law [Eq. (5)] is used to calculate the amount of metal cations dissolved during the reactions at the anode (Chaturvedi 2013, Roopashree and Lokesh 2014, Singh and Ramesh 2014, Khaled et al. 2015):

$$m = \frac{ItM_{W}}{zF} \tag{5}$$

where I is the current (A), t is the operation time (s), M_{w} is molecular weight of the substance (g/mol), F is Faraday's constant (96,485 C/mol), z is the number of electrons involved in the reaction (2 for Fe²⁺ and 3 for Fe³⁺ and Al³⁺), and *m* is the quantity of metal dissolved (g).

Thus, at the cathode the reaction occurs by formation of OH⁻ [Eq. (6)] or by consumption of hydronium ions/ protons [Eq. (7)] (Chaturvedi 2013, Khandegar and Saroha 2013a,b,c):

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$$
 (6)

$$2H^{+}(aq) + 2e^{-} \rightarrow H_{2}(g) \tag{7}$$

At high pH, aluminum dissolves as aluminate as shown in Eq. (8) (Barrera-Díaz et al. 2012):

$$2Al(s) + 6H_2O + 2OH^-(aq) \rightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g)$$
 (8)

During the hydrolysis or dehydrolysis reactions in the aluminum ion solution, aluminate ions are produced on the electrodes. A green rust manifests when iron electrodes are used, which contains both Fe(II) and Fe(III) hydroxides, and anions such as Cl⁻, CO₃⁻², and SO₄⁻² (Moreno et al. 2009). Figure 3 gives the mononuclear hydrolysis products of Fe(III) and Al(III) as a function of pH. It is possible that similar polynuclear species are produced in EC and chemical coagulation (Vepsäläinen 2012, Khaled et al. 2015).

3.2 Secondary reactions

There is possibility of occurrence of other reactions like dissolution of aluminum and iron production in EC system apart from the conventional reaction (Chaturvedi 2013, Khandegar and Saroha 2013a,b,c, Ukiwe et al. 2014, Khaled et al. 2015). The following is the list of probable reactions:

- Hydrogen formation at the cathodes through Eqs. (6)-(8).
- The upsurge of pH because of formation of hydroxyl ions or the consumption of hydronium ions/protons [Eqs. (6) and (7)].
- 3. Reduction of metal ions on the cathodes.

Several literature reported formation of oxygen on the anode (Chen 2004, Dalvand et al. 2011, Al Aji et al. 2012, Khandegar and Saroha 2013a,b,c, Khaled et al. 2015). Generally, this may not take place under typical conditions (electrochemical potential) of EC systems as the dissolution of anodes follows Faraday's law (Mouedhen et al. 2008). It is possible that some other reactions also occur, because the dissolution of iron at the anodes is lower than the calculated value according to Faraday's law under alkaline conditions.

There is a technology called EF, which can be used to produce bubbles that can effectively separate particles from the solution Matis and Peleka (2010). In EF, oxygen bubbles are deposited on the anodes when the potential is satisfactorily high [Eq. (9)], while hydrogen bubbles on the cathodes. However, in EC technology only hydrogen bubbles are formed on the cathodes (Phalakornkule et al. 2010a,b, Al Aji et al. 2012, Vepsäläinen 2012, Khaled et al. 2015).

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 (at anode) (9)

The size of the bubbles plays an important role in the efficiency of EC and EF systems. Smaller bubbles are more favorable as these provide a higher surface area for particles. EF promotes formation of smaller diameter bubbles than the usual dissolved air flotation (DAF) technology. The suggested mean diameter of the hydrogen and oxygen bubbles produced in EF ranges from 17 to 50 µm, whereas in DAF the mean diameters of the bubbles range from 48 to 60 µm. Electrode material, current density, and pH play a vital role in determining the bubble size. The smallest hydrogen bubbles are produced at neutral or acidic pH. Stainless steel plates have been found to produce the smallest bubbles. There has been some controversy in the reported effects of current density on the bubble size (Comninellis and Chen 2010). Sarkar et al. (2010) found that a major part of hydrogen produced on the cathodes can be dissolved in the solution in which bubble size diameter depends on the rate of hydrogen production. Hydrogen production rate increases with increase in current density, bubble nucleation rate, and dissolved gas concentration field.

In comparison with chemical coagulation, EC surges the pH of the solution if acidic, neutral, or slightly alkaline and declines when it is extremely alkaline. This ultimately affects the speciation of aluminum and iron hydroxides. Building up alkalinity in highly acidic (pH 2) systems is not adequate to raise the pH of the solution, while at pH 3 and higher, pH increases during the treatment (Mouedhen et al. 2008). If the initial nature of the solution is highly alkaline (pH > 9), then pH lowers down because of the formation of aluminate [Al(OH) $_4$ -], which eats away alkalinity as shown in Eq. (8) (Kobya et al. 2006, Barrera-Díaz et al. 2012, Khaled et al. 2015). This indicates that the change in pH and final steady-state pH relies on the concentration of anions in the solution.

The concentration of reaction products is highest at the electrode surface, and the concentration gradient exists from the surface towards the bulk solution because electrochemical reactions occur at the surface of the electrodes. Therefore, pH decreases at the vicinity of the anode and vice versa at the cathode surface. This can lead to precipitation of inorganic salts on the electrode surface in a system like precipitation of calcium carbonate on the cathodes where the solubility changes with pH (Hasson et al. 2008).

Direct electrochemical reduction of metal cations occurs at the cathode surface if electrochemical potential at the cathodes is in the specific area [Eq. (10)] (Al Aji et al. 2012, Khaled et al. 2015):

$$Me^{n+}(aq) + ne^{-} \rightarrow Me^{0}(s)$$
 (10)

The reduction of metal ions directly affects contaminant removal efficiency, regardless of their reduction to metallic state. Heidmann and Calmano (2008) projected that Zn(II), Cu(II), Ni(II), and Ag(I) are eliminated from the solution by hydrolyzation and co-precipitation, however, Cr(VI) may be reduced to Cr(III), and precipitated as hydroxide. It is likely that dissolving of aluminum at the cathodes prevents plating of the cathode with other metals. Coating with metal ions like Ni(II) and Cu(II) should be preferred while using iron or inert metals.

3.3 Sludge characteristics

The properties of the produced sludge are important because sludge treatment and disposal are among the major cost factors in water and wastewater treatment, especially when sludge has been produced by chemicals. The dried EC sludge produced by different configuration of electrodes can be characterized by FTIR, XRD, XPS, SEM-EDS, and EDX (Aoudj et al. 2010, Vasudevan et al. 2011a, Vepsäläinen 2012, Pirkarami and Olya 2014).

Dried sludge formed by aluminum electrodes contained amorphous aluminum hydroxide and/or aluminum oxyhydroxide. Iron electrodes produced crystalline phases, such as magnetite, and poorly crystalline phases, such as iron oxyhydroxides and lepidocrocite. Sludge produced by combining aluminum with iron electrodes contain the aforementioned products as well as mansfeldite, diaspora, and iron oxide. The crystallinity of iron species decreased possibly due to the substitution of iron by aluminum (Vepsäläinen 2012).

Un and Aytac (2013) investigated the sludge produced after EC process with iron electrodes for textile wastewater treatment and described by X-ray diffraction (XRD) to determine the main elimination pathway in the reactor. According to the results, the only by-product of EC is maghemite. Maghemite can be produced from ferric hydroxide (Fe(OH).).

Vasudevan et al. (2011a) analyzed the sludge of an EC process with aluminum electrodes for fluoride removal using XRD and energy-dispersive X-rays (EDX). XRD spectrum of aluminum coagulant showed very broad and shallow diffraction peaks. These broad bands indicate that the coagulant is amorphous or at best very poorly crystalline in nature. The presence of fluoride, aluminum, and oxygen is apparent in the EDX spectrum thus providing direct evidence that fluoride is adsorbed on the aluminum hydroxide. Other elements detected in the aluminum hydroxide come from adsorption of the conducting electrolyte, chemicals used in the experiments, alloying, and the scrap contaminations of the anode and cathode.

Aoudj et al. (2010) used the FTIR spectrum to analyze the obtained sludge of EC with aluminum electrodes and to recognize the nature of removal of dye (Direct red 81). The results show a broad and intense band at 3452 cm⁻¹, which can be attributed to extending vibrations of OH groups. The sharp bands at 1500 and 1411 cm⁻¹ show the existence of azo group (-N=N-). The robust bands at 1114, 1049, and 617 cm⁻¹ may be attributed to S-O stretching vibrations of sulfonate group (SO₃-). The noticed dissimilarities may be because of the adsorption of dye on aluminum hydroxide flocs. However, no previous studies observed the type of reaction of EC process whether physio-adsorption or chemo-adsorption especially in dye removal.

Emamjomeh and Sivakumar (2009) studied the sludge produced during the fluoride removal by EC using XRD. The identified components are aluminum fluoride hydroxide complexes and aluminum hydroxide.

