Electrocoagulation applications for industrial wastewaters: a critical review

I. Kabdaşlı , I. Arslan-Alaton , T. Ölmez-Hancı & O. Tünay

Taylor & Francis
Taylor & Francis Group

Electrocoagulation applications for industrial wastewaters: a critical review

I. Kabdaşlı*, I. Arslan-Alaton, T. Ölmez-Hancı and O. Tünay

Istanbul Technical University, Faculty of Civil Engineering, Department of Environmental Engineering, Istanbul, Turkey

Cost-effective methods are required to treat a wide range of wastewater pollutants in a diverse range of conditions. As compared with traditional treatment methods, electrocoagulation provides a relatively compact and robust treatment alternative in which sacrificial metal anodes initiate electrochemical reactions that provide active metal cations for coagulation and flocculation. The inherent advantage of electrocoagulation is that no coagulants have to be added to the wastewater and hence the salinity of the water does not increase after treatment. Electrocoagulation is a complex process involving a multitude of pollutant removal mechanisms operating synergistically. Although numerous publications have appeared in the recent past, the lack of a holistic and systematic approach has resulted in the design of several treatment units without considering the complexity of the system and process control mechanisms. Due to the fact that electrocoagulation is thought to be an enigmatic, promising treatment technology and a cost-effective solution for sustainable water management in the future, it will become increasingly important to provide a deeper insight into the pollutant removal mechanisms involved, kinetic modelling and reactor design. Considering the abovementioned facts, in this paper, industrial wastewater electrocoagulation applications have been reviewed with special emphasis placed on the major reaction mechanisms involved in these applications. Evaluation was based on specific pollutant parameters of the sector as well as operation costs including solid waste management, sacrificial electrode materials and electrical energy requirements.

Keywords: electrocoagulation; industrial wastewater; removal mechanisms; design and process parameters; operation costs

1. General principles of the electrocoagulation process

1.1. Historical development and reaction mechanism

Electrocoagulation was first proposed by Vik et al. [1], describing a sewage treatment plant in London built in 1889 where electrochemical treatment was employed via mixing the domestic wastewater with saline (sea)water. In 1909, J.T. Harries received a patent for wastewater treatment by electrolysis using sacrificial aluminium and iron anodes in the United States [1]. Matteson et al. [2] described the 'Electronic Coagulator', which electrochemically dissolved aluminium from the anode into the reaction solution that interacted with the hydroxyl ions produced at the cathode to form aluminium hydroxide. The hydroxides flocculated and coagulated the suspended solids, purifying the polluted water. A similar process was used in Great Britain in 1956 [2], in which iron electrodes were used to treat polluted river water. Thereafter, a wide range of water and wastewater applications followed under a variety of conditions.

In early reports, the electrocoagulation process was applied to remove suspended solids [2]; heavy metals [3]; petroleum products [4]; colour from dye-containing solution [5]; aquatic humus [1]; fluorine from water [6]; and urban wastewater [7]. In the last two decades the application has been greatly expanded, and there is currently much interest in using electrocoagulation for treatment of a variety of effluents containing metals, foodstuff, olive oil, textile dyes, fluorine, polymeric wastes, organic matter from landfill leachate, turbidity, chemical and mechanical polishing wastes, aqueous suspensions of ultrafine particles, nitrate, phenolic waste and arsenic [8–15] as well as municipal wastewater [16].

The electrocoagulation process basically involves the dissolution of metal cations from the reactor anode with the simultaneous formation of hydroxyl ions and hydrogen gas at the cathode:

$$M \rightarrow M^+ + ne^- \tag{1}$$

$$2H_2O(l) \rightarrow OH^- + H_2(g) \tag{2}$$

A current is passed through a metal electrode, oxidising the metal (M) to its cation (M^+) (Equation (1)). Simultaneously, water is reduced to hydrogen gas and the hydroxyl ion (OH^-) (Equation (2)). Electrocoagulation thus introduces metal cations in situ, using sacrificial anodes (typically iron, stainless steel or aluminium) that need to be periodically replaced [17,18]. The overall reaction mechanism is a combination of removal mechanisms functioning synergistically. The dominant mechanism may vary throughout

*Corresponding author. Email: kabdasli@itu.edu.tr

the dynamic process as the reaction progresses, and will certainly shift with changes in treatment conditions, operating parameters and in particular pollutant types [19–21]. During electrocoagulation, highly charged cations (Al^{3+}; Fe^{2+}) formed at the anode destabilize colloidal particles by the formation of monomeric and polymeric hydroxo complex species. These metal hydroxo complexes have high adsorption properties, forming strong aggregates with pollutants [22]. The extent of metal hydrolysis depends upon the total metal cation concentration and the pH, as well as the type and concentration of other species present in solution [23]. Electrolysis in the presence of an iron electrode produces Fe^{2+} upon anodic oxidation and iron hydroxide, $Fe(OH)_n$, where n can be 2 or 3. The $Fe(OH)_n(s)$ remains in the aqueous phase as an amorphous suspension, which can remove the pollutants from the wastewater by either complexation or electrostatic attraction followed by coagulation. In surface complexation mode, the pollutant acts as a ligand (L) to chemically bind hydrous iron [24]:

$$\text{L-H(aq)} + \text{(OH)OFe(s)} \rightarrow \text{L-OFe(s)} + H_2O(l) \quad (3)$$
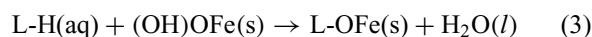
The pre-hydrolysis of ferric iron ions also leads to the formation of reactive clusters for wastewater treatment [25]. Ferric iron ions generated by electrochemical oxidation of the iron electrode may form $Fe(OH)_3$, monomeric and polymeric hydroxo complexes depending on the pH of the aqueous medium [26]. These impart a strong affinity for dispersed particles as well as (negatively charged) counter ions to cause coagulation [24,27]. The gases (H_2, O_2) evolved at the electrodes may be strong enough to cause flotation of the coagulated materials. Once the floc is generated, the electrolytic gas creates a flotation effect, removing the pollutants to the floc-foam layer at the liquid surface [28]. In the case of aluminium electrodes, soluble and insoluble pollutants can be coagulated by aluminium hydrates and hydroxides and then effectively removed from effluent owing to the existence of monomeric and polymeric species of aluminium. Upon hydrolysis, aluminium ions generate many monomeric and polymeric species over a wide pH range [29]. Major interactions taking place in the reaction solution during electrocoagulation are listed as: (i) migration to an oppositely charged electrode (electrophoresis) and aggregation due to charge neutralization; (ii) the metallic cation or the hydroxyl ion forms a precipitate with the pollutant; and (iii) the metallic cation interacts with hydroxyl ions to form a hydroxide depending upon the pH [28,30]. The metal hydroxide usually has high adsorption properties, thus bonding to the pollutant (bridge coagulation), or the hydroxides form larger lattice-like structures and sweep through the water (sweep coagulation), entrapping particles; depending on reaction conditions, electrode type and oxygen concentration, oxidation or reduction of the pollutants to less toxic species may occur (decolourization, dehalogenation, etc.), as well as removal by electroflotation and adhesion to rising gas bubbles.

Due to the multitude of reactions occurring simultaneously, it becomes very difficult to model and control the process and its removal mechanism. Consequently, adequate scale-up parameters, a systematic approach for process optimization and performance prediction of the electrocoagulation reactor are yet to be established. Advantages and benefits of using electrochemical techniques include environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation and cost effectiveness. In addition, the following advantages can be added for the treatment of pollutants with the electrocoagulation process: compact and simple reactors due to rapid reactions instead of using chemicals (coagulants, oxidants) and microorganisms; and the systems employ only electrons to facilitate water treatment. The formed aluminium and iron hydroxide flocs are relatively dense and easier to dewater, having a low sludge volume index (SVI). Hence, sludge management through electrocoagulation becomes more attractive than via coagulation and precipitation methods with conventional coagulants and hydrated lime [28,31]. On the other hand, electrocoagulation has several disadvantages [28]: the sacrificial electrodes are dissolved and hence lost into wastewater streams as a result of oxidation and need to be regularly replaced periodically; the use of electricity may result in high electrical energy costs, and electrical energy costs are very high in some countries; operation costs (sludge disposal, electrical energy consumption and electrode replacement) may become high, depending on the case in question; an impermeable oxide film may be formed on the cathode, leading to loss of efficiency; and high conductivity of the wastewater suspension is required. In some cases electrolytes have to be added to the wastewater; gelatinous metal hydroxides may tend to solubilize in some cases; the presence of high electrolyte concentrations (chloride) may result in the formation of toxic, organically bound halogens (AOX, EOX, POX); and in some cases pretreatment (pH adjustment, equalization, etc.) may be required prior to electrocoagulation.

1.2. Process parameters

1.2.1. Current density

Current density is one of the most critical operation parameters in electrocoagulation, having an integral effect on process efficiency [20,30,32,33]. This parameter determines both the rate of electrochemical metal dosing to the water and the density of electrolytic bubble production. Literature sources report a wide range of current densities applied between 1–100 mA/cm^2 depending on the case study. Obviously, different current densities are desirable in different situations. High current densities are needed for separation processes involving flotation cells or large settling tanks, while small current densities are appropriate for electrocoagulators that are integrated with conventional sand and coal filters. A systematic analysis is required

to define and refine the relationship between the applied current density and targeted removal (separation) effects. In a typical electrocoagulation experiment, the electrode or electrode assembly is usually connected to an external direct current source [34]. The amount of metal dissolved or deposited is directly proportional to the amount of electricity passed through the electrolytic solution. A simple relationship between current density (mA/cm^2) and the amount of substances (M) dissolved (g of M/cm^2) can be derived from Faraday's law [30]:

$$W = J \times t \times (M/n) \times F \qquad (4)$$

where W is the quantity of electrode material dissolved (g of M per cm^2); J is the applied current density (mA/cm^2); t the electrolysis time in s; M the relative molar mass of the electrode material under study; n the number of electrons in oxidation/reduction reaction; and F is Faraday's constant (96,500 C/mol).

1.2.2. Reaction pH

The pH of the reaction solution changes during the electrocoagulation process, and the final pH of the effluent actually affects the overall treatment performance [35,36]. It has been reported that when the initial pH value is less than 4 (acidic), the effluent pH increases, while it tends to decrease when the initial pH value is higher than 8 (basic), and the pH of the effluent changes only slightly when the initial pH value is in the neutral range (around 6–8). This situation indicates a pH buffering effect during electrocoagulation which is different from traditional chemical coagulation. This pH buffering capacity can be attributed to the balance between the production and consumption of hydroxyl ions during electrocoagulation and the need for charge neutralization before the ultimate transformation of soluble aluminium compounds into aluminium hydroxides. Thus, the formation of Al(OH)$_3$ near the anode may lead to the decrease of pH. On the other hand, it has also been reported that ultimate pH values increase rapidly during electrocoagulation such that the ultimate pH values reached at the end of electrocoagulation are always greater than 8–9 [24]. This is not surprising, since continuous hydroxyl ion production occurs at the cathode (see Equation (2)). Under alkaline conditions, the formation of Al(OH)$_4^-$ complexes is the major reason for a decrease in pH. Moreover, hydrogen bubbles produced at the cathode are smallest and finest at neutral pH, providing sufficient surface area for gas–liquid–solid interfaces and mixing efficiency to favour the aggregation of tiny destabilized particles and colloids [23,37].
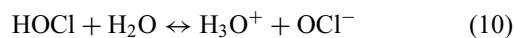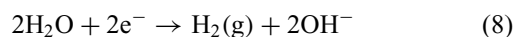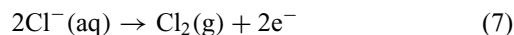
1.2.3. Electrolyte type and concentration

Sodium chloride (NaCl) is usually employed to increase the conductivity of the water or wastewater to be treated.

Wastewater conductivity affects the Faradic yield, cell voltage and therefore energy consumption in electrocoagulation cells. In addition, increasing water conductivity using NaCl has other advantages; for example, chloride anions can significantly reduce the adverse effects of other anions, such as HCO$_3^-$ and SO$_4^{2-}$ [38]. Indeed, the existence of carbonate anions may lead to the precipitation of Ca^{2+} ions. These ions can form an insulating layer on the surface of the cathode, which can increase the ohmic resistance of the electrochemical cell:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \qquad (5)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s) \qquad (6)$$
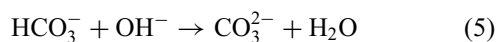
Conversely, an excessive amount of NaCl induces an overconsumption of the aluminium electrodes due to 'corrosion pitting'; aluminium dissolution may become irregular [38]. This is the reason why NaCl addition should be limited and optimized. Salts of monovalent ions appear to be the best electrolytes [20,28]. NaCl is usually employed as the electrolyte to increase the conductivity of wastewater to be treated by an electrochemical process, and decreases the passivation of the aluminium surface to promote electrocoagulation efficiency [36]. The addition of NaCl can also reduce the electrical energy consumption of electrocoagulation, as it increases the conductivity of the wastewater. Compared with no addition of electrolyte, NaCl addition in the 'g/L' range usually saves much electrical energy, and hence decreases operating costs. This can be explained by the fact that the cell voltage decreases with an increase of conductivity at constant current density; moreover, the total resistance in the solution decreases and thereby the consumed electrical energy is decreased. Considering that an excessive concentration of NaCl causes overconsumption of the anode material due to corrosion pitting, electrode dissolution may become irregular at NaCl overdoses [30]. On the other hand, during electrocoagulation in the presence of NaCl, formation of hypochlorite (OCl$^-$) and hypochlorous acid (HOCl) is possible so that besides serving as an electrolyte, NaCl may also provide an additional, in situ-formed oxidizing agent to the reaction solution provided that the pH remains below 11 and the reaction temperature does not increase significantly [39]:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \qquad (7)$$

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \qquad (8)$$

$$Cl_2(g) + H_2O \rightarrow HOCl(aq) + HCl \qquad (9)$$

$$HOCl + H_2O \leftrightarrow H_3O^+ + OCl^- \qquad (10)$$

Adsorbable, organically bound halogens (AOX) includes chemicals of different structures and toxicological profiles [40]. It is known that the use of low-cost disinfectants such as sodium hypochlorite can create AOX in wastewater. On the other hand, both chemical oxidation (e.g. chlorination

and ozonation) may lead to the formation of chlorinated organic compounds [40]. Although the environmental significance of AOX is controversial, many jurisdictions have adopted strict regulatory requirements limiting its discharge [13]. For instance, according to the German Sewage Water Administration Regulation, the AOX threshold limit is given as $500\,\mu g/L$ [41]. AOX formation during electrocoagulation due to the reaction of hypochlorous acid with the high organic carbon content of reactive dyebath effluent ingredients and its subsequent abatement cannot be ruled out [39].

1.2.4. Electrode type and arrangement

In most studies reported in the scientific literature, aluminium (Al), iron (Fe), mild steel and stainless steel (SS) electrodes have been used as the electrode materials [42]. Do and Chen [5] compared the performance of iron and aluminium electrodes for removing colour from dye-containing solutions. Their conclusion was that the optimum electrocoagulation operation conditions varied with the choice of iron or aluminium electrodes, which in turn were determined by Holt et al. [43]: namely, initial pollutant concentration, pollutant type, solution pH and stirring rate. Baklan and Kolesnikova [42] investigated the relationship between 'size' of the cation introduced and treatment efficiency. The size of the cation produced (10–$30\,\mu m$ for Fe^{3+} compared with 0.05–$1\,\mu m$ for Al^{3+}) was suggested to contribute to the higher efficiency of iron electrodes. Hulser et al. [34] observed that electrocoagulation was strongly enhanced at aluminium surfaces in comparison with steel electrodes. This was attributed to the in situ formation of dispersed aluminium–hydroxide complexes through hydrolysis of the aluminate ion, which does not occur when employing steel electrodes. In a monopolar electrode arrangement of an electrocoagulation cell, each pair of sacrificial electrodes is internally connected with each other, and has no interconnections with the outer electrodes [28]. This arrangement of monopolar electrodes with cells in series is electrically similar to a single cell with many electrodes and interconnections. In series cell arrangement, a higher potential difference is required for a given current to flow because cells connected in series have higher resistance. In this arrangement the same current flows through all the electrodes. On the other hand, in a parallel arrangement the electric current is divided between all electrodes in relation to the resistance of the individual cells. Some authors have used bipolar electrodes [28] with cells connected in parallel, where the sacrificial electrodes are placed between two parallel electrodes without any electrical connection. Only the two monopolar electrodes are connected to the electric power source, with no interconnections between the sacrificial electrodes. This type of cell arrangement provides a simple set-up, which facilitates easy maintenance during operation. When an electric current is passed through the two electrodes, the neutral sides of the conductive plate will be transformed to charged sides, which have opposite charge compared with the parallel side beside it. The sacrificial electrodes, in this case, are also known as bipolar electrodes [28].

1.2.5. Electrode passivation

One of the greatest operational issues with electrocoagulation is electrode passivation. The passivation of electrodes is a serious concern for the longevity of the process. Passivation of aluminium electrodes has been reported in several studies [3,44,45]. Passivation was also observed when, during electrocoagulation with iron electrodes, deposits of calcium carbonate and magnesium hydroxide were formed at the cathode and an oxide layer was formed at the anode. Nikolaev et al. [44] suggested various methods to minimize/prevent electrode passivation, such as changing the polarity of the electrode, hydromechanical cleaning of the electrodes, mechanical cleaning of the electrodes and introducing inhibiting agents.

1.2.6. Reactor design

Electrocoagulation reactors have been built in a number of configurations. Each system has its own set of advantages and disadvantages, among which are varying degrees of treatment ability. Often the electrocoagulation units are used simply as a replacement for chemical dosing systems and do not always take advantage of the electrolytic gases produced in the electrocoagulation process. To date, no single empirical or systematic approach has emerged over the years in the design of electrocoagulation reactors [21]. Therefore, it becomes very difficult to compare the performance of different reactor configurations. Reactor geometry affects several operational parameters, including bubble path and size, flotation effectiveness, floc formation, fluid flow regime and mixing/settling characteristics. From the scientific literature, the most common approach involves aluminium and iron plate electrodes with batch or continuous operation mode. In a continuous system, water to be treated is dosed with dissolved metal ions as it passes through the electrocoagulation cell. A downstream unit is often required to separate the pollutant from the water. The surface area to volume ratio (S/V) has been shown to be a significant scale-up parameter [43]. The electrode area influences current density, position and rate of cation dosing, as well as bubble production and bubble path length. Mameri et al. [6] reported that as the S/V ratio increases the optimal current density decreases. In a study conducted by Zolotukhin [46], an electrocoagulation–flotation system was scaled up from laboratory to industrial size. The following dimensionless scale-up parameters were chosen to ensure correct sizing and proportioning of the reactors: the Reynolds number (fluid flow regime), the Froude number (buoyancy), Weber criteria (surface tension), gas saturation and reactor geometry were kept similar.

2. Textile industry wastewater

Textile industries are among the major polluting industries in terms of discharged volume and characteristics. Textile preparation, dyeing and finishing operations contribute to the complexity of the total effluent, rendering its treatment a rather difficult task. Due to their colour content, dyebath effluents, in particular, are not only aesthetic pollutants, but may also interfere with light penetration in the receiving bodies of water, thereby disturbing biological processes [47]. Furthermore, textile industry effluent contains a variety of dye-assisting chemicals (wetting, scouring, sequestering, cleaning, anti-creasing agents, acid donors, etc.), which are in some cases bio-inhibitory, toxic and/or refractory, as well as a significant amount of salts, creating an additional ecotoxicological impact in receiving water bodies [48]. Conventionally, textile industry wastewaters are treated through different biological, physical and chemical methods [47]. Biological treatment processes are often ineffective in removing dyes, which are highly branched and structured macromolecules with high stability and hence low biodegradability [49]. On the other hand, various physicochemical treatment methods including chemical coagulation–flocculation [50,51], adsorption on to low-cost materials [52] and activated carbon beds, reverse osmosis and ultrafiltration [53] are also available for dye removal. However, these phase-transfer treatment processes have had rather limited success and applicability in the effective decolourization of textile effluent. Further, the main drawback of chemical coagulation is the addition of further chemicals. In recent years, ozonation [54], electrochemical [55,56] photochemical, photocatalytic [57] and photoelectrocatalytic [58] advanced oxidation processes have been proposed as alternative treatment techniques because they were qualified as being very effective. However, the high operating costs of these advanced alternative treatment methods have limited their feasibility and full-scale implementation [59]. More recently, electrochemical processes, and in particular electrocoagulation, have been proposed to treat complex waste streams including textile industry wastewater. These promising applications are reviewed in this paper on the basis of characteristic/target pollutant parameters of the effluent produced by this industrial sector.

2.1. Colour

Many studies have been devoted to the electrocoagulation of single aqueous dye solutions or synthetically prepared dyehouse samples containing a mixture of dyes and NaCl as the common electrolyte. In these treatability studies, it could be demonstrated that colour caused by the presence of dyes could be effectively removed at a range of 95–99% during electrocoagulation using iron or aluminium electrodes. Decolourization kinetics were typically followed by spectrophotometry and obeyed the first-order law on the basis of absorbance (colour) abatement profiles. Most of these studies aimed at finding optimal operation conditions for colour removal from dye solutions or synthetic dyehouse effluent by controlling/modifying the process variables. The highest colour-removal efficiencies were usually obtained at near neutral to slightly acidic pH values, whereas the current intensity, and hence treatment time, had to be increased to improve colour removal efficiencies. This is because the key process parameter for electrocoagulation is in fact the amount of electrogenerated coagulant, which is directly related to the product of applied current density and treatment time. Colour removal is typically observed earlier than organic carbon (chemical oxygen demand (COD), total organic carbon (TOC)) removal, since in electrocoagulation several mechanisms play a significant role and this treatment process is not solely based on a phase-transfer mechanism. Interpretation based on Infrared and Fourier Transform Infrared Spectrometric analyses revealed that in addition to coagulation, precipitation and adsorption, colour removal is also attributable to the cleavage of colour-causing bonds in the dye structure. This cleavage is speculatively not due to direct anodic oxidation, but occurs indirectly in parallel to the oxidation of ferrous iron to ferric iron via the reductive pathway. A limited number of studies have been reported for real textile industry wastewater, and only a few works investigated the treatability of both dye solutions and actual effluent via electrocoagulation. It should be noted that experimental dye solutions cannot represent real textile industry wastewater, the latter bearing a broad spectrum of organic and inorganic chemicals known as dye auxiliaries. The ingredients of dyehouse effluent are extremely variable in time and composition according to customer orders, fabric type, fashion and period of the year.

Merzouk et al. [60] studied the efficiency of electrocoagulation using Al electrodes for the removal of COD, TOC, colour and turbidity from a real textile wastewater (COD: 1065 mg/L; TOC: 354 mg/L, pH: 7.2), two aqueous 2-naphthoic acid and 2-naphthol solutions (two disperse dyes, concentration: 100 mg/L; absorbance at 503 nm-λ_{max}: 0.2 cm^{-1}), and the same real textile effluent containing the abovementioned disperse dyes. Treatment efficiencies were compared and modelled by considering adsorption equilibrium and mass balances for single and multiple substrates (pollution parameters) adsorbed on the formed aluminium hydroxide flocs. The removal of colour from the dyestuff solutions was satisfactory, whereas that of the real textile wastewater appeared to be less efficient. The higher removal efficiency obtained for the single aqueous dye solutions as compared with the real textile wastewater was attributed to the complexity and higher organic carbon content of the wastewater. The decrease in the removal efficiencies with increasing pollution load was more additive than synergistic.

The performance of continuous electrocoagulation employed for decolourization and COD removal from a synthetically prepared textile wastewater (COD: 2500 mg/L; initial dye concentration: 200 mg/L) using aluminium electrodes was examined by Merzouk et al. [61]. In this work, electrocoagulation was optimized in terms of key operating conditions and parameters conductivity (1500–5000 mg/L), influent pH (3–9) and inlet dye concentration (25–200 mg/L), as well as current density and hydraulic residence time (Q: 25.2–78 L/h). The length of the electrodes was maximized to reduce their height to enhance H_2 bubble formation; this design was used to enhance mixing in the first compartment, using both the liquid flow and H_2 bubbles for this purpose. An increase in current density from 20.83 to 62.5 mA/cm^2 yielded an increase in colour removal efficiency from 78% to 93%. The results showed that the colour induced by a red disperse dye was effectively removed by at least 85% when the pH ranged from 6–9, the hydraulic residence time was 14 min, the current density was 31.25 mA/cm^2 (I: 1.5 A) and the conductivity was 2.4 mS/cm for an inter-electrode distance of 1 cm. As the disperse dye concentration was increased from 25 to 100 mg/L, not only did the dye removal yield increase, but also the final dye concentration in the effluents decreased from about 11 to 4 mg/L. However, the adsorption capacity of flocs became exhausted when the initial dye concentration was increased further from 100 to 200 mg/L. At lower current densities, increasing the electric conductivity of the wastewater had no notable effect on colour removal efficiency, but at high current densities specific colour and COD removal yields, as well as specific electrical energy consumption, decreased appreciably. Two basic removal mechanisms are generally considered to explain disperse dye removal via electrocoagulation: (i) precipitation for pH lower than 4; and (ii) adsorption for higher pH values (6–9). Under these conditions, COD abatement was at least 80%, indicating that colour and COD parameters were removed in parallel.

The work of Cerqueira et al. [62] reports the viability of the electrocoagulation process for COD, turbidity and colour removal from a raw effluent originating from a particular textile industry related to hemp manufacture (COD: 1179–2553 mg/L; colour (absorbance): 0.503–0.842 cm^{-1}; conductivity: 2.20–4.61 mS/cm; pH: 9.9–11.6). Current density, initial pH, electrolysis time, material of the electrode (iron, aluminium, or iron–aluminium) and inter-electrode distance were optimized, and thereafter the effects of these parameters on specific electrical energy consumption were studied under optimized electrocoagulation conditions. The highest removal efficiencies were obtained as 93% for colour, 99% for turbidity and 87% for COD using aluminium electrodes, an initial pH of 5, a cell operation time of 30 min and a current density of 1.5 mA/cm^2. Higher colour removal efficiency was obtained when the process was conducted with aluminium electrodes at an initial pH of 5, probably due to the higher production of

solid Al(OH)$_3$ becoming significant at this pH value. In the case of iron electrodes, higher removal efficiencies were obtained at an initial pH of 7, where higher production of amorphous Fe(OH)$_3$ occurs; this ferric hydroxide complex may be responsible for the removal of the major part of the impurities in the textile wastewater. A hybrid (Fe + Al) electrode configuration was also developed with the purpose of a simultaneous release of both iron and aluminium ions into the solution, and to assess its effect on treatment efficiencies. The system was constructed with eight plates, four being Al and four Fe plates. The experiment was run at an initial pH of 6, which is an intermediate value of pH used for the iron and aluminium electrodes, that is, pH 5 and pH 7, respectively. With variation of the current density from 2.5–12.5 mA/cm^2 the highest removal efficiencies of COD (56% and 55%), colour (81% and 88%) and turbidity (96% and 97%) were obtained. As far as pollutant removal is concerned, the results obtained with the hybrid electrode are very promising. Under the studied treatment conditions, electroflocculation of these effluents may constitute a viable alternative for removal of COD, turbidity and colour.

Phalakornkule et al. [63] investigated the operation of a continuous upflow electrocoagulation reactor for the removal of the azo dye Direct Red 23 (disodium 3-[(4-acetamidophenyl)azo]-4-hydroxy-7-[[[[5-hydroxy-6-(phenylazo)-7-sulphonato-2-naphthyl] amino] carbonyl] amino] naphthalene-2-sulphonate). A sample of 100 mg/L aqueous Direct Red 23 solution was treated at an initial pH adjusted to 9.6 with NaOH and an electric conductivity of 850–890 μS/cm with NaCl. Batch-mode operation was employed first to optimize the process for the parameters of electrode type, electrode distance, current density and electrocoagulation time. Except at a current density of 4 mA/cm^2, electrocoagulation with aluminium anode required at least 5 min to achieve a removal efficiency >80%, whereas during electrocoagulation with iron electrodes colour removal efficiencies of >90% could be achieved with a 2 min treatment. Based on removal efficiencies and energy consumption, optimum conditions were found to be iron anode, an electrode distance of 8 mm and a current density of 3 mA/cm^2 at contact time of 5 min. The continuous upflow reactor performed satisfactorily, resulting in 95% colour removal and energy consumption in the order of 0.6–0.7 kWh/m^3. This set of parameters was further employed to treat real textile wastewater. The initial COD of the textile wastewater ranged between 278–736 mg/L. The colour removal efficiency was not always satisfactory; from six samplings, four were satisfactory (>80%), but two failed (<80%). Removal of colour from the textile wastewater was more difficult than from the synthetically prepared wastewater. On the other hand, direct dyes have been generally reported to be more easily removed by the electrocoagulation method than reactive dyes, which are more polar and water soluble. Another possible explanation was that the real textile wastewater may have contained some chemicals which may inhibit the

electrocoagulation mechanism. The electrical energy consumption ranged from 0.2–0.9 kWh/m^3 for the real textile effluent.