The ability of the sludge produced by EC to settle during paper mill (Zodi et al. 2011) and textile wastewater treatment has been studied (Zodi et al. 2009). When paper mill wastewater was treated, the sludge volume index was 0.207–0.310 l/g and 0.081–0.091 l/g for aluminum and iron electrodes, respectively. The sludge formed by iron electrodes was heavier and produced a more compact layer. The authors observed similar results with textile wastewaters. Hydrogen produced during the EC induces flotation of particles and decreases settling velocity. The combination of EC and electrode watering has been studied for the reduction of water content in sewage sludge (Shin and Lee 2006). The combination of EC and electrode watering reduced water content of the sludge to 55%, whereas water content in sludge treated with only pressure filtration was 78%.

3.4 Operating parameters affecting electrocoagulation treatment

Several parameters affect the efficiency of the EC in pollutant removal from wastewater. The parameters include the following: electrode materials, arrangement of electrodes, current density supply and time of treatment, effect of pH solution, conductivity of solution, effect of temperature, initial concentration of pollutant, effect of anions concentration, effect of agitation speed, interelectrode distance, and power supply type.

3.4.1 Electrode materials

Electrode material defines which electrochemical reactions take place in the EC system. Both aluminum and iron electrodes have been used successfully in EC systems. Aluminum dissolves in all cases as Al(III), whereas there is some controversy as to whether iron dissolves as Fe(II) or Fe(III) (Roopashree and Lokesh 2014, Khaled et al. 2015).

Iron dissolves as Fe(II) and is oxidized in bulk solution to Fe(III) in the presence of oxidants like oxygen (Linares-Hernández et al. 2009, Al Aji et al. 2012, Un and Avtac 2013, Roopashree and Lokesh 2014, Un and Ocal 2015). Fe(II) is a weak coagulant compared to Fe(III) because of higher solubility of hydroxides and lower positive charge (Un and Ocal 2015). For example, some poor results have been achieved with iron electrodes by Bagga et al. (2008). Ideal material selection depends on the type of contaminants and the chemical characteristics of the electrolyte. Generally, aluminum is better than iron in most cases when the effectiveness of the treatment is the only criterion (Lekhlif et al. 2014). However, aluminum is more expensive. In some cases, wastewater has a substantial quantity of calcium or magnesium ions. Hence, the inert cathode materials like metal oxide coated titanium and graphite are recommended (Chen 2004, Daghrir et al. 2012). The reports on combinations of aluminum and iron electrodes are also available in the literature.

Linares-Hernández et al. (2009) obtained high removal of color with aluminum electrodes, while the iron was more effective than aluminum in reducing chemical oxygen demand (COD) from industrial wastewater. A combination of iron and aluminum removes both color (71%) and COD (69%) with high efficiency. Similar results were obtained when paper mill wastewaters were treated with various aluminum and iron electrode combinations (Katal and Pahlavanzadeh 2011). Aluminum electrodes were most effective in removing the color of the wastewater, whereas iron electrodes removed COD and phenol from the wastewater more effectively than aluminum electrodes. A combination of aluminum and iron electrodes removed color, COD, and phenol with high efficiency. Combination electrodes have been studied for arsenic removal from groundwater (Gomes et al. 2007). The use of iron electrodes and a combination of iron and aluminum electrodes demonstrated higher efficiency in arsenic removal. Similar results were obtained for copper, chromium and nickel removal from metal plating wastewater (Heidmann and Calmano 2010, Akbal and Camci 2011).

3.4.2 Arrangement of electrodes

There are a number of methods for the arrangement of electrodes. In EC systems, normally plate electrodes are built and water passes through the space between the

electrodes (Khaled et al. 2015). Arrangement of electrodes could be monopolar or bipolar. In monopolar arrangements, the performance improvement is achieved by using EC cells with monopolar electrodes either in parallel or series combinations (Figures 5 and 6). The parallel connections entail a couple of conductive metal plates positioned between two parallel electrodes and a direct current (DC) power source. Further, each pair of 'sacrificial electrodes' is internally linked without interconnections with the outer electrodes. This prearrangement of monopolar electrodes with cells in series is electrically similar to a single cell with many electrodes and interconnections (Mollah et al. 2004, Gunukula 2011, Vepsäläinen 2012, Khandegar and Saroha 2013a,b,c, Demirci et al. 2015).

A resistance box is used in experimental setup to control the flow of current and a multimeter to record the current. Sacrificial anodes are conductive metal plates or rods deployed in EC construction. These lower the dissolution potential of the anode and lower the reduction or reductive deposition of elemental metals on the cathode. The same or different metal can be used for the making of sacrificial electrodes and the cathodes (Mollah et al. 2004). Due to the higher resistance of series connected cells, a higher potential difference is necessary for the

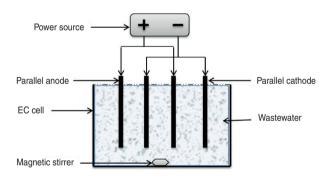


Figure 5: Schematic diagram of EC reactor with monopolar electrodes in parallel adopted from Mollah et al. (2004).

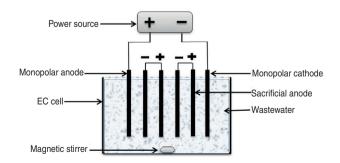


Figure 6: Schematic diagram of EC reactor with monopolar electrodes in series adopted from Mollah et al. (2004).

required current to flow. However, the same current will flow through all the electrodes. In a parallel arrangement, the electric current is distributed between all the electrodes in proportion to the resistance of the individual cells (Demirci et al. 2015, Khaled et al. 2015).

Figure 7 presents bipolar electrodes with cells in parallel showing that sacrificial electrodes are located amid the two parallel electrodes without electrical linking. Only the two monopolar electrodes are linked to the electric power source with no interconnections between the sacrificial electrodes. This pre-arrangement of the system offers flexible maintenance during use. The neutral sides of the conductive plate become the charged sides when an electric current is passed through the two electrodes, with opposite charges compared to the parallel side. Therefore, the sacrificial electrodes are called bipolar electrodes (Mollah et al. 2004, Gunukula 2011, Vepsäläinen 2012, Khandegar and Saroha 2013a,b,c, Demirci et al. 2015).

The contaminant removal efficacies and operating costs of monopolar and bipolar configurations are compared in several studies. Khaled et al. (2015) investigated the influence of electric configuration (bipolar and monopolar) using four aluminum electrodes for 60 min reaction time under the same current density for cadmium removal from industrial wastewater. For the bipolar configuration, the removal efficiency reached 92% with power consumption of 4.15 kW h/m³. However, for monopolar configuration, the removal efficiency attained 87% and the power consumption is 1.20 kW h/m³. Thus, the choice of monopolar configuration exhibited high removal efficiency negligibly lower than that of bipolar configuration and a significant reduction in power consumption. This is attributed to higher surface area exhibited by bipolar connection, which results in a more anodic oxidation compared to that of monopolar connection. Other authors studied textile wastewater removal by EC with four aluminum electrodes connected inside a reactor in three different configurations: monopolar-parallel (MP-P),

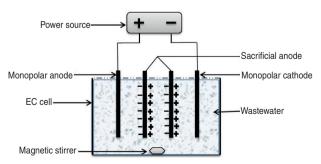


Figure 7: Schematic diagram of EC reactor with dipolar electrodes in parallel adopted from Mollah et al. (2004).

monopolar-serial (MP-S), and bipolar-parallel (BP-P). The results showed that MP-P mode is the most cost effective for both electrode connection types (Demirci et al. 2015). All connection types show similar results in reducing color and turbidity. However, Kobya investigated the treatment of potable water containing a low concentration of arsenic and compared the performances of the three electrode connection modes (MP-P, MP-S, and BP-P) as a function of wastewater pH, current density, and operating time. The results showed that MP-P mode is the most cost effective for both aluminum and iron electrodes (Kobya et al. 2011). Monopolar configuration has been reported to be better in the treatment of laundry wastewater (Wang et al. 2009a), oily bilge water (Asselin et al. 2008), and textile wastewater (Bayramoglu et al. 2007).

From the above-mentioned studies, it can be concluded that monopolar configuration has lesser operating cost, whereas larger removal of impurities can be attained with bipolar configuration, mainly because of side reactions. Moreover, no report is available on removal of pollutants by the combination of electrode configurations in a single EC reactor.

3.4.3 Current density supply and time of treatment

Current density is regarded as an important factor because it analyzes the coagulant dosage rate, bubble formation rate, size, and development of flocs, as they affect the efficiency of the EC process. The anode dissolution rate is directly proportional to the current density. However, an increase in current density beyond the optimal value has no effect on the contaminant removal efficiency (Barrera-Díaz et al. 2012, Khaled et al. 2015). On the other hand, for the aluminum and iron anodes, dissolution reaction is the primary reaction, and the proportion of other reactions is minor at typical current densities and electrode potentials when pH is neutral or acidic (Mouedhen et al. 2008, Vepsäläinen 2012, Verma et al. 2012). The dissolution rate of iron anodes may be lower than the calculated values by Faraday's law at alkaline pH. This shows the possibility of other reactions at the anode under these conditions (Sasson et al. 2009, Vepsäläinen 2012, Un and Ocal 2015).

Coagulant produced by electrolysis can usually be calculated according to Faraday's law when current and treatment times are known (Eq. 5). Coagulant concentration produced by electrolysis on anodes is typically directly proportional to the electric charge added per volume (coulombs per liter). However, the total amount of coagulant dissolved also includes chemical dissolution of the electrodes in low pH and the dissolution of aluminum

cathodes. Current density probably has some influence on the chemical dissolution of aluminum cathodes because it affects the rate of hydroxyl ion production at the cathodes (Khandegar and Saroha 2013a,b,c). Mouedhen et al. (2008) studied aluminum dissolution from the cathodes with an electrochemical cell constructed of platinized titanium anode and aluminum cathode. They used constant charge per volume (540 C/L) and various current densities. According to their results, as the current density decreases, the amount of aluminum generated increases. The produced amount of aluminum on the cathodes depends more on the treatment time than the electric charge added per volume.

The removal rate of pollutant is also a function of the electrolysis time. The pollutant removal efficiency increases with an increase in the electrolysis time. However, beyond the optimum electrolysis time, the removal rate becomes constant and does not increase with an increase in the electrolysis time. Metal hydroxides are formed by dissolution of the anode. For a fixed current density, the number of generated metal hydroxide increases with an increase in the electrolysis time. For a longer electrolysis time, there is an increase in the generation of flocs resulting in an increase in the pollutant removal efficiency (El-Ashtoukhy et al. 2013, Lekhlif et al. 2014).

3.4.4 Effect of pH solution

The pH of the solutions is perceived as an important parameter before treatment because it affects the conductivity of the solution, dissolution of the electrodes, speciation of hydroxides, and ζ -potential of colloidal species. An optimal pH of the solution is desirable for any pollutant streams for better removal efficiency of contaminants as it helps in precipitation of pollutants. Both low and high pH values from the optimal value decrease the removal efficiency (Vepsäläinen 2012).

Aluminum and iron cations and hydroxides destabilize colloids. Active coagulant species are produced in acidic, neutral, and slightly alkaline solutions. In highly alkaline pH, Al(OH), and Fe(OH), ions are produced, which have weaker coagulating efficiency. Figure 3 shows that Fe(III) is more result oriented in a wider pH range than Al(III) and works also under slight alkaline pH. The competing anions affect the optimum pH of the coagulating system. The effect of water pH on the efficiency of contaminant removal is also documented in literature in detail (Aoudj et al. 2010, Barrera-Díaz et al. 2012, Gupta and Ali 2012, Vepsäläinen 2012, Khaled et al. 2015).

Mechanistic studies are rather difficult to conduct for the EC treatment processes, as the pH tends to increase as the EC process proceeds. For example, the release rate of aluminum during electrolysis with a constant charge per volume is lower in solutions with pH <3 and higher for

above 3 (Mouedhen et al. 2008). Chemical dissolution of aluminum cathodes happens due to increase in pH to a level where formation of aluminate occurs. It is likely that acidic bulk solution hinders this reaction as the formed hydroxyl ions are utilized by acid in the solution. In acidic pH, the dissolution of iron electrodes is substantial even without electricity, whereas oxidation of Fe(II) to Fe(III) takes place only at pH above 5 (Sasson et al. 2009). The dissolution rate falls at high pH, which is comprehensible as the corrosion rate of iron declines in alkaline pH in the presence of oxygen due to the formation of an inactive layer on the surface (Vepsäläinen 2012). The maximum efficiency has been reported at the pH of 4, where the pH of the synthetic solution increased after the EC process with the passage of electrolysis time because of the formation of OH⁻ in the EC process (Verma et al. 2013).

The initial pH of the solutions plays a key role in the wastewater treatment process, either in chemical coagulation or EC (Cañizares et al. 2009a,b). However, EC is more appropriate in a wide range of pH, while chemical coagulation is preferred if pH is high. EC process of textile industrial wastewater treatment was investigated to determine the impact of initial pH (3, 5, and 9.01) using packed bed iron electrodes. Investigation shows that the efficiency of the system is found not to be pH reliant. However, it does not affect substantially the COD and color removal. COD elimination efficiency of over 90% was noticed for all pH levels studied (Un and Aytac 2013).

Water impurities have their own specific pH values for their removal, for example, phosphorus and metal cations. Literature shows some investigations indicating the effect of pH on contaminant removal from wastewater by EC (Irdemez et al. 2006a). The phosphorus removal from laundry wastewater was investigated using aluminum electrodes. The result shows poor removal rate when initial pH was lower than 6 or higher than 8 (Janpoor et al. 2011), while another study explained that the elimination effectiveness improved when the initial pH of the wastewater was augmented during the removal of Cu(II), Mn(II), and Zn(II) using aluminum electrodes (Hanay and Hasar 2011).

3.4.5 Conductivity of solution

In the electrolysis process, the contaminant elimination efficiency and working cost are direct functions of the solution conductivity. The conductivity of the solution helps the flow of the electric current through it. Salt additives, such as sodium chloride or sodium sulfate, are added to the solution before treatment for adjusting the pH. At a constant cell voltage or reduction in the cell voltage, the current density increases with increase in conductivity (Merzouk et al. 2010, Dalvand et al. 2011, El-Ashtoukhy et al. 2013), thereby decreasing the energy consumption.

3.4.6 Effect of temperature

The effect of temperature on the removal of pollutants through EC has been studied in a few articles. The effect of solution temperature on boron removal by EC is studied in the range of 293–333 K (Yilmaz et al. 2008). When temperature increased from 293 K to 333 K, the boron removal efficiency increased from 84% to 96%. The reverse is the case when paper mill wastewater was treated at temperatures between 293 and 333 K. Removal of color, COD, and phenol decreased by 10–20% when temperature increased from 293 K to 333 K (Katal and Pahlavanzadeh 2011).

When the electrode used is aluminum and temperature is too high, there is a shrinkage of large pores of the Al(OH), gel, which causes the formation of dense flocs that are more likely to be deposited on the electrode surface (Chen 2004, Vepsäläinen 2012). Temperature increase also enhances the solubility of aluminum. This shows that temperature increase has both positive and negative effects on removal efficiency. It is possible that the effect of temperature on removal efficiency depends on the pollutant's removal mechanism. A previous study showed the effect of temperature on the percentage removal of phenol using a fixed bed aluminum electrode. The percentage removal increases from 88% to 95% as the temperature increases from 25 to 45°C. Further increase in temperature has a little effect on removal efficiency (El-Ashtoukhy et al. 2013). However, another study by Khaled et al. (2015) showed the effect of initial temperature (18, 30, 50, and 70°C) for the removal of cadmium from industrial wastewater through EC process using two aluminum electrodes. They found that increase in temperature and reduction of electrolysis time significantly improved the removal efficiency without difference in cost and energy consumption. In fact, due to the increase in temperature, the mass transfer increased, and the kinetics of particle collision improved. In addition, high temperature favors formation of large hydrogen bubbles, enhanced flotation speed, and reduction in the adhesion of suspended particles. The maximum elimination of 98% was obtained at a temperature of 50°C and an electrolysis time of 30 min.

Thus, 50°C is the optimum initial EC temperature based on removal efficiency in a short treatment time without change in the cost.

3.4.7 Initial concentration of pollutant

The pollutant removal efficiency decreases with an increase in the initial concentration of the pollutant for a constant current density. This is because the amount of metal hydroxide flocs formed may be insufficient to settle the huge amount of pollutant molecules at higher initial pollutant concentrations (Dalvand et al. 2011, Khandegar and Saroha 2013a,b,c). When the initial concentration of pollutants is high, there is no significant effect of current densities on removal rate especially at the early stage of the reaction (Ajeel et al. 2015).

3.4.8 Effect of anions concentration

The concentration of anions in the solution affects the stability of the passive layer of an electrode. Sulfate anions are passivation agents and therefore reduce the production of metal cations. Chlorides, on the other hand, induce the breakdown of the passive layer and pitting corrosion (Khandegar and Saroha 2013a,b,c). Some salts can precipitate on the cathodes if the concentration of the salt in water is sufficiently high (Hasson et al. 2008).

According to a previous study, fluoride and arsenate compete with phosphate ion and reduce its removal by EC (Vasudevan et al. 2011a). The effect of supporting electrolytes on the efficiency of an EC system has been studied by treating unskimmed milk samples and a cutting oil emulsion by aluminum electrodes in the presence of NaCl, Na₂SO₄, NH₄Cl, and (NH₄)₂SO₄ (Trompette and Vergnes 2009). According to the results, sulfate anions increase electrical consumption and have a negative effect on EC efficiency. The ratio of [Cl⁻]/[SO₄-2] should be 0.1 or higher to ensure the breakdown of the passive film. Another study investigated fluoride removal in the presence of chloride, nitrate, and sulfate anions. The best results were obtained in the absence of these anions. However, sulfate ion concentration had a significant effect on the removal efficiency of the fluoride, probably because it can compete with fluoride ions from Al(III) (Vepsäläinen 2012).