Essadki et al. [64] reported the performance of a 14–20 L capacity external-loop airlift reactor being used as an electrochemical cell to treat polluted water using batch electrocoagulation without mechanical agitation, pumping requirements or air injection. Mixing and complete flotation of the pollutants were achieved using only the overall liquid recirculation induced by hydrogen microbubbles generated by water electrolysis. A red dye mixture (2-naphthoic acid and 2-naphtol) typically used in the Moroccan textile industry was used to validate this novel application. The conductivity of the dye solution was adjusted with NaCl to the range 1.0–29 mS/cm. Colour removal was measured as the absorbance at 450 nm (A_{450}). The specific electrical energy consumption per kg dye removed and the specific electrode consumption per kg dye were calculated. The objective was to achieve A_{450} in the treated water lower than 0.07 cm^{-1}. This gave a condition on colour and turbidity removal. In addition 80% COD removal was demanded, to achieve the Moroccan limits for COD in textile wastewater. It was shown that the axial position of the aluminium electrodes and the residence time in the separator section were the key parameters to achieve good mixing conditions, to avoid bubbles/particles recirculation in the down-comer and to prevent floc break-up/erosion by hydrodynamic shear forces. The above-explained conditions corresponded to an optimum liquid recirculation velocity that was correlated to the applied electric current, electrode position and dispersion height. The electrocoagulation time required for 80% COD and 80% colour removals was modelled as a function of the applied current density. Similarly, specific energy and electrode consumptions were correlated to current, electrode gap and conductivity, which provided the necessary tools for scale-up and process optimization. The time required to achieve 80% colour and COD removals did not follow first-order kinetics; the amount of pollution removed was not proportional to the amount of aluminium ions released by the electrodes. This may be due to the complexity of dye removal; the dye is formed by two constituents, the second being an oxidized form of the first. Consequently, their affinity for flocculation may differ and vary with current density. In addition, at a high current density, other parallel reactions may be encountered at the anode, such as the direct oxidation of one or both constituents of the dye, but also oxygen formation at the anode, which plays a negative role in electrocoagulation:

$$4OH^- \rightarrow O_2(g) + 2H_2O + 2e^- \qquad (11)$$
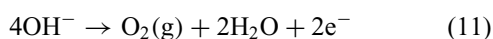
Conversely, high current density allows passivation of the cathode to be reduced, but an increase in energy consumption induces heating by the Joule effect. As a result, too high current densities have generally to be avoided. Operation time and removal efficiencies were similar to those reported in conventional electrocoagulation cells, but the specific energy and electrode consumptions were less since there was no need for mechanical agitation, pumping requirements and air injection, consumption efficiencies which could not be achieved in other kinds of conventional gas–liquid contactors.

Arslan-Alaton et al. [65] examined the treatability of real reactive dyebath effluent (COD: 500 mg/L; A_{436}: 3.00 cm^{-1}; A_{525}: 5.50 cm^{-1}; A_{620}: 0.70 cm^{-1}; conductivity: 27.6 mS/cm; chloride: 7800 mg/L; total suspended solids (TSS): 220 mg/L; pH: 11.2) comprising an exhausted reactive dyebath and its sequential rinses with electrocoagulation using aluminium (Al) and stainless steel (SS) electrodes. The experimental study focused on the effect of applied current density (22–87 mA/cm^2 at an initial optimized pH of 5.5) on decolourization and COD removal rates using Al and SS as electrode materials. Colour removal rates could be fitted to first-order kinetics. Results indicated that treatment efficiency was enhanced appreciably by increasing the applied current density when Al electrodes were used for electrocoagulation. No clear correlation existed between current density and removal rates for electrocoagulation with SS electrodes; the treatment efficiency could only be improved when the applied current density was in the range of 33–65 mA/cm^2. Electrocoagulation with SS electrodes was superior in terms of decolourization (99–100% colour removal obtained after 10–15 min electrocoagulation at all studied current densities), whereas electrocoagulation with Al electrodes was more beneficial for COD removal in terms of electrical energy consumption (5 kWh/m^3 wastewater for electrocoagulation with Al electrodes instead of 9 kWh/m^3 wastewater for electrocoagulation with SS electrodes). Regarding colour removal mechanisms for electrocoagulation with Al and SS electrodes, the following conclusions could be drawn from this work: Al electrodes cannot act as reducing agents since they enter the solution only in the '+III' valence state. In contrast, SS (or Fe) anodes cause ferrous iron release that may act as the reducing agent for azo dyes when all dissolved oxygen in the reaction medium is consumed. Moreover, it has been postulated that the reduction potentials and dissolved oxygen concentrations are appreciably lower during electrocoagulation with steel electrodes than those measured for Al electrodes, providing evidence that conditions are more favourable for reduction reactions when steel electrodes are employed. The observed colour and COD abatement profiles clearly revealed that electrocoagulation involving SS (or Fe electrodes) is a two-stage redox process, and hence proceeds more slowly than electrocoagulation with Al electrodes, due to the following anodic reactions taking place sequentially:

$$2Fe(s) \rightarrow 2Fe^{2+}(aq) + 4e^- \qquad (12)$$

$$2Fe^{2+}(aq) + 5H_2O + 1/2O_2 \rightarrow 2Fe(OH)_3(s) + 4H^+ \qquad (13)$$
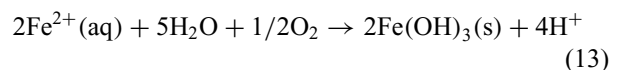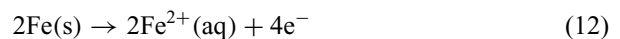
Unlike most chemical and biological treatment processes, no increase in electrical conductivity (salinity) was observed, which is clearly attributable to the removal mechanism of electrocoagulation. In this study, bicarbonate and carbonate ions may have been removed by the same reaction mechanisms so that the overall electrical conductivity did not change significantly after applying electrocoagulation. Similar amounts of iron or aluminium hydroxide sludges (range: 5000–6000 mg/L) were formed after treatment with Al and SS electrodes.

Zaroual et al. [66] studied electrocoagulation with iron electrodes to treat real textile wastewater (COD: 485 mg/L; BOD_5; 80 mg/L; chloride: 27,069 mg/L; A_{620}: 0.663 cm^{-1}; A_{525}: 0.415 cm^{-1}; A_{436}: 0.286 cm^{-1}; pH: 10.6) in a batch reactor. The effects of the operating parameters electrocoagulation time (2–8 min) and electrolysis potential (300–700 mV) on decolourization and COD removal efficiency were investigated. The findings indicated that 100% colour accompanied with 84% COD removal could be achieved after a 3 min treatment at a potential of 600 mV. The effluent quality of the wastewater by far exceeded the discharge criteria. In addition, the removal mechanism could be explained by employing zeta potential measurement. Zeta potential measurements demonstrated that $Fe(OH)_2$ is probably responsible for the electrocoagulation process.

Daneshvar et al. [67] investigated the decolourization of the azo dye Orange II (Acid Orange 7) by direct current electrocoagulation. The effects of initial pH, stirring rate, dye concentration, electrode distance, current density and temperature were tested. The experimental results revealed that the colour of the dye solution was effectively removed (>98%) accompanied by a significant COD reduction (>84%) when iron was used as the sacrificial anode and the concentration of Orange II was lower than 200 mg/L. The optimum current density was found as 3.5 mA/cm^2 with an optimal initial pH of around 8. After 20 min of treatment, adsorbed dyes desorbed into the solution, and consequently the removal efficiency decreased. The ease of desorption may be the reason for the physical adsorption mechanism. A temperature raise to 30°C caused an increase in dye removal efficiency which could be explained by the increase of mobility and collision of ions with hydroxyl polymers. On the other hand, at higher temperatures the removal efficiency decreased because of the formation of unsuitable flocs and/or the increase of solubility of formed precipitates. Pollutants desorbed from the ferric hydroxide sludge were separated and their structures were identified in order to propose a removal mechanism for Orange II electrocoagulation. Ultraviolet, Fourier Transform Infrared spectrometry and nuclear magnetic resonance analyses indicated that one of the compounds was sulphanilic acid and the other was Orange II. It could be concluded that Orange II was reduced and cleaved into 1-amino-2-naphtol and sulphanilic acid salt. The 1-amino 2-naphtol was not extractable.

Overall, several mechanisms have been proposed for colour removal during electrocoagulation. It may involve, besides adsorption, complexation with the metal hydroxide, forming ionic bonds. Colour removal can also take place if reaction conditions (dissolved oxygen concentrations) are suitable to allow reduction processes to occur simultaneously with iron oxidation in the solution bulk (Fe^{2+} to Fe^{3+}). Further studies are necessary in order to increase the reliability of the electrocoagulation technique for decolourization of real textile wastewater.

2.2. Organic matter

The mechanism of electrocoagulation for wastewater treatment is known to be very complex. It has been postulated that organic matter (COD, TOC) removal may involve electrochemical oxidation, adsorption by electrostatic attraction and physical entrapment. Textile industry wastewater is known to contain a variety of complex organics including pigments, dyestuffs, surfactants, sequestering agents, wetting agents and carboxylic acids that impart the effluent a medium-to-high strength organic carbon load. Moreover, the biodegradability of these compounds is relatively poor, creating problems in conventional activated sludge systems.

Arslan-Alaton et al. [68] examined the treatability of simulated reactive dyebath effluent (COD: 300 mg/L; chloride: 12,955 mg Cl$^-$/L; alkalinity: 12,955 mg $CaCO_3$/L; $A_{436} = 0.532$ cm^{-1}, $A_{525} = 0.693$ cm^{-1} and $A_{620} = 0.808$ cm^{-1}; pH: 11.23) employing electrocoagulation with Al and SS electrodes. Optimization of critical operation parameters such as initial pH (3–11), applied current density (22–87 mA/cm^2) and electrolyte type (either NaCl or Na_2SO_4) improved the overall treatment efficiencies, resulting in effective decolourization (99% using SS electrodes after 60 min, 95% using Al electrodes after 90 min electrocoagulation) and COD abatement (93% with SS electrodes after 60 min, 86% with Al electrodes after 90 min). Optimum electrocoagulation conditions were established as follows: an initial pH of 5 and an applied current density of 22 mA/cm^2 for both electrode materials. An applied current density value of 22 mA/cm^2 was already sufficient to achieve the desired treatment goals. COD and colour-removal efficiencies also depended on the electrolyte type. Formation of AOX associated with the use of NaCl as the electrolyte during electrocoagulation was also detected. A dramatic retardation of colour and COD removal rates was observed when Na_2SO_4 was used as the electrolyte instead of NaCl. This could be attributed to the passivating effect of sulphate ions hindering effective anodic dissolution of the electrode materials. On the other hand, it should also be pointed out that the higher COD and colour removals recorded while using NaCl as the electrolyte material were at least partially a consequence of hypochlorous acid formation, which contributed to oxidation of dyebath ingredients at pH values below

11, in addition to COD and colour removals achieved via co-precipitation with metallic sludge. An economical evaluation was also carried out within the frame of the study; for a COD removal efficiency of 83–84%, 1.8 and 3.6 kWh/m^3 electrical energy were consumed when Al and SS electrodes were employed, respectively. These electrical energy requirements are appreciably lower than those reported for degradation of recalcitrant pollutants with advanced oxidation processes.

Ozonation has often been applied to industrial wastewater prior to biological treatment in order to enhance its biodegradability by destroying – or at least converting – recalcitrant organic pollutants to less toxic and/or degradable oxidation intermediates. It has been reported that an increase in the BOD$_5$/COD ratio refers to an enhancement in the biodegradability of a wastewater, and this positive impact has often been reported for ozonation applications. However, studies where real industrial wastewater has been treated by ozonation alone did not achieve high levels of pollutant removal. In a study conducted by Hernández-Ortega et al. [69] it was demonstrated that the final quality of real industrial wastewater could be improved significantly when the existing biological treatment process was enhanced with electrocoagulation and ozonation pre-treatments. The wastewater (COD: 2142 mg/L; colour: 8440 Pt-Co; turbidity: 400 NTU) used in this study originated from an industrial complex of 140 large factories. The combined electrocoagulation and ozonation process was found to be a suitable pre-treatment option for traditional biological processes, and a very useful combination to treat the effluent parameter values down to the required environmental standards set for discharge into municipal wastewater treatment works (sewers). The combined treatment systems were able to decrease the colour and the turbidity of the wastewater by more than 90% and the COD by more than 60%. The COD removal mechanism by electrocoagulation was explained by sweep coagulation. A significant increase in the COD removal rate was obtained with iron in the solution, improving the efficiency by 20% (0.120 mg COD/mg O$_3$ without iron versus 0.144 mg COD/mg O$_3$ with iron). This synergistic effect supports the use of this technology as a complement to the electrocoagulation process. This was also verified by the BOD$_5$/COD relationship: it was observed that the biodegradability of the wastewater, originally around 0.07, increased considerably by the coupled electrocoagulation + ozonation process for ultimate treatment with the biological system. With ozonation it was possible to reduce the pollutant load of the wastewater, but results obtained with stand-alone ozonation were relatively poor as compared with electrocoagulation. None of the stand-alone treatment methods appeared to be efficient in textile wastewater treatment, emphasizing the requirement for combined treatment systems.

The electrocoagulation method offers several advantages over traditional chemical treatment processes in that less coagulant ion is required. Can et al. [70] studied the effect of preliminary chemical coagulant (polyaluminium chloride or alum) addition on COD removal from textile wastewater (COD: 3422 mg/L; TOC: 900 mg/L; TSS: 1112 mg/L; conductivity: 3.99 mS/cm; turbidity: 5700 NTU; pH: 6.95) by employing electrocoagulation in batch mode (treated volume: 250 mL) with aluminium electrodes. The two coagulants exhibited the same performance, but in the combined electrocoagulation, polyaluminium chloride was found to significantly enhance the COD removal rate and efficiency, depending on the amount of the total aluminium supplied by initial addition and in situ electrochemical generation. The highest COD removals were obtained during electrocoagulation at slightly acidic pH (5.5), resulting in 60–65% COD removal (the final pH was 7.8). Addition of aluminium salt to the wastewater shifted the initial pH towards more acidic and stabilized the solution pH during electrolysis, depending upon the amount of aluminium salt but not its type. A comparative operation cost analysis was also provided, and it was found that for the same operation cost per mass of COD removed, the combined electrocoagulation performance was 80% in contrast to electrocoagulation, which was limited to only 23% for an operation time of 5 min for an addition of 800 mg/L polyaluminium chloride.

Kobya et al. [71] demonstrated that the use of iron and aluminium as sacrificial electrode materials in the treatment of textile wastewater (COD: 3422 mg/L; TOC: 900 mg/L; TSS: 1112 mg/L; conductivity: 3.99 mS/cm; turbidity: 5700 NTU; pH: 6.95) by electrocoagulation was strongly pH dependent. According to their findings, in a slightly acidic medium (pH around 5–6) COD and turbidity removal efficiencies for aluminium were higher than those for iron, while in neutral and alkaline medium (7–9) iron was the preferable electrode material. High conductivity favours high process performances. On the other hand, for the same turbidity and COD removal efficiencies, electrocoagulation with iron electrodes required a current density of 8–10 mA/cm^2, while for aluminium electrodes a current density of 15 mA/cm^2 had to be applied for an operation time of 10 min. The experiments delineated that operation time and current density exhibited similar effects on the process performances, electrical energy and electrode consumption values. Finally, the energy consumption calculated in kWh per kg COD removed was found to be lower for iron electrodes, while the electrode consumption per kg COD removed was generally lower with aluminium. It is obvious that these two important operation costs (electrical energy and electrode material) will affect the decision about the type of sacrificial electrode material for given wastewater characteristics. Ultimately the COD, colour and turbidity (TSS) removal levels required by environmental consents for industrial process effluents may determine whether electrocoagulation should be applied to remove the target pollutants.

2.3. Toxicity

It is expected that after application of electrocoagulation using iron or aluminium electrodes and NaCl as the electrolyte, residual iron and aluminium as well as chlorinated organics will be present in the treated reaction solution. As a consequence, toxicity assessment of the effluents being subjected to electrocoagulation is an important task. However, only few case studies exist where the toxicity of the treated dyehouse effluent has been reported. Palácio et al. [72] studied the electrocoagulation with iron electrodes of a textile dyeing wastewater (COD: 1640 mg/L; sulphate: 2680 mg/L; NH_3-N: 1.3 mg/L; Org-N: 4.6 mg/L; Cl^-: 3850 mg/L; turbidity: 310 NTU; pH: 12.5) containing the commercial fibre direct dyes Solophenyl Orange TGL, Solophenyl Blue 71, Solophenyl Scarlet BNLE, Solophenyl Yellow ARL, Solophenyl Black FR and Navy Blue 98. From their respective stock solutions, a mixture of dyeing standards was also prepared, resulting in a final dyeing concentration of 8.33 mg/L, and then a sufficient amount of NaCl was added in order to reach the same conductivity value (16.88 mS/cm) of the dyehouse effluent samples for electrocoagulation measurements. The treatment system was optimized by the application of a 3^3 full factorial experimental design. The process response was evaluated on the basis of COD and colour removals. Analysis of variance (ANOVA) indicated that the variables treatment time and current density were statistically significant parameters for COD and colour removals. For a current density of 14.3 mA/cm^2 and an initial pH of 7, after 15 min treatment, 92%, 62% and 41% removals were achieved for turbidity, COD and TOC parameters, respectively. For the sulphate parameter, 75% removal was reached in the first 5 min. Moreover, complete decolourization was achieved above 30 min electrocoagulation. Acute toxicity was examined with lettuce seeds (*Lactuca sativa*) and brine shrimps (*Artemia salina*). The lowest toxicity levels were achieved after 5 min electrocoagulation, and extending the treatment time to 30 min did not decrease the high toxicity level, suggesting that this electrochemical process could only be used as part of a complete effluent treatment system.

2.4. Other pollution parameters

Zongo et al. [73] carried out electrocoagulation of two textile industry wastewaters (WW$_1$; COD: 1790 mg/L; turbidity: 115 NTU; conductivity: 2.8 mS/cm; pH: 7; WW$_2$: COD: 1240 mg/L; turbidity: 110 NTU; conductivity: 2.4 mS/cm; pH: 9) in a batch system provided with aluminium or iron electrodes as well as liquid recirculation. The system was examined on the basis of COD, turbidity and colour (A$_{436}$) removals. The two electrode metals were found to be of comparable efficiency. The applied current density was varied in the range of 5–20 mA/cm^2. The results could be interpreted by a simple model involving the overall equilibrium between the metal ion dissolved in the form of hydroxides and the removed pollutant. Turbidity and absorbance at 436 nm could be totally removed, while COD abatement ranged from 74–88% for the two effluent types, respectively. Abatement of the turbidity parameter was observed to obey another kinetic, with a sharp reduction after a preliminary phase, while electrocoagulation accumulation of metal hydroxide has no effect on this variable. Taking into account the stoichiometry of the metal dissolution, the molecular weight of these metals and the current efficiency of metal dissolution, the energy consumption for the treatment of 1000 mg/L COD was estimated at 1.75 kWh/m^3 with iron electrodes and 1.53 kWh/m^3 with aluminium electrodes. These values could be reduced by 30% with a two-fold increase in the effluent conductivity; the addition of NaCl at 1000 mg/L would allow such a reduction in the electric energy consumption.

When electrocoagulation is considered as a treatment application, the costs of aluminium and iron sludge management should be taken into account. Hence, sludge volume and settlability are critical parameters that need to be minimized to reduce sludge management costs. Zodi et al. [74] dealt with the treatment of textile wastewater (COD: 3260 mg/L; turbidity: 310 NTU; conductivity: 1.9 mS/cm; TSS 1700 mg/L; pH: 7) by electrocoagulation with emphasis on the subsequent sludge settling process. The influence of electrode material, current density, pH, treatment period on sludge settling characteristics was investigated in detail. The textile wastewater under study had a high suspended solids and turbidity together with a fair COD. The initial pH and conductivity (NaCl concentration) of the reaction solutions were adjusted before electrocoagulation. The current density was supplied in the range of 5–20 mA/cm^2. The electric current was kept constant for each run. The reaction solution was stirred at 200 rpm and continuously circulated in the flow circuit by means of a peristaltic pump at 50 mL/min. The total duration of the electrolysis was 60 min unless stated otherwise. Iron or aluminium electrodes were used for electrocoagulation, with various conditions of initial pH ranging from 3–9, current density and electrolysis time. The proposed treatment process consisted of a sequential electrocoagulation + settling system. Sludge settling velocity after electrocoagulation was measured depending on the operating conditions and used to compare the efficiency of various empirical models for estimation of sludge settling velocity. Finally, the sludge aptitude to settling was studied in terms of SVI to determine the most suitable operating conditions. For electrocoagulation with iron electrodes, more rapid settling was observed than with aluminium electrodes. The interface velocity was determined as 4.00, 3.75, 3.15 and 3.85 cm/min at 5, 10, 15 and 20 mA/cm^2, respectively. For the effluent treated with aluminium electrodes at an initial pH of 9, the solid/liquid interface descended with an initial velocity of 2.15 cm/min, whereas for the initial pH values of 3, 5, 6 and 7, the initial velocity was determined as 0.53, 0.55,

0.74 and 2.05 cm/min, respectively. In addition, the sediment height for electrocoagulation conducted at an initial pH of 9 was lower. The settling velocity after electrocoagulation with iron electrodes was found as 1.90, 2.80, 3.20, 3.75 and 3.13 cm/min for the pH values of 3, 5, 6, 7 and 9, respectively. With aluminium electrodes, SVI varied with the applied current density and the lowest value of 125 mL/g was obtained at 10 mA/cm^2, whereas the highest SVI was found as 215 mL/g for 15 mA/cm^2. The treatment was more efficient with iron electrodes with regards to obtained SVI values, varying from 61 mL/g at 5 mA/cm^2 down to 52 mL/g at 20 mA/cm^2. SVI values decreased with increasing pH reaching a minimum level at alkaline pH, attaining 73 and 61 mL/g with aluminium and iron electrodes, respectively. In accordance with the performance observed in terms of settling velocity, suspended solids and turbidity abatements, electrocoagulation with iron electrodes seems to be more efficient for the treatment of textile wastewaters. The results presented probably depend on the dimensions of the settling chamber.

2.5.   Economic analysis

As with other treatment processes, electrocoagulation requires comprehensive study discerning the effects of continuous variables such as pH, current density and electrolysis time as well as electrode material, electrode distance and connection mode. In some studies devoted to electrocoagulation applications, special emphasis has been placed on electrical energy and operating costs (i.e. costs of electrode materials, electricity, electrode replacement, chemicals used for pH and electric conductivity adjustment). Due to the fact that among the prevailing chemical treatment processes electrocoagulation appears to be the most promising in terms of full-scale implementation potential, attention has been paid to the economic issues of the application of electrocoagulation.

Essadki et al. [64] used an external-loop airlift reactor to carry out batch electrocoagulation experiments without mechanical agitation, pumping requirements or air injection. Mixing and complete flotation of the pollutants were achieved using only the overall liquid recirculation induced by the hydrogen gas bubbles produced in situ. A red dye from the Moroccan textile industry was used to assess the performance of the airlift reactor. Results showed that best treatment conditions corresponded to an optimum liquid overall recirculation velocity that was correlated to current, electrode position and dispersion height. Colour (80%) and COD (80%) removal efficiencies, specific energy requirements and electrode consumptions were correlated to current, electrode gap and conductivity, which provided the major tools for scale-up and process optimization. Operation time and removal efficiencies were similar to those reported in conventional electrocoagulation cells, but specific energy and electrode consumptions were smaller than those experienced with conventional gas–liquid contacting

devices. For the application studied in this work, four key points were established: (i) from the economic point of view that accounts both for specific energy and electrode consumption, the optimal conditions correspond to a low current (1 A) and a high operation time (36 min); (ii) on the other hand, considering capital/investment costs, the size of the equipment and hence the operation time should be limited by increasing the current density; (iii) considering the full-scale implementation procedure, it is preferable to operate at medium current densities 15 mA/cm^2 (about 2 A) to avoid unnecessary Al(OH)$_3$ sludge formation in the treated effluent; (iv) it is important to avoid extreme current density (more than 30 mA/cm^2) due to the sludge-formation issue addressed above, as well as to optimize specific removal efficiencies and minimize operation costs.

Specific electrical energy consumptions for COD and colour removals (15–20 kWh/kg COD and dye, respectively) decreased considerably with increasing conductivity. However, high chloride content usually exceeded the maximum acceptable concentration in receiving waters destined for reuse. A conductivity of 5 mS/cm seems to be a reasonable compromise because it offers a moderate value of electrical energy consumption by the Joule effect, while preventing a rapid degradation of the electrode surface (corrosion pitting).

Kobya et al. [75] conducted a detailed techno-economic evaluation for electrocoagulation of a textile industry wastewater (COD: 2031 mg/L; TSS: 102 mg/L; conductivity: 2.31 mS/cm; turbidity: 671 NTU; pH: 8.88) using aluminium and iron electrodes connected in three modes, namely monopolar-parallel (1), monopolar-serial (2) and bipolar-serial (3). Different cost items including electrical, sacrificial electrodes, labour, sludge handling, maintenance and depreciation costs have been considered in the calculation of the total operating cost. Results indicated that the monopolar-parallel mode was more cost effective for both electrode types. Although both electrode materials show similar results in terms of COD and turbidity removals, Fe should be preferred as it is a low-cost material. It was also evident that electrocoagulation was fast and efficient, rendering it an economically attractive process. As compared with chemical coagulation, electrocoagulation consumed fewer chemicals and produced less sludge, and the effluent pH was more stable. The lowest energy consumption was calculated as 0.63 kWh/m^3 for iron and 0.70 kWh/m^3 for aluminium for the monopolar-parallel electrode connection. Sludge production varied between 0.65–1.00 kg/m^3 for iron and 0.90–1.30 kg/m^3 for aluminium electrodes. Electrocoagulation of textile wastewater using iron electrodes under the experimental conditions pH 7, 3 mA/cm^2 and 15 min electrocoagulation resulted in a treatment cost of 0.245 USD/m^3 wastewater.

Bayramoglu et al. [76] examined economic performance for the electrocoagulation of a textile effluent (COD: 2031 mg/L; TSS: 102 mg/L; conductivity: 2.31 mS/cm; turbidity: 671 NTU; pH: 8.88) from a plant producing

wastewater at a rate of 1000 m^3/d. Aluminium and iron electrode materials were used as sacrificial electrodes in parallel and serial connection modes. An initial pH of 7 for iron electrodes and an initial pH of 5 for aluminium electrodes were found to be the most suitable in terms of COD and turbidity removals, respectively. Increasing the applied current density from 3 to 6 mA/cm^2 did not increase the energy requirements and associated operating costs considerably when monopolar-parallel electrode connections were used.

Bayramoglu et al. [77] studied the effects of various parameters such as electric conductivity and pH, current density and operating time on the operating cost for electrocoagulation of a textile industry effluent (COD: 3420 mg/L; TOC: 900 mg/L; TSS: 1112 mg/L; conductivity: 3.88 mS/cm; turbidity: 5700 NTU; pH: 6.95) with aluminium and iron electrode materials, separately. The preliminary analysis of the total operating cost included material (electrodes) cost, electrical energy cost as well as well as labour, maintenance and other fixed costs. The latter costs items are largely independent of the type of the electrode material. Thus energy and electrode material costs were taken into account as major cost items in the present work as kWh per kg of COD removed:

$$\text{Total operation cost} = \text{Operation cost} + C_{\text{energy}}$$
$$+ C_{\text{electrode}} \quad (14)$$

where C_{energy} and $C_{\text{electrode}}$, are consumption quantities per kg of COD removed, which were obtained experimentally in this work.

Cost calculations showed that in the case of iron electrodes, the operational cost was approximately 0.10 USD/kg COD removed, and for aluminium electrodes it was calculated as 0.3 USD/kg COD removed. Electrode consumption cost accounted nearly 50% of the total cost for iron and 80% of the total cost for aluminium. The electrocoagulation process also comprised additional and different equipment than an electrolysis unit. A detailed economic and technical analysis of the entire process is necessary for more exact comparison of the electrode materials.

3. Leather tanning industry

Electrocoagulation for the treatment of leather tanning industry wastewaters has recently attracted great attention. This process, utilizing aluminium, iron and steel electrodes, has proven very effective in removing organic matter as well as some specific inorganic pollutants such as sulphide, trivalent chromium, oil and grease, and ammonia from leather tanning industry effluents. The high chloride content of the wastewaters (2000–8000 mg/L), originating from soaking and washing of salted hides and sheepskins, offers an inherent advantage for treating leather tanning industry effluents with electrocoagulation, since the presence of high amount of chloride leads to a decrease in energy consumption for the process owing to the increase in conductivity. Moreover, high concentration of chloride induces in situ electrochemical generation of the chlorine/hypochlorite couple acting as oxidants [20,78,79].

3.1. Organic matter, colour and turbidity

Two mechanisms involved in the abatement of organic matters in terms of COD and TOC via electrocoagulation are of importance for the leather tanning industry effluents [78,80]. The first mechanism is the removal of organic matters by indirect oxidation, apparently through chlorine species formed from chloride ions. The second mechanism with a role in the removal of organic matter, particularly in the colloidal form, is adsorption/entrapment on freshly produced metal hydroxide flocs. This mechanism is also responsible for the removal of the suspended solids corresponding to turbidity from the leather tanning industry effluents [80]. Therefore, it has been commonly inferred that increasing the amount of metal hydroxide flocs results in an improvement in the removal of organic matter and turbidity. Current density or cell current plays a determining role on the floc formation rate and on the rate and size of the bubble production. At higher cell current or current density, the larger amount of metal dissolution from sacrificial anode accelerates, and brings about a greater amount of metal hydroxide flocs for the removal of pollutants [78]. Furthermore, bubble density increases and bubble size diminishes with elevating cell current or current density, resulting in faster removal of pollutants. Hence, a number of laboratory-scale studies have been carried out to reveal the influence of this key process variable on organic matter, colour and turbidity removal performance.

Studies performed to determine the effect of cell current on organic matter removal from raw leather tanning industry effluents by electrocoagulation using either iron or aluminium electrodes in plate form have revealed that COD removal as well as TOC abatement were enhanced with elevating cell current due to acceleration of the rate of formation of metal hydroxide flocs [78,80,81]. In these studies, combined leather tanning industry effluents with COD concentrations ranging between 2000–8000 mg/L underwent an electrocoagulation process performed at low cell currents, and up to 90% COD removals were achieved [78,80,81]. On the other hand, Şengil and co-workers [82] have reported that there was an optimum current density value (35 mA/cm^2) yielding the highest COD removal efficiency (82%) for the treatment of tannery liming drum wastewater with electrocoagulation, since COD abatement efficiency did not improve further when the current density was elevated from 35 to 70 mA/cm^2. As their effluent was more concentrated in terms of COD (25,300 mg/L) and sulphide (3000 mg/L) than the combined leather tanning industry effluents, elevated current densities were required to attain satisfactory COD removal efficiencies. Taking into account that the lowest current density applied in their study was in the range of the low cell current employed for the

treatment of combined leather tanning industry effluents, it can be concluded that the increase in cell current or current density up to an optimum value has a positive influence on organic matter and turbidity abatement rates.