Zeta potential analysis is an effective tool for measurement of the destabilization degree of particles/flocs (Gregory and Carlson 2003). It helps to understand the stability of contaminant particles in EC process for pollutant removal under different salt concentrations. The zeta

potential values of the pollutant-aluminum flocs formed in EC increased gradually with electrolysis time in the presence of various initial Cl- concentrations (Gao et al. 2010). This is attributed to the increase of released Al3+ in the presence of Cl⁻ in comparison with the absence of Cl⁻. During the EC process, more polymeric aluminum species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{34}^{7+}$, and Al₁₃(OH)₃₆ might be generated through the consecutive hydrolysis reactions with the increase of Al3+ concentration (Cañizares et al. 2007). These polynuclear cations could be adsorbed on the surface of negatively charged pollutant particles, thus increasing the zeta potential through charge neutralization. This could promote the aggregation and removal of pollutants. The influence of Cl⁻ on the zeta potential is similar to that on Al³⁺ release and the pollutant removal by the EC.

3.4.9 Effect of agitation speed

Agitation helps to maintain uniform conditions and avoids the formation of the concentration gradient in the electrolysis cell. Further, the agitation in the electrolysis cell imparts velocity for the movement of the generated ions. With an increase in agitation speed up to the optimum agitation speed, there is an increase in the pollutant removal efficiency. This is because of early floc formation attributed to increase in the mobility of the generated ions. Further, the pollutant removal efficiency at a particular electrolysis time increases. However, further increase in the agitation speed beyond the optimum value decreases the pollutant removal efficiency as the flocs degrade by collision attributed to high agitation speed (Bayar et al. 2011, Khandegar and Saroha 2013a,b,c, Lekhlif et al. 2014, Khaled et al. 2015).

3.4.10 Interelectrode distance

The inter-electrode distance plays a significant role in EC process because the electrostatic field depends on the distance between the anode and cathode. Maximum pollutant removal efficiency is obtained by maintaining an optimum distance between the electrodes. At the minimum inter-electrode distance, the pollutant removal efficiency is low. This is because the generated metal hydroxides which act as the flocs and remove the pollutant by sedimentation degrade as they collide with each other due to high electrostatic attraction (Khandegar and Saroha 2013a,b,c, Verma et al. 2013). The pollutant removal efficiency increases with an increase in the inter-electrode

distance from the minimum till the optimum distance between the electrodes. This is because further increase in the distance between the electrodes decreases the electrostatic effects resulting in a slower movement of the generated ions. It provides more time for the generated metal hydroxide to agglomerate to form the flocs resulting in an increase in the removal efficiency of the pollutant in the solution (Verma et al. 2013, Khaled et al. 2015). Further increase in the electrode distance above the optimum value reduces the pollutant removal efficiency. This is because the travel time of the ions increases with an increase in the electrodes distance. Further, there is a decrease in the electrostatic attraction, which lowers the formation of flocs needed to coagulate the pollutant (Verma et al. 2013, Singh and Ramesh 2014).

3.4.11 Power supply type

In the EC process, there is an in situ generation of metal hydroxide ions by electrolytic oxidation of the sacrificial anode. These metal hydroxide ions act as a coagulant and remove the pollutants from the solution by sedimentation. Several studies in the literature used DC for EC process. The use of DC leads to the corrosion of the anode due to oxidation. An oxidation layer also forms on the cathode, which reduces the flow of current between the cathode and the anode thereby lowering the pollutant removal efficiency (Khandegar and Saroha 2013a,b,c). However, several studies used alternating current (AC) to activate EC process. Vasudevan et al. (2011a) studied fluoride removal from water using DC and AC EC systems comparatively. The results showed similar removal efficiency with both technologies. However, the energy consumption was slightly lower with AC technology. The same authors investigated the effect of AC and DC on the removal of cadmium from water using aluminum electrodes. They obtained a removal efficiency of 97.5% and 96.2% with the energy consumption of 0.454 and 1.002 kWh/kL at a current density of 0.2 A/dm² and pH of 7 using AC and DC, respectively. The results indicate that the problem of corrosion formation at the electrodes can be reduced by the use of AC in place of DC in the EC process (Vasudevan et al. 2011b). The report of Mansour and Hasieb (2012) also corroborates the above reports for removal of Ni(II) and Co(II) from synthetic drinking water using EC with AC current.

4 Batch and continuous flow EC reactor

Wide ranges of wastewater have been treated using batch and continuous EC techniques. The use of batch reactor is mainly to study the effect of the operating parameters. By contrast, a continuous system operates under steady state conditions particularly a constant pollutant concentration and effluent flow rate. Therefore, continuous flow reactors are more suitable for industrial process studies with large effluent volumes, while the batch reactors are suited to laboratory and pilot plant studies. In some cases, the small-scale experiments of the continuous system were used to steady the materials and energy balance of largescale EC unit (Fekete et al. 2016). The continuous mode of operation is preferred due to its better control than the batch mode of operation. Figure 8 illustrates a typical batch mode of operation and schematic diagram for continuous mode of operation (Khandegar and Saroha 2013a,b,c). Batch method of EC reactors exhibits time dependence as the coagulant is persistently produced in the reactor with the anode dissolution. The anode material is hydrolyzed and is equipped for collecting the pollutants. Accordingly,

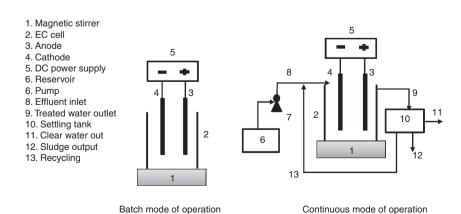


Figure 8: Schematic diagram of batch and continuous flow of EC reactor adopted from Khandegar and Saroha (2013a,b,c).

the pollutant concentration, coagulant produced, and pH continue changing with respect to time. A batch system has neither inflow nor outflow of effluent during the electrolysis time.

5 Design of the EC cell

Electrode potential describes which reactions take place on the electrode surface. The overall voltage (U/V) is dependent on equilibrium potential difference $(E_{r_k} - E_{r_a})$, anode and cathode overpotentials (η_a, η_k) , mass transfer overvoltage (η_{Mt}) , and ohmic potential drop in the solution (η_{1D}) according to the following equation (Daous and El-Shazly 2012, Shreesadh et al. 2014, Lekhlif et al. 2014, Kraljić Roković et al. 2014, Valero et al. 2015):

$$U = |E_{r,k} - E_{r,a}| + \eta_a + |\eta_k| + \eta_{Mf} + \eta_{IR}$$
 (11)

Alteration in analyte concentration occurs near the electrode surface because the electrode reaction causes concentration overpotential (η_{Mt}/V), also called as mass transfer or diffusion overpotential. This is attributable to the variation in the electroactive species concentration between the bulk solution and the electrode surface. This takes place if the electrochemical reaction is significantly fast to the inferior surface concentration of electroactive species below that of the bulk solution. The concentration overpotential is negligibly less when reaction rate constant is much smaller than the mass transfer coefficient. The increase in masses of the metal ions transported from the anode surface to the bulk of the solution reduces mass transport overpotential. This mass transportation is achievable by increasing the turbulence of the electrolyte solution using some mechanical means. Enrichment of ionic mass transport twisted from the dissolution of the anode by creating turbulence is not reported in the literature. Kinetic and concentration overpotential surge up as the current goes up. Internal resistance (IR-drop, $\eta_{\text{\tiny IP}}$) between electrodes or solution resistance can be expressed by the equation shown below (Khaoula et al. 2013, Kraljić Roković et al. 2014, Khaled et al. 2015, Valero et al. 2015):

$$\eta_{ID} = \text{Id} / \text{AK} \tag{12}$$

where d is the distance between the electrodes (cm), A is the surface area of the cathode (cm²) K is specific conductivity of the solution (μ S/cm), and I is the current (A).

To get the maximum efficiency from an EC reactor, the following factors must be considered (Mollah et al. 2004, Nasrullah et al. 2012):

The IR-drop between the electrodes must be minimized;

- The accumulation of O₂ and H₃ gas bubble nucleates at the electrode surfaces need to be minimized;
- Impairment to mass transfer through the spaces between the electrodes should be minimized.

The IR-drop depends on the following (Khaoula et al. 2013, Khaled et al. 2015):

- The conductivity of the electrolyte solution;
- The distance between the two electrodes;
- The electrode geometry.

A solution with high conductance and increased crosssectional area of electrodes can minimize the internal resistance between electrodes (Mansour and Hasieb 2012, Khaoula et al. 2013). The pollutant removal efficiency of EC system is affected by the geometry of the electrodes (Kuroda et al. 2003, Nielsen and Andersson 2009).

The produced hydrogen and oxygen bubble gathers onto the electrode surface to produce an insulating layer initiated by electrode passivation. This phenomenon is unwanted for anode dissolution and EC operation producing weak mass transfer that minimizes the removal rate of contaminants. The primary control of inertness is the galvanostatic mode of operation. The current and the potential are reliant on the system's total resistance. Any resistance from a passivation layer raises the cell potential by increasing the η_{1D} . In addition, these impermeable layers avoid the effective current transport between the anode and cathode. Because of these layers, a high electrical energy intake will result in high cost due to increase in the cell potential to achieve optimum removal efficiency (Khandegar and Saroha 2013a,b,c).

Previously, reactor design for EC process has been achieved using various model configurations. These include parallel electrodes (Chafi et al. 2011, Merzouk et al. 2011a,b, Al Aji et al. 2012, Shalaby et al. 2014), 25 pairs of circular shape electrode (Phalakornkule et al. 2010a,b), a packed bed cylindrical electrode (Un and Aytac 2013), fixed bed reaching electrode (El-Ashtoukhy et al. 2013), and hollow cylindrical electrode (Un et al. 2013). However, the design of these electrodes did not consider reduction of fouling films on the surface of the electrode without adding any chemicals (Aoudj et al. 2010, El-Ashtoukhy et al. 2013). A turbulence level in the wastewater is recommended to enhance the mass transfer between electrodes (Martínez-Delgadillo et al. 2013b) and to mitigate the accumulation of bubbles where the flow of the electrolyte surrounding the electrodes must be increased to push the bubbles out (Mollah et al. 2004). Den and Huang (2006) corroborated this by electrodes arrangement in a horizontal zigzag manner to produce a hydraulic turbulence in their experimental work for removal of silica by EC continuous flow.

6 Mass transfer measurement

The mass transfer coefficient is one of the most significant constraints for design and operation of chemical reactors. Coefficient of mass transfer mainly depends on fluid flow either under laminar or turbulent conditions. Mass transfer takes place from a range of high chemical potential to a range of low chemical potential, minimizing any difference within the system. Generally, chemical species transfer between two phases through an interface or by diffusion through one phase. The convective mass transfer is the transport process that takes place between a solid surface and a moving fluid (Xiang 2014). To measure these coefficients experimentally, electrochemical method or limiting current method was used. The technique has been widely used in evaluating solid-liquid mass transfer coefficients for a rough surface in complex flow regimes or chemical reaction systems. It is based on measurement of the maximum achievable current through an electrode for a particular electrochemical process (Burns and Jachuck 2005). The limiting current is achieved, when the potential is applied between the cathode and the anode. Hence, the electric current increases exponentially with increase in potential until it reaches a constant value. The mass transfer coefficient can be expressed in the following equation (Ponce-De-Leon et al. 2007, Abdel-Aziz et al. 2011, Sulaymon and Abbar 2012, Ibrahim et al. 2013):

$$K_{m} = i_{r} / nFAC_{h}, \qquad (13)$$

where i_L is the limiting current (A), n is electron moles (3 for Al and 2 for Fe), F is Faraday's constant (96,500 C/mol), A is the surface area of the electrode (cm²), and C_b is bulk concentration (mol/cm³).

The limiting current technique can be used for various electrochemical reactors to analyze the effect of electrode configuration on mass transfer rates (Hong et al. 2008, Su et al. 2011). The electrode materials and liquid vary from study to study. The process of cathodic copper deposition for the measurement of limiting current was chosen for the assessment of mass transfer performance at a spinning disc electro-oxidation reactor system (Burns and Jachuck 2005). A cupric acid-copper sulfate electroplating system was also adopted to examine the effects of the anode size and location on the limiting currents of natural convection mass transfer experiments in a vertical pipe (Kang and Chung 2010). Another electrolytic cell,

ferri-ferrocyanide system, and nickel electrodes, was used to obtain the mass transfer coefficients in an annular duct with an obstruction (Weyns et al. 2009). Additionally, Abdel-Aziz et al. (2011) studied the mass transfer rate at a horizontal cylinder placed in a cylindrical vertical column under different hydrodynamic conditions by measuring the limiting current of the cathodic reduction of $K_3Fe(CN)_6$ using a solution containing $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ and excess NaOH as supporting electrolyte.

The accuracy of measuring the mass transfer coefficient is better than that obtained using other techniques such as dissolution method that depends on removal efficiency of pollutants to find the mass transfer coefficient (Xiang 2014). However, mass transfer coefficient was not previously adopted by limiting current method during the EC process. The most important advantages of limiting current methods include controllability of the driving forces and *in situ* current monitoring (Cañizares et al. 2006). Furthermore, the degradation of the electrolyte can lead to variation in local mass transfer coefficients (Xiang 2014).

In EC treatment, the particle diffusivity (D, cm²/s) inside the reactor can be calculated using Stoke-Einstein equation [Eq. (14)] after measuring the particle size of the ionic aluminum or iron as follows (Geankoplis 2003, Den and Huang 2006):

$$D = K_{R} \cdot T / 3\pi \cdot \mu \cdot d_{o}, \qquad (14)$$

where K_B is the Boltzmann constant (1.388×10⁻¹⁶ g·cm²/ s·k), T refers to temperature (298 K), μ is the viscosity of the solution (g/cm·s), and d_o is the particle (ionic aluminum or iron) size (cm).

Dimensional analysis technique can be used to study mass transfer phenomenon of EC process when using rotating electrodes. The application of this analysis to the description of mass transfer yields three nondimensional groups, namely, the Reynolds (Re), Sherwood (Sh), and Schmidt numbers (Sc), respectively (Sulaymon and Abbar 2012, Fouad et al. 2013):

$$Sh=K_{m}d/D,$$
 (15)

$$Re = \rho Nd^2 / \mu, \tag{16}$$

$$Sc = \mu / \rho D, \tag{17}$$

where d, D, N, ρ , and μ represent effective diameter (cm), diffusion coefficient (cm²/s), rotational speed (rps), fluid density (g/cm³), and fluid viscosity (g/cm·s), respectively. However, no previous studies use rotating electrodes in the EC process.

Accordingly, mass transfer data are correlated experimentally using the following dimensionless relationship, which is considered valid for a great variety of electrolytic reactor designs (Rajeshwar and Ibanez 1997, Tamas et al. 2007, Almazán-Ruiz et al. 2012, Fouad et al. 2013):

$$Sh = bRe^aSc^{0.33},$$
 (18)

where b is a mass transfer correlation constant and a is the exponent of Reynolds number. The values of these parameters can be obtained experimentally, or from differential equations.

A number of correlations have been observed for various configurations of electrochemical systems (Rajeshwar and Ibanez 1997, Abdel-Aziz et al. 2011, Fouad et al. 2013, Xiang 2014):

Spinning disk electrode:

$$Sh = 0.62 \text{ Re}^{0.5} \text{ Sc}^{0.33} \text{ (laminar flow)}$$
 (19)

$$Sh = 0.01 \text{ Re}^{0.87} \text{ Sc}^{0.33} \text{ (turbulent flow)}$$
 (20)

Parallel plates:

$$Sh = 0.023 \text{ Re}^{0.45} \text{ Sc}^{0.33} \text{ (turbulent flow)}$$
 (22)

Packed bed:
$$Sh = 0.32 Re^{0.66} Sc^{0.33}$$

(for $100 < Re < 10,000$) (23)

Rotating cylinder:
$$Sh = 0.079 \text{ Re}^{0.7} \text{ Sc}^{0.33}$$
 (turbulent flow) (24)

Such mass transfer correlations are useful for reactor design optimization, as well as for analysis of chemical kinetics. The development of these mass transfer correlations is crucial to understanding mass transfer processes.

7 Computational fluid dynamics modelling

Computational fluid dynamics (CFD) has become an essential means for engineering problems. CFD simulations provide insight into the details of how processes work and allow the evaluation and optimization of the simulated system by a computational solution, even before prototypes have been built. The features of simulation, such as low cost, short lead times, and satisfactory accuracy, enable CFD to be a convenient and useful method to study many engineering processes (Andersson et al. 2011). In the fluid flow (hydrodynamics) equipment design, CFD gives better understanding and information for design. The flow analyses comprises turbulence, chemical reactions, and/or heat and mass transfer, which limit and reduce design accuracy due to the three-dimensional nature of the problems. However, CFD handles all three parameters appropriately; being a powerful technique, it helps to overcome many of the limitations influencing traditional analysis. Flow field variables like velocities, temperatures, or a mass concentration are considered in CFD. CFD codes contain three main elements: (i) a pre-processor, (ii) a solver, and (iii) a post-processor (Thilakavathi et al. 2012).

Prior to simulation of mass transfer processes in chemical engineering, investigation of the flow pattern is required. The fluid is described as a continuum, and the leading equations of fluid dynamics, the mass, momentum, and energy equations provide the cornerstone for CFD. These equations have significant commonalities so that a general variable Ø can be used to describe the traditional form fluid flow equations, including scalar quantities such as temperature and concentration. This common governing equation is written in the following form (Xiang 2014):

$$\frac{\partial(\rho\varnothing)}{\partial t} + \nabla \cdot (\rho \cup \varnothing) + \nabla \cdot (D_{\varnothing} \nabla \varnothing) + S_{\varnothing} \tag{25}$$

where the variable Ø can be velocity along x, y, and z direction, U is temperature or mass fraction, ρ is the density of fluid, D_{α} is the diffusion coefficient, and S_{α} is the source

For the electrochemical systems, the governing equation [Eq. (25)] is simplified by the mass continuity equation and Navier-Stokes equation (Versteeg and Malalasekera 2007), which are expressed as

$$\nabla \cdot \cup = 0 \tag{26}$$

$$\frac{\partial \cup}{\partial t} + \nabla \cdot (\cup \cup) - \nabla \cdot \nu \nabla \cup = -\nabla \frac{p}{\rho}$$
 (27)

where \cup is the velocity, ν is the kinematic viscosity, ρ is the density, and ρ is the pressure. For the case of mass transfer into the fluid bulk, the dimensionless concentration of species in solution, α , was modeled using a scalar transport equation with turbulent diffusivity contributions:

$$\frac{\partial \alpha}{\partial t} + \nabla \cdot (\cup \alpha) - \nabla \cdot D_{\text{turb}} \nabla \alpha = 0$$
 (28)

where D_{turb} is the diffusion coefficient of species in turbulent liquid phase, consisting of the binary diffusivity, D_{AB} , and an enhancement factor dependent on the turbulent

eddy viscosity, v_{turb} , and a turbulent Schmidt number, Sc_{trub} :

$$D_{\text{turb}} = D_{AB} + (u_{\text{turb}} / Sc_{\text{trub}}) \tag{29}$$

Turbulent flow is the most common condition simulated in CFD, which forms eddies in extensive choices of length and time scales. The eddies interact in a dynamically complex way (Martínez-Delgadillo et al. 2013b, Xiang 2014). Several literatures investigated the use of CFD-based modeling to simulate electrochemical reactor. Thilakavathi et al. (2012) used RuO₂/Ti and stainless steel sheet of 6.5×5 cm² as anode and cathode, respectively, in an electrochemical model with CFD simulations by means of a commercial code FLUENT 6.3. They aimed to have a better understanding of the flow performance in continuous stirred electrochemical reactor. The authors found a good agreement between experimental and modeling results.