Anodic material plays a major role in electrocoagulation process performance. Three types of anodic materials, namely aluminium, steel and iron, have been commonly employed to treat leather tanning industry effluents. Findings indicate that the relative performance of the electrode material is variable and depends on the target pollutant to be removed. In a study by Benhadji and co-workers [80], electrocoagulation was performed using an aluminium anode and either an aluminium or steel cathode in plate form to treat leather tanning industry effluent. Aluminium was selected as an anode material because this material required relatively less oxidation potential. In their study, the best COD removal efficiencies as well as BOD_5 and turbidity abatement rates were obtained when the aluminium cathode was used, and good performance of the aluminium electrode as both anode and cathode was attributed to its low hydrogen overvoltage during electrocoagulation. Results from another comparative study indicated that electrocoagulation with aluminium electrode pairs yielded better effluent quality than electrocoagulation with aluminium and iron electrodes used in different combinations as anode and cathode, respectively, for the treatment of leather tanning industry effluent [83]. Contrary to these findings, iron or steel electrodes were found to be more effective in reducing COD from leather tanning industry effluents in the work of Şengil et al. [82]. In their study, the effectiveness of aluminium electrodes in removing colour and turbidity has also been reported. Feng and co-workers [78] proposed a two-stage electrocoagulation application as a pretreatment step to treat leather tanning industry effluent, instead of using a combination of anodic materials. In their trial, sulphide removal was targeted together with COD, TOC and ammonia abatements in the first-stage electrocoagulation with mild steel sheets, and in the following stage aluminium sheets were used to facilitate coagulation and flotation. The best pollutant removal performances were obtained by applying two-stage electrocoagulation. On the other hand, data obtained by Espinoza-Quiñones et al. [84] showed that electrocoagulation using aluminium electrodes exhibited better organic matter removal performance than that using iron electrodes, while iron electrodes were more effective in removing some inorganic pollutants such as chromium, calcium and zinc. It can be deduced from the published data that the selection of the appropriate anodic material with respect to the target pollutant is of great importance in order to achieve acceptable or satisfactory process performance.

Electrolysis time or circulation flow rate is an important operating parameter affecting pollutant removal performance as well as operational and maintenance costs. Electrolysis time is a function of process variables such as current density and wastewater character [85]. As mentioned earlier, current density governs the formation rate of metal hydroxide flocs and the rate and size of H_2 bubbles evolved [33]. Hence, the floc formation rate appreciably accelerates by increasing either the current density or electrolysis time. Considering that adsorption/entrapment on freshly produced metal hydroxide flocs is a dominant removal mechanism for organic matter from leather tanning industry effluents, organic matter removal efficiency improves with increasing current density or extending electrolysis time providing that the electrocoagulator is designed properly and other process variables, such as initial pH etc., are selected correctly. On the other hand, in the relevant literature it is clearly evident that the organic matter abatement rate is very fast for the first 10–30 min of electrocoagulation applications [78,80,82–84,86]. Therefore, an electrolysis time interval varying between 10 and 30 min, corresponding to low energy consumption, has been recommended as an optimum time period to achieve satisfactory pollutant removal efficiencies. Similar to electrolysis time, high circulating flow rates provide high organic matter removal efficiencies, since they can promote either turbulent flow or collision between active species and pollutant molecules [81].

As mentioned earlier, initial pH is important process variable influencing process performance. Therefore, the effect of this process variable on the organic matter removal from leather tanning industry effluents has been sought in some scientific works. The results have revealed that an initial pH in the range of 6.5–9.0 provided practically the same level of organic matter removal efficiencies for both iron and aluminium electrodes [81,84,86]. Hence, it can be concluded that the effect of initial pH on the organic matter removal efficiency is not significant within the pH range of 6.5–9.0.

In the electrocoagulation process, COD or TOC removal efficiency is closely related to initial organic matter concentration. The study results of Gilpavas and co-workers [83] indicated that both COD and TOC abatement rates were highly dependent on their initial concentrations, and an increase in the initial organic matter concentration caused a deceleration in both COD and TOC abatements.

Reaction kinetics for removal of organic matter, sulphide and oil-grease from source-based liming effluent by an electrocoagulation process operated in batch mode were expressed as pseudo-second-order kinetics [82]. Table 1 summarises the pseudo-second-order rate coefficients calculated by Şengil et al. [82]. As can be seen from the table, the regression coefficients are greater than 0.98, indicating very good fitness in all pollutants.
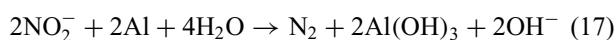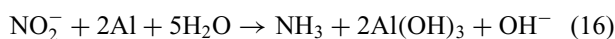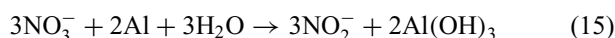
3.2. *Ammonia and nitrate*

Since ammonia salts are the most common chemicals used in the deliming process following the unhairing step, leather tanning industry effluents contain high concentrations of ammonium [87]. Two mechanisms are involved

Table 1. Pseudo-second-order reaction rate coefficients [82].

$k \times 10^5$ (L/mg $\times$ min)	R^2	Electrocoagulation operation conditions	Electrode
2.5_{COD}	0.991	$J = 7.85 \, \text{mA/cm}^2$; $pH_o = 3$; $t = 10 \, \text{min}$	Mild steel
$4.25_{sulfide}$	0.987	$J = 7.85 \, \text{mA/cm}^2$; $pH_o = 3$; $t = 10 \, \text{min}$	Mild steel
$2.97_{oil\text{-}grease}$	0.996	$J = 7.85 \, \text{mA/cm}^2$; $pH_o = 3$; $t = 10 \, \text{min}$	Mild steel

in ammonia removal from leather tanning industry effluent via electrocoagulation [78]. The first mechanism is the volatilization of ammonia, taking place at the pH values above 9.5. Therefore, ammonia elimination by this mechanism is closely related to pH increases experienced during the electrocoagulation process. When electrocoagulation is commenced near neutral pH values, the solution pH continuously increases as a consequence of cathodic hydroxyl formation and may reach alkaline pH values greater than 9.5, resulting in ammonia volatilization. Feng et al. pointed out that the H_2 bubbles produced during electrocoagulation helped the stripping of ammonia gas [78]. The second mechanism is the decomposition of ammonia to nitrogen gas by means of the chlorine/hypochlorite couple generated in situ [78]. The reactions responsible for the second mechanism are analogous to those of break-point chlorination [78]. The data obtained by Feng et al. [78] indicated that under the same electrocoagulation operation conditions, both aluminium and mild steel electrodes yielded the same level of ammonia removal efficiencies (around 30%). They have also reported that ammonia elimination performance could be improved by applying two-stage electrocoagulation, which would provide an additional 13% ammonia removal efficiency.

Nitrate is another nitrogen form originating from leather tanning industry effluents [87]. The mechanism and efficiency of electrochemical nitrate reduction depend on the cathode material used in the electrocoagulation application. Nitrate can be reduced by many metals such as magnesium, iron, tin, aluminium, etc. [88,89]. Therefore, the main mechanism of nitrate removal by electrocoagulation/floatation process with aluminium electrodes has been explained based on the reduction of nitrate by powdered aluminium [88,89]. According to this, aluminium oxidizes at the anode that can decompose and reduce nitrate to nitrite from water. Then, nitrite is converted to ammonia and nitrogen gas by the following reactions [80,89]:

$$3NO_3^- + 2Al + 3H_2O \rightarrow 3NO_2^- + 2Al(OH)_3 \quad (15)$$

$$NO_2^- + 2Al + 5H_2O \rightarrow NH_3 + 2Al(OH)_3 + OH^- \quad (16)$$

$$2NO_2^- + 2Al + 4H_2O \rightarrow N_2 + 2Al(OH)_3 + 2OH^- \quad (17)$$

The results of the study carried out by Emamjomeh et al. [89] using synthetically prepared samples containing nitrate indicated that (i) ammonia was the primary reaction product (40–70%) for electrocoagulation/floatation process using aluminium electrodes performed under different operation conditions; (ii) nitrate removal efficiency decreased with increasing initial nitrate concentration; (iii) an increase in initial pH in the range of pH 8–12 enhanced nitrate removal efficiency; and (iv) an increase in current density or an extension in electrolysis time significantly improved nitrate removal performance. Similar conclusions were also reached by Benhadji et al. [80] for nitrate removal from a leather tanning industry effluent by electrocoagulation with aluminium electrodes.

3.3. Sulphide

In the leather tanning industry, the unhairing process is commonly accomplished using sodium sulphide and lime in order to eliminate the hair on the skin [87]. Hence, sulphide concentrations may reach several thousand mg/L in the effluents originating from the beamhouse in leather tanning facilities [90]. In combined leather tanning effluents, sulphide concentrations vary in the range of 20–278 mg/L if the unhairing process is employed [91]. Henceforth, control of sulphide compounds is an important task in the wastewater management of such leather tanning facilities.

When iron or steel electrodes are used in the electrocoagulation process, the produced ferrous and ferric iron ions may react with sulphide species in two different ways. Ferrous iron tends to precipitate with sulphide species to form a variety of precipitants [92]. Ferric iron oxidizes sulphide to either sulphite or sulphate while being reduced itself into ferrous iron [92]. The reaction of ferrous iron with sulphide can be simplified as follows:

$$Fe^{2+} + S^{2-} \rightarrow FeS(s) \downarrow \quad (18)$$
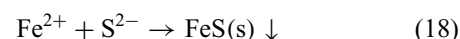
Other possible reactions between ferrous iron and sulphide have been described by Wei and Osseo-Asare [93]. The precipitation reaction proceeds via formation of intermediate species before precipitating FeS(s). The formation of intermediate species is a rapid reaction and completes in the first few minutes (Equation (18)). On the other hand, the conversion rate of these intermediate species to FeS(s) is slow (Equation (19)). These reactions can be presented as follows [92,93]:

$$Fe^{2+} + nHS^- \rightarrow Fe(HS)_n^{2-n} \quad (19)$$

$$Fe(HS)_n^{2-n} \rightarrow FeS(s)\downarrow + H^+ + (n-1)HS^- \quad (20)$$
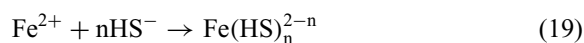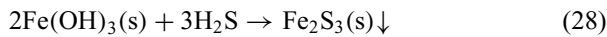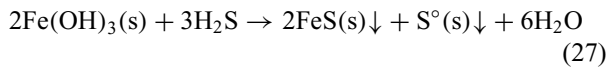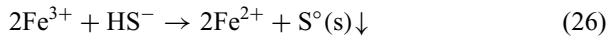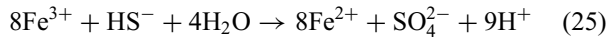
In addition, one of the abovementioned intermediates may involve in the precipitation of solid pyrite (FeS_2) under anaerobic conditions according to the following reactions [92,94]:

$$FeS + H_2S \rightarrow Fe(HS)_2 \tag{21}$$

$$Fe(HS)_2 \rightarrow FeS_2(s)\downarrow + H_2 \tag{22}$$
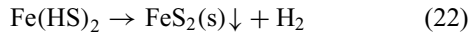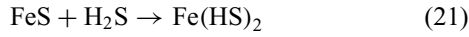
Under aerobic conditions, the following reactions have been suggested for the pyrite precipitation [92,95]:

$$FeS + S^\circ \rightarrow FeS_2(s)\downarrow \tag{23}$$

$$Fe^{2+} + 2HS^- + 0.5O_2 \rightarrow FeS_2(s)\downarrow + H_2O + H^+ \tag{24}$$
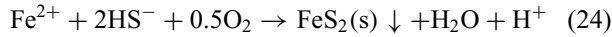
In the case of ferric iron, either ferric iron or insoluble ferric hydroxide solid reacts with HS^- or H_2S to form a variety of species according to the following reactions [92,96]:

$$8Fe^{3+} + HS^- + 4H_2O \rightarrow 8Fe^{2+} + SO_4^{2-} + 9H^+ \tag{25}$$

$$2Fe^{3+} + HS^- \rightarrow 2Fe^{2+} + S^\circ(s)\downarrow \tag{26}$$

$$2Fe(OH)_3(s) + 3H_2S \rightarrow 2FeS(s)\downarrow + S^\circ(s)\downarrow + 6H_2O \tag{27}$$

$$2Fe(OH)_3(s) + 3H_2S \rightarrow Fe_2S_3(s)\downarrow \tag{28}$$

It has been also suggested that more stable and insoluble species, for example FeS_2 and greigite (Fe_3S_4), may be produced via further transformation of $Fe_2S_3(s)$ [92,96].

In the case of aluminium, the following reaction between aluminium and sulphide takes place [78,97]:

$$2Al^{3+} + 3S^{2-} \rightarrow Al_2S_3(s)\downarrow \tag{29}$$
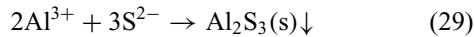
As Al_2S_3 is an unstable solid phase, it converts into stable $Al(OH)_3$ and sulphide releases into the solution as a consequence of this transformation [78].

Sulphide removal from combined leather tanning effluents and source-separated beamhouse effluents by electrocoagulation using either aluminium, mild steel or iron anodes has been investigated in a few studies [78,82,97]. The results of a study carried out using a combined leather tanning industry effluent revealed that the initial elimination of sulphide (91.9%) was quite fast and realized within 5 min when mild steel anodes were used. In the study of Feng et al. [78] mild steel anodes were found to be superior to aluminium anodes, since less than 12% sulphide removal was obtained by aluminium anodes at the end of 60 min of electrolysis time and the initial pH of 7.85. This low sulphide removal efficiency was attributed to the conversion of Al_2S_3 into $Al(OH)_3$. A similar conclusion has been made by Şengil et al. [82], as aluminium and mild steel anodes yielded around 20% and 60% sulphide removal efficiencies, respectively, under the same electrocoagulation operating conditions ($J = 6.42\,mA/cm^2$ and $pH_o = 3.0$). For sulphide removal from a tannery liming drum effluent, optimum electrocoagulation operating conditions were determined as a current density of $35\,mA/cm^2$, an electrolysis time of 10 min and an initial pH of 3.0 in their experimental study. Under optimum operation conditions, 90% sulphide removal was achieved. It should be pointed out that the initial pH of 3.0, determined as the optimum pH in their study, may speed up the evolution and volatilization of toxic H_2S gas, causing serious health problems. In addition to this, as the liming drum streams contain extremely high amounts calcium resulting in a pH than higher 12, addition of a large amount of acid is required to decrease the liquor pH to 3.0. Presumably because of these disadvantages, electrocoagulation applications were commenced at the original pH (11.86) of a beamhouse effluent in the study of Murugananthan et al. [97]. Compared with the experimental data of Şengil et al. [82], initiating the electrocoagulation process at an alkali pH value had a deleterious effect on sulphide removal efficiency. When iron anodes were used 73% sulphide removal efficiency was obtained. Although the effectiveness of iron anodes in removing sulphide has also been reported in their study, sulphide removal efficiency was only 4% higher than that of aluminium anodes (69%) under the same electrocoagulation operating conditions ($J = 47\,mA/cm^2$, $pH_o = 11.86$ and $t = 20\,min$).

It should be pointed out that, in the literature cited here, the reaction liquor turns into a dark colour as a result of insoluble FeS formation, and the sulphide concentration drops rapidly in the case of iron and mild steel electrodes.

3.4.   Trivalent chromium

When tanning and retanning processes are undertaken using trivalent chromium salts, trivalent chromium-bearing effluents are generated from the leather tanning facilities [87]. Trivalent chromium concentrations vary in the range of 5–1329 mg/L in combined leather tanning industry effluents [91]. Although chemical precipitation is a fully proven trivalent chromium removal method when applied to combined leather tanning industry wastewaters, electrocoagulation using either aluminium or iron-based electrodes has been recently nominated as a candidate technique for the treatment of trivalent chromium-bearing wastewaters originating from the leather tanning industry due to its several inherent advantages.

The main mechanism in the treatment of trivalent chromium by electrocoagulation is hydroxide precipitation, which occurs as a consequence of hydroxyl ion production at the cathode. Hydroxide precipitation is based on the low solubility of metal hydroxides at a specific pH value, termed as optimum pH [98]. Solubility of a certain metal reaches minimum at the optimum pH, which is a characteristic value for each metal. Although the optimum pH of trivalent chromium is 9.0, resulting in 0.007 mg/L chromium solubility, chromium solubilities of less than 0.01 mg/L can be obtained by hydroxide precipitation at a wide range of pH values varying between 7.0 and 11.0 [98].

Published data have disclosed that complete trivalent chromium removal can be achieved by applying electro-coagulation using either aluminium or iron-based anodes [80,81,83,84,86]. As mentioned above, trivalent chromium removal performance is closely related to the solution pH reached through the electrocoagulation process. Hence, researchers have focused on the effect of initial pH on trivalent chromium removal efficiency. The results demonstrated that trivalent chromium removal efficiency did not depend on initial pH, and almost complete trivalent chromium removal could be attained when electrocoagulation was commenced at initial pH values of 6.5–9.0. This independence can be attributed to the low solubility of trivalent chromium in the pH range of 7.0–11.0. On the other hand, it has been reported that other electrocoagulation operational parameters, such as current density and electrolysis time, affected trivalent chromium removal from leather tanning industry effluents. An increase in current density or an extension in electrolysis time improved trivalent chromium removal efficiencies. Nevertheless, it has been pointed out that an electrolysis time in the range of 15–45 min would be enough to attain cost-effective trivalent chromium removal [80,81,84,86]. In addition, it has been reported that (i) the removal rate was very low at low initial trivalent chromium concentrations; (ii) at high initial trivalent chromium concentrations the removal efficiency decreased very quickly, owing to electrode saturation as a result of the formation of an oxide layer on the electrode surface; and (iii) higher trivalent chromium concentrations required a longer electrolysis times to achieve the same removal efficiency [83].

Gilpavas and co-workers [83] have implemented a response surface method in order to establish optimal electrocoagulation operation conditions for maximum trivalent chromium abatement from leather tanning industry effluent. By applying a quadratic regression model they obtained the following equation to represent the percentage trivalent removal efficiency (%R) as a function of the current density (J), the distance between electrodes (G) and the initial chromium concentration (C_o):

$$\%R = 109.41 + 0.293 \times J + 28.87 \times C_o - 42.26 \times G$$
$$- 0.0024 \times J - 0.028 \times J \times C_o + 0.016 \times J \times G$$
$$- 10.98 \times C_o^2 + 1.08 \times C_o \times G + 9.5 \times G^2 \quad (30)$$

The optimal operation conditions based on statistical analysis for trivalent chromium removal by electrocoagulation process were determined by Gilpavas et al. as a current density of $57.87 \, mA/cm^2$, an electrode gap of 0.5 cm, an initial trivalent chromium concentration of 3596 mg/L, and aluminium as the electrode material [83]. In another study, a fractional factorial 2^3 experimental design was applied in order to determine optimal values of the system variables [84]. ANOVA for effluent trivalent chromium concentration has confirmed the model predicted by the experimental design within a 95% confidence level.

3.5. Other pollutants

Electrocoagulation is also an effective technique in the treatment of oil and grease-bearing wastewaters. The capability of the process in the removal of oil and grease from several industrial effluents has been well documented. Therefore, the effectiveness of the process in the treatment of oil and grease originating from the leather tanning industry has been investigated in a few works [81,82]. The results indicated that almost complete oil and grease removal could be achieved by electrocoagulation operated under optimum conditions. In these studies, the best oil and grease removal performances were obtained when aluminium anodes were used. Results revealed that (i) oil and grease removal efficiency was not significantly affected by electrocoagulation operating parameters such as the initial pH, the electrolysis time, the flow rate and the current density; and (ii) an electrolysis time in the range of 5–10 min was enough to achieve almost complete oil and grease removal.

3.6. Energy consumption

Table 2 outlines the energy consumptions that have been reported for the treatment of leather tanning industry effluents by electrocoagulation. As seen from the table, there is no correlation among the reported energy consumptions, and energy consumption varies significantly depending on electrocoagulation operating conditions and the target pollutant to be treated.

4. Pulp and paper industry

The pulp and paper industry is water intensive, consuming large volumes of water in the preparation of feed material

Table 2. Electrical energy consumptions (EEC) for the treatment of leather tanning industry wastewater by electrocoagulation.

EEC kWh/m^3	Electrocoagulation operation conditions	Electrode	[Ref]
0.13	$J = 22.4 \, mA/cm^2$; $pH_o = 7-9$; $t = 20$ min; general	Aluminium	[81]
5.768	$J = 35 \, mA/cm^2$; $pH_o = 3$; $t = 10$ min; for COD	Mild steel	[82]
0.524	$J = 35 \, mA/cm^2$; $pH_o = 3$; $t = 10$ min; for S	Mild steel	[82]
1.5×10^{-4}	$J = 3.5 \, mA/cm^2$; $pH_o = 3$; $t = 10$ min; for oil and grease	Mild steel	[82]
0.25	$J \cong 0.57 \, mA/cm^2$; $pH_o = 7.85$; $t = 20$ min; for COD	Aluminium	[78]

and in the overall production process. The most significant sources of pollution among various operation stages in pulp and paper industry are wood debarking, pulping, pulp washing, pulp bleaching and papermaking processes. Pulp and paper industry wastewaters are characterized by high levels of organic matter (e.g. COD and TOC), suspended solids and strong colour. The strong colour of the wastewater is mainly attributed to the complex compounds derived from polymerization between lignin-degraded products and tannin during pulping/bleaching operations. Pulp and paper industry wastewaters also contain various toxic chemicals including organic substances (resin acids, tannins, phenols, chlorinated organic compounds), heavy metals, alkali and alkaline earth metals, and metalloids. Thus, the presence of strongly toxic species, or species that are difficult to degrade, (e.g. lignin), not only affects the wastewater COD levels but also renders their disposal very problematic. The effects of pulp and paper industry wastewaters on the environment are bacterial and algal slime growth, thermal impacts, scum formation, colour problems and loss of both biodiversity and aesthetic beauty [99]. The toxic pollutants in pulp and paper industry wastewaters can cause long-term toxic effects on animal life, such as respiratory stress, toxicity, mutagenicity and genotoxicity.

Several authors have reported that current density has significant influence on the efficiency of the electrocoagulation process. This can be attributed to the fact that the applied current density determines the coagulant and bubble production rate, size and floc growth. In addition, it has been demonstrated that bubble density increases and size decreases with increasing current density, resulting in a greater upwards flux and a faster removal of pollutants and sludge flotation. It is also advisable to limit the applied current density in order to avoid excessive oxygen evolution, as well as to eliminate other adverse effects such as heat generation. Hence, researchers have focused on the effects of current density on the treatment of pulp and paper industry wastewaters by electrocoagulation. In these studies it has been reported that removal efficiencies in terms of COD, BOD_5, turbidity and colour as well as phenol content were increased with increasing current density to an optimum value; however, further increase did not show any significant improvement in treatment performance. In the study of Zaied and Bellakhal [100] the highest current ($16.7\,mA/cm^2$) produced the quickest treatment, with 80% COD reduction occurring after only 30 min by using aluminium electrodes. Khansorthong and Hunsom [101] investigated colour and COD removal efficiencies at different current densities in the range of 1.04–$3.11\,mA/cm^2$ with a fixed circulating flow rate of wastewater of 6.9 L/min by iron plate electrodes. The initial wastewater pH, colour and total COD values were 7.90, 1909 Pt-Co unit and 623 mg/L, respectively. Colour reduction was very fast, with approximately 80% reduction within 15 min at all current densities, and attained a constant level by 30 min. In their study, the optimum current density chosen as $2.07\,mA/cm^2$ yielded

93.7% and 73.6% reductions in colour and total COD levels, respectively, leaving remnant levels of colour (119 Pt-Co units) and total COD (237 mg/L) in the treated wastewater. Electrocoagulation was proposed as a suitable technology to meet standards of water discharge and, even better, as a treatment option for removal of turbidity by Terrazas et al. [102]. In their work, electrocoagulation using aluminium plate electrodes was evaluated in terms of turbidity removal, and the effects of current density and cell voltage in the overall process were discussed. The turbidity removal efficiency showed a slight improvement as the current density increased but, as expected, there was also an increase in cell voltage and therefore energy consumption, which was attributed to the decrease in conductivity. The highest turbidity removal was achieved as 92% where the removal of COD and BOD_5 was not higher than 1322 mg/L (50%) and 1012 mg/L (60%), respectively. The results of Uğurlu et al. [10] have also confirmed that the removal of lignin, phenol, BOD_5 and COD increased with increasing current intensity. In experiments carried out at different current intensities, higher removal levels were explained through a decrease in intra-resistance of the solution and consequently an increase in the transfer speed of organic species to electrodes. In addition, it was observed that a range of 2.5–$5\,mA/cm^2$ was sufficient for the removal of the pollutants investigated.

Vepsäläinen et al. [103] studied the removal of dissolved sulphide and phosphorus in pulp and paper industry wastewater by electrocoagulation. According to their results, current density did not have a noticeable effect on the electric charge or iron concentration required per unit of sulphide precipitated. This is important when considering full-scale applications, where the required electrode surface area of the system depends on the current (A) and current density (mA/cm^2) targets of the treatment. However, high current density increases the voltage and power consumption of the system, and consequently the operating cost of the electrocoagulation process. In their study, current density did not show a significant effect on phosphorous removal rates at $3.6\,mA/cm^2$, $7.1\,mA/cm^2$ and $10.7\,mA/cm^2$. However, current efficiency decreased slightly when current densities were $14\,mA/cm^2$ and $17.9\,mA/cm^2$, and this was attributed to a faster flotation and a shorter contact time between pollutants and the coagulants produced.

The electrocoagulation process was proposed as a pre-treatment step for pulp and paper industry wastewaters by Soloman et al. [104]. In their study, the best operational conditions giving maximum improvement in biodegradability of the effluent were determined using response surface methodology. Their study demonstrated that the biodegradability index was directly related to both electrolysis time and current density. There was a decrease in the resulting biodegradability index after treatment duration of 6.9 min and current density of $11.29\,mA/cm^2$. At the early stage of treatment, long-chain organic matter such as lignin was converted into lower molecular weight components that did not considerably reduce COD but increased BOD_5,

resulting in an increase in biodegradability. The effect of current density on biodegradability index was also explained as a result of the relative contribution of the oxidation and coagulation mechanisms. At a higher current density, the optimal time for maximum biodegradability index was expected to be reached at the early stages of electrocoagulation. In the investigation, the oxidation and coagulation mechanisms started attacking the more easily degradable part at $11.29 \, \text{mA/cm}^2$ when compared with lower current density values, which may result in a decrease in the biodegradability index.

The influence of electrode material on the treatment of pulp and paper industry wastewaters has been extensively studied. Aluminium and iron electrodes were used as anode and cathode materials in these studies. Different combinations of these materials were also tested and the treatment performances of electrocoagulation processes were evaluated. Both electrode materials as well as their combinations were found to be effective in the treatment of pulp and paper industry wastewaters by electrocoagulation. However, the results indicated that aluminium electrodes produce better treatment performance than iron electrodes. Zaied and Bellakhal [100] found that both materials (aluminium and iron) showed similar efficiency in reducing COD and polyphenol index. Nevertheless, with increasing time, rates of COD and polyphenol removal obtained with the aluminium electrode were slightly higher than those achieved with iron electrodes. In addition, aluminium is more effective than iron in removing colour. Similar observations were also made by Zodi et al. [105] for COD and arsenic removal. In their study, the maximum COD removal at 10 and $15 \, \text{mA/cm}^2$ were 47% and 68%, respectively, with aluminium electrodes, and 32% and 41%, respectively, with iron electrodes. In their study, more than 91.5% of arsenic was removed with aluminium electrodes at $10 \, \text{mA/cm}^2$. Arsenic removal efficiency reached 86% and 88% at 10 and $15 \, \text{mA/cm}^2$, respectively, when iron electrodes were used. Treatment with iron and aluminium electrodes had different kinetics in terms of turbidity removal [105]. In fact, with iron electrodes, turbidity decreased rapidly during the early stages of electrocoagulation; nevertheless, at the end of the treatment, removal remained incomplete. In contrast, with aluminium electrodes there was no turbidity abatement during the early stages of electrocoagulation, but in the later stages aluminium electrodes had higher removal efficiency than that of iron electrodes. On the contrary, Parama Kalyani et al. [106] concluded that the COD and colour removals were higher in the case of a mild steel anode than the aluminium anode for the same operating conditions. Katal and Pahlavanzadeh [107] recommended effective electrode combinations for removal efficiencies in treating pulp and paper industry wastewater in the following order: (i) aluminium–aluminium electrode combination for removing colour; (ii) iron–iron electrode combination for removing COD and phenol; and (iii) aluminium–iron or iron–aluminium electrode combination for removing

colour, COD and phenol at high efficiencies. Uğurlu et al. [10] concluded that formation of the coagulate depends on the structures of the contaminants, thus on the ability of contaminant molecules to be adsorbed on hydrolysis products or flocs. In their study, it was observed that experiments carried out at 12 V, treatment time of 2 min and a current intensity of 77.13 mA were sufficient for the removal of lignin, phenol, BOD_5 and COD with aluminium and iron electrodes. The removal capacities of the process using an aluminium electrode were 80% of lignin, 98% of phenol, 70% of BOD_5 and 75% of COD after 7.5 min. By using iron electrodes the removal capacities were found to be 92%, 93%, 80% and 55%, respectively.

Electrode material also plays a major role on the sludge characteristics generated during the electrocoagulation process. Sludge volume index (SVI) was used by Zodi et al. [105] in order to characterize the settling characteristics of electrocoagulation sludge generated by aluminium and iron electrodes. The high SVI values obtained for aluminium electrodes were due to the fact that the sludge formed was light and fluffy, hence settleability was hindered. On the contrary, SVI values obtained for the sludge formed by iron electrodes was considerably lower than the sludge formed by aluminium electrodes. This was attributed to the fact that the sludge formed by iron electrodes was heavy enough to produce a compact layer.

The effect of the electrode gap (electrode distance) on the treatment performance of electrocoagulation has been evaluated in some studies [102,108]. It was reported that the treatment performance of the electrocoagulation process decreased with gap increment. This effect was associated with the process of flocculation, as the clots would be more disperse and therefore floc formation would be retarded. However, it was also reported that lower electrode gaps resulted in inefficient removal of pollutants, as the close gap between anode and cathode obstructed solid and fluid transfer [108]. The results of the study carried out by Terrazas et al. [102] showed that a separation gap of 1 cm produced a faster build-up of sludge; however, it favoured better turbidity removal and lower energy consumption than larger separations gaps. The electrode gap should be considered very carefully for reactor design, as it greatly impacts the performance of the process.