Electrodes are important for process and design as they affect the inner flow of the reactor, ultimately influencing the performance. Numerous researchers reported the influence of the hydrodynamic limitations on the performance of reactor such as turbulence intensity, velocity and vorticity distribution map for the fluid (Vegini et al. 2008, Martínez-Delgadillo et al. 2010a,b, 2013a, Santos et al. 2010, Frías-Ferrer et al. 2011, Su et al. 2011).

Enciso et al. (2012) used CFD modeling to describe the fluid flow in three-dimensional electrochemical rotating cylinder reactor and to show the influence of the counterelectrode geometry. Authors explored four design configurations, wherein both size and number of counterelectrodes were varied. They observed that electrode arrangement and counterelectrodes affect the streamlines of the flow. This generates high-velocity zones within the reactor, mainly at the surface of the electrode and at the bottom of the reactor. However, further research, using state-of-the-art CFD tools to examine the electrochemical reactor with rotating ring electrodes for removal of hexavalent chromium (Cr(VI)) from industrial wastewaters are needed. The results showed that the flow velocity field and turbulence intensity were not homogeneous in the reactor (Martínez-Delgadillo et al. 2013b). Moreover, no previous studies used CFD simulation to present the mass transfer inside the electrochemical reactor special in EC process as in a "black box" where the coagulants are produced from dissolution of anode.

The standard $K-\varepsilon$ model is suitable for predicting flows with low curvature, whereas when the curvature increases, the RNG K- ε model is more precise for capturing the turbulence fluctuation of swirl flows (Delgadillo and Rajamani 2005, Enciso et al. 2012). Rivero et al. (2010) applied the RANS software approach in three dimensions to model the hydrodynamic behavior of a rotating cylinder electrode. The simulated results were validated by modelling the kinetics of copper retrieval, presenting an adequate promise with the experimental results.

8 Applications of EC

EC application can be categorized as follows:

- Elimination of contaminants from a different type of wastewaters, which is summarized in Table 1.
- Removal of dyes and textile industry effluent, which are shown in Table 2.

9 Comparison EC with conventional coagulation treatment

There is not much comparison provided in open domain literature for conventional coagulation and EC. Table 3 provides a detailed comparison of the technologies based on their efficiencies.

10 Combinations of EC with other treatment technologies

Besides the sludge separation technologies, filtration, flotation, and sedimentation, other water treatment technologies have also been combined with EC. The combination of various techniques for the treatment of effluent leads to a higher removal efficiency as compared to a single treatment method. EC in combination with other treatment methods is a safe and effective way for removal of pollutants. Some studies on the combination of EC with other treatment techniques have been reported in the literature and are summarized in Table 4. However, no previous study dealswith the combination of EC process with other electrochemical technologies such as EO for the treatment of textile wastewater to reduce the sludge toxicity.

The EO process is an electrochemical mechanism that is commonly used to treat effluents that contain refractory organic compounds such as textile effluents (Wang et al. 2004), landfill leachates (Deng and Englehardt 2007), olive oil wastewater, sewage sludge (Morao et al. 2004), and tannery effluent (Panizza and Cerisola 2004). The

 Table 1:
 EC process used for treatment of different types of wastewater under optimal conditions.

Type of wastewater	Current density or current	Time (min)	Н	Anode-cathode	COD removal (%)	Reference
Dairy industry	62 A/m ²	25	5.00	Al-Al	25	Valente et al. (2015)
Textile industry	10.4 mA/cm^2	120	9.00	Al-Al, Fe-Fe	69,64	Demirci et al. (2015)
Olive mill	10 mA/cm^2	09	4.80	Fe-Fe	80	Kraljić Roković et al. (2014)
Dairy industry	50 mA/cm^2	300	5.10	Al-Al	06	Shivayogimath and Naik (2014)
Hospital effluent	60 mA/cm ²	09	3.00	Fe-Fe	87	Dehghani et al. (2014)
Textile industry	80 mA/cm^2	80	4.65	Al-Al, Fe-Fe, SS-SS	90, 85, 82	Roopashree and Lokesh (2014)
Oil refinery	8.59 mA/cm ²	180	7.00	Al-Al	80	El-Ashtoukhy et al. (2013)
Sugar industry	50 mA/cm ²	300	00.9	Fe-Fe	06	Shivayogimath and Jahagirdar (2013)
Hospital operation theater	12.2 mA/cm^2	75	6.75	Fe-Fe, Fe-Al	93,90	Mahajan et al. (2013)
Transport container washing	$100 \mathrm{A/m^2}$	09	6.90	Al-Al, Fe-Fe	76,79	Kara (2013)
Textile industry	20 mA/cm^2	90	9.01	Fe-Fe	96	Un and Aytac (2013)
Textile industry	0.3 A	09	7.00	Fe-SS	82	Wei et al. (2012)
Surfactant-aided soil-remediation processes	7.5 mA/cm ²	90	8.25	Al-Al, Fe-Fe	90,88	Lopez-Vizcaino et al. (2012)
Marble processing	20 A/m^2	20	7.80	Fe-Al	92	Ozyonar and Karagozoglu (2012)
Lack water	$13.33 \mathrm{mA/cm^2}$	120	8.10	Al-Al	92	Ahmed et al. (2012)
Distillery spent wash	0.817 A/cm ²	120	3.00	Al-Al, Al-Fe	81,71	Khandegar and Saroha (2012)
Paint manufacturing	35 A/m^2	35	6.90	Fe-Fe, Al-Al	90,92	Akyol (2012)
Baker's yeast	80 A/m^2	30	4.50	Al-Al	48	Gengec et al. (2012)
Landfill leachate	30 mA/cm^2	180	6.54	Fe-Fe	99	Orescanin et al. (2012)
Olive mill	1 A	45	4.30	Al-Al, Fe-Fe	53, 51	Coskun et al. (2012)
Domestic effluent	0.25 A	20	6.70	Fe-Fe	92	Sarala (2012)
Poultry slaughterhouse	1 mA/cm^2	30	8.20	Al-Al	80	Bayar et al. (2011)
Town landfill leachate	500 A/m^2	30	8.20	Al-Al, Fe-Fe	70,68	Bouhezila et al. (2011)
Paper mill	70 mA/cm^2	30	7.00	Fe-Fe	88	Katal and Pahlavanzadeh (2011)
Landfill leachate	4.96 mA/cm ²	90	6.70	Fe-Fe, Al-Al	49, 32	Li et al. (2011)
Tannic acid	10 mA/cm^2	120	9.00	Fe-Fe	06	Mansouri et al. (2011)
Landfill leachate	$15.90 \mathrm{mA/cm^2}$	30	7.00	Al-Al	45	Top et al. (2011)
Raw wastewater	24.70 mA/cm^2	30	8.40	Fe-Fe	77	Saleem et al. (2011)
Pulp and paper	15 mA/cm^2	30	7.00	Al-Al	06	Sridhar et al. (2011)
Dairy	15 mA/cm^2	30	7.00	Fe-Al	79	Yavuz et al. (2011)
Laundry	0.2 A	90	9.00	Al-Al	92	Janpoor et al. (2011)
Chemical mechanical polishing	6.8 mA/cm ²	20	00.9	Fe-Fe, Al-Al	86,88	Chou et al. (2010)
Olive mill	250 A/m^2	25	4.20	Al-Al	80	Hanafi et al. (2010)
Distillery spent wash	0.03 A/cm ²	120	3.00	Al-Al	72	Krishna et al. (2010)
Biodiese	50 mA/cm^2	25	90.9	Al-Graphite	55	Chavalparit and Ongwandee (2009)
Petroleum refinery	13 mA/cm^2	09	9.50	Al-Al, SS-Al, SS-Fe	45, 43, 23	El-Naas et al. (2009)
Bio-digester	44.65 mA/cm ²	120	2.80	Fe-Fe	20	Kumar et al. (2009)
Mixed wastewater	45.45 mA/cm ²	09	8.00	Al-Fe	69	Linares-Hernández et al. (2009)
Vegetable oil refinery	35 mA/cm ²	90	7.00	Al-Al	06	Un et al. (2009)