Another important parameter is the retention time or treatment (electrolysis) time of the wastewater in the reactor. The literature has indicated that electrocoagulation treatment performance increases by increasing the treatment time, due to the acceleration effect of treatment time on floc formation rate [10,100,106]. In the electrocoagulation process, metal hydroxide flocs ($Al(OH)_3$ or $Fe(OH)_3$) are generated in situ once the charge is applied, and the generated flocs adsorb the organic molecules present in the effluent, resulting in the removal of pollutants with treatment time. It is also thought that increasing the treatment time improves the efficiency of removal by inducing faster aggregation of the hydrolysed products [10]. On the

other hand for lignin removal, when an aluminium electrode was used, initially a rapid increase was observed with increasing treatment time; however, after a certain treatment time period, the percentage of lignin removal remained approximately constant [10].

Depending upon the degree of acid re-treatment and bleaching of wood pulp, along with the local water pH for washings, pulp and paper industry wastewater may range in pH from acidic to mildly alkaline; these conditions will potentially affect the electrocoagulation process [101]. All reported experimental results have revealed that treatment efficiency was very poor either at low ($<$2.0) or high pH ($>$8.0) values, with the optimal pH at around 7.0 at which higher phenol, colour, COD and BOD_5 removal efficiencies could be reached, by using either aluminium or iron electrodes. [100,106–108]. It was concluded that at these pH values freshly formed amorphous $Al(OH)_3$ or $Fe(OH)_3$ has large surface areas, which are beneficial for fast adsorption of soluble organic compounds and entrapping of colloidal particles, and hence more reduction of phenol, colour, COD and BOD_5. Further increasing the pH beyond 7.0 decreased the reduction of phenol, colour, COD and BOD_5, mainly due to the formation of $Al(OH)_4^-$ or $Fe(OH)_4^-$ which did not contribute to the reduction of phenol, colour, COD and BOD_5 [106–108].

As previously noted, the electrocoagulation process requires the presence of salts as supporting electrolytes to increase solution conductivity. Solution conductivity affects cell voltage, current efficiency and consumption of electrical energy in electrolytic cells [109]. The effect of solution conductivity on electrocoagulation performance for the treatment of pulp and paper industry wastewaters has been investigated in a number of studies. In these studies, NaCl was used as the supporting electrolyte to increase solution conductivity, and it was concluded that increasing the solution conductivity increased the removal efficiencies up to an optimum value. However, beyond this value, removal efficiencies were not enhanced by increasing the solution conductivity [106,108]. The enhancement of removal efficiencies can be explained as follows: when chlorides are present in the solution, the products of anodic discharge are Cl_2 and OCl^-. The OCl^- itself a strong oxidant and capable of oxidizing the organic molecules present in the effluent. Thus, the supporting electrolyte not only increases the conductivity but also contributes as a strong oxidizing agent.

In the study of Parama Kalyani et al. [106], it was stated that the COD removal percentage is proportional to pollutant concentration and the amount of hydroxide flocs generated for the treatment of pulp and paper industry wastewaters by electrocoagulation. Uğurlu et al. [10] also used a pseudo-first-order kinetic approach for expressing the kinetics of COD, lignin, phenol and BOD_5 removal. Table 3 provides the pseudo-first-order reaction rate constants (k, 1/min), and respective R^2 values for phenol, lignin, COD and BOD_5 removals from the relevant scientific literature. The data obtained by Khansorthong and Hunsom [101] indicated that the kinetics of the rate of colour and total COD removal were directly proportional to the applied current density, and the rate constant of colour removal was a little higher (faster) than that of total COD under the same conditions.

One of the integral parameters that must be evaluated prior to implementation of the electrocoagulation process is the operating cost (the costs of electricity, electrodes and sludge treatment). Selection of appropriate operational conditions (optimum operating parameters) should be performed to meet all economic aspects for successful implementation [110]. Table 4 summarizes the energy consumptions that have been reported for the treatment of the pulp and paper industry wastewaters by the electrocoagulation process.

5. Olive mill wastewaters

Olive mill wastewater is one of the most complex effluents generated by industrial activities. Due to the unique features associated with this type of agro-wastewater, namely seasonal and localized production and a high organic carbon content quite resistant to biodegradation, olive mill wastewater constitutes a serious environmental problem [111–113]. The characteristics of olive mill wastewater largely depend on the type (two- or three-phase process) as well as mode (continuous or batch) of the olive oil extraction technique employed. The strong organic carbon content of olive oil wastewaters − often associated with a COD level in excess of 30,000 mg/L−inherently involves a great variety complex organic pollutants, including several aromatic (e.g. p-coumaric acid, benzofurane, hydroxytyrosol, tyrosol) and aliphatic (e.g. hexane, decanoic acid, dichloropropene) compounds [114,115]. Olive mill wastewater also contains inorganics such as potassium and sodium chlorides, sulphates and phosphates, as well as calcium, iron, magnesium, sodium, copper and traces of other elements. Treatment of olive mill wastewater has always been considered as a challenging issue for scientists. Consequently, the wastewater has served as a platform of trial and error for a large spectrum of different treatment options [116]. In the recent past, electrocoagulation has been tested for the treatment of olive mill wastewater [117–123]. In these studies, numerous experimental runs have been carried out in order to determine the performance of the electrocoagulation process as a function of operating conditions such as current density, electrode material, initial pH, etc., and the response of the process has been evaluated in terms of removal efficiencies of pollutants and energy consumption. However, the reported results also identified significant drawbacks, and indicated that no single technology could be applied to olive mill wastewater as a stand-alone treatment option.

Electrocoagulation prior to biological treatment was considered a suitable pretreatment stage owing to the treatment performance of the process [120,123]. Khoufi et al.

Table 3. Summary of the kinetic data of the pulp and paper industry wastewaters by the electrocoagulation process.

Parameter	k (1/min)	R^2	Electrocoagulation operation conditions	Electrode	[Ref]
COD	0.085	0.990	CP* $= 12$ V; $pH_o = 7.6$; $t = 5$ min	Iron	[10]
	0.118	0.810	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min	Aluminium	[10]
	0.050	-	$J = 10$ mA/cm^2; $pH_o = 5.0$; NaCl $= 400$ mg/L	Aluminium	[106]
	0.058	-	$J = 10$ mA/cm^2; $pH_o = 5.0$; NaCl $= 400$ mg/L	Mild Steel	[106]
	0.046	-	$J = 10$ mA/cm^2; $pH_o = 7.0$; NaCl $= 400$ mg/L	Aluminium	[106]
	0.070	-	$J = 10$ mA/cm^2; $pH_o = 7.0$; NaCl $= 400$ mg/L	Mild Steel	[106]
	0.046	-	$J = 10$ mA/cm^2; $pH_o = 9.0$; NaCl $= 400$ mg/L	Aluminium	[106]
	0.061	-	$J = 10$ mA/cm^2; $pH_o = 9.0$; NaCl $= 400$ mg/L	Mild Steel	[106]
	0.021	-	$J = 5$ mA/cm^2; $pH_o = 7.0$; NaCl $= 400$ mg/L	Aluminium	[106]
	0.023	-	$J = 5$ mA/cm^2; $pH_o = 7.0$; NaCl $= 400$ mg/L	Mild Steel	[106]
	0.051	-	$J = 10$ mA/cm^2; $pH_o = 7.0$; NaCl $= 400$ mg/L	Aluminium	[106]
	0.073	-	$J = 10$ mA/cm^2; $pH_o = 7.0$; NaCl $= 400$ mg/L	Mild Steel	[106]
	0.051	-	$J = 15$ mA/cm^2; $pH_o = 7.0$; NaCl $= 400$ mg/L	Aluminium	[106]
	0.073	-	$J = 15$ mA/cm^2; $pH_o = 7.0$; NaCl $= 400$ mg/L	Mild Steel	[106]
	0.038	-	$J = 10$ mA/cm^2; $pH_o = 7.0$; NaCl $= 200$ mg/L	Aluminium	[106]
	0.057	-	$J = 10$ mA/cm^2; $pH_o = 7.0$; NaCl $= 200$ mg/L	Mild Steel	[106]
	0.055	-	$J = 10$ mA/cm^2; $pH_o = 7.0$; NaCl $= 400$ mg/L	Aluminium	[106]
	0.071	-	$J = 10$ mA/cm^2; $pH_o = 7.0$; NaCl $= 400$ mg/L	Mild Steel	[106]
	0.058	-	$J = 10$ mA/cm^2; $pH_o = 7.0$; NaCl $= 600$ mg/L	Aluminium	[106]
	0.082	-	$J = 10$ mA/cm^2; $pH_o = 7.0$; NaCl $= 600$ mg/L	Mild Steel	[106]
BOD$_5$	0.119	0.800	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min	Iron	[10]
	0.159	0.910	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min	Aluminium	[10]
Lignin	0.086	0.920	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min	Iron	[10]
	0.281	0.890	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min	Aluminium	[10]
Phenol	0.456	0.990	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min	Iron	[10]
	0.335	0.900	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min	Aluminium	[10]

*Cell potential.

Table 4. Summary of the energy consumption data for the treatment of pulp and paper industry wastewaters by the electrocoagulation process.

SEC* kWh/kg of pollutant	EEC kWh/m^3	Electrocoagulation operation conditions	Electrode	[Ref]
	10.1–12.9	$J = 15$ mA/cm^2; $pH_o = 7.0$; $t = 20$ min; NaCl $= 0.5 - 2$ g/L; Rotational Speed $= 50$–200 rpm; for colour	Aluminium	[108]
	<1.2	$J = 1.04 - 3.11$ mA/cm^2; $pH_o = 5.57 - 9.33$; for colour and COD	Iron	[101]
1.17–1.21	-	$J = 11.29$ mA/cm^2; $pH_o = 7.3$; $t = 6.9$ min; for COD	Iron	[104]
≈1.6	-	$J = 10$ mA/cm^2; $pH_o = 12.0$; $t = 50$ min; for COD	Iron	[100]
≈5.0	-	$J = 10$ mA/cm^2; $pH_o = 12.0$; $t = 50$ min; for polyphenols	Iron	[100]
≈1.4	-	$J = 10$ mA/cm^2; $pH_o = 12.0$; $t = 50$ min; for COD	Aluminium	[100]
≈4.0	-	$J = 10$ mA/cm^2; $pH_o = 12.0$; $t = 50$ min; for polyphenols	Aluminium	[100]
0.6	0.136	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min; for COD	Iron	[10]
0.5	0.105	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min; for COD	Aluminium	[10]
11.0	0.113	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min; for BOD$_5$	Iron	[10]
5.1	0.091	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min; for BOD$_5$	Aluminium	[10]
7.13×10^4	96.25	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min; for lignin	Iron	[10]
7.15×10^4	95.52	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min; for lignin	Aluminium	[10]
17.37×10^4	92.93	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min; for phenol	Iron	[10]
14.89×10^4	79.66	CP $= 12$ V; $pH_o = 7.6$; $t = 5$ min; for phenol	Aluminium	[10]

*Specific energy consumption

[120] investigated the effect of the electrocoagulation process, in which most phenolic compounds were polymerised, as a pretreatment to detoxify olive mill wastewater for anaerobic post treatment. For that aim, investigation of the main chemical and physical characteristics of olive mill wastewater was carried out on crude and electrocoagulated

wastewater. Biodegradability was measured according to the ratio between the BOD_5 and COD, whose value must be less or equal to 0.5. After electrocoagulation the soluble COD of olive mill wastewater decreased to approximately 33.6% of the initial value (initial COD = 36, 900 mg/L) and the BOD_5/COD ratio was increased to 0.58 (initial BOD_5/COD = 0.33). This result highlighted the ability of the electrocoagulation process using iron electrodes to eliminate soluble compounds present in olive mill wastewaters. Chromatography analysis and the Folin–Ciocalteu method confirmed the removal of most low molecular mass phenolics (removal efficiency = 76.2%) and ortho-diphenols (removal efficiency = 47.5%). The pretreatment of olive mill wastewater by electrocoagulation also decreased the inhibition of *Vibrio fisheri* luminescence by 66.4%, whereas untreated olive mill wastewater exhibited 100% inhibition. The electrocoagulation process applied to olive mill wastewater resulted in the removal of a large amount of recalcitrant polyphenolic compounds, and consequently a decrease in toxicity [124]. Using electrocoagulation for the removal of phenolic compounds and possibly other toxic materials that inhibit the growth of anaerobic microorganisms contributed significantly to increasing the efficiency of anaerobic digestion.

In another study conducted by Hanafi et al. [123] olive mill wastewater was pretreated first by electrocoagulation using aluminium electrodes, and then by a biological process using a selected strain of *Aspergillus niger* van Tieghem. The effects of the treatments were assessed through COD removal, reduction of total phenols and the decrease of phytotoxicity using durum wheat (*Triticum durum*) seeds. In their study the concentration of phenolics (removal efficiency = 76%) was significantly reduced during electrocoagulation. The authors concluded that the effluent quality of the olive mill wastewater pretreated by the electrocoagulation process was excellent, and it could be directly fed as influent to the aerobic treatment stage.

The electrocoagulation process has also been combined with ultrafiltration as a post-treatment method to treat olive mill wastewater [125]. In the study conducted by Yahiaoui et al. [125], an ultrafiltration process equipped with a CERAVER membrane was used as pretreatment for electrocoagulation application. The obtained permeate for ultrafiltration with an average COD of about 1.1 g/L was treated in a electrochemical reactor equipped with bipolar iron plate electrodes. The results obtained from this study showed that the optimum COD removal rate was obtained at a current density of 9.33 mA/cm² and pH ranging from 4.5–6.5. At the optimum operational parameters for the experiments, the electrocoagulation process was able to reduce COD from 1.1 g/L to 78 mg/L, allowing direct discharge of the treated olive mill wastewater by meeting the wastewater discharge standards (<125 mg/L).

The collision between particles, floc growth and the potential for material removal, both pollutant and coagulant, by coagulation and/or flotation are determined by the applied current density. As reported in the relevant scientific literature, for a given treatment time, the performance of the electrocoagulation process increases significantly with the increase of applied current density. It should be also mentioned that as the current density decreases, the time needed to achieve similar efficiencies increases. The effect of current density on the treatment performance of electrocoagulation as applied to olive mill wastewaters has been discussed by several researchers [117,119,122]. Hanafi et al. [122] have observed an optimum current density value of 25 mA/cm² where the removal efficiencies of COD, polyphenols and colour were 80%, 77% and 88%, respectively. The electrodes (anode + cathode) consumption was calculated as 0.6–0.7 kg Al/m³ at the conditions investigated. In their study, a further increase in current density (38 mA/cm²) induced a relatively high increase in electrode consumption (1.4 kg Al/m³), but no more COD and polyphenol removal occurred regardless of the current used. Arslan-Alaton et al. [121] also studied the effect of current density on the removal of COD, TOC and antioxidant activity from olive mill wastewaters. It can be inferred from their data that increasing the applied electrical current (from 33 mA/cm² to 44 mA/cm²) resulted in a significant acceleration in COD and TOC removals. Accordingly, the highest overall COD and TOC removal efficiencies (46% and 49%, respectively) were obtained at the run with the higher electrical current value (44 mA/cm²). Based on published data it can be concluded that the applied current density used in the electrocoagulation process should be optimized with a reasonable treatment time to achieve an acceptable treatment performance for the lowest total investment and operational cost.

Electrode assembly is the heart of an electrochemical treatment facility. Therefore, Adhoum and Monser [117] and Tezcan Ün et al. [119] conducted studies in order to determine the most appropriate electrode material for the treatment of olive mill wastewaters by electrocoagulation. In their research it appeared that both materials were almost equally effective in the removal of COD and polyphenols. However, aluminium was found to be more effective than iron in removing colour from olive mill wastewater [117]. Indeed, they specified that the effluent treated with iron as the sacrificial anode first appeared yellow and then turned brown. This behaviour was attributed to the excess of Fe(II) and Fe(III) species generated during the electrocoagulation and characterized by their yellow-brown colour, and to the occurrence of a complexing reaction between iron ions and polyphenol molecules leading to brown soluble compounds.

The polarity of the electrodes also played an important role in the treatment of wastewater. To determine the effects of polarization, Tezcan Ün et al. [119] conducted a 1 h experiment at the same current for each case. In their study, when the stirrer acted as positive electrode-anode, colloids, which carry mostly negative charges, merged to the centre of the reactor. As a result, the concentration of

colloids increased and coalescence occurred at the centre of the reactor. When the reactor was used as positive electrode-anode, the particles moved radially outwards, which did not enhance the coalescence process significantly. In this experiment, an increase of 8% in the removal efficiency was obtained when the stirrer acted as positive electrode-anode.

A limited number of studies have investigated the effect of treatment time on olive mill wastewater treatment by electrocoagulation. It was demonstrated that the percentage of COD, polyphenols and colour removal depended on the process duration for both types of anode; however, the aluminium anode performed better. In the study of Inan et al. [118], aluminium provided 28% COD removal compared with 20% for iron for a 4 min treatment time, whereas the corresponding values were 52% (aluminium) and 42% (iron) for a 30 min treatment time. The data obtained by Inan et al. [118] showed that the treatment time in the interval of 10–15 min was optimal for COD removal, and any further increase in treatment time did not enhance COD removal. Hanafi et al. [122] have explored the effect of treatment time on removal of polyphenols and colour. In their study, the treatment of the olive mill wastewater by electrocoagulation was monitored by spectrophotometric measurements, which provided a straightforward way of following the elimination of the polyphenols (at absorbance 278 nm) and colour (at absorbance 395 nm). For the first 3 min of treatment time, 10% of polyphenols were removed, whereas the colour intensity increased. This has been attributed to the oxidative polymerization of phenols and tannins originally present in the sample that contributed to the increase of coloured organic compounds [120]. After 15 min of electrocoagulation treatment, 72% and 80% of polyphenols and colour were removed, respectively. Similar to COD, further treatment time had only a slight influence on the elimination of polyphenols and decolourization.

The initial pH of the wastewater, a critical process parameter, influences the treatment performance of olive mill wastewaters by electrocoagulation. It has been reported that treatment efficiency was very poor either at low (<2) or high pH (>10) using aluminium electrodes [117,122]. In these studies, maximum removal efficiencies in terms of COD, polyphenols and colour were observed at pH in the range of 4–6. Considering the fact that typical pH values of olive mill wastewaters vary between 4 and 5.5, these wastewaters can be directly treated by electrocoagulation without requiring pH adjustment. In a study conducted by Inan et al. [118], a low level of COD removal was observed for iron anodes under pH 4.6. A 10 min processing of the olive mill wastewater yielded only 20% COD removal. In their study, increasing the pH increased the COD removal efficiencies, and maximal value of 47% was reached under pH 9.

To date, only limited data have been available dealing with the effect of electrolyte concentration/conductivity on treatment of olive mill wastewaters by electrocoagulation [121,122]. Hanafi et al. [122] have examined the effects of chloride concentration on the removal of COD, polyphenols and colour by the electrocoagulation process. The olive mill wastewater – diluted five times – used in this study had a COD value of 20,000 mg/L, conductivity of 3.6 mS/cm and acidic pH (4.2). The removal efficiency was greatly enhanced by adding 2 g/L NaCl to the olive mill wastewater, obtaining a removal efficiency of 84% of COD, 87% of polyphenols and 92% of colour. This enhancement in removal efficiencies was explained by the oxidation of pollutants by ClO^-. However, these investigators also pointed out that an excess amount of chloride in the solution was detrimental to electrocoagulation performance. This negative effect was explained by the transitory compounds that finally dissolved in the solution with excess chloride, as a form of $AlCl_4^-$, resulting in a decrease in the amount of $Al(OH)_3$ coagulant [109]. Another study conducted by Arslan-Alaton et al. [121] indicated that increasing the electrolyte concentration (from 1000 to 2000 mg/L) resulted in a significant acceleration in COD and TOC removals for olive mill wastewater treatment by electrocoagulation.

One of the most important parameters that must be determined to evaluate electrocoagulation as a treatment process for olive mill wastewater is cost. However, to date only a limited number of studies have been published that deal with the operating cost analysis of olive mill wastewater treatment by electrocoagulation. In these studies the amount of energy consumed per unit mass of COD removed (SEC; kWh/kg $COD_{removed}$) were estimated and used for the calculation of operating cost, expressed as capita per kg $COD_{removed}$. A summary of SEC and energy consumption values as well as operating costs for olive mill wastewaters by electrocoagulation reviewed in this subsection is given in Table 5. As can be seen in Table 5, an increase in current density causes a proportional increase of ohmic voltage losses in the cell, and also increases the SEC values as well as operating costs. A sufficiently high chloride concentration caused a decrease of the anode potential that resulted in considerably reduced SEC values. The energy cost of electrochemical coagulation applied in the study of Tezcan Ün et al. [119] was determined to be in the range of €0.18–6.75/kg $COD_{removed}$.

6. Metal-bearing industrial effluents

To date, a huge number of scientific works have been published on the treatment of metals with electrocoagulation using a variety of electrode materials such as aluminium, iron and steel. The data obtained from this research have indicated that metals, particularly in the free form, can be successfully eliminated via electrocoagulation if the operating conditions are optimized. This research has mostly been performed using synthetically prepared samples comprising a single metal such as cadmium, nickel, copper, zinc, chromium, etc., without considering other pollutants which may be carried along with the metals. In other words, individual and/or combinative synergistic effects of other

Table 5.   Summary of SEC values and operating costs for olive mill wastewaters by electrocoagulation reviewed.

SEC kWh/ kgCOD$_{removed}$	EEC kWh/m^3	Operating Cost €/kgCOD$_{removed}$	Electrocoagulation operation conditions	Electrode and Electrode Consumption	[Ref]
0.12–4.04	–	0.03–0.38	$J = 25$–$250\,mA/cm^2$; pH$_o$ = 4.2; $t = 15\,min$; Conductivity = 3.6 mS/cm	Aluminium 0.020– 0.085 kg/kgCOD$_{removed}$	[122]
3.41–2.63	–	0.27	$J = 250\,mA/cm^2$; pH$_o$ = 4.2; $t = 15\,min$; [NaCl] = 0.5–2 g/L	Aluminium 0.085 kg/kgCOD$_{removed}$	[122]
2.54–2.63	–	0.27	$J = 250\,mA/cm^2$; pH$_o$ = 5 − 8; $t = 15\,min$; [NaCl] = 2 g/L	Aluminium 0.066 kg/kgCOD$_{removed}$	[122]
3.35	–	0.396	$J = 25\,mA/cm^2$; pH$_o$ = 4.68; $t = 15\,min$; Conductivity = 3.24 mS/cm	Aluminium	[123]
–	13–55	–	$J = 20$–$75\,mA/cm^2$; pH$_o$ = 6.5; $t = 1\,h$; Conductivity = 6.9 mS/cm for COD	Iron	[119]
–	29–188	–	$J = 20$–$75\,mA/cm^2$; pH$_o$ = 6.5; $t = 3\,h$; Conductivity = 6.9 mS/cm for COD	Iron	[119]
–	62	–	$J = 75\,mA/cm^2$; pH$_o$ = 5.5; $t = 1\,h$; Conductivity = 6.9 mS/cm for COD	Aluminium	[119]
–	302	–	$J = 75\,mA/cm^2$; pH$_o$ = 5.5; $t = 3\,h$; Conductivity = 6.9 mS/cm for COD	Aluminium	[119]

pollutants on electrocoagulation performance have been disregarded in these studies. Due to the fact that these data reported for metal removal from synthetically prepared samples may not be representative of real-world cases, our emphasis will be placed on the treatment of real metal finishing industry effluents by electrocoagulation.

Metal-bearing industrial effluents can be classified with respect to their characteristics and treatment requirements [87]. Wastewaters containing mainly metals in free form, namely not bound by strong complex formers, which can be handled by conventional metal treatment techniques such as hydroxide precipitation without need for pretreatment, are referred to as common metal effluents [98]. Hexavalent chromium-carrying effluents are excluded from this group as they are strictly segregated due to the high toxicity of hexavalent chromium. These effluents are commonly subjected to hexavalent chromium reduction before hydroxide precipitation [87]. Complexed metals represent the third group of effluents, bearing complexed metals, being in the form of metals which are bound to strong complex formers keeping them in solution [98,126]. This group also requires stream segregation and pretreatment before hydroxide precipitation. In the following subsections, electrocoagulation applications will be introduced on the basis of this classification.

6.1.   Common metals

As explained earlier (in subsection 3.4), hydroxide precipitation is the main process playing a key role in metal removal in electrocoagulation. Adsorption or entrapment on freshly produced metal hydroxide flocs through the electrocoagulation process also contributes to metal removal from industrial effluents. Thus, the solution pH attained and the

amount of freshly produced hydroxide flocs composed of parent metal ions of the sacrificial anode during or at the end of the electrocoagulation process determine metal removal performance.

Most electrocoagulation applications have been devoted to the removal of zinc, copper, nickel and cadmium from the metal-bearing effluents which result from metal processing and finishing operations. This research has targeted the optimization of process variables such as current density, initial pH, electrolyte concentration, and electrode material and configuration. The findings related to current density have mostly indicated that metal removal efficiency significantly improves with increasing current density. Akbal and Camcı [127] examined the removal of copper, chromium and nickel from a metal plating effluent by electrocoagulation using aluminium and iron electrodes. A wide range of current density, varying between 2.5 and $10\,mA/cm^2$, was applied in their electrocoagulation applications. All metals were almost completely removed by increasing the current density from 2.5 to $10\,mA/cm^2$ in the case of both aluminium and iron electrodes. Their highest current density yielded the quickest treatment resulting in the highest amount of metal hydroxide flocs. Similar observations were also reported by Adhoum et al. [128]. In another study by Akbal and Camcı [129], electrocoagulation using four different combinations of aluminium and iron electrodes as anodes and cathodes was applied to the same effluent in order to investigate the effect of current density with respect to anode and cathode materials on metal removal efficiency. At the same current density range as applied in their previous study, similar results were obtained as expected. In addition to this, an iron anode and aluminium cathode pair was reported to be the most effective combination, as complete copper, nickel and chromium removals were

achieved by electrocoagulation operated at a current density of $10\,mA/cm^2$ and an initial pH of 3 for a treatment time of 20 min. Kobya et al. [130] explored the effect of current density on zinc and phosphate abatements from a spent rinse water originating from the zinc phosphate coating process of an automotive assembly plant by electrocoagulation using either iron or aluminium electrodes. When the current density was elevated from $1\,mA/cm^2$ to $6\,mA/cm^2$, zinc removal efficiency was remarkably enhanced from 4.8% to 97.8% for iron electrodes, and from 28% to 96.7% for aluminium electrodes. Further increase in current density up to $10\,mA/cm^2$ did not provide an additional enhancement in zinc removal efficiency. A similar behaviour was also observed with phosphate removal. In another study by Kobya et al. [131] the removals of cadmium and nickel as well as cyanide from two different cyanide-bearing electroplating rinse waters by electrocoagulation using cast iron plate electrodes were studied. The results of the study performed using cadmium-cyanide electroplating rinse water indicated that cadmium removal efficiency was practically independent of the current density and proceeded very quickly at the beginning of the electrocoagulation applications, but levelled off after 30 min of operation time for all applied current densities (0.5, 1, 3 and $6\,mA/cm^2$). A similar pattern was observed for cyanide removal from cadmium-cyanide electroplating rinse water. On the other hand, an increase in current density and an extension in electrocoagulation treatment time notably promoted nickel and cyanide abatements from nickel-cyanide electroplating rinse water, and the lowest remaining nickel and cyanide concentrations were obtained at the highest current density ($6\,mA/cm^2$) and at the longest operation period (80 min). Nickel removal efficiencies were 33.1, 43.6, 54.3 and 99.2% at the current densities of 0.5, 1, 3 and $6\,mA/cm^2$, respectively [131]. In the same current density range, cyanide removal efficiency increased from 38.5% to 99.8%. Similarly, Heidmann and Calmano [132] have reported that nickel abatement from a galvanic wastewater by electrocoagulation improved by increasing current density. Golder et al. [133] reached a similar conclusion for copper removal from a copper plating rinse effluent.

Charge loading, describing the quantity of electricity per unit volume, affects metal removal efficiency [127,130], and the authors stated that there was an optimum charge loading value at which maximum metal removals could be obtained; beyond this value, the improvement in metal abatement rate was negligible. Kobya et al. [130] determined the optimum charge loading as $8.18\,F/m^3$ and $12.29\,F/m^3$ for aluminium and iron electrodes, respectively. Similar optimum charge loading values have been reported as $8.2\,F/m^3$ for aluminium electrodes and $12\,F/m^3$ for iron electrodes by Akbal and Camcı [127].

Configurations of reactor and electrodes are important design parameters affecting the performance of the electrocoagulation process. Since the success of electrocoagulation is strictly related to the electrode material used,

an appropriate electrode material with respect to the target pollutant has to be selected so as to attain satisfactory treatment performance. This selection may become a crucial issue when the effluent contains hexavalent chromium, complex former or cyanide together with other metals. If the effluent bears these type pollutants together with metals, an iron electrode should be selected, since the aluminium electrode generally exhibits low process performance or failures in their treatment. Upon closer inspection of the data, it can be said that the same electrode materials sometimes exhibit variable performance in the treatment of the same pollutants, such as nickel and copper, depending on the connection of electrodes or on the operating conditions. In a few studies, iron or the combination of iron and aluminium electrodes proved to be superior in the treatment of nickel by electrocoagulation operated under optimized operational conditions and where the electrodes were arranged in a monopolar mode [127,129,131]. For the combination of bipolar mode and slightly acidic reaction conditions, the best nickel removal efficiency was attained by using the combination of aluminium and iron electrodes, whereas the lowest nickel removal was obtained by iron electrodes in the study of Heidmann and Calmona [132]. Their results obtained for copper also conflicted with the data obtained for monopolar connections. In their study, the combination of aluminium and iron electrodes yielded the best copper removal efficiency, whereas iron or its combination with aluminium electrodes in monopolar mode found to be the most effective materials for copper removal by Akbal and Camcı [127,129]. On the other hand, Golder et al. [133] reported that both mild steel and aluminium electrodes had a similar performance for copper removal under the same operational conditions, and a bipolar electrode arrangement was more efficient than a monopolar electrode arrangement for the same cell current. These findings indicate that both material and connection of electrodes, as well as the electrocoagulation operation conditions, play important roles in treatment of metal-bearing effluents. Furthermore, the number or the active surface area of electrodes used is another design parameter which has an important role in the process performance. When the electrode number is increased or the active surface area is enlarged, a significant enhancement in metal removal efficiency can be achieved under the same operating conditions [127,133]. In parallel with this, in the case of insufficient electrode numbers or active surface area, the electrode materials may be evaluated as inadequate.