Table 1 (continued)

(2008) (2008) Zaied and Bellakhal (2009) 3arrera-Díaz et al. (2006) Sayramoglu et al. (2004) (irzhner et al. (2008) Orouiche et al. (2007) (2006) Zaroual et al. Thakur et al. (2009) Asselin et al. (2008) Murthy et al. (2007) Jğurlu et al. (2008) eng et al. (2007) (urt et al. (2008) 78 60 52 50,72 90, 85 90 71, 69 75, 55 COD removal 75 88 90 84 Anode-cathode Al-Al, Fe-Fe Al-Al, Fe-Fe e-Fe, Al-Al Al-Al, Fe-Fe 6.75 7.00 7.00 7.00 7.60 7.60 7.40 6.80 6.00 7.00 7.00 7.00 7.00 7.00 표 **Current density** 18.20 A/m² 70 mA/cm² 20 ma/cm 125 A/m² or current ma/cm² 0.12 A 1.5 A Chemical mechanical polishing **Slack liquor-paper industry** Distillery spent wash Type of wastewater Food processing Dairy wastewater **Fextile industry** Textile industry Oily bilge water 3aker's yeast Restaurant Paper mill Domestic **Fannery** Winery

interest in using EO is based on its capability of reacting on the pollutants by using both direct and indirect effects of electrical current.

In direct oxidation, the pollutants are adsorbed by the anode and removed through the transfer of the electron. Direct oxidation may be achieved through mineralization with hydroxide radical (OH') produced by dimensionally stabilized anodes (DSA) with high oxygen overvoltages, such as SnO₂, PbO₂, and IrO₂. In fact, OH' radicals are exclusively generated on the anode electrodes from the oxidation of water, and organic compounds can be completely transformed or degraded by reaction with adsorbed OH' radicals (Zaviska et al. 2012).

Indirect oxidation can be achieved through electrochemical generation of a mediator in solution (such as HClO, H₂O₂, Cl₂, HBrO, H₂S₂O₈, Fenton reagent, O₃, and others) to convert toxic organics to a less harmful product by using graphite or noble metal anodes. This technique has widely proved to be a clean, flexible and powerful tool for development of new methods for waste and water treatment (Stergiopoulos et al. 2014, Da Silva et al. 2015).

A number of experimental studies demonstrated that the metallic oxide anodes (Ti/IrO₂, Ti/SnO₂, and Ti/PbO₂) could be successfully utilized for pollutant removal (Zhou et al. 2005, Wang et al. 2006). The hydroxyl radicals (OH') and Cl⁻ produce HClO, which is characterized among the powerful oxidants to remove the pollutants. It is formulated in the following equations (Wang et al. 2009b, Zaviska et al. 2012):

$$MO_x + H_2O \rightarrow MO_x(OH^*) + H^+ + e^-$$
 (30)

$$Cl^{-} + OH^{\bullet} + H^{+} \rightarrow HClO + H_{2}O$$
 (31)

where MO_x represents metal oxide electrodes. The formation of HClO occurs as an effect of Cl₂ hydroxylation based on the equations below (Zaviska et al. 2009):

$$2Cl^{-} \rightarrow Cl_{2} + 2e^{-} \tag{32}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^-$$
 (33)

11 Economical side

Cost analysis plays an important role in industrial wastewater treatment technique. The costs involved in EC process include the cost of energy consumption, cost of dissolved electrode, and cost of external chemical (for increasing the solution conductivity or varying the pH of the solution). The operating cost using EC process is

Table 2: EC process used for removal of various type of dyes.

DVe	Callello		Anode-	Kemoval	Kererence
	current density	(min)	cathode	efficiency (%)	
Reactive Red 120	75 A/m²	09	Fe-Fe	95	Pirkarami and Olya (2014)
CI Reactive Blue 25	2.5 mA/cm ²	06	AI-AI	26	Singh and Ramesh (2014)
Reactive Orange 16	20 mA/cm ²	30	Fe-Fe	95	Alizadeh et al. (2014)
Brilliant Green	139A/m^2	30	Fe-Fe	93	Nandi and Patel (2013)
Acid Yellow 23	120 A/m^2	09	Fe-Fe	93	Modirshahla et al. (2013)
Acid Red 73	80 A/cm^2	90	Al-Al	95	Mahmoodi and Dalvand (2013)
CI Direct Blue 1 CI Fast Red B base CI Green G	1 A	20	Al-Al	88, 90, 92	Lambert et al. (2011)
Reactive Blue 19	30 mA/cm ²	06	Fe-Fe	86	Khoomsab and Khummongkol (2013)
Reactive orange 84	130 A/m^2	06	SS-SS, Fe-Fe	92, 76	Yuksel et al. (2013)
Acid red 131, Reactive yellow 86, Indanthrene	0.0625A/m^2	09	Al-Al	26	Khandegar and Saroha (2013a)
blue KS, Basic GK 4, Reactive yellow 145		,		(-
Reactive black B, Orange 3K, Yellow GK	0.0625 A/m²	09	Al-Al	88	Knandegar and Sarona (2013b)
Azo, Anthraquinone, Xanthene	0.3 A	06	Fe-Fe, Fe-SS	86	Wei et al. (2012)
Acid black 52, Acid yellow 220	40 A/m^2	06	Al-Al	92, 94	Pajootan et al. (2012)
Levafix brilliant blue E-B	100 A/m^2	120	Al-Al, Fe-Fe	95, 83	Akbal and Kuleyin (2011)
Acid, Reactive	4 mA/cm ²	120	Fe-Carbon	95	Körbahti et al. (2011)
Dispersered	$20.8 \mathrm{mA/cm^2}$	06	Al-Al	95	Merzouk et al. (2011a)
Acid brown 14	6.329A/m^2	09	AI-SS	Bench scale: 91	Parsa et al. (2011)
				Pilot scale: 80	
Reactive black 5	7.5 mA/cm^2	09	Fe-SS	06	Patel et al. (2011)
Indigo carmine	54.45 mA/cm²	120	SS-SS	66	Secula et al. (2011)
Direct red 81	$1.875 \mathrm{mA/cm^2}$	09	Al-Al	86	Aoudj et al. (2010)
Crystal violet	28 A/m^2	06	Fe-Al, Al-Fe	96,98	Durango-Usuga et al. (2010)
Remazol red 3B	15 mA/cm^2	90	Fe-Fe	26	Kobya et al. (2010)
Reactive blue 140, Direct red 1	40 A/m^2	120	Fe-Fe, Al-Al	> 95	Phalakornkule et al. (2010a)
Orange II	160 A/m^2	06	Al-Al	94	Mollah et al. (2010)
Reactive black 5	4.575 mA/cm ²	09	Al-Al	95	Şengil and Özacar (2009)
Direct red 23	30 A/m^2	80	Fe-Fe, Al-Al	> 94	Phalakornkule et al. (2009)
Acid Red 14	102 A/m^2	09	Fe-SS	> 91	Aleboyeh et al. (2008)
Levafix blue CA	$35.5 \mathrm{mA/cm^2}$	06	Fe-Fe	96	Körbahti and Tanyolaç (2008)
Acid yellow 23	112.5A/m^2	09	AI-SS	86	Daneshvar et al. (2007)
Basic red 46, Basic blue 3	80 A/m^2	120	Fe-SS	86	Daneshvar et al. (2006)
Acid yellow 36	127.8 A/m^2	90	Fe-Fe	83	Kashefialasl et al. (2006)
Reactive blue 19, Acid red 266, Disperse	1.6 A	120	Al-Graphite,	95	Yang and McGarrahan (2005)
yellow 218			Fe-Graphite		
Methylene blue, Eosin yellowish	16.1 mA/cm^2	06	SS-SS	95, 75	Golder et al. (2005)
Acid red 14	80 A/m^2	120	Fe-SS	93	Daneshvar et al. (2004)
Remazol red RB 133	15 mA/cm ²	09	Al-Al	92	Can et al. (2003)

Table 3: Comparison of EC with conventional coagulation.