Some research has focused on the influence of wastewater conductivity on metal removal performance [129,133]. In these studies, conductivity was elevated using NaCl, and a variable effect of conductivity was observed. Golder et al. [133] reported that an increase in the NaCl from 1000 mg/L (1.96 mS/cm) to 4000 mg/L (6.19 mS/cm) yielded a significant loss in copper removal in the case of mild steel electrodes, due to the decreased passivating oxide layer on the electrodes; a similar but less pronounced effect was also

Table 6.   Optimum pH values for hydroxide precipitation.

Metal	Optimum pH	pH range
Nickel	10.2	8.8–13.4
Zinc	9.2	8.5–10.4
Copper	8.8	6.9–13.5
Cadmium	11.1	9.9–12.2
Chromium (3+)	9.0	5.4–13.6

observed in the case of aluminium electrodes. In contrast, the results of another study performed at almost the same conductivity range (2–6 mS/cm) revealed that (i) the highest conductivity produced the quickest treatment with an effective removal of copper, chromium and nickel; (ii) metal removal efficiency, particularly for nickel, was significantly enhanced with increasing conductivity; and (iii) an increase in conductivity resulted in a decrease in electrical energy consumption as a result of the reduction in cell voltage and a reduction in electrode consumption [129].

Considering that the dominant removal mechanism is hydroxide precipitation, selection of the initial pH is of great importance in terms of metal removal performance. When the initial pH is selected as an acidic value, depending on other process variables such as current density and wastewater conductivity, insufficient metal removal efficiencies may be obtained as a result of effluent pH values being lower than the optimum pH. When the initial pH optimum is chosen as an alkaline value, that is, a pH value closer to the optimum pH of metal, the partial precipitation of metal will occur and the initial metal concentration will be decreased before electrocoagulation. In addition, when electrocoagulation is commenced at alkaline pH values, higher pH values will be attained within shorter reaction times. Therefore, comparing metal removal performance for such cases will create a misleading platform for discussion. Table 6 summarizes the optimum pH of the metals cited in the present review [98]. This table also covers the pH ranges at which metal concentrations are lower than 1 mg/L for hydroxide solubility. These pH ranges make it possible to evaluate which mechanism is responsible for the metal removal.

Kobya and co-workers [131] determined the optimum initial pH range as 8–10 for yielding maximum nickel removal from nickel cyanide plating effluent by electrocoagulation using cast iron plate electrodes. Nickel concentration was reduced from 175 mg/L to 1.92 and 0.35 mg/L at an initial pH of 8 (original pH of the effluent) and 10, respectively. In the same study, the optimum initial pH range was found as 7.6–10.6 for maximum cadmium removal from cadmium cyanide plating effluent by electrocoagulation with cast iron plate electrodes. The cadmium concentration was decreased from 102 mg/L to 1.7 and 0.6 mg/L at an initial pH of 7.6 and 10.6, respectively. The authors concluded that hydroxide precipitation was one of the removal mechanisms for both nickel and cadmium at alkaline effluent pH values, and the other mechanism contributing to

metal removal was adsorption onto ferrous hydroxide flocs produced during the electrocoagulation process.

In another Kobya et al. study [130], the optimum initial pH values for zinc removal from zinc phosphate coating effluent by electrocoagulation were determined as 3.0 and 4.0 for iron and aluminium electrodes, respectively. In the case of iron electrodes, the final pH value was obtained as 5.6, and zinc concentration was reduced from 40 to 0.9 mg/L. For the aluminium electrodes, the final pH reached 7.6, resulting in a remaining zinc concentration of 1.1 mg/L. As can be seen in Table 6, zinc concentrations lower than 1 mg/L can be achieved by hydroxide precipitation at pH values in the range of 8.5–10.4. Out of this pH range, particularly for the final pH values obtained in the run, zinc hydroxide solubility was extremely high and may exceed a few hundred mg/L. From this standpoint, the high zinc removals obtained at slightly acidic pH values were attributed to the precipitation of other zinc solid phases such as $Zn_3(PO_4)_2$, co-precipitation of $FeZnPO_4$ or $AlZnPO_4$, and adsorption onto metal hydroxide flocs produced throughout electrocoagulation process [130].
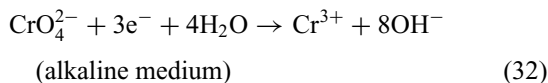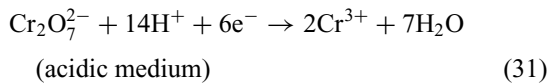
The effect of initial pH on the removal of copper, chromium and nickel from metal plating effluent was explored by Akbal and Camcı in the pH range of 3–9, at a current density of 5 mA/cm^2 using four different combinations of aluminium and iron electrodes [129]. The results obtained for copper removal indicated that an increase in initial pH from 3 to 9 yielded an enhancement in removal efficiency from 73.2% to 97.4% for aluminium anode and cathode, from 95.5% to 98.7% for iron anode and cathode, from 75.1% to 99.6% for iron anode and aluminium cathode, and from 67.8% to 95.5% for aluminium anode and iron cathode after 10 min of electrocoagulation. When the initial pH was elevated from 3 to 9, chromium removal efficiencies improved from 82.7% to 93.5% for aluminium–aluminium electrode pairs, from 91.1% to 95.1% for iron–iron electrode pairs, from 82.3% to 97.4% for iron–aluminium electrode pairs, and from 91.7% to 97.2% for aluminium–iron electrode pairs after the same electrocoagulation operation time. For the same initial pH elevation and 30 min of electrocoagulation treatment, nickel abatement efficiencies enhanced from 84.9% to 99.1% for aluminium–aluminium electrode pairs, from 76.9% to 99.3% for iron–iron electrode pairs, from 74.4% to 99.9% for iron–aluminium electrode pairs, and from 73.4% to 99.1% for aluminium–iron electrode pairs. At the initial pH of 9, complete copper and chromium removals were achieved at 30 min of treatment time in the case of iron–aluminium electrode pairs, and the lowest remaining nickel concentrations were obtained for all electrode pairs. The improvement in metal removal efficiency by increasing the initial pH was ascribed to the precipitation of their hydroxides at the cathode [129].

Golder and co–workers [133] commenced all electrocoagulation runs at the original pH of the copper plating rinse water (4.8), and pH changes during the process were followed. They recorded a significant increase in the
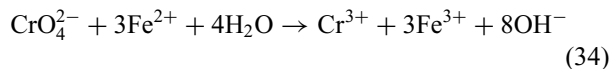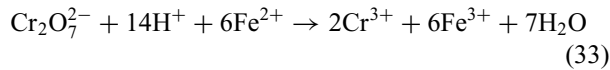
solution pH with increasing current density and prolonging treatment time in the case of both aluminium and mild steel electrodes. The effects of current density and treatment time on solution pH were more clearly observed in the case of aluminium electrodes. Although pH elevation rates were faster with aluminium electrodes, higher copper removals were obtained with mild steel electrodes. These high removal efficiencies were attributed to another copper removal mechanism, namely electrodeposition, taking palace on the mild steel cathodes along with hydroxide precipitation. Their mass balance analysis for copper revealed that the amount of copper electrodeposited on the mild steel cathodes was much greater than that of the aluminium cathode. Therefore, the authors concluded that electrodeposition also contributed to copper removal from the copper plating effluent, particularly in the case of mild steel cathodes.

6.2. Hexavalent chromium

When electrocoagulation is operated by iron electrodes, one of the following reductions takes place at the cathode, depending on the solution pH [134–136]:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$\text{(acidic medium)} \quad (31)$$

$$CrO_4^{2-} + 3e^- + 4H_2O \rightarrow Cr^{3+} + 8OH^-$$
$$\text{(alkaline medium)} \quad (32)$$

In addition to the abovementioned reactions, ferrous iron ions produced at the cathode can directly reduce hexavalent chromium to trivalent chromium according the following reactions [136]:

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \quad (33)$$

$$CrO_4^{2-} + 3Fe^{2+} + 4H_2O \rightarrow Cr^{3+} + 3Fe^{3+} + 8OH^- \quad (34)$$

Furthermore, hydroxide ions formed at the cathode induce the precipitation of trivalent chromium ions as insoluble $Cr(OH)_3$ [136].

The reaction pH plays a determining role on the hexavalent chromium removal rate. Under acidic conditions (pH < 4.0) the reduction rate of hexavalent chromium decreases with increasing pH, whereas at pH values greater than 4.0 it increases with increasing pH [137–140]. This accelerated removal rate can be explained by the increase in concentrations of $FeOH^+$ and $Fe(OH)_2^o$ hydroxo complex species in bulk solution at pH values above 4 [137].

Although a number of researchers have focused on hexavalent chromium removal by electrocoagulation, synthetically prepared samples were commonly used in these studies. Our literature survey revealed that only a few studies have been published on hexavalent chromium removal from metal-bearing effluents by electrocoagulation.

Heidmann and Calmano [132] investigated hexavalent chromium removal from a galvanic wastewater by electrocoagulation. In their study, the electrodes were operated in bipolar mode, and three different electrode arrangements were applied so as to find out the best electrode combination: (i) four iron electrodes; (ii) four aluminium electrodes; and (iii) two aluminium and two iron electrodes. The combination of iron and aluminium electrodes yielded the lowest remaining chromium concentration. Initial pH was varied from the original pH of the effluent (1.5) to 5 in order to evaluate the effect of initial pH on hexavalent chromium removal by electrocoagulation with the combination of iron and aluminium electrodes. After 140 min of treatment time, the lowest remaining chromium concentration (8 mg/L) was obtained at initial pH values of 4 and 5. As the removal efficiencies of the other metals were low for pH 4, the optimum initial pH was selected as 5.0. The results obtained for different applied currents indicated that increasing the applied current led to acceleration of the process without deterioration of the hexavalent chromium removal rate.

Ölmez [134] implemented a response surface method in order to determine the optimal electrocoagulation operating conditions for maximum hexavalent chromium abatement from a hard chromium coating process effluent with a high hexavalent chromium concentration of 1450 mg/L by electrocoagulation with stainless steel electrodes. The author stated that increasing the electrolyte (NaCl) concentration accelerated hexavalent chromium removal, decreased power consumption and shortened treatment time. Hexavalent chromium removal efficiency improved by increasing the applied current density. Although the electrocoagulation runs were initiated at the original pH (1.84) of the effluent, the solution pH values increased to 11.0 at the end of all electrocoagulation runs. For complete chromium removal the optimum conditions were determined as an applied current density of 31.7 mA/cm^2, an electrolyte (NaCl) concentration of 33.6 mM and a treatment time of 70 min by implementing the central composite design. Ölmez [134] expressed an empirical relationship between hexavalent chromium removal efficiency (R %) and the process variables (applied electric current (X_1), electrolyte (NaCl) concentration (X_2) and application time (X_3)) by the following second-order polynomial equation:

$$\begin{aligned} Y(\%) = {}& -35.47743 - 2.52778X_1 + 3.17792X_2 \\ & + 1.61104X_3 + 0.35667X_1X_2 + 0.12167X_1X_3 \\ & - 2.25 \cdot 10^{-3}X_2X_3 - 1.22222X_{12} \\ & - 0.084000X_2^2 - 0.010236X_3^2 \end{aligned} \quad (35)$$

For the optimum electrocoagulation operational conditions, the sludge mainly comprised $Fe(OH)_3$ and $Cr(OH)_3$ and the SVIs were measured as 11.6 g/L and 80 mL/g, respectively. The specific resistance to filtration of the sludge produced varied between 7.8×10^{12} and $10.1 \times$

10^{12} m/kg, corresponding to good dewaterability characteristics. The result of the leaching test proved that the sludge produced by the process was of non-hazardous nature, as the chromium concentration in the leachate was lower than 0.5 mg/L.

6.3. Complexed metals

Three mechanisms are involved in the electrocoagulation process for the removal of complexed heavy metals when stainless steel electrodes are employed in presence of chloride [141]. One of these mechanisms is the conversion of the complexed metal into the free metal form through the structural change of the organic complex former by indirect oxidation with chloride. The second mechanism is the hydroxide precipitation of the metal in free form through increasing solution pH. The last mechanism is the removal of colloidal material through the formation of $Fe(OH)_3$ flocs via adsorption or entrapment. This last mechanism enhances the removal of metal hydroxide solids existing in the colloidal form.

Kabdaşlı et al. [141] investigated the treatability of a metal plating wastewater containing complexed metals originating from the nickel and zinc plating process by electrocoagulation using stainless steel electrodes. The effect of varying operating parameters such as the applied current density, initial pH of solution, electrolyte concentration and energy consumption on heavy metal removal were explored. Organic matter removal was also studied.

As mentioned above, first of all, the complex former has to undergo a structural change by which it loses its complexing ability. In the study of Kabdaşlı et al. [141], for the case of nickel this conversion was realized after achieving 40–50% TOC removal. However, zinc removal was observed to be independent of TOC abatement, indicating that the organic complex former used in the investigated metal plating bath did not form complex species with zinc, and it was only able to bind the nickel as a complexed metal. Complete removals were achieved with this TOC abatement when the solution pH attained or exceeded the optimum pH of nickel. These prerequisites were achieved at the applied current densities of 9 and 22.5 mA/cm^2 in 180 and 90 min, respectively. Complete zinc removals were obtained at solution pH values in the range of 6.5–7.5 in all electrocoagulation applications. Since the pH range was much lower than the optimum pH of zinc, zinc removal other than hydroxide precipitation was attributed to binding onto freshly produced $Fe(OH)_3$ flocs.

Kabdaşlı et al. [141] pointed out that increasing the applied current density from 2.25 to 9.0 mA/cm^2 appreciably enhanced TOC removal efficiency from 20% to 66%, and in the range of 22.5–56.25 mA/cm^2 practically the same TOC removal efficiencies (60%) were attained within relatively shorter reaction times. A linear increase was obtained for the pseudo-first-order TOC rate constants (k_{TOC}) versus the applied current densities (J) ranging from 2.25–56.25 mA/cm^2 as $k_{TOC} = -0.0004 \times J$ ($R^2 = 0.98$). An increase in electrolyte (KCl) concentration resulted in a slight decrease in TOC removal performance, and the highest TOC removal efficiency (66%) accompanied with complete nickel and zinc removals was achieved at the lowest chloride concentration, corresponding to the original chloride concentration of the effluent (1515 mg/L). The fastest TOC removal was obtained at the original pH of the effluent (6.0), and the TOC concentration was reduced from 170 mg/L to 85 mg/L for electrocoagulation operated without any electrolyte addition at this initial pH value and an applied current density of 9 mA/cm^2. Nickel removal performance was adversely affected by decreasing of the initial pH from its original value of 6.0. Optimum operation conditions for the electrocoagulation process were established as an applied current density of 9 mA/cm^2, the original electrolyte concentration ($\approx$1500 mg Cl/L) and original pH (6) of the effluent. As expected, sludge production during electrocoagulation increased upon increasing applied current density. Surprisingly, the amounts of sludge produced during electrocoagulation remained unchanged with increasing electrolyte concentration.

Kabdaşlı et al. [142] also investigated the effect of H_2O_2 addition to the electrocoagulation (combined electrocoagulation/Fenton treatments) process in order to enhance the organic matter removal efficiency for the abovementioned effluent. All the combined electrocoagulation/Fenton treatments were performed at an initial pH of 2.6 and at a current density of 22 mA/cm^2, and a wide range of H_2O_2 concentrations varying between 15–230 mM was tested. The highest COD and TOC removal efficiencies were obtained for the combined electrocoagulation/Fenton process in the presence of 20 mM H_2O_2. At this dosage, the organic matter mineralization level increased from 50% to near 70%, accompanied with complete heavy metal removals. The authors stated that the combined electrocoagulation/Fenton process provided better results compared with plain electrocoagulation.

6.4. Economic analysis

As mentioned earlier, electrical energy requirement and electrode material consumption are the main expenses accounting for the operational cost of the electrocoagulation process. Therefore, an economical evaluation based on these master process variables is an easy tool to assess the feasibility of this treatment technique for the removal of metals from metal-bearing effluents. Obviously, electrocoagulation operation conditions such as current density, initial pH and electrolyte concentration or conductivity of the effluent have critical roles in the optimization of the technique. As the operational cost is generally affected by the operating parameters, researchers have focused on their effects on process performance. A number of authors have pointed out that current density is directly proportional to operational cost [127,129–132]. In other words,

increasing current density produces increases in the electrical energy requirement and electrode material consumption. Kobya and co-workers [131] reported that an increase in current density from 0.5 to 6 mA/cm^2 elevated the electrical energy requirement and electrode material consumption from 0.33 to 11.65 kWh/m^3 and from 0.52 to 2.85 kg/m^3, respectively, for almost complete removal of cyanide and cadmium from cadmium cyanide electroplating rinse water. The operational cost escalated correspondingly, from 0.171 to 2.445 €/m^3 [131]. At the same current density range, the electrical energy requirement and electrode material increased from 0.28 to 11.95 kWh/m^3 and from 0.46 to 1.62 kg/m^3, respectively, for almost complete removal of cyanide and nickel from nickel cyanide electroplating rinse water. The corresponding escalation in operational cost was approximately tenfold for this case [131]. In another study by Kobya et al. [130], the electrical energy requirement increased from 0.18 to 11.29 kWh/m^3 and 0.24 to 8.47 kWh/m^3 with an increase in current density from 1 to 10 mA/cm^2 in the treatment of the zinc phosphate coating effluent by electrocoagulation using aluminium and iron electrodes, respectively. At this current density range, electrode consumption increased from 0.2 to 0.62 kg/m^3 for iron electrodes and from 0.01 to 0.35 kg/m^3 for aluminium electrodes. It was also stated in the same study that an increase in initial pH value caused remarkable increases both electrical energy requirement and electrode consumption. Electrical energy requirements were 3.1–8.4 kWh/m^3 for aluminium electrodes at initial pH values of 2 and 5, and 1.38–6.80 kWh/m^3 for iron electrodes at initial pH values of 2 and 3. Corresponding electrode consumptions were determined as 0.15–0.50 kg/m^3 and 0.14–0.54 kg/m^3 for iron and aluminium electrodes, respectively.

The abovementioned adverse effects observed with increases in current density and initial pH can be reversed by increasing the conductivity of the effluent. The positive influence of conductivity is due to the shortened electrolysis time. This improvement in operational cost has been proven in the work of Akbal and Camcı [129].
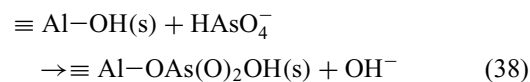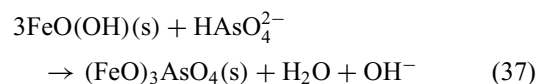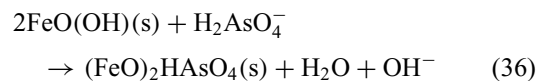
Total operational cost of the electrocoagulation process was compared with that of conventional chemical coagulation for the removal of nickel, copper and chromium from metal plating effluent by Akbal and Camcı[127]. They estimated total operational costs accounting for energy, electrode material and sludge disposal expenses as 0.59 and 0.97 US$/m^3 for electrocoagulation with iron and aluminium electrodes, respectively. Total operational costs of conventional chemical coagulation were calculated as 0.89 US$/m^3 for FeCl$_3$ and 1.176 US$/m^3 for alum.

7. Arsenic-containing wastewaters

Arsenic, although, acquires −3 (arsine), 0, −1 (alkyl arsenic) valences exists in nature as major forms As(III), arsenious acid (H$_3$AsO$_3$) and As(V), arsenic acid and their ionized forms. Arsenic in the trivalent state exists in reducing conditions such as groundwater. Pentavalent arsenic species predominate and are stable in oxygen-rich aerobic environments such as surface waters. Arsenious acid yields the species H$_2$AsO$_3^-$, HAsO$_3^{2-}$, and AsO$_3^{3-}$ with the ionization constants (25°C, 1 atm) pK$_{a,1}$: 9.1, pK$_{a,2}$: 12.1, pK$_{a,3}$: 13.4. Uncharged H$_3$AsO$_3$ predominates below pH 9. Arsenic (III) is a hard acid and complexes with oxides and nitrogen. Arsenic acid H$_3$AsO$_4$ forms the species H$_2$AsO$_4^-$, HAsO$_4^{2-}$ AsO$_4^{3-}$ with ionization constants (25°C, 1 atm) pK$_{a,1}$: 2.1, pK$_{a,2}$: 6.7, pK$_{a,3}$: 11.3; between pH 4–10 practically only H$_2$AsO$_4^-$ and HAsO$_4^{2-}$ species exist. Around neutral pH their concentrations are comparable. Arsenic (V) behaves like a soft acid, forming complexes with sulphides. It forms bi-dentate binuclear bridging complexes at high iron to arsenic ratio, which is used for the removal of arsenic [143–145]. Although several methods are available for the treatment of arsenic-containing wastewaters, such as adsorption and chemical precipitation, coagulation with ferric or aluminium salts is an effective and simple method.

Recently, electrocoagulation has been used for the treatment of arsenic. Electrocoagulation where ferric or aluminium hydroxocomplexes and various oxide/hydroxide solid phases are generated in situ is an effective method. In the process of coagulation with ferric salts or electrocoagulation with iron electrodes, a number of hydrated species such as Fe(H$_2$O)$_6^{3+}$, Fe(H$_2$O)(OH)$_2^+$ and Fe$_2$(H$_2$O)$_6$(OH)$_4^{4+}$, and solid phases such as goethite FeO(OH) are formed, depending on pH of the solution. Both As(III) and As(V) are adsorbed onto iron solid phases. Among them, the oxides with which arsenic interacts strongly are hydrous ferric oxide (Fe$_2$O$_3 \times$ H$_2$O) and goethite (FeO(OH)). Arsenate anions form naturally occurring arsenate minerals (FeAsO$_4$.2H$_2$O, corodite; Fe$_3$(AsO$_4$)$_2$.H$_2$O, symplesite) with dominant solid phases. Polymeric aluminium hydroxides formed through hydrolysis provide also large surfaces for adsorption of arsenic species to form insoluble arsenic complexes. Examples of these reactions are given as follows:

$$2FeO(OH)(s) + H_2AsO_4^-$$
$$\rightarrow (FeO)_2HAsO_4(s) + H_2O + OH^- \quad (36)$$
$$3FeO(OH)(s) + HAsO_4^{2-}$$
$$\rightarrow (FeO)_3AsO_4(s) + H_2O + OH^- \quad (37)$$
$$\equiv Al-OH(s) + HAsO_4^-$$
$$\rightarrow \equiv Al-OAs(O)_2OH(s) + OH^- \quad (38)$$

Studies have shown that in situ precipitation of ferrihydrite removes arsenic more efficiently than addition of prepared ferrihydrite [146]. Arsenite and arsenate adsorptions on ferrihydrite were compared by Raven et al. [147]. Arsenite was found to react more quickly; however, arsenate adsorption was faster at low arsenic concentrations and low pH values. Arsenite was retained in larger amounts

than arsenate at high pH values or at higher arsenic concentrations. Jain et al. [148] evaluated the As(III) and As(V) adsorption mechanism on ferrihydrite in the pH range of 4–10. Lenoble et al. [149] studied arsenic adsorption on iron-based adsorbents and found that arsenate adsorption was favoured in acidic pH values; however, maximum adsorption was realized between pH 4–9. Ranjan et al. [150] also reported that arsenate adsorption on hydrous iron oxide depended on pH, while arsenite adsorption was insensitive to pH. Goldberg and Johnston [151] stated that arsenate formed inner-sphere surface complexes on both amorphous aluminium and iron oxides, and arsenite formed both inner- and outer-sphere complexes on amorphous aluminium oxide. Qiao et al. [152] conducted coagulation experiments by using $FeCl_3$ to remove arsenic species. They concluded that As(III) was removed in larger quantities than As(V) at pH 7 and 8. The pH range where As(III) was removed preferentially to As(V) by $FeCl_3$ coagulation was broader at higher initial As/Fe molar ratios. Lakshmanan et al. [153] used NSFI-53 challenge water and added As(III) or As(V) at 0.05 mg/L to assess the performance of coagulation with $FeCl_3$. As(V) removals increased with decreasing pH values. With pH in the range 6.5–8.5 and with 2 mg/L Fe(III) dose, almost complete As(V) removal could be obtained at pH 6.5. As(III) removals were pH independent in the pH range 6.5–8.5. When $FeSO_4$ was used instead of $FeCl_3$, As(V) removals obtained with 2.5 mg/L Fe^{2+} were lower than 10%.

Electrocoagulation studies for arsenic removal have been commonly realized with the low arsenic concentrations encountered in natural waters. These studies indicate the basic features of the process, therefore some studies and their results are summarized here. Gomes et al. [8] applied electrocoagulation to As(III) removal with initial concentrations between 1.42–1230 ppm and at 30 mA/cm^2 current density. They used Fe−Fe, Al−Al and Al−Fe electrode pairs. They found that the Fe−Fe electrode pair provided removal of over 99% As(III) at all concentrations. The Al−Fe electrode pair yielded 78.9–99.6% removal depending on initial As(III) concentration. The Al−Al electrode pair performance reached 97.8%. Wan et al. [154] used electrocoagulation with iron electrodes for the removal of As(III) and As(V) at initial concentrations between 100–1000 μg/L. The reactor was operated with a current of 22 mA. Air was sparged at the bottom of the reactor to provide oxygen for ferrous iron oxidation. The electrocoagulation operation time required to reach As(III) concentrations less than 1.0 μg/L was 90 min for an initial concentration of 100 μg/L and initial pH between 5–9, while the same residual concentration was attained in 120 min operation time for 1000 μg/L initial concentration at initial pH 7. The same residual arsenic concentration was achieved in the case of As(V) with initial concentration of 100 μg/L between 15–75 min for initial pH values of 5–8, but at initial pH 9 the required time was over 120 min to reach less than 1.0 μg/L at initial pH of 7. An initial concentration of

As(V) of 1000 μg/L similarly needed more than 120 min. In the same study, field trials of electrocoagulation were undertaken with water samples containing arsenic concentrations in the range 400–700 μg/L. In all trials, final filtered water samples had As concentrations of less than 10 μg/L. Kobya et al. [155] studied the removal by electrocoagulation of As(III) using iron and aluminium electrodes. An As(III) solution was added to potable water to make an initial As (III) concentration of 150 μg/L. The highest removal efficiencies for a monopolar in-series electrode connection were 99.3 % for iron electrodes at pH 6.5, and 98.9 % for aluminium electrodes at pH 7. Lakshmanan et al. [153] used NSFI-53 challenge water containing 50 μg/L arsenic to study As(III) and As(V) removals by electrocoagulation using iron electrodes at 1.2 A current for 110 cm^2 anode surface area. As(V) removals were found to be erratic at pH 6.5, while more consistent results were obtained at pH 7.5 and 8.5. At pH 6.5, most of the iron was found to be soluble Fe^{2+} after 2 min of operation, while at pH 7.5 about 70–80% iron was determined as an insoluble $Fe(OH)_3$ solid being capable of adsorbing As(V). Complete As(V) removals could be obtained only at pH 7.5 with a total iron dose of about 6 mg/L. At pH 8.5, removal was reduced to below 90%. The As(III) removal efficiencies in the system showed a slight dependency on pH, and the removal efficiency slightly improved with increasing pH. All removal efficiencies were, however, below 80%. Kumar et al. [156] in their study, carried out at pH 6–8 with current densities 0.65–1.53 mA/cm^2 and using iron electrodes, concluded that As(III) removal was through oxidation to As(V) and adsorption on hydrous ferric oxides. Wan et al. [154] observed that in all experiments with As(III), the As(V) was measured with increasing concentrations, which then decreased with increasing time. They concluded that at least 25% oxidation of As(III) to As(V) during the electrocoagulation process was predicted. Lakshmanan et al. [153] did not find any significant oxidation of As(III) to As(V) during electrocoagulation with iron electrodes. The use of a combination of graphite and iron electrodes had no significant advantage for As(III) removal compared with iron electrodes. However, a two-stage electrocoagulation process with graphite anode at Stage 1 and iron anode in Stage 2 was effective for As(III) oxidation. On the other hand, Pallier et al. [157] found that As(III) oxidation to As(V) was achieved in electrocoagulation using iron electrodes. These results indicate that oxidation of As(III) to As(V) during electrocoagulation is strongly dependent on operational conditions, but at any rate a complete conversion may not be attainable. There is some research into enhancing the oxidation of As(III) to As(V) within the electrocoagulation operation, in order to avoid optimization for both species and to achieve As removal in a one-step operation. Arienzo et al. [158] employed the electrocoagulation process with iron electrodes and added H_2O_2 to the system to oxidize As(III) to As(V), which was considered to be more strongly retained by hydrous ferric oxides. Parga et al. [159] used an air injection system to increase arsenic

removal in the electrocoagulation process. Zhao et al. [160] used a DSA electrode in combination with an iron electrode for the removal of As(III), first by oxidation to As(V) and then removal with adsorption. They concluded that nearly compete oxidation of As(III) was achieved in the process.

Although high arsenic removals are obtainable by electrocoagulation, the above information indicates that operational parameters need to be closely controlled. A brief evaluation of the effect of operational parameters on electrocoagulation performance is given below.

pH is a determining factor in electrocoagulation for arsenic removal, particularly if more than one species exist in solution. In their study to remove As(V) by electrocoagulation with iron electrodes, Vasudevan et al. worked in a wide pH range of 2–12 [161]. They found that the removal efficiency increased up to pH 7 and then slightly decreased. Kumar et al. [156] did not find a significant change in removal of As(III) and As(V) in an electrocoagulation operation in the pH range of 6–8. Gomes et al. [8] reported the optimum pH as 6 for As(III) removal in electrocoagulation with an aluminium and iron electrode pair. Wan et al. [154] determined the solid phase in an electrocoagulation operation using iron electrodes of lepidocrocite, which had an isoelectric point pH of 7.0. They noted that As(V) removal at pH 8 and 9 was slow as compared with lower pH values. A similar observation was made for As(III). Although the rates were different, removal of arsenic was found to be at the same capacity between pH values 5–8. However, the decreasing rate at higher pH values was explained by less favourable adsorption above the isoelectric point, due to like charges of ions and solid surfaces. Kobya et al. [155] gave optimum pH values for the electrocoagulation treatment of As(III) as 6.5 and 7.0 for iron and aluminium electrodes, respectively.

Initial arsenic concentrations were also evaluated in some studies. Vasudevan et al. [161] reported that the uptake of arsenate in the electrocoagulation process increased with increasing initial concentration from 0.5–1.5 mg/L. The amount of arsenate adsorbed increased from 0.451 to 1.483 mg As/g iron hydroxide sludge as the initial concentration increased from 0.5–1.5 mg/L. Gomes et al. [8] showed that with an aluminium and iron electrode pair and an initial As(III) concentration varying in a wide range of 1.42–1230 ppm, arsenic removal values did not change significantly. As a result of their experiments on the removal by electrocoagulation of As(III) and As(V) with initial concentrations varying between 100–1000 μg/L, Wan et al. [154] concluded that arsenic removal was limited by the production of a solid phase, and arsenic removal efficiencies were independent of initial concentration.

Current density and related parameters are another important issue for the assessment and design of electrocoagulation. Some researchers have indicated that an increase in current density increases arsenic removal efficiency [155]. However, most authors have claimed that an increase in current density might increase the rate of the process, but had no effect on final arsenic removal [156]. Kumar et al. [156] suggested using the charge density parameter. Vasudevan et al. [161] observed that in their electrocoagulation process operation, an initial As(V) concentration of 0.5 mg/L was removed with higher efficiency as the current density was increased from 0.5 to 2 mA/cm^2 and stayed unchanged with further increase. It seems that in the case of arsenic removal, current density is related to the production of adsorbing material, so in this respect it may emerge as a rate-limiting mechanism for the electrocoagulation process.

The effect of co-existing ions on arsenic removal by electrocoagulation is important for water treatment; however, it may gain even greater importance for the treatment of wastewaters. Studies have indicated that many parameters common in both natural wasters and wastewaters interfere with arsenic removal by electrocoagulation. Vasudevan et al. [161] observed a very high level of interference of carbonate at 250 mg/L, phosphate at 50 mg phosphate/L, fluoride at 5 mg/L and silica at 15 mg/L. They explained the interaction of phosphate, fluoride and silica by preferential adsorption and carbonate by passivation of the anode. Wan et al. [154] determined that presence of 1–4 mg P/L phosphate inhibited the removal of arsenic by electrocoagulation. Their explanation was not only competitive adsorption, but also a decrease in the rate of oxidation of Fe^{2+} to Fe^{3+} in the presence of phosphate. The authors did not observe any significant effect of dissolved silica between 5–20 mg/L concentration. Also, 10–50 mg/L sulphate did not affect the process. Lakshmanan et al. [153] determined silica interference at 20 mg/L; the effect was found to increase with increasing pH. The authors also observed the negative effect of phosphate at a level of 40 μg/L; they noted, however, that the effect decreased with increasing pH. Pallier et al. [157] noted a significant negative effect of humic acids at 10 mg/L DOC level for removal of both As(III) and As(V). Kumar and Goel [162] investigated arsenic and nitrate removal by electrocoagulation and found no significant difference in the removal of these substances in tap water versus distilled water.

Research dealing with the kinetic and thermodynamic aspects of arsenic removal by electrocoagulation is limited. Vasudevan et al. [161] indicated that arsenate adsorption by Fe(OH)$_3$ is an endothermic process. The authors also determined that this adsorption could be represented by Langmuir adsorption, and followed second-order kinetics. Balasubramanian et al. [163] reported that arsenate removal by electrocoagulation using stainless steel electrodes could be represented by first-order kinetics, and the adsorption data fitted well the Langmuir isotherm.

A limited number of works have focused on the energy requirements and cost of arsenic removal by electrocoagulation. Kobya et al. [155] calculated electrode consumption and energy requirements for a specific electrode connection. The energy requirements for the treatment of water containing 150 μg/L As(III) were found to be 0.0140 kWh/m^3

and $0.0254\,\mathrm{kWh/m^3}$ for iron and aluminium electrodes, respectively. Kumar and Goel [162] gave the electrode consumption for As(V) treatment using iron electrodes. Martinez-Villafane et al. [164] made an analysis of energy and electrode consumption for the removal of arsenic from underground water containing $131\,\mu\mathrm{g/L}$ arsenic. In their work, very short retention time $(20\,\mathrm{s})$ was assumed for the electrocoagulation process.

Arsenic can be adsorbed onto several adsorbents such as activated carbon, agricultural products, hydrotalcites and metal-based absorbents, of which iron oxides are of importance; however, there are other metal-based methods making use of metals such as titanium, copper and zirconium [144]. Different metals are also used in the electrocoagulation process as electrode materials. A copper–copper electrode was shown to remove 67% arsenic at low pH values. Titanium–titanium electrodes provided a mediocre efficiency of 58%. It was reported that As(III) was less adsorbed as compared with As(V) on TiO_2. Other electrode types such as Cu−Zn, Cu−Fe and Cu−Al pairs have also been used for arsenic removal with varying efficiencies [143]. Kumar et al. [156] obtained up to 58% As(III) removal with titanium electrodes.

Arsenic as a wastewater pollutant is found in metal finishing and mining industry wastewaters. Pyrometallurgic copper processing is an important source of wastewater [165]. There are studies, although limited in number, for the removal of arsenic using electrocoagulation at higher arsenic concentrations in parallel with, or representing, arsenic-containing wastewaters. Hansen et al. [165] studied electrocoagulation treatment with iron electrodes using a continuous system. A stock solution was prepared to contain 100 mg As/L as As(III) or As(V). The As(V) solution was prepared from As(III) solution by oxidation using hydrogen peroxide. At a current density of $12\,\mathrm{mA/cm^2}$ and a residence time of 9.4 min, more than 98% of As(V) was removed. An increase in current density from 12 to $15\,\mathrm{mA/cm^2}$ did not change the efficiency. Under the same operating conditions, As(III) removal was less than 10%. Hansen et al. [166] used the arsenic solutions as described in their earlier work [165] to contain 100 mg/L As(III) or As(V). They used three different electrocoagulation units, all equipped with iron electrodes: a modified flow, a turbulent flow and an air-lift reactor. As(V) removal was over 98% for both modified flow and turbulent flow at a current density of $12\,\mathrm{mA/cm^2}$. Increasing the current density did not improve the efficiency further. The electrocoagulation process was applied to solutions containing As(III) and As(V) by Lakshmipathiraj et al. [167]. Mild steel electrodes were used with different electrolytes; 0.01 M NaCl, Na_2SO_4, and $NaNO_3$ were used at $5.2\,\mathrm{mA/cm^2}$ with initial As(III) concentration of 25 mg/L. While arsenic removal of 98% was obtained with NaCl, arsenic removal was 80% and 75% for Na_2SO_4 and $NaNO_3$, respectively. The reduction in the efficiencies for Na_2SO_4 and $NaNO_3$ was attributed to their passivating effect. The process took 35 min and

pH was elevated over 9 at the end of the application of electrocoagulation. The effect of initial concentrations was tested using several dilutions, from 5–100 mg/L As(III) concentration, using 0.01 M NaCl and at a current density of $5.2\,\mathrm{mA/cm^2}$. For all As(III) concentrations, 98% removal was obtained nearly in 90 min. The effect of current density was tested using 25 mg/L As(III) with current densities varying from 5.2–$20.8\,\mathrm{mA/cm^2}$. The rate of arsenic removal was found to increase with increasing current density, which was attributed to the increased generation rate of Fe^{2+}. The removal of As(III) and As(V) was studied in another experiment conducted at $5.2\,\mathrm{mA/cm^2}$ current density and with 0.01 M NaCl. The initial concentration of the arsenic solutions was 10 mg/L. Removal of both As(III) and As(V) was almost the same, although As(V) removal was slightly better at the initial stage. Lacasa et al. [168] applied electrocoagulation with iron and aluminium electrodes to arsenic removal at 20 mg/L As(V) concentration. For both electrodes and at current densities of 0.5 and $3.0\,\mathrm{mA/cm^2}$, arsenic concentrations were reduced below $10\,\mu\mathrm{g/L}$. The pH was increased with increasing current density, however, and for $0.5\,\mathrm{mA/cm^2}$ the final pH values were between 7 and 8. Balasubramanian et al. [163] studied As(V) removal by electrocoagulation, using mild steel electrodes, with an initial concentration 100 mg/L. Although a sharp reduction was observed in the initial stages of the operation, the removal, particularly after 30 min, was gradual. Maximum efficiency was found at $15\,\mathrm{mA/cm^2}$. The efficiency of the process was enhanced as the initial pH was increased from 4 to 7, but no significant difference was observed when the initial pH value was increased from 7 to 11.

The research conducted so far has demonstrated that removal of arsenic by the use of electrocoagulation, at least with the use of iron electrodes, is an effective technology for natural waters. However, there is still a need for further research on various aspects of the process, such as As(III) oxidation and removal and the effect of coexisting anions. For the area of wastewater treatment the need for the future research is even greater, due to the high arsenic concentration and complex ionic matrix of these wastewaters.
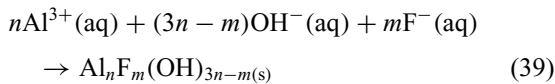
8. Fluoride-containing wastewaters

8.1. The basis of fluoride removal and electrocoagulation

Electrocoagulation with aluminium electrodes has proved to be effective in reducing fluoride concentrations found in water resources to drinking water standards of 0.5–1.5 mg/L. The process has also been applied to fluoride-bearing wastewaters. The mechanism of the process has long been understood from work in several areas of research, mostly adsorption and coagulation. A brief description of the process mechanism and its applications through the coagulation process is given below.
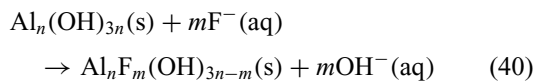
When an aluminium salt is added to water in a quantity exceeding the solubility of aluminium hydroxide, the metal ion, Al^{3+} is hydrated to form $Al(H_2O)_6^{3+}$ which yields mononuclear, dinuclear and polynuclear complexes such as $Al(OH)^{2+}$, $Al_7(OH)_{17}^{4+}$ and $Al_{13}(OH)_{34}^{5+}$ through a series of hydrolysis reactions. The hydrolysis reactions produce hydrogen ions, which reduce the pH of the solution. Data exist in the literature on hydroxo species, their polymerization reactions and stability constants [169,170] as well as the optimal conditions for the preparation of polymeric aluminium (III) hydroxide species for water treatment [171]. The positively charged polymeric hydroxo metal ions prevail below the isoelectric point, which is between 9.2 and 11.5 [172].

At an initial pH of 8, however, the concentration of negatively charged $Al(OH)_4^-$ and aluminium solubility significantly increase, and the solution loses its destabilization capacity for negatively charged colloids. Below pH 8, positively charged aluminium species, particularly the highly charged polymers, carry out effective destabilization through charge neutralization. In saturated solutions, polymeric hydroxy complexes eventually yield solid $Al(OH)_3$ through complex reactions. The optimum pH range of alum coagulation, therefore, is assumed to be between pH 6–8. The fluoride removal mechanism is based on the reactions that take place during alum coagulation. One of the mechanisms is the formation of insoluble $Al_nF_m(OH)_{3n-m(s)}$ through co-precipitation:

$$nAl^{3+}(aq) + (3n - m)OH^-(aq) + mF^-(aq)$$
$$\rightarrow Al_nF_m(OH)_{3n-m(s)} \qquad (39)$$

or, adsorption:

$$Al_n(OH)_{3n}(s) + mF^-(aq)$$
$$\rightarrow Al_nF_m(OH)_{3n-m}(s) + mOH^-(aq) \qquad (40)$$

In these mechanisms $Al_n(OH)_{3n}$ represents the polymeric aluminium hydroxo species, which are also called reactive polymers. Hydroxy aluminium polymers are metastable with respect to precipitation, but they persist in solution for a long time.

The formation of Al-Fe-OH was determined, and started to be used for fluoride removal in the 1980s, and was studied intensively in the 2000s [173–176]. Hao et al. [177] studied the adsorption characteristics of fluoride onto hydrous alumina and developed a surface complexation model. They also noted that a polynuclear complex may be formed at high loading. Schmitt and Pietrzyk [178], in their study of the separation of inorganic anions on an alumina column, analysed the anion adsorption mechanism and presented the anion retention order for 16 anions where fluoride was the first anion. In Saha's study to remove to fluoride with $AlCl_3$, a complex consisting of Ca, Al, and F was formed [179]. Szczepaniak and Koscielna [180] conducted a similar study to determine specific adsorption of halogen anions

on hydrous γ-Al_2O_3 and found that fluoride had the greatest affinity, and while Cl^-, Br^- and I^- were adsorbed through formation of ion pair complexes in the outer-coordination sphere, sorption of IO_4^- and F^- involved the formation of surface complexes in the inner-coordination sphere. Kasprzyk-Hordern [181] evaluated the chemistry of alumina and its aqueous solution reactions in relation to water treatment. In this paper, the inner-coordination sphere complex of fluoride was represented as an exchange reaction with hydroxyl ions:

$$\equiv Al-OH + F^- \leftrightarrow \equiv Al-F + OH^- \qquad (41)$$

Further, a number of studies were conducted to experimentally verify the complex [182–184]. The process conditions for maximum removal were also assessed. Buffle and co-workers [173] experimentally analysed the speciation of polymers for fluoride removal. In their paper, they also accounted for the formation of insoluble Na_3AlF_6. Mekonen et al. [175] discussed the effect of pH on fluoride removal by alum and recommended the pH range 6.5–7.5 for alum–PAC slurry defluoridation. Ayoob et al. [172] in their overview of defluoridation technologies of drinking water pointed out that high pH values play a role in fluoride removal through the reaction:

$$Al(OH)_4^- + F^- \rightarrow Al(OH)_3F + OH^- \qquad (42)$$
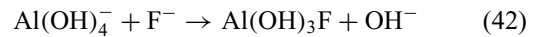
Since at high pH values residual aluminium concentrations increase beyond drinking water standards, this mechanism is avoided. To make use of the positively charged polymers for fluoride removal by complex formation, the pH should be kept below the isoelectric pH of alum. Hu et al. [185] pointed out the importance of pH in defluoridation by alum coagulation, and stated that the pH was changing through the reaction because the hydroxide ions were liberated as the fluoride complex was formed, and control of pH in the range 5.5–6.5 was rather difficult. They proposed to use γ_{OH} defined as:

$$3 + \frac{[OH^-]_0}{[Al^{3+}]_t} - \frac{[H^+]}{[Al^{3+}]_t} \qquad (43)$$

or γ_{Alk} defined as:

$$2 \times \frac{[CO_3^{2-}]}{[Al^{3+}]} \qquad (44)$$

or to use γ_{OH+F}

$$3 + \frac{[OH^-]_0}{[Al^{3+}]_t} - \frac{[H^+]}{[Al^{3+}]_t} + \frac{[F^-]_0}{[Al^{3+}]_t} \qquad (45)$$

as a criterion whose value was taken as 3. Sujana et al. [176] studied defluoridation by alum coagulation between pH 3–9 and found the optimum pH as 6. They explained this optimum as stronger competition from hydroxide ions at and above pH 6, and the adsorption was less in the acidic range

due to the formation of unionized hydrofluoric acid. These researchers also conducted a desorption test on fluoride-bearing sludge at pH 6.5 for 48 h and found no release of fluoride. The authors found that the percent of adsorption increased with sludge dose, and the adsorption reached equilibrium conditions in 2 h. The rate of the reaction was represented by the Lagergren equation and first-order kinetics. On the other hand, the adsorption efficiency was found to decrease from 85% to 72% at pH 6 and for 20 mg/L initial fluoride concentration for an increase in temperature from 307 to 337 K. They also reported that sulphate and nitrate adversely affected fluoride removal at 10 mg/L concentration, while phosphate and silicate demonstrated an adverse effect at higher concentrations of 10–50 mg/L. Yang and Dluhy [186] prepared aluminium hydroxide sludge in an electrochemical reactor and then used this fresh sludge for fluoride adsorption, reducing the fluoride concentration from 16 to 0.1 mg/L by adjusting the pH to 6.3. Capacity determination, kinetic and thermodynamic studies for fluoride adsorption by aluminium hydroxides are rather rare. Liu et al. [187] found a capacity of 110 mg F/g Al for freshly precipitated aluminium hydroxide in the pH range from 5.0–7.2. The reaction rate fitted a pseudo-second-order model and equilibrium was reached in 2 h. Sujana et al. [176] determined equilibrium time as 240 min at pH 6 for fluoride removal by alum sludge. The adsorption data fitted the Langmuir isotherm, and they found the reaction rate to obey the first-order kinetics. Sujana et al. [188] used amorphous F/Al mixed hydroxides for fluoride adsorption and reported that the data fitted both Langmuir and Freundlich isotherms well. The maximum capacity was determined as 91.7 mg/g. The reaction rate was represented by first-order kinetics.

Electrocoagulation applications for fluoride removal are undertaken using aluminium anodes to generate Al(III) ions. The process in other ways is similar to alum coagulation. However, the defluoridation efficiency using electrocoagulation has been considered superior to coagulation. This is explained by the electro-condensation effect, which is originated by the attraction of negatively charged ions, fluoride to the anode; fluoride concentration near the anode exceeds that in the bulk solution, leading to higher efficiency. Another mechanism that may work is the formation of AlF_6^{3-} ions near the anode where both fluoride and Al^{3+} ions exist in high concentration, and eventually transform to the insoluble salt Na_3AF_6 as [172,189]:

$$Al^{3+} + 6F^- \rightarrow AlF_6^{3-} \qquad (46)$$

$$AlF_6^{3-} + 3Na \rightarrow Na_3AlF_6 \qquad (47)$$
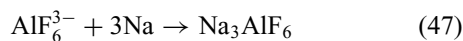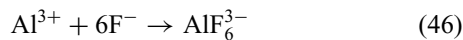
Zhu et al. [190] divided the fluoride into three parts: that remaining in water, that adsorbed by the flocs, and that removed by the gelatinous layer attached to the electrodes resulting from electrophoresis and/or electrocondensation effects in the electric field. They proposed the existence of an $Al_n(OH)_mF_k^{3n-m-k}$ complex which, depending on the charge, could form a colloid in the reactor or be adsorbed onto the anode or cathode surfaces. The results of their study showed that over 50% of the fluoride was removed on the electrodes at an optimum pH of 6.5. Emamjomeh et al. [191] conducted a study to better understand the defluoridation mechanism of electrocoagulation by aluminium electrodes, and accounted for the fluoride complexes $AlFe^{2+}$, $AlFe_2^+$, AlF_3^o and AlF_4^-. They found that solid cryolite appeared in the pH range of 5–6, and by increasing the pH to 6–8 aluminium hydroxofluoride formation was maximized, which was the main mechanism for defluoridation. They also found that fluoroaluminium complexes predominated in the acid solution until $Al(OH)_3$ precipitated. The fluoride removal efficiency decreased as the pH was increased from 8 to 10. Mameri et al. [6] evaluated the effect of pH on defluoridation by electrocoagulation. The process was commenced at different initial pH values varying between 4.4 and 9.0. Their results indicated that the final pH of the solution converged to pH 7.6 independent of the initial pH. pH 7.6 was evaluated as a point where fluoroaluminium complexes AlF_3^o, $AlOHF_3^-$ and $Al(OH)_2F_2^-$ were strongly present, inducing an efficient fluoride removal. Hu et al. [185] used the molar ratio of hydroxide ions to Al(III) ions as a criterion, and concluded that the hydroaluminium polymer formed if the γ_{OH} was less than 2.46. Zhao et al. [192] also studied the effect of alkalinity on defluoridation by electrocoagulation. They concluded that as the OH^- was the only source of alkalinity in raw water, the highest efficiency could be obtained when the molar ratio of alkalinity and fluoride to Al(III) was controlled at 3.0. These studies showed the importance of the pH in defluoridation by electrocoagulation.

Another important issue in electrocoagulation for fluoride removal is passivation of electrodes. Passivation is a common problem in electrocoagulation. An oxide film formed on aluminium is stable between pH values 4 and 10, which increases resistance and reduces efficiency [6,193]. Several methods have been proposed to overcome the problem of passivation. Mameri et al. [6] used bipolar electrodes for this purpose. Bipolar electrodes are formed by placing conductive plates between two electrodes without electric connection. Opposite electric charges on the plates that face the electrodes will develop, and anodic and cathodic reactions take place on the positively and negatively charged surfaces, respectively. This application provides more efficient current distribution and reduced drop in electric potential. Addition of chloride to the solution, periodical reversal of the current direction, and use of alternating current (AC) are other methods that have been tried to resolve the passivation problem. Mameri et al. [6] applied bipolar electrodes and concluded that this application induced a reduction in defluoridation time while the mass ratio of Al/F^- obtained with the bipolar electrodes was of the same order as the ratio determined with a system

of monopolar electrodes. Mameri et al. [194] employed aluminium electrodes in bipolar mode for defluoridation of Sahara water. Emamjomeh and Sivakumar [195] stated that the Al^{3+}/F^- mass ratio was not significantly different between monopolar and bipolar electrocoagulation systems. Ghosh et al. [183] observed better removal of fluoride for a bipolar connection than for a monopolar connection. They also reported that with the same current density applied for both kinds of connections, the density was higher in the bipolar connection. Vasudevan et al. [196] used both AC and direct current for defluoridation by electrocoagulation, using aluminium electrodes at $10\,mA/cm^2$ current density and initial pH 7, and reported that both removal efficiency and energy consumption were favourable for use of AC.

The chloride ion is often used in the electrocoagulation process to increase conductivity; however, it also has corrosive properties, and even at low concentrations results in breakdown of the passivating film through pitting corrosion [193]. Cheng [197] added chloride to an electrocoagulation solution to alleviate the passivation problem in defluoridation by electrocoagulation.

Hu et al. [189] evaluated the effects of co-existing anions on fluoride removal in the electrocoagulation process using aluminium electrodes. They conducted potentio-dynamic polarization tests for both monopolar and bipolar electrode connections to assess defluoridation efficiency, current efficiency and applied potential. They used 25 mg/L F^- solution as the reference and added Cl^-, NO_3 and SO_4^{2-} anions separately or as $SO_4^{2-} + Cl^-$ and $SO_4^{2-} + NO_3^-$ combinations. The concentration of the added anions varied between 1–10 mM. No obvious pitting was observed for F^- and SO_4^{2-}-containing solutions; however, in the presence of Cl^- and NO_3^- anions the current density rose as the applied potential was increased above the pitting potential. This was explained by lyotropic series of the anions for Al(III) given as $F > SO_4^{2-} \gg Cl^- > NO_3^-$ and also by the lower solubility of fluoro-hydro-aluminium and sulfa-hydro-aluminium complexes as the affinity of F^- or SO_4^{2-} ions for Al(III) was greater than Cl^-. Their conclusion was that defluoridation occurred on the surface of the anode without co-existing anions due to electro-condensation effect, and with near 100% efficiency. However, in systems with co-existing anions the defluoridation reaction took place in solution, and the residual fluoride was controlled by Al(III) dosage. Here the effect of SO_4^{2-} on defluoridation by electrocoagulation is significant. The authors further pointed out that SO_4^{2-} not only exerted a competitive effect on the formation of Al-OH-F complex, it also reduced the accumulation of fluoride ions near the anode. Therefore, most of the defluoridation reactions in systems with co-existing anions occurred in bulk solution. Zuo et al. [198] also emphasized the effect of SO_4^{2-} and Cl^- on defluoridation by electrocoagulation. Based on sulphur measurements in dried electrocoagulation sludge, they explained that the increase in sulphur content of the sludge

indicated an increased concentration of SO_4^{2-} in the solution, by the competition between SO_4^{2-} and F^- with the reaction:

$$Al(OH)_{3-x}F_x + ySO_4^{2-} \leftrightarrow Al(OH)_{3-x}F_{x-2y}(SO_4)_y + 2yF^-$$
(48)
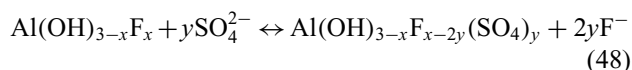
The effect of chloride was also explained by the authors based on the ability of chloride to rupture the passive films of aluminium electrodes [198]. It was concluded that as Cl^- concentration increased, the current efficiency of electrocoagulation and therefore production of aluminium species increased. Although less so than SO_4^{2-}, Cl^- also exerted a competition for complexation with aluminium. However, the positive effects of Cl^- could be offset by the negative role, and Cl^- had only a small effect on defluoridation by electrocoagulation. The authors also evaluated the effect of Ca^{2+} on the process, and found that Ca^{2+} at 250 mg/L concentration enhanced defluoridation by reducing the final fluoride concentration to 0.23 mg/L, with respect to 0.87 mg/L when no Ca^{2+} was present in the water. They explained the positive effect of Ca^{2+} with the probability of co-precipitation of Al^{3+} and Ca^{2+}:

$$mAl^{3+} + nCa^{2+} + (3m + 2n)H_2O$$
$$\leftrightarrow Al_mCa_n(OH)_{3m+2n} + (3m + 2n)H^+ \quad (49)$$
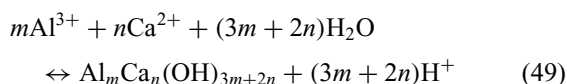
and as the Ca^{2+} had stronger affinity to F^-, incorporation of Ca^{2+} into the aluminium hydroxide might enhance fluoride removal.

Trompette and Vergnes [199] evaluated the effects of supporting electrolytes during electrocoagulation with aluminium electrodes for the treatment of unskimmed milk and cutting oil emulsions, and concluded that SO_4^{2-} ions were quite harmful both for electrical consumption and electrocoagulation efficiency. They also found that chloride and ammonium ions were beneficial, while the role of sodium cations was neutral. The authors also indicated that electrocoagulation could be realized in the presence of sulphate when the $[Cl^-]:[SO_4^{2-}]$ ratio was around or greater than 1:10.

Kolics et al. [200] applied radioactive labelling and electrochemical techniques to evaluate the adsorption of sulphate and chloride ions on aluminium. They demonstrated that sulphate ions bound on the surface increased with solution pH and exposure time. The surface coverage of chloride increased with anodic polarization even above the pitting potential.

Mouedhen et al. [201] conducted a study to assess the behaviour of aluminium electrodes in the electrocoagulation process. They used an electrolyte solution containing 1 g/L Na_2SO_4 and added NaCl to assess the effect of chloride concentrations. They found that a minimum Cl^- concentration of 60 ppm was required to break down the anodic passive film and considerably reduce the cell voltage during electrolysis. They also pointed out that the global

amount of coagulant was originated not only by electro-chemical oxidation of anode; chemical attack at the cathode also yielded soluble aluminium species, resulting in a total amount exceeding the value calculated from Faraday's law.

Zhao et al. [202] evaluated the effects of Ca^{2+} and Mg^{2+} on defluoridation in the electrocoagulation process using an aluminium anode and copper cathode. They indicated that an increase in Ca^{2+} concentration improved defluoridation efficiency, but could not change the optimal molar ratio of OH^- and F^- to Al^{3+} (r_{OH+F}). r_{OH+F} was defined as:

$$r_{OH+F} = \frac{[OH^-]_o + [OH^-]_{EC} + [F^-]_o - [H^+]_o}{[Al^{3+}]_T} \quad (50)$$

where $[OH^-]_o$, $[H^+]_o$ and $[F^-]_o$ are initial concentrations of OH^-, H^+ and F, respectively. $[Al^{3+}]_T$ is the total concentration of Al^{3+} and $[OH]_{EC}$ is the concentration of OH^- generated in the electrolysis process. The highest defluoridation efficiency was obtained at $r_{OH+F} = 3$. Only a small portion of Ca^{2+} was found to enter into the flocs, and Ca^{2+} did not influence the mechanism of defluoridation by electrocoagulation. For the Mg^{2+}-containing system, the optimal r_{OH+F} increased with increasing Mg^{2+} concentration. About 50–70% of the total Mg^{2+} was found to enter into the flocs. This incorporation was explained with the formation of $Mg-Al-F$ layered double hydroxides. Vasudevan et al. [203] used a $Mg-Al-Zn$ alloy as an anode for fluoride removal by electrocoagulation. They obtained a maximum removal efficiency of 96% at the current density of $2\,mA/cm^2$ and a pH of 7.0. They concluded that fluoride was adsorbed onto magnesium hydroxide. However, the mechanism may be the formation of the $Mg-Al-F$ complex found by Zhao et al. [202] rather than magnesium hydroxide, which seems unlikely to form at any significant amount at pH 7.0. In the same work, the effects of carbonate, silicate, phosphate and arsenic on the process were also evaluated. Carbonate, silicate and phosphate inhibited the process beginning at $5\,mg/L$, all causing about 30% loss of fluoride removal efficiencies. The carbonate inhibition was attributed to its passivating effect on the anode. The effects of phosphate and silicate were interpreted as their preferential adsorption over fluoride. The effect of arsenic was the most drastic in that fluoride removal reduced from 96% to 38% by increasing the arsenate concentration from 0.2 to $5\,mg/L$. The effect of arsenate was also explained by preferential adsorption of arsenate over fluoride.

In general, there is an agreement on optimum ranges for the operational parameters of the electrocoagulation process for fluoride removal. The optimum pH range was accepted by some researchers as the wider 6–8 [184]. However, a narrower range has been suggested by many authors. Zuo et al. [198] adopted the optimum influent pH range as 6.0–7.0, while Zhu et al. [190] assumed the optimal pH range of 5.5–6.5. Mameri et al. [6] also found more efficient defluoridation pH between 5 and 7.6. Zhao et al. [204] pointed

out that the removal rate decreased greatly when the pH was higher than 7. Vasudevan et al. [196] also reported that fluoride removal efficiency increased up to pH 7.0 and then decreased with further increase in pH. Gwala et al. [205] determined the optimum pH range as 6–7.

In general, it has been found that treatment time required to attain a certain residual fluoride value increases as the initial fluoride concentration increases [6,183,196,198]. Zhu et al. [190] stated that 'defluoridation efficiency of electrodes tended to decrease although defluoridation capacity increased relatively with the initial F^- concentration rising', implying that this generalization may have a limit.