Effluent	Removal parameter	Results (%)	Reference
Landfill leachate	COD, BOD, Turbidity	EC: COD (90), BOD (87), Turbidity (96)	Brkanac et al.
		Coagulation (CaO + FeCl ₃ ·6H ₂ O): COD (80), BOD (70), Turbidity (92)	(2014)
Electroplating	Cr(III), Cr(VI)	EC: 100 for both Cr(III) and Cr(VI)	Verma et al.
		Coagulation (Ferric chloride): Cr(III) (52.6), Cr(VI) (25.8)	(2013)
Textile	Color	EC: 97	Khandegar and
		Coagulation (Alum): 90	Saroha (2013a)
Textile	Color	EC: 98	Khandegar and
		Coagulation (Alum): < 50	Saroha (2013b)
Synthetic kaolin	_	EC flocs are more porous as compared toflocs formed by alum	Harif et al.
solution		coagulation	(2012)
Landscape	Algae	EC: 80	Wang et al.
	(Chlorophyll-a)	Coagulation (Aluminum sulfate): 74	(2012)
		Coagulation (Polyaluminum chloride): 71	
Synthetic dye	Orange II dye	EC: 93	Chafi et al.
solution		Coagulation (Aluminum sulfate): 53	(2011)
Synthetic	Reactive red dye	EC: 95	Merzouk et al.
wastewater		Coagulation (Aluminium sulphate): 91	(2011a)
		Coagulation (Ferric chloride: 85	
Metal plating	Cu, Cr, Ni	EC: 98	Akbal and
		Coagulation (Aluminum sulfate and ferric chloride): 90	Camcı (2010)
Aqueous suspension	Turbidity	EC: 92	Kıliç and
of kaolinite		Coagulation (Aluminum sulfate): 85	Hoşten (2010)
Synthetic	COD, Turbidity	EC: COD (82), Turbidity (90)	Cañizares et al.
wastewater		Coagulation (Alum): COD (72), Turbidity (90)	(2009b)
		Coagulation (aluminum polychloride): COD (70), Turbidity (83)	
Aqueous solution	Cr(VI)	EC: 53.5	Golder et al.
		Coagulation (Aluminum sulfate): 14.9	(2007)
		Coagulation (Alum): 13.8	

obtained from the following equations (Dalvand et al. 2011, Ghosh et al. 2011). Electrode consumption ($C_{electrode}$, kg/m³: kg of electrode dissolved/m³ of effluent):

$$C_{\text{electrode}} = I \times RT \times M / n \times F \times V \tag{34}$$

Electrical energy consumption (C_{energy}, kW h/m³):

$$C_{\text{energy}} = U \times I \times RT / V \tag{35}$$

Chemical consumption (C_{chemicals}, kg of chemical/m³):

$$C_{chemicals} = Chemicals used / m^3 of effluent$$
 (36)

Operating cost (cost/m³) =
$$aC_{electrode} + bC_{energy} + cC_{chemicals}$$

(37)

where I = electrical current (A), U = voltage (V), RT = reaction time of treatment (s), M = molecular mass of Al (26.98 g/Mol) and Fe (55.84 g/Mol), Z = amount of electron moles (3 for Al, 2 for Fe), F = Faraday's constant (96,500 c/Mol), V = volume of wastewater (L), a = cost of aluminum or iron (US\$/kg), b=electricity costs (US\$/kWh), and c=cost of chemicals which can be added (US\$/kg).

The operational cost at optimum conditions of EC process for dye removal was investigated. Electrode consumption, energy consumption, and operating cost were 0.052 kg/m³, 1.303 kW h/m³, and 1.856 US\$/m³, respectively (Dalvand et al. 2011), while the economic analysis for EC treatment of pulp and paper industry effluents was carried out, and the operating costs varied from 1.62 US\$/m³ to 1.92 US\$/m³ (Sridhar et al. 2011). Kobya et al. (2011) employed EC process for removal of cadmium and nickel from electroplating rinse water. The removal efficiencies were 90% for cadmium, 93% for nickel, and 95% for cyanide. The treatment cost was 1.85 US\$/m³ for cadmium and 2.45 US\$/m3 for nickel and cyanide at optimum conditions. The same authors investigated Remazol Red 3B decolorization using iron electrodes and found that 95% decolorization was possible under optimum conditions. The energy consumption was 3.3 kWh/kg dye at a cost of 1.6 Euro/m³ (Kobya et al. 2010). EC with mild steel electrodes was used for treating agroindustry (meat processing, cereal, and food beverages) wastewater. About 82% COD removal was achieved with treatment costs of about 4.93 US\$/m³. The cost includes

 Table 4:
 EC process combined with other methods.

TFS (37), TVS (95), Cr (92) 7), Fe (98.56)	Torres-Sánchez et al. (2014) García-Morales et al. (2013) Daous and El-Shazly (2012) Secula et al. (2012) Asaithambi et al. (2012) Módenes et al. (2012) Sbizzaro Filho et al. (2012) Bellebia et al. (2012) Orescanin et al. (2011) Mahvi et al. (2011) Yahiaoui et al. (2011) Yahiaoui et al. (2011) Yahao et al. (2011) Chang et al. (2011)
70), TFS (37), TVS (95), Cr (92)), 10.17), Fe (98.56) 5 (85.5),	Daous and El-Shazly (2012) Secula et al. (2012) Asaithambi et al. (2012) Módenes et al. (2012) Sbizzaro Filho et al. (2012) Bellebia et al. (2012) Orescanin et al. (2012) Deshpande et al. (2011) Mahvi et al. (2011) Yahiaoui et al. (2011) Yahao et al. (2011) Yavuz et al. (2011)
), no.17), Fe (98.56)	Sbizzaro Filho et al. (2012) Bellebia et al. (2012) Orescanin et al. (2012) Deshpande et al. (2011) Baudequin et al. (2011) Mahvi et al. (2011) Yahiaoui et al. (2011) Yahao et al. (2011) Chang et al. (2011)
), 10.17), Fe (98.56) S (85.5),	Orescanin et al. (2012) Deshpande et al. (2011) Baudequin et al. (2011) Mahvi et al. (2011) Yahiaoui et al. (2011) Zhao et al. (2011) Yavuz et al. (2011) Chang et al. (2010)
5 (85.5),	Deshpande et al. (2011) Baudequin et al. (2011) Mahvi et al. (2011) Yahiaoui et al. (2011) Zhao et al. (2011) Yavuz et al. (2011) Chang et al. (2010)
SS (85.5),	Mahvi et al. (2011) Yahiaoui et al. (2011) Zhao et al. (2011) Yavuz et al. (2011) Chang et al. (2010)
	Zhao et al. (2011) Yavuz et al. (2011) Chang et al. (2010)
	Chang et al. (2010)
	Merzouk et al. (2010)
Mixed industrial COD (91), lurbidity (98), color (97) Textile COD (70), Turbidity (90) Synthetic milk powder solution COD (75.5), SS (30.6)	Rodriguez et al. (2010) Zodi et al. (2010) Nouri et al. (2010)
COD (85) COD (80), BOD (70) Color (> 92)	Hernández-Ortega et al. (2010) Vilhunen et al. (2010) Aouni et al. (2009)
OD (83), SS (86.5) Irbidity (91)	Merzouk et al. (2009) Boroski et al. (2009)
	Narayanan and Ganesan (2009) Wang et al. (2009a) Un et al. (2009) Raiu et al. (2008)
	Barrera-Díaz et al. (2008) He et al. (2007)
	Linares-nemandez et al. (2007) Can et al. (2006) Parga et al. (2005) Shen et al. (2003) liang et al. (2002)
Cr(VI) (92) COD (62) COD (96) COD (93) COD (85), BOD (84), BOD (COD (84), BOD (COD (70), TSS (COD (70), TSS (COD (70), TSS (60)) F- (86) Dissolved organ	Cr(VI) (92) COD (62) COD (96) COD (93) COD (85), BOD (75) COD (84), BOD (75) COD (84), BOD (78), Color (95), Turbidity (96), Coli form (90) COD (70), TSS (80) CT (95), As (90) F- (86) Dissolved organic carbon (67), Color (89)

electrical power, chemical, and electrode consumption (Drogui et al. 2009).

Espinoza-Quiñones et al. (2009) investigated the removal of organic and inorganic pollutants from lather finishing industry wastewater by using EC. Authors found that EC is cheaper than that of the conventional method. In comparison with EC method, the cost of the conventional method is almost twice that of EC. Another study found that the operating cost of chemical coagulation is 3.2 times higher than that of EC for the treatment of textile wastewater (Bayramoglu et al. 2007).

Under the lab scale, the oil bilge wastewater using iron and aluminum electrodes with bipolar and monopolar configuration were investigated. At optimal condition, the cost was estimated as 1.96 US\$/m³, which accounts for energy and electrode intake, chemicals, and discarding of sludge (Asselin et al. 2008). Using EC process, aluminum electrodes for removal of iron [Fe(II)] from tapwater with a concentration of 15 mg/l Fe(II) would cost around 6.05 US\$/m³ of tap water (Ghosh et al. 2008).

12 Conclusions

The selection of an effluent treatment method is administered by several parameters such as pollutants type and concentration and wastewater volume and toxicity. EC technique has been applied for effective removal of a wide range of pollutants from wastewaters. EC shows a better performance compared to the traditional treatment methods. EC is a simple technique, which consumes less reaction time at adequate cost. It is characterized by low sludge production and high settleability. However, to improve the performance of EC process, the following studies are necessary:

- The effect of shape and geometry of the electrodes, which could enhance the conductivity of the cell and minimize energy consumptions.
- The suggested EC process with rotating electrodes, which could reduce the passivation film, enhance homogeneity of electrolyte, and increase the rate of flocs formation. This is necessary because the former design of EC process reactor could not reduce fouling films from the surface of the electrode (passivation phenomenon) without the use of chemical.
- Combination of EC process with other electrochemical technologies such as EO for the treatment of textile wastewater.
- The use of CFD simulation to evaluate the mass transfer inside the EC reactor. This is necessary towards limiting current method during the EC process.

- The mechanism of EC process reaction such as physioadsorption or chemo-adsorption particularly for dye
- The effect of temperature on the removal of pollutants through EC process.

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