The effect of current density on the electrocoagulation process has a similar effect. Zhu et al. [190] concluded that current density had little effect on defluoridation by the flocs for current densities $0.463–9.259\,mA/cm^2$. They also found that charge loading increased fluoride removal up to $1.55\,F/m^3$, above which a plateau was reached. Mameri et al. [6] also stated that electrocoagulation was controlled by the formation of fluoroaluminium complexes, and it was not necessary to work with a current density greater than an optimum value for a chosen area/volume (A/V) ratio. Emamjomeh and Sivakumar [184] also found increasing fluoride removals with increasing current density. Ghosh et al. [183] found an increase in fluoride removal with increasing current densities between $37.5–62.5\,mA/cm^2$. Their general comment on this behaviour was that increasing current density caused the anodic oxidation to take place more readily, favouring the formation of amorphous aluminium hydroxide species for adsorption.

The modelling of fluoride removal by electrocoagulation has been attempted by several researchers. The adsorption of F^- has been fitted to the Langmuir isotherm [190,196,206]. Essadki et al. [207] used a combined version of the Langmuir and the Freundlich models.

The effect of temperature on the electrocoagulation process has also been evaluated. Mameri et al. [6] conducted electrocoagulation experiments on Sahara ground water between 20–55°C, and indicated that process efficiency decreased with increasing temperature; they explained the results as desorption of fluoride from aluminium hydroxide and the destruction of fluoroaluminium complexes at high temperature. Vasudevan et al. [196] showed that the adsorption of fluoride was exothermic and spontaneous in nature.

Defluoridation by electrocoagulation has been also analysed for the assessment of reaction kinetics. In some of the studies first-order kinetics was assumed [6,195,208]. However, the first-order kinetic constant changed with operational parameters such as current density, pH and initial fluoride concentration [207]. Emamjomeh and Sivakumar [195] applied first-order kinetics but expressed the rate constant in terms of current concentration (I/V), initial fluoride concentration and electrodes distance. Hu et al. [206] proposed a variable-order kinetics (VOK), which was based on a combination of a first-order kinetics between fluoride

removal and aluminium production and the Langmuir adsorption equilibrium as:

$$\Gamma = \frac{\Gamma_{max}[F^-]}{1 + k[F^-]} \qquad (51)$$

where Γ_{max} represents the maximum Γ (mole of removed fluoride ions per mol Al(III) ions at a given equilibrium pH). If $1/k \gg [F^-]$ the proposed model turns to first-order kinetics, and if $[F^-] \gg 1/k$ the order of reaction is zero. Essadki et al. [207] modified this model considering a combined Langmuir and Freundlich isotherm. Vesudevan et al. [196] worked with both alternating and direct current in their study and found that using both forms of current the adsorption of fluoride fitted the Langmuir isotherm and followed second-order kinetics.

There are a few studies on the optimization, applicability and cost of the defluoridation process by electrocoagulation. Behbahani et al. [208] applied response surface methodology for the optimization of the process. They found that initial fluoride concentration, current density and reaction time were the main parameters affecting fluoride removal in the electrocoagulation process. When the operational cost of the process was calculated as the sum of energy and electrode consumptions and energy consumption was calculated as $E = V \times I \times t$ (V: voltage, I: current intensity, t: time), their analysis showed that the cost of the process was dependent on current density and reaction time values. They obtained maximum operating costs of 1.27–1.48 US\$/m³ for initial fluoride concentrations of 25–100 mg/L. Gwala et al. [205], however, in their optimization study, found that an increase in current density substantially reduced treatment duration but increased residual aluminium level. Ghosh et al. [209] in their techno-economic analysis for the electrocoagulation of fluoride-contaminated drinking water found that fluoride removal efficiency increased with the increase in current density and decreased with an increase in inter-electrode distance. They observed that a 40 min reaction time was required to achieve 1 mg/L fluoride in the electrocoagulation bath for the initial fluoride concentration of 10 mg/L, at 62.5 mA/cm² current density and 5 mm inter-electrode distance. They calculated the operating cost for this system as 0.38 US\$/m³, which was significantly lower than that calculated by Behbahani et al. [208]. Emamjomeh and Sivakumar [184] reported the maximum total operational cost for the electrocoagulation process as 0.6 AUD/m³ treated water for 5 mg/L initial fluoride concentration. Zuo et al. [198] calculated the energy consumption of the electrocoagulation process for 4.0 mg/L initial F^- and 2.2 mA/cm² current density as 1.2 kWh/m³ water.

8.2. Electrocoagulation applications for fluoride-bearing effluents

Fluoride as a wastewater pollutant exists in several industrial wastewaters such as glass treatment, fertilizer, semiconductor manufacturing and metal finishing industries. Studies on the electrocoagulation treatment of fluoride conducted on actual or simulated wastewaters are summarized below.

Cook and Uhrich [210] reported the use of electrocoagulation with aluminium electrodes for the treatment of semiconductor wastewaters pretreated with lime precipitation. The continuous pilot testing of the system was successful in bringing down the fluoride concentrations 1.8 mg/L, but severe passivation problems occurred. Shen et al. [182] used synthetically prepared wastewater to assess the treatability of fluoride using electrocoagulation with bipolar aluminium electrodes. In their study, 15 mg/L influent fluoride concentration was reduced lower than 2 mg/L at initial pH 6, charge loading 4.97 F/m, and a residence time of 20 min. Lower fluoride concentrations were obtained by adding 50 mg/L of Fe^{3+} or Mg^{2+} into the coagulation unit.

Hu et al. [211] effectively removed dissolved fluoride and CaF_2 particles in semiconductor wastewater pretreated with CaF_2 precipitation, using electrocoagulation and flotation. Sodium dodecyl sulphate was used to improve flotation performance in their work. They reported that the fluoride treatment efficiency was optimal when the initial acidity was very close to the initial fluoride concentration ($[H^+]_o \approx [F^-]_o = 27.8$ mg/L) and the final pH was around 7.

Hu et al. [212] used synthetically prepared wastewater with a high fluoride content. Following calcium precipitation, the effluent was used for the evaluation of electrocoagulation–flotation performance using sodium dodecyl sulphate. They compared batch and continuous systems, and found that fluoride removal was the same for both systems for charge loading of about 1000 C/L.

Drouiche et al. [213] prepared a synthetic fluoride solution to represent photovoltaic wastewater and assessed the performance of electrocoagulation with bipolar aluminium electrodes using this sample. An initial fluoride concentration of 25 mg/L was reduced to 9.5 mg/L with 30 V applied potential and at initial pH 6–8. Addition of NaCl up to 100 mg/L further decreased the fluoride concentration.

Khatibikamal et al. [214] applied the electrocoagulation process with aluminium electrodes to steel industry wastewater containing 5 mg/L F; 219 mg/L Cl^- and 180 mg/L SO_4^{2-}. Fluoride removal efficiency of 90% was obtained under 30 V fixed potential in 5 min in the monopolar reactor. The performance was further enhanced by adding extra aluminium plates, turning the system to bipolar. The pH changed from 7 to 4.68 in the first 15 min, and then increased to 9.48 at the end of 40 min. The effect of voltage was also tested between 5–30 V; fluoride was reduced to under 1 mg/L at an initial 10 V for which the current was 0.49 A. The adsorption kinetics was represented by the second-order model.

Beyza et al. [215] investigated the treatability of aluminium surface treatment effluent by electrocoagulation using aluminium electrodes. The wastewater was strong, containing over 6000 mg/L fluoride, almost 5000 mg/L

aluminium as well as 340–370 mg/L COD. High fluoride removals of over 90% were obtained by electrocoagulation. The final fluoride concentrations were affected by initial fluoride levels. For 1500 mg/L chloride concentration as electrolyte, optimum fluoride removals were obtained with current densities between 22.3 and 29.8 mA/cm^2. The process required close control of variables to keep the residual aluminium and COD concentrations at a minimum.

There are two studies which evaluated fluoride removal from wastewaters by electrocoagulation using iron electrodes. Drouiche et al. [216] studied fluoride removal by electrocoagulation using iron electrodes with a synthetically prepared wastewater to simulate the characteristics of photovoltaic wastewater after calcium precipitation. A fluoride concentration of 25 mg/L could be reduced to below 15 mg/L F$^-$, which was the discharge standard value, in 40 min under 30 V potential. When actual wastewater with the same fluoride concentration was used the discharge standard could still be achieved, but longer treatment times were needed. The cost of the process was calculated to be 0.059 US\$ per litre of wastewater treated. Drouiche et al. [217] used simulated photovoltaic wastewater after precipitation with lime to evaluate the performance of electrocoagulation with iron electrodes. The optimum pH for the process was found as 6. The initial concentration of 25 mg/L F$^-$ was reduced to below 15 mg/L in 40 min and with 30 V potential.

Fluoride removal by electrocoagulation technology has achieved a level of applicability for water treatment with some precautions, such as the control of residual aluminium, and technical and economical optimization of the process according to the quality of water being treated. However, studies on its application to wastewaters are limited, although they are promising. Further studies are required with actual wastewaters containing high concentrations of fluoride to elucidate the capability and limitations of the process, as well as to consider interference from factors such as calcium, since they are known to exist in effluents as a component of wastewaters as well as through the pretreatment processes preceding electrocoagulation treatment.

9. Conclusions

In the present review, it was demonstrated that electrocoagulation has successfully been applied for the removal of specific problematic factors (such as colour, recalcitrance and toxicity) that cannot be removed effectively via conventional treatment methods. To date, electrocoagulation has been applied to a wide range of industrial wastewaters, revealing that previous research has focused on the application of electrocoagulation to specific situations and case studies (wastewater treatment plants and waste streams). However, it should be kept in mind that case-related on-site process optimization has limited success, and a more detailed approach is required to predict

reaction performance globally. Mechanisms are expected to change through the process but the dominant mechanisms and their role are yet to be identified. The lack of a fundamental, methodical approach at a mechanistic level is reflected by the lack of similarities in reactor design and application. To date, adequate scale-up parameters have not been defined and the scales of operation parameters vary by more than one magnitude. A logical, systematic approach to a fundamental understanding of electrocoagulation is apparently missing and thus needs further dedicated effort. Only then can an appropriate design phase, based on solid scientific and engineering knowledge, proceed on safe terrain. Obviously, a huge number of key mechanisms are dependent on only few operation parameters. Certainly, dozens of individual optimization studies exist, for example for pH and applied current, to maximize removal efficiencies, but these experimental case studies often conflict with other locally optimized conditions. As a consequence, a trade-off between various competing factors must be evaluated to provide a scientific basis for global optimum operation conditions. From the above facts it is also obvious that the full potential of the electrocoagulation process as an emerging wastewater treatment alternative is yet to be fully realized. Until now, the process has only been empirically optimized and hence requires more fundamental understanding for improved engineering design and full-scale application. In addition, the process involves a not yet fully investigated, complex reaction mechanism related to a variety of surface and interfacial phenomena that limits the engineering and design aspect of electrocoagulation. For optimum performance and future progress in the application of this novel and innovative technology, better reactor design, understanding and process control has to be provided. In this review, special emphasis was placed on the discussion of critical process parameters, fundamentals and reaction mechanism. It is apparent that this enigmatic technology will continue to make inroads into the wastewater treatment arena because of its numerous advantages and changing strategic global water needs.

References

[1] E.A. Vik, D.A. Carlson, A.S. Eikun, and E.T. Gjessing, *Electrocoagulation of potable water*, Water Res. 18 (1984), pp. 1355–1360.
[2] M.J. Matteson, R.L. Dobson, R.W. Glenn Jr., N.S. Kukunoor, W.H. Waits III, and E.J. Clayfield, *Electrocoagulation and separation of aqueous suspensions of ultrafine particles*, Colloids Surfaces A 104 (1995), pp. 101–109.
[3] V.D. Osipenko and P.I. Pogorelyi, *Electrocoagulation neutralization of chromium containing effluent*, Metallurgist 21 (1977), pp. 44–45.
[4] V.V. Amosov, A.G. Zil'berman, E.I. Kucheryavykh, É.I. Sorkin, L. Ya. Tsarik, S.A. Éppel', V.E. Timoshekand and I.P. Titov, *Experience in local treatment of wastewaters from petrochemical production*, Chem. Tech. Fuels Oil 12 (1976), pp. 850–852.

[5] J.-S. Do and M.-L. Chen, *Decolourization of dye-containing solutions by electrocoagulation*, J. Applied Electrochem. 24 (1994), pp. 785–790.

[6] N. Mameri, A.R. Yeddou, H. Lounici, D. Belhocine, H. Grib, and B. Bariou, *Defluoridation of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes*, Water Res. 32 (1998), pp. 1604–1612.

[7] M.-F. Pouet and A. Grasmick, *Urban wastewater treatment by electrocoagulation and flotation*, Water Sci. Technol. 31 (1995), pp. 275–283.

[8] J.A.G. Gomes, P. Daida, M. Kesmez, M. Weir, H. Moreno, J.R. Parga, G. Irwin, H. McWhinney, T. Grady, E. Peterson, and D.L. Cocke, *Arsenic removal by electrocoagulation using combined Al-Fe electrode system and characterization of products*, J. Hazard. Mater. 139 (2007), pp. 220–231.

[9] F. Zidane, P. Drogui, B. Lekhlif, J. Bensaid, J.F. Blais, S. Belcadi, and K. El Kacemi K, *Decolourization of dye-containing effluent using mineral coagulants produced by electrocoagulation*, J. Hazard. Mater. 155 (2008), pp. 153–163.

[10] M. Uğurlu, A. Gurses, C. Doğar, and M. Yalçin, *The removal of lignin and phenol from paper mill effluents by electrocoagulation*, J. Environ. Manage. 87 (2008), pp. 420–428.

[11] K. Bensadok, S. Benammar, F. Lapicque, and G. Nezzal, *Electrocoagulation of cutting oil emulsions using aluminium plate electrodes*, J. Hazard. Mater. 152 (2008), pp. 423–430.

[12] I. Heidmann and W. Calmano, *Removal of Zn(II), Cu(II), Ni(II), Ag(I) and Cr(VI) present in aqueous solutions by aluminium electrocoagulation*, J. Hazard. Mater. 152 (2008), pp. 934–941.

[13] I. Arslan-Alaton, I. Kabdasli, B. Vardar, and O. Tünay, *Electrocoagulation of simulated reactive dyebath effluent with aluminum and stainless steel electrodes*, J. Hazard. Mater. 164 (2009), pp. 1586–1594.

[14] U. Tezcan-Un, A.S. Koparal, and U.B. Ogutveren, *Electrocoagulation of vegetable oil refinery wastewater using aluminum electrodes*, J. Environ. Manage. 90 (2009), pp. 428–433.

[15] M.M. Emamjomeh and M. Sivakumar, *Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes*. J. Environ. Manage. 90 (2009), pp. 1663–1679.

[16] A. Bukhari, *Investigation of the electro-coagulation treatment process for the removal of total suspended solids and turbidity from municipal wastewater*, Bioresour. Technol. 99 (2008), pp. 914–921.

[17] P. Cañizares, M. Carmona, J. Lobato, F. Martinez, and M.A. Rodrigo, *Electrodissolution of aluminum electrodes in electrocoagulation processes*, Ind. Eng. Chem. Res. 44 (2005), pp. 4178–4185.

[18] P. Cañizares, C. Jimenez, F. Martinez, C. Saez, and M.A. Rodrigo, *Study of the electrocoagulation process using aluminum and iron electrodes*, Ind. Eng. Chem. Res. 46 (2007), pp. 6189–6195.

[19] X.M. Chen, G.H. Chen, and P.L. Yue, *Separation of pollutants from restaurant wastewater by electrocoagulation*, Sep. Purif. Technol. 19 (2000), pp. 65–76.

[20] G.H. Chen, *Electrochemical technologies in wastewater treatment*, Sep. Purif. Technol. 38 (2004), pp. 11–41.

[21] P.K. Holt, G.W. Barton, and C.A. Mitchell, *The future for electrocoagulation as a localised water treatment technology*, Chemosphere 59 (2005), pp. 355–367.

[22] J. Goodwin (ed.), *Colloidal Dispersion*, Royal Society of Chemistry, London, 1981, pp. 47.

[23] J.Th.G. Overbeek, *Recent developments in the understanding of colloid stability*, J. Colloid. Interface Sci. 58 (1977), pp. 408–422.

[24] M. Rebhun and M. Lurie, *Control of organic-matter by coagulation and floc separation*, Water Sci. Technol. 27 (1993), pp. 1–20.

[25] X. Xu and X. Zhu, *Treatment of refectory oily wastewater by electro-coagulation process*, Chemosphere 56 (2004), pp. 889–894.

[26] W. Schneider and B. Schwyn, *Aquatic Surface Chemistry,* Wiley/Interscience, New York, 1987.

[27] P.N. Johnson and A. Amirtharajah, *Ferric-chloride and alum as single and dual coagulants*, J. AWWA 75 (1983), pp. 232–239.

[28] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, and D.L. Cocke, *Fundamentals, present and future perspectives of electrocoagulation*, J. Hazard. Mater. 114 (2004), pp. 199–210.

[29] X. Carrier, E. Marceau, J.F. Lambert, and M. Che, *Transformations of gamma-alumina in aqueous suspensions 1. Alumina chemical weathering studied as a function of pH*, J. Colloid. Interface Sci. 308 (2007), pp. 429–437.

[30] M.Y.A. Mollah, R. Schennach, J.R. Parga, and D.L. Cocke, *Electrocoagulation (EC) – science and applications*, J. Hazard. Mater. 84 (2001), pp. 29–41.

[31] P.K. Holt, G.W. Barton, M. Wark, and C.A. Mitchell, *A quantitative comparison between chemical dosing and electrocoagulation*, Colloid. Surf. A-Physicochem. Eng.Asp. 211 (2002), pp. 233–248.

[32] J.G. Ibanez, M.M. Singh, and Z. Szafran, *Laboratory experiments on electrochemical remediation of the environment. Part 4: Color removal of simulated wastewater by electrocoagulation-electroflotation*, J. Chem. Educ. 75 (1998), pp. 1040–1041.

[33] I. Linares-Hernandez, C. Barrera-Diaz, G. Roa-Morales, B. Bilyeu, and F. Urena-Nunez, *Influence of the anodic material on electrocoagulation performance*, Chem. Eng. Journal 148 (2009), pp. 97–105.

[34] P. Hulser, U.A. Krüger, and F. Beck, *The cathodic corrosion of aluminium during the electrodeposition of paint: electrochemical measurements*, Corrosion Science 38 (1996), pp. 47–57.

[35] N. Daneshvar, A. Oladegaragoze, and N. Djafarzadeh, *Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters*, J. Hazard. Mater. 129 (2006), pp. 116–122.

[36] Y.Ş. Yıldız, A.S. Koparal, and B. Keskinler, *Effect of initial pH and supporting electrolyte on the treatment of water containing high concentration of humic substances by electrocoagulation*, Chem. Eng. J. 138 (2008), pp. 63–72.

[37] J. Lyklema, *Fundamentals of Interface and Colloid Science*, Vol. IV: Particulate Colloids, Chapter 3: Pair Interactions, Elsevier Ltd., Amsterdam, 2005.

[38] L. Sánchez-Calvo, J.-P. Leclerc, G. Tanguy, M.-C. Cames, G. Paternotte, G. Valentin, A. Rostan, and F. Lapicque, *An electrocoagulation unit for the purification of soluble oil wastes of high COD*, Env. Progress 22 (2003), pp. 57–65.

[39] H. Liu, S. Liss, and D. Allen, *The influence of anoxic conditioning of sludge on enhanced AOX (adsorbable organic halogen) removal in aerobic biological treatment system*, Water Sci. Technol. 35 (1997), pp. 77–84.

[40] E. Emmanuel, G. Keck, J.M. Blanchard, P. Vermande, and Y. Perrodin, *Toxicological effects of disinfections using sodium hypochlorite on aquatic organisms and its contribution to AOX formation in hospital wastewater*, Environ. Int. 30 (2004), pp. 891–900.

[41] German Sewage Water Administration Regulation, Appendix 51 of the German Sewage Water Administration Regulation, Part I No. 86, 1998 (Anhang 51 der Rahmenabwasserverordnung 1998 Teil I Nr. 86, ausgegeben zu Bonn, 29. Dezember 1998).

[42] V.Y. Baklan and I.P. Kolesnikova, *Influence of electrode material on the electrocoagulation*, J. Aerosol Sci. 27 (1996), pp. S209–S210.

[43] P. Holt, G. Barton, and C. Mitchell, *Electrocoagulation as a Wastewater Treatment*, The Third Annual Australian Environmental Engineering Research Event, 23–26 November Castlemaine, Victoria, 1999, pp. 6.

[44] N.V. Nikolaev, A.S. Kozlovskii, and I.I. Utkin, *Treating natural waters in small water systems by filtration with electrocoagulation*, Sov. J. Water Chem. Technol. 4 (1982), pp. 244–247.

[45] S.P. Novikova and T.L. Shkorbatova, *Purification of effluents from the production of synthetic detergents by electrocoagulation*, Sov. J. Water Chem. Technol. 4 (1982), pp. 353–357.

[46] I.A. Zolotukhin, *A pilot-scale system for the treatment of mine water by electrocoagulationflotation*, Sov. J. Water Chem. Technol. 11 (1989), pp. 147–151.

[47] J. Shore, *Cellulosics Dyeing*, Society of Dyers and Colorists, Alden Press, Oxford, 1995.

[48] I. Arslan-Alaton, *A review of the effect of dye assisting chemicals on advanced oxidation of reactive dyes in wastewater*, Color. Technol. 199 (2003), pp. 345–353.

[49] C. Máximo, M.T. Pessoa-Amorim, and M. Costa-Ferreira, *Biotransformation of industrial reactive azo dyes by Geotrichum sp. CCMI 1019*, Enzyme Microb. Technol. 32 (2003), pp. 145–151.

[50] C. Allegre, M. Maisseu, F. Charbit, and P. Moulin, *Coagulation-flocculation-decantation of dyehouse effluents: concentrated effluents*, J. Hazard. Mater. B116 (2004), pp. 57–64.

[51] I. Kabdaşlı, I. Arslan-Alaton, B. Vardar, and O. Tünay, *Comparison of electrocoagulation, coagulation and the Fenton process for the treatment of reactive dyebath effluent*, Water Sci. Technol. 55 (2007), pp. 125–134.

[52] R. Sanghi and B. Bhattacharya, *Review on decolorization of aqueous dye solutions by low cost adsorbents*, Color. Technol. 118 (2002), pp. 256–269.

[53] I. Koyuncu, *Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinyl sulphone dyes: effects of feed concentration and cross flow velocity*, Desalination 143 (2002), pp. 243–253.

[54] I. Kabdaşlı, T. Ölmez, and O. Tünay, *The factors affecting color removal from reactive dye bath by ozonation*, Water Sci. Technol. 45 (2002), pp. 261–270.

[55] M.C. Gutièrrez, M. Pepió, M. Crespi, and N. Mayor, *Control factors in the electrochemical oxidation of reactive dyes*, Color. Technol. 117 (2001), pp. 356–361.

[56] X. Chen, G. Chen, and P.L. Yue, *Anodic oxidation of dyes at novel Ti/B-diamond el*ectrodes, Chem. Eng. Sci. 58 (2003), pp. 995–1001.

[57] I. Arslan-Alaton, I. Balcioglu, and D.W. Bahnemann, *Advanced oxidation of a reactive dyebath effluent: comparison of O_3, H_2O_2/UV-C and TiO_2/UV-A processes*, Water Res. 36 (2002), 1143–1154.

[58] M. Hepel and J. Luo, *Photoelectrochemical mineralization of textile diazo dye pollutants using nanocrystalline WO_3 electrodes*, Electrochem. Acta 47 (2001), pp. 729–740.

[59] *Handbook Advanced Photochemical Oxidation Processes*, US EPA, Cincinnati, OH, 1998.

[60] B. Merzouk, M. Yakoubi, I. Zongo, J.-P. Leclerc, G. Paternotte, S. Pontvianne, and F. Lapicque, *Effect of modification of textile wastewater composition on electrocoagulation efficiency*, Desalination 275 (2011), pp. 181–186.

[61] B. Merzouk, B. Gourich, A. Sekki, K. Madani, C. Vial, and M. Barkaoui, *Studies on the decolorization of textile dye wastewater by continuous electrocoagulation process*, Chem. Eng. J. 149 (2009), pp. 207–214.

[62] A. Cerqueira, C. Russo, and M.R.C. Marques, *Electroflocculation for textile wastewater treatment*, Braz. J. Chem. Eng. 26 (2009), pp. 659–668.

[63] C. Phalakornkule, S. Polgumhang, and W. Tongdaung, *Performance of an electrocoagulation process in treating direct dye: batch and continuous upflow processes*, World Acad. Sci. Eng. Technol. 57 (2009), pp. 277–282.

[64] A.H. Essadki, M. Bennajah, B. Gourich, Ch. Vial, M. Azzi, and H. Delmas, *Electrocoagulation/electroflotation in an external-loop airlift Reactor-Application to the decolorization of textile dye wastewater: a case study*, Chem. Eng. Processing 47 (2008), pp. 1211–1223.

[65] I. Arslan-Alaton, I. Kabdaşlı, D. Hanbaba, and E. Kuybu, *Electrocoagulation of a real reactive dyebath effluent using aluminum and stainless steel electrodes*, J. Hazard. Mater. 150 (2008), pp. 166–173.

[66] Z. Zaroual, M. Azzi, N. Saib, and E. Chain, *Contribution to the study of electrocoagulation mechanism in basic textile effluent*, J. Hazard. Mater. B131 (2006), pp. 73–78.

[67] N. Daneshvar, H. Ashassi-Sorkhabi, and A. Tizpar, *Decolorization of Orange II by electrocoagulation method*, Sep. Purif. Technol. 31 (2003), pp. 153–162.

[68] I. Arslan-Alaton, I. Kabdaşlı, B.Vardar, and Olcay Tünay, *Electrocoagulation of simulated reactive dyebath effluent with aluminum and stainless steel electrodes*, J. Hazard. Mater. 164 (2009), pp. 1586–1594.

[69] M. Hernández-Ortega, T. Ponziak, C. Barrera-Díaz, M.A. Rodrigo, G. Roa-Morales, and B. Bilyeu, *Use of a combined electrocoagulation-ozone process as a pretreatment for industrial wastewater*, Desalination 250 (2010), pp. 144–149.

[70] O.T. Can, M. Kobya, E. Demirbas, and M. Bayramoglu, *Treatment of the textile wastewater by combined electrocoagulation*, Chemosphere 62 (2006), pp. 181–187.

[71] M. Kobya, O.T. Can, and M. Bayramoglu, *Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes*, J. Hazard. Mater. B100 (2003), pp.163–178.

[72] S.M. Palácio, F.R. Espinoza-Quiñones, A.N. Módenes, C.C. Oliveira, F.H. Borbab, and F.G. Silva Jr., *Toxicity assessment from electro-coagulation treated-textile dye wastewaters by bioassays*, J. Hazard. Mater. 172 (2009), pp. 330–337.

[73] I. Zongo, A.H. Maiga, J. Wéthé, G. Valentin, J.-P. Leclerc, G. Paternotte, and F. Lapicque, *Electrocoagulation for the treatment of textile wastewaters with Al or Fe electrodes: compared variations of COD levels, turbidity and absorbance*, J. Hazard. Mater. 169 (2009), pp. 70–76.

[74] S. Zodi, O. Potier, F. Lapicque, and J.-P. Leclerc, *Treatment of the textile wastewaters by electrocoagulation: Effect of operating parameters on the sludge settling characteristics*, Sep. Purif. Technol. 69 (2009), pp. 29–36.

[75] M. Kobya, M. Bayramoglu, and M. Eyvaz, *Technoeconomical evaluation of electrocoagulation for the textile wastewater using different electrode connections*, J. Hazard. Mater. 148 (2007), pp. 311–318.

[76] M. Bayramoglu, M. Eyvaz, and M. Kobya, *Treatment of the textile wastewater by electrocoagulation.*

Economical evaluation, Chem. Eng. J. 128 (2007), pp. 155–161.

[77] M. Bayramoglu, M. Kobya, O.T. Can, and M. Sozbir, *Operating cost analysis of electrocoagulation of textile dye wastewater*, Sep. Purif. Technol. 37 (2004), pp. 117–125.

[78] J.W. Feng, Y.B. Sun, Z. Zheng, J.B. Zhang, S. Li, and Y.C. Tian, *Treatment of tannery wastewater by electrocoagulation*, J. Environ. Sci. 19 (2007), pp. 1409–1415.

[79] H.M. Wong, C. Shang, Y.K. Cheung, and G. Chen, *Chloride Assisted Electrochemical Disinfection*, the Eighth Mainland-Taiwan Environmental Protection Conference, Tsin Chu, Taiwan, 2002.

[80] A. Benhadji, M.T. Ahmed, and R. Maachiv, *Electrocoagulation and effect of cathode materials on the removal of pollutants from tannery wastewater of Rouïba*, Desalination 277 (2011), pp. 128–134.

[81] S. Kongjao, S. Damronglerd, and M. Hunsom, *Simultaneous removal of organic and inorganic pollutants in tannery wastewater using electrocoagulation technique*, Korean j. Chem. Eng. 25 (2008), pp. 703–709.

[82] I.A. Şengil, S. Kulaç, and M. Özacar, *Treatment of tannery liming drum wastewater by electrocoagulation*, J. Hazard. Matter. 167 (2009), pp. 940–946.

[83] E. Gilpavas, I. Dobrosz-Gómez, and M. Á. Gómez-García, *The removal of trivalent chromium from the leather tanning wastewater: the optimisation of the electrocoagulation process parameters*, Water Sci. Technol. 63 (2011), pp. 385–394.

[84] F.R. Espinoza-Quiñones, M.T.M. Fornari, A.N. Módenes, S.M. Palácio, D.E.G. Trigueros, F. H. Borba, and A.D. Kroumov, *Electrocoagulation efficiency of the tannery effluent treatment using aluminium electrodes*, Water Sci. Technol. 60 (2009), pp. 2173–2185.

[85] C.A. Martínez-Huitle and E. Brillas, *Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review*, Appl. Catal. B-Environ. 87 (2009), pp. 105–145.

[86] F.R. Espinoza-Quiñones, M.T.M. Fornari, A.N. Módenes, S.M. Palácio, F.G. da Silva Jr, N. Szymanski, A.D. Kroumov, and D.E.G. Trigueros, *Pollutant removal from tannery effluent by electrocoagulation*, Chem. Eng. J. 151 (2009), pp. 59–65.

[87] O. Tünay, I. Kabdaşlı, I. Arslan-Alaton, T. Ölmez-Hancı, *Chemical Oxidation Applications for Industrial Wastewaters*, IWA Publishing, London, 2010.

[88] A.P. Murphy, *Chemical removal of nitrate from water*, Nature 350 (1991), 223–225.

[89] M.M. Emamjomeh, M. Sivakumar, *Denitrification using a monopolar electrocoagulation/flotation (ECF) process*, J. Environ. Management 91 (2009), pp. 516–522.

[90] G. Zengin, T. Ölmez, S. Doğruel, I. Kabdaşlı and O. Tünay, *Assessment of source-based nitrogen removal alternatives in leather tanning industry wastewater*, Water Sci. Technol. 45 (2002), pp. 205–215.

[91] O. Tünay, I. Kabdaşlı, D. Orhon, and E. Ateş, *Characterization and pollution profile of leather tanning industry in Turkey*, Water Sci. Technol. 32 (1995), pp. 1–9.

[92] D. Firer, E. Friedler, and O. Lahav, *Control of sulfide in sewer systems by dosage of iron salts: comparison between theoretical and experimental results, and practical implications*, Sci. Total Environ. 392 (2008), pp. 145–156.

[93] D. Wei and K. Osseo-Asare, *Formation of iron monosulfide: a spectrophotometric study of the reaction between ferrous and sulfide ions in aqueous solutions*, J Colloid Interface Sci. 174 (1995), pp. 273–282.

[94] E. Drobner, H. Huber, G. Wachtershauser, D. Rose, and K.O. Stetter, *Pyrite formation linked with hydrogen evolution under anaerobic conditions*, Nature 346 (1990), pp. 742–744.

[95] N.A. Padival, W.A. Kimbell, and J.A. Redner, *Use iron salts to control dissolved sulfide in trunk sewers*, J. Environ. Eng. ASCE 121(1995) pp. 824–829.

[96] A. Davydov, K.T. Chuang, and A.R. Sanger, *Mechanism of H_2S oxidation by ferric oxide and hydroxide surfaces*, J. Phys. Chem. B 102(1998), pp. 4745–4752.

[97] M. Murugananthan, G.B. Raju, and S. Prabhakar, *Removal of sulphide, sulfate and sulfite ions by electro coagulation,* J. Hazard. Mat. B109 (2004), pp. 37–44.

[98] O. Tünay, I. Kabdaşlı, and Y-T. Hung, *Treatment of metal finishing wastes*, in *Handbook of Industrial Hazardous Waste Treatment*, L.K. Wang, Y-T. Hung, H.H. Lo, and C. Yapijakis, 2nd ed, Marcel Dekker Inc., Boca Raton, 2007, pp. 289–359.

[99] D. Pokhrel and T. Viraraghavan, *Treatment of pulp and paper mill wastewater – a review*, Sci. Total Environ. 333 (2004), pp. 37–58.

[100] M. Zaied and N. Bellakhal, *Electrocoagulation treatment of black liquor from paper industry*, J. Hazard. Mater. 163 (2009), pp. 995–1000.

[101] S. Khansorthong and M. Hunsom, *Remediation of wastewater from pulp and paper mill industry by the electrochemical technique*, Chem. Eng. J. 151 (2009), pp. 228–234.

[102] E: Terrazas, A. Vázquez, R. Briones, I. Lázaro, and I. Rodríguez, *EC treatment for reuse of tissue paper wastewater: Aspects that affect energy consumption*, J. Hazard. Mater. 181 (2010), pp. 809–816.

[103] M. Vepsäläinen, J. Selin, P. Rantala, M. Pulliainen, H. Särkkä, K. Kuhmonen, A. Bhatnagar, and M. Sillanpää, *Precipitation of dissolved sulphide in pulp and paper mill wastewater by electrocoagulation*, Environ. Technol. 32 (2011), 1393–1400.

[104] P.A. Soloman, C. Ahmed Basha, M. Velan, N. Balasubramanian, and P. Marimuthu, *Augmentation of biodegradability of pulp and paper industry wastewater by electrochemical pre-treatment and optimization by RSM*, Sep. Purif. Technol. 69 (2009), pp. 109–117.

[105] S. Zodi, J-N. Louvet, C. Michon, O. Potier, M-N. Pons, F. Lapicque, and J-P. Leclerc, *Electrocoagulation as a tertiary treatment for paper mill wastewater: Removal of non-biodegradable organic pollution and arsenic*, Sep. Purif. Technol. 81 (2011), pp. 62–68.

[106] K.S. Parama Kalyani, N. Balasubramanian, and C. Srinivasakannan, *Decolorization and COD reduction of paper industrial effluent using electro-coagulation*, Chem. Eng. J. 151 (2009), pp. 97–104.

[107] R. Katal and H. Pahlavanzadeh, *Influence of different combinations of aluminum and iron electrode on electrocoagulation efficiency: Application to the treatment of paper mill wastewater*, Desalination 265 (2011), pp. 199–205.

[108] R. Sridhar, V. Sivakumar, V. Prince Immanuel, and J. Prakash Maran, *Treatment of pulp and paper industry bleaching effluent by electrocoagulant process*, J. Hazard. Mater. 186 (2011), pp. 1495–1502.

[109] C-T. Wang, W-L. Chou and Y-M. Kuo, *Removal of COD from laundry wastewater by electrocoagulation/ electroflotation*, J. Hazard. Mater. 164 (2009), pp. 81–86.

[110] T. Olmez-Hanci, Z. Kartal, and I. Arslan-Alaton, *Electrocoagulation of commercial naphthalene sulfonates: Process optimization and assessment of implementation potential*, J. Environ. Manage. 99 (2012), pp. 44–51.

[111] M. Gotsi, N. Kalogerakis, E. Psillakis, P. Samaras, and D. Mantzavinos, *Electrochemical oxidation of olive oil mill wastewaters*, Water Res. 39 (2005), pp. 4177–4187.

[112] W. Najjar, S. Azabou, S. Sayadi, and A. Ghorbel, *Catalytic wet peroxide photo-oxidation of phenolic olive oil mill wastewater contaminants Part I. Reactivity of tyrosol over (Al-Fe)PILC*, Appl. Catal. B74 (2007), pp. 11–18.

[113] P. Cañizares, J. Lobato, R. Paz, M.A. Rodrigo, and C. Sáez, *Advanced oxidation processes for the treatment of olive-oil mills wastewater*, Chemosphere 67 (2007), pp. 832–838.

[114] E.S. Aktas, S. Imre, and L. Ersoy, *Characterization and lime treatment of olive mill wastewater*, Water Res. 35 (2001), 2336–2340.

[115] M. Drouiche, V. Le Mignot, H. Lounici, D. Belhocine, H. Grib, A. Pauss, and N. Mameri, *A compact process for the treatment of olive mill wastewater by combining UF and UV/H_2O_2 techniques*, Desalination 169 (2004), pp. 81–88.

[116] P. Paraskeva and E. Diamadopoulos, *Technologies for olive mill wastewater (OMW) treatment: A review*, J. Chem. Technol. Biotechnol. 81 (2006), pp. 1475–1485.

[117] N. Adhoum and L. Monser, *Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation*, Chem. Eng. Process. 43 (2004), pp. 1281–1287.

[118] H. Inan, A. Dimoglo, H. Şimşek, and M. Karpuzcu, *Olive oil mill wastewater treatment by means of electro-coagulation*, Sep. Purif. Technol. 36 (2004), 23–31.

[119] Ü. Tezcan Ün, S. Uğur, A.S. Koparal, and Ü. Bakır Öğütveren, *Electrocoagulation of olive mill wastewaters*, Sep. Purif. Technol. 52 (2006), pp. 136–141.

[120] S. Khoufi, F. Feki, and S. Sayadi, *Detoxification of olive mill wastewater by electrocoagulation and sedimentation processes*, J. Hazard. Mater. 142 (2007), pp. 58–67.

[121] I. Arslan-Alaton, T. Olmez-Hanci, E. Dulekgurgen, and D. Orhon, *Assessment of organic carbon removal by particle size distribution analysis*, Environ Eng. Sci. 26 (2009), pp. 1239–1248.

[122] F. Hanafi, O. Assobhei, and M. Mountadar, *Detoxification and discoloration of Moroccan olive mill wastewater by electrocoagulation*, J. Hazard. Mater. 174 (2010), pp. 807–812.

[123] F. Hanafi, A. Belaoufi, M. Mountadar, and O. Assobhei, *Augmentation of biodegradability of olive mill wastewater by electrochemical pre-treatment: Effect on phytotoxicity and operating cost*, J. Hazard. Mater. 190 (2011), pp. 94–99.

[124] S. Khoufi, H. Aouissaoui, M. Penninckx, and S. Sayadi, *Application of electro-Fenton oxidation for the detoxification of olive mill wastewater phenolic compounds*, Water Sci. Technol. 49 (2004), 97–102.

[125] O. Yahiaoui, H. Lounici, N. Abdi, N. Drouiche, N. Ghaffour, A. Pauss, and N. Mameri, *Treatment of olive mill wastewater by the combination of ultrafiltration and bipolar electrochemical reactor processes*, Chem. Eng. Process. 50 (2011), 37–41.

[126] O. Tünay and N.I. Kabdaşlı, *Hydroxide precipitation of complexed metals*, Water Res. 28 (1994), pp. 2117–2124.

[127] F. Akbal and S. Camcı, *Comparison of electrocoagulation and chemical coagulation for heavy metal removal*, Chem. Eng. Technol. 33 (2010), pp. 1655–1664.

[128] N. Adhoum, L. Monser, N. Bellakhal, and J.E. Belgaied, *Treatment of electroplating wastewater containing Cu^{2+}, Zn^{2+} and Cr(VI) by electrocoagulation*, J. Hazard. Mater. B112 (2004), pp. 207–213.

[129] F. Akbal and S. Camcı, *Copper, chromium and nickel removal from metal plating wastewater by electrocoagulation*, Desalination 269 (2011), pp. 214–222.

[130] M. Kobya, E. Demirbas, A. Dedeli, and M.T. Sensoy, *Treatment of rinse water from zinc phosphate coating by batch and continuous electrocoagulation processes*, J. Hazard. Mater. 173 (2010), pp. 326–334.

[131] M. Kobya, E. Demirbas, N.U. Parlak, and S. Yigit, *Treatment of cadmium and nickel electroplating rinse water by electrocoagulation*, Environ. Technol. 31 (2010), pp. 1471–1481.

[132] I. Heidmann and W. Calmano, *Removal of Ni, Cu and Cr from a galvanic wastewater in an electrocoagulation system with Fe- and Al-electrodes*, Sep. Purif. Technol. 71 (2010), pp. 308–314.

[133] A.K. Golder, V.S. Dhaneesh, A.N. Samantac, and S. Ray, *Electrotreatment of industrial copper plating rinse effluent using mild steel and aluminium electrodes*, J. Chem. Technol. Biotechnol. 84 (2009), pp. 1803–1810.

[134] T. Ölmez, *The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology*, J. Hazard. Mater. 162 (2009), pp. 1371–1378.

[135] M.G. Arroyo, V. Pérez-Herranz, M.T. Montañéz, J. García-Antón, and J.L. Guiñón, *Effect of pH and chloride concentration on the removal of hexavalent chromium in a batch electrocoagulation reactor*, J. Hazard. Mater. 169 (2009) pp. 1127–1133.

[136] G. Mouedhen, M. Feki, M. De Petris-Wery, and H.F. Ayedi, *Electrochemical removal of Cr(VI) from aqueous media using iron and aluminium as electrode materials: Towards a better understanding of the involved phenomena*, J. Hazard. Mater. 168 (2009), pp. 983–991.

[137] D.L. Sedlak and P.G. Chan, *Reduction of hexavalent chromium by ferrous iron*, Geochim. Cosmochim. Acta 61 (1997), pp. 2185–2192.

[138] M.A. Schlautman and I. Han, *Effects of pH and dissolved oxygen on the reduction of hexavalent chromium by dissolved ferrous iron in poorly buffered aqueous systems*, Water Res. 35 (2001), pp.1534–1546.

[139] M. Pettine, L. D'Ottone, L. Campanella, F.J. Millero, and R. Passino, *The reduction of chromium(IV) by iron(II) in aqueous solutions*, Geochim. Cosmochim. Acta 62 (1998), pp. 1509–1519.

[140] I.J. Buerge and S.T. Hug, *Kinetics and pH dependence of chromium (VI) reduction by iron(II)*, Environ. Sci. Technol. 31 (1997), pp. 1426–1432.

[141] I. Kabdaşlı, T. Arslan, T. Ölmez-Hancı, I. Arslan-Alaton, and O. Tünay, *Complexing agent and heavy metal removals from metal plating effluents by electrocoagulation with stainless steel electrodes*, J. Hazard. Mater. 165 (2009), pp. 838–845.

[142] I. Kabdaşlı, T. Arslan, I. Arslan-Alaton, T. Ölmez-Hancı, and O. Tünay, *Organic matter and heavy metal removals from complexed metal plating effluent by the combined electrocoagulation/Fenton process*, Water Sci. Technol. 61 (2010), pp. 2617–2624.

[143] A. Imran, A.K. Tabrez, and A. Mohd, *Removal of arsenic from water by electrocoagulation and electrodialysis techniques*, Sep. Purif. Rev. 40 (2011), pp. 25–42.

[144] D. Mohan and C.U. Pittman Jr., *Arsenic removal from water/wastewater using adsorbents - A critical review*, J. Hazard Mater. 142 (2007), pp. 1–53.

[145] C. Sullivan, M. Tyrer, C.R. Cheeseman, and N.J.D. Graham, *Disposal of water treatment wastes containing arsenic - A review*, Sci. Total Environ. 408 (2010), pp. 1770–1778.

[146] D.E. Giles, M. Mohapatra, T.B. Issa, S. Anand, and P. Singh, *Iron and aluminium based adsorption strategies for removing arsenic from water*, J. Environ. Manage. 92 (2011), pp. 3011–3022.

[147] K.P. Raven, A. Jain, and R.H. Loeppert, *Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes*, Environ. Sci. Technol. 32 (1998), pp. 344–349.

[148] A. Jain, K.P. Raven, and R.H. Loeppert, *Arsenite and arsenate adsorption on ferrihydrite: Surface charge reduction and net OH^- release stoichiometry*, Environ. Sci. Technol. 33 (1999), pp. 1179–1184.

[149] V. Lenoble, O. Bouras, V. Deluchat, B. Serpaud, and C. Bollinger, *Arsenic adsorption onto pillared clays and iron oxides*, J. Colloid Interface Sci. 255 (2001), pp. 52–58.

[150] M.B. Ranjan, D.Soumen, D. Sushanta, and G.U. De Chand, *Removal of arsenic from ground water using crystalline hydrous ferric oxide (CHFO)*, Water Qual. Res. J. Can. 38 (2003), 193–210.

[151] S. Goldberg and C.T. Johnston, *Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling*, J. Colloid Interf. Sci. 234 (2001), pp. 204–216.

[152] J. Qiao, Z. Jiang, B. Sun, Y. Sun, Q. Wang and X. Guan, *Arsenate and arsenite removal by $FeCl_3$: Effects of pH, As/Fe ratio, initial As concentration and co-existing solutes*, Sep. Purif. Technol. (2012), doi:10.1016/j.seppur.2012.03.023 (in press).

[153] D. Lakshmanan, D.A. Clifford, and G. Samanta, *Comparative study of arsenic removal by iron using electrocoagulation and chemical coagulation*, Water Res. 44 (2010), pp. 5641–5652.

[154] W. Wan, T.J. Pepping, T. Banerji, S. Chaudhari, and D.E. Giammar, *Effects of water chemistry on arsenic removal from drinking water by electrocoagulation*, Water Res. 45 (2011), pp. 384–392.

[155] M. Kobya, F. Ulu, U. Gebologlu, E. Demirbas, and M.S. Oncel, *Treatment of potable water containing low concentration of arsenic with electrocoagulation: Different connection modes and Fe-Al electrodes*, Sep. Purif. Technol. 77 (2011), pp. 283–293.

[156] P.R. Kumar, S. Chaudhari, K.C. Khilar, and S.P. Mahajan, *Removal of arsenic from water by electrocoagulation*, Chemosphere 55 (2004), pp. 1245–1252.

[157] V. Pallier, G. Feuillade-Cathalifaud, and B. Serpaud. *Influence of organic matter on arsenic removal by continuous flow electrocoagulation treatment of weakly mineralized waters*, Chemosphere 83 (2011), pp. 21–28.

[158] M. Arienzo, P. Adamo, J. Chiarenzelli, M.R. Bianco, and A. De Martino, *Retention of arsenic on hydrous ferric oxides generated by electrochemical peroxidation,* Chemosphere 48 (2002), pp. 1009–1018.

[159] J.R. Parga, D.L. Cocke, J.L. Valenzuela, J.A. Gomes, M. Kesmez, G. Irwin, H. Moreno, and M. Weir, *Arsenic removal via electrocoagulation from heavy metal contaminated groundwater in La Comarca Lagunera Mexico*, J. Hazard. Mater. 124 (2005), pp. 247–254.

[160] X. Zhao, B. Zhang, H. Liu, and J.H. Qu, *Removal of arsenite by simultaneous electro-oxidation and electro-coagulation process*, J. Hazard. Mater. 184 (2010), pp. 472–476.

[161] S. Vasudevan, J. Lakshmi, and G. Sozhan, *Studies relating to removal of arsenate by electrochemical coagulation: optimization, kinetics, coagulant characterization*, Sep. Sci. Technol. 45 (2010), pp. 1313–1325.

[162] S. N. Kumar and S. Goel, *Factors influencing arsenic and nitrate removal from drinking water in a continuous flow electrocoagulation (EC) process*, Hazard. Mater. 173 (2010), pp. 528–533.

[163] N. Balasubramanian, T. Kojima, C.A. Basha, and C. Srinivasakannan, *Removal of arsenic from aqueous solution using electrocoagulation*, J. Hazard. Mater. 167 (2009), pp. 966–969.

[164] J.F. Martinez-Villafane, C. Montero-Ocampo, and A.M. Garcia-Lara, *Energy and electrode consumption analysis of electrocoagulation for the removal of arsenic from underground water*, J. Hazard. Mater. 172 (2009), pp. 1617–1622.

[165] H.K. Hansen, P. Nunez, and R. Grandon, *Electrocoagulation as a remediation tool for wastewaters containing arsenic*, Miner. Eng. 19 (2006), pp. 521–524.

[166] H.K. Hansen, P. Nunez, D. Raboy, I. Schippacasse, and R. Grandon, *Electrocoagulation in wastewater containing arsenic: Comparing different process designs*, Electrochim. Acta 52 (2007), pp. 3464–3470.

[167] P. Lakshmipathiraj, S. Prabhakar, and G.B. Raju, *Studies on the electrochemical decontamination of wastewater containing arsenic*, Sep. Purif. Technol. 73 (2010), pp. 114–121.

[168] E. Lacasa, P. Canizares, C. Saez, F.J. Fernandez, and M.A. Rodrigo, *Removal of arsenic by iron and aluminium electrochemically assisted coagulation*, Sep. Purif. Technol. 79 (2011), pp. 15–19.

[169] D. Hendricks, *Water Treatment Unit Processes Physical and Chemical*, CRC Press, Taylor and Francis Group, Boca Raton, 2006.

[170] J. Duan and J. Gregory, *Coagulation by hydrolyzing metal salts*, Adv. Colloid Interfac. 100–102 (2003), pp. 475–502.

[171] N. Parthasarathy and J. Buffle, *Study of polymeric aluminium(III) hydroxide solutions for application in waste water treatment, Properties of the polymer and optimal conditions of preparation*, Water Res. (1985), pp. 25–36.

[172] S. Ayoob, A.K. Gupta, and T. Bhat Venugopal, *A conceptual overview on sustainable technologies for the defluoridation of drinking water*, Crit. Rev. Env. Sci. Tech. 38 (2008), pp. 401–470.

[173] J. Buffle, N. Parthasarathy, and W. Haerdi, *Importance of speciation methods in analytical control of water treatment processes with application to fluoride removal from waste waters*, Water Res. 19 (1985), pp. 7–24.

[174] L. Ming, S.R. Yi, Z.J. Hua, B.Y.W. Lei, L. Ping, and K.C. Fuwa, *Elimination of excess fluoride in potable water with coacervation by electrolysis using aluminium anode*, Fluoride 20 (1983), pp. 54–63.

[175] A. Mekonen, P. Kumar, and A. Kumar, *Integrated biological and physiochemical treatment process for nitrate and fluoride removal*, Water Res.35 (2001), pp. 3127–3136.

[176] M.G. Sujana, R.S. Thakur, and S.B. Rao, *Removal of fluoride from aqueous solution by using alum sludge*, J. Colloid Interf. Sci. 206 (1998), pp. 94–101.

[177] O.J. Hao and C.P. Huang, *Adsorption characteristics of fluoride onto hydrous alumina*, J. Environ. Eng-Asce 112 (1986), pp. 1054–1069.

[178] G.L. Schmitt and D.J. Pietrzyk, *Liquid-chromatographic separation of inorganic anions on an alumina column*, Anal. Chem. 57 (1985), pp. 2247–2253.

[179] S. Saha, *Treatment of aqueous effluent for fluoride removal*, Water Res. 27 (1993), pp. 1347–1350.

[180] W. Szczepaniak and H. Koscielna, *Specific adsorption of halogen anions on hydrous gamma-Al_2O_3*, Anal. Chim. Acta 470 (2002), pp. 263–276.

[181] B. Kasprzyk-Hordern, *Chemistry of alumina, reactions in aqueous solution and its application in water treatment*, Adv. Colloid Interfac. 110 (2004), pp. 19–48.

[182] F. Shen, X.M. Chen, P. Gao, and G.H. Chen, *Electrochemical removal of fluoride ions from industrial wastewater*, Chem. Eng. Sci. 58 (2003), pp. 987–993.

[183] D. Ghosh, C.R. Medhi, and M.K. Purkait, *Treatment of fluoride containing drinking water by electrocoagulation using monopolar and bipolar electrode connections*, Chemosphere 73 (2008), pp. 1393–1400.

[184] M.M. Emamjomeh and M. Sivakumar, *Fluoride removal by a continuous flow electrocoagulation reactor*, J. Environ. Manage. 90 (2009), pp. 1204–1212.

[185] C.Y. Hu, S.L. Lo, and W.H. Kuan, *Effects of the molar ratio of hydroxide and fluoride to Al(III) on fluoride removal by coagulation and electrocoagulation*, J. Colloid Intref. Sci. 283 (2005), pp. 472–476.

[186] C.L. Yang and R. Dluhy, *Electrochemical generation of aluminum sorbent for fluoride adsorption*, J. Hazard Mater 94 (2002), pp. 239–252.

[187] R.P. Liu, W.X. Gong, H.C. Lan, Y.P. Gao, H.J. Liu, and J.H. Qu, *Defluoridation by freshly prepared aluminum hydroxides*, Chem. Eng. J. 175 (2011), pp. 144–149.

[188] M.G. Sujana, G. Soma, N. Vasumathi, and S. Anand, *Studies on fluoride adsorption capacities of amorphous Fe/Al mixed hydroxides from aqueous solutions*, J. Fluorine Chem. 130 (2009), pp. 749–754.

[189] C.Y. Hu, S.L. Lo, and W.H. Kuan, *Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes*, Water Res. 37 (2003), pp. 4513–4523.

[190] J. Zhu, H.Z. Zhao, and J. Ni, *Fluoride distribution in electrocoagulation defluoridation process*, Sep. Purif. Technol. 56 (2007), pp. 184–191.

[191] M.M. Emamjomeh, M. Sivakumar, and A.S. Varyani, *Analysis and the understanding of fluoride removal mechanisms by an electrocoagulation/flotation (ECF) process*, Desalination 275 (2011), pp. 102–106.

[192] H.Z. Zhao, W. Yang, J. Zhu, and J.R. Ni, *Defluoridation of drinking water by combined electrocoagulation: Effects of the molar ratio of alkalinity and fluoride to Al(III)*, Chemosphere 74 (2009), pp. 1391–1395.

[193] W.A. Badawy, F.M. Al-Kharafi, and A.S. El-Azab, *Electrochemical behaviour and corrosion inhibition of Al, Al-6061 and Al-Cu in neutral aqueous solutions*, Corros. Sci. 41 (1999), pp. 709–727.

[194] N. Mameri, H. Lounici, D. Belhocine, H. Grib, D.L. Piron, and Y. Yahiat, *Defluoridation of Sahara water by small plant electrocoagulation using bipolar aluminium electrodes*, Sep. Purif. Technol. 24 (2001), pp. 113–119.

[195] M.M. Emamjomeh and M. Sivakumar, *An empirical model for defluoridation by batch monopolar electrocoagulation/flotation (ECF) process*, J. Hazard Mater. 131 (2006), pp. 118–125.

[196] S. Vasudevan, B.S. Kannan, J. Lakshmi, S. Mohanraj, and G. Sozhan, *Effects of alternating and direct current in electrocoagulation process on the removal of fluoride from water*, J. Chem. Technol. Biotechnol. 86 (2011), pp. 428–436.

[197] L.S. Cheng, *Electrochemical method to remove fluorine from drinking water*, Water Supp. 3 (1985), pp. 177–186.

[198] Q.H. Zuo, X.M. Chen, W. Li, and G. Chen, *Combined electrocoagulation and electroflotation for removal of fluoride from drinking water*, J. Hazard. Mater. 159 (2008), pp. 452–457.

[199] J.L. Trompette and H. Vergnes, *On the crucial influence of some supporting electrolytes during electrocoagulation in the presence of aluminum electrodes*, J. Hazard. Mater. 163 (2009), pp. 1282–1288.

[200] A. Kolics, J.C. Polkinghorne, and A. Wieckowski, *Adsorption of sulfate and chloride ions on aluminum*, Electrochim. Acta. 43 (1998), pp. 2605–2618.

[201] G. Mouedhen, M. Feki, M. De Petris Wery, and H.F. Ayedi, *Behavior of aluminum electrodes in electrocoagulation process*, J. Hazard. Mater. 150 (2008), pp. 124–135.

[202] H.Z. Zhao, B. Zhao, W. Yang, and T.H. Li, *Effects of Ca(2+) and Mg(2+) on defluoridation in the electrocoagulation process*, Environ. Sci. Technol. 44 (2010), pp. 9112–9116.

[203] S. Vasudevan, J. Lakshmi, and G. Sozhan, *Studies on a Mg-Al-Zn alloy as an anode for the removal of fluoride from drinking water in an electrocoagulation process*, Clean 37 (2009), 372–378.

[204] X. Zhao, B. Zhang, H. Liu, and J. Qu, *Simultaneous removal of arsenite and fluoride via an integrated electro-oxidation and electrocoagulation process*, Chemosphere 83 (2011), pp. 726–729.

[205] P. Gwala, S. Andey, V. Mhaisalkar, P. Labhasetwar, S. Pimpalkar, and C. Kshirsagar, *Lab scale study on electrocoagulation defluoridation process optimization along with aluminium leaching in the process and comparison with full scale plant operation*, Water Sci. Technol. 63 (2011), pp. 2788–2795.

[206] C.-Y. Hu, S.L. Lo, and W.-H. Kuan, *Simulation the kinetics of fluoride removal by electrocoagulation (EC) process using aluminum electrodes*, J. Hazard. Mater. 145 (2007), pp. 180–185.

[207] A.H. Essadki, B. Gourich, M. Azzi, Ch. Vial, and H. Delmas, *Kinetic study of defluoridation of drinking water by electrocoagulation/electroflotation in a stirred tank reactor and in an external-loop airlift reactor*, Chem. Eng. J. 164 (2010), pp. 106–114.

[208] M. Behbahani, M.R. Alavi Moghaddam, and M. Arami, *Techno-economical evaluation of fluoride removal by electrocoagulation process: Optimization through response surface methodology*, Desalination 271 (2011), pp. 209–218.

[209] D. Ghosh, C.R. Medhi, and M.K. Purkait, *Techno-economic analysis for the electrocoagulation of fluoride-contaminated drinking water*, Toxicol. Environ. Chem. 93 (2011), pp. 424–437.

[210] S.L. Cook and K.D. Uhrich, *Electrochemical fluoride removal in semiconductor wastewater*, 44th Purdue University Industrial Waste Conference Proceedings, (1990), Lewis Publishers, Imc., Chelsea, Michigan, pp. 373–383.

[211] C.Y. Hu, S.L. Lo, W.H. Kuan, and Y.D. Lee, *Removal of fluoride from semiconductor wastewater by electrocoagulation-flotation*, Water Res. 39 (2005), pp. 895–901.

[212] C.-Y. Hu, S.L. Lo, W.-H. Kuan, and Y.D. Lee, *Treatment of high fluoride-content wastewater by continuous electrocoagulation-flotation system with bipolar aluminum electrodes*, Sep. Purif. Technol. 60 (2008), pp. 1–5.

[213] N. Drouiche, S. Aoudj, M. Hecini, N. Ghaffour, H. Lounici, and N. Mameri, *Study on the treatment of photovoltaic wastewater using electrocoagulation: Fluoride removal with aluminium electrodes −Characteristics of products*, J. Hazard. Mater. 169, (2009), pp. 65–69.

[214] V. Khatibikamal, A. Torabian, F. Janpoor, and G. Hoshyaripour, *Fluoride removal from industrial wastewater using electrocoagulation and its adsorption kinetics*, J. Hazard. Mater. 179 (2010), pp. 276–280.

[215] B. Samuk, I. Kabdaşlı, O. Tünay, and M. Karpuzcu, *Fluoride abatement from aluminium surface treatment effluents by electrocoagulation,* Fresenious Environ. Bullet. (2012) in press.

[216] N. Drouiche, N. Ghaffour, H. Lounici, N. Mameri, A. Maallemi, and H. Mahmoudi, *Electrochemical treatment of chemical mechanical polishing wastewater: removal of fluoride – sludge characteristics – operating cost*, Desalination 223 (2008), 134–142.

[217] N. Drouiche, S. Aoudj, H. Lounici, M. Drouiche, T. Ouslimane, and N. Ghaffour, *Fluoride removal from pretreated photovoltaic wastewater by electrocoagulation: An investigation of the effect of operational parameters*, Procedia Engineering 33 (2012), pp. 385–391.