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Role of turbulent flow and gas bubbles in enhancing mass transfer in batch electrocoagulation: a brief review

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ABSTRACT

Electrocoagulation (EC) has now become a popular choice in wastewater treatment owing to its easy operation, low sludge production and small quantity of chemicals used. Electrocoagulation is an electrochemical method that involves the release of active coagulant precursors (usually aluminium or iron cations) from corroded sacrificial anodes in a solution with the simultaneous formation of hydroxyl ions and hydrogen gas at the anode and cathode, respectively. The conventional design of the electrodes in an EC cell, however, does not take into consideration the impact of electrode passivation. It has been shown that the accumulation of hydrogen bubbles around the electrodes will result in a high internal resistance between the electrodes and will hinder the transfer of ions, which eventually, the efficiency of the EC cell will be reduced. While providing an extensive review of electrocoagulation, the main focus of this paper has been to highlight recent works on EC cells such as investigations into the geometry of electrodes and the utilization of gas bubbles to improve the removal efficiency. Interestingly, the improvements have not only been shown to have had a strong influence on the mass transfer of the EC cell but have also indirectly reduced the impact of passivation and the accumulation of bubbles on the electrodes. The roles of agitation through mechanical stirring and gas bubbles in enhancing mass transfer during electrocoagulation have also been discussed in this paper.

Keywords: Batch electrocoagulation; Electrode passivation; Mass transfer; Turbulent flow; Gas bubbles

1. Introduction

With the rapid growth of industrialization, the increase in industrial and manufacturing activities has resulted in a tremendous production of wastewater that pollutes rivers, lakes and oceans. Therefore, as the demand for clean and safe water to meet the needs of a growing population becomes increasingly acute, it is crucial to have an adequate wastewater treatment system. Of all the wastewater treatment methods in use today, the electrocoagulation (EC) process recently sparked renewed interest due to its potential to remove wastewater pollutants. It has been

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proven that this technology is able to effectively remove harmful substances from various wastewater sources, for example, the chemical mechanical polishing of wastewater from the semiconductor industry [1,2], the removal of heavy metals from textile wastewater [3], crude oil from petroleum wastewater [4], palm oil mill effluent [5] as well as leachate from municipal wastewater [6–8].

Similar to coagulation–flocculation, electrocoagulation can be generally defined as the destabilization of a colloidal suspension or solution, where the destabilized particles are propagated to gather and agglomerate into larger flocs [9]. This technique, however, is different from the coagulation–flocculation method as the electric current is applied to the connecting aluminium (Al) or iron (Fe) electrodes, which are placed in the wastewater. Coagulants are then formed by the dissolution of the anode, where the precipitates can either be removed by sedimentation or flotation [10]. Theoretically, the release of cations during the electrocoagulation process is expected to reduce the repulsive energy (energy barrier) between the particles. With less repulsive forces between them, the particles can then be destabilized to form agglomerates that allow for easier separation of the sludge from the treated water [11].

Despite the successful treatment of wastewater demonstrated by EC, as reported in various literature, this method still has to be subjected to various technical improvements before it can be considered as a reliable wastewater treatment technology. According to Moussa et al. [11], further research should be conducted with regard to the EC technology, particularly on fitting its actual operation for industrial applications. Several approaches have been recommended to overcome this issue such as a modified EC reactor design and its operation and modelling behaviour, and a continuous flow mode of operation with a focus on its economic feasibility. Apart from proposing changes to the EC design and its mode of operation, there have also been suggestions on preventing electrode passivation in the EC process [12,13].

Electrode passivation is the formation of an impermeable oxide film on the sacrificial anode during the electrocoagulation process. The formation of this film hinders metal dissolution by reducing the ionic transfer between the anode and cathode as well as indirectly preventing the formation of a metal hydroxide [14]. The evolution and accumulation of hydrogen and oxygen gases in the form of gas bubbles at the respective cathode and anode will also reduce the performance of the EC by increasing the electrical resistance of the cell [15]. This may result in a higher consumption of electrical energy and lead to higher operational costs for EC.

Since most of the past studies focused on measures to reduce electrode passivation, this paper was aimed at analysing the recent approaches that were used to improve the EC process, particularly with regard to the changes made to the electrode in the EC reactor. Besides explaining the mechanism of electrode passivation in EC and the role of a turbulent flow under the influence of mechanical agitation and non-agitation in enhancing the EC process, the role of gas bubbles in separating the particles from the bulk solution in the EC process of coupling with dissolved air flotation (DAF) and sono-electrocoagulation were also discussed in this paper.

2. Concept of electrocoagulation

2.1. Differences between coagulation and electrocoagulation

Both electrocoagulation and coagulation involve the destabilization of particles, where the electrostatic interparticle repulsion is reduced by the combined metal cations and negative particles to the extent that the Van der Waals force predominates and a zero net charge is produced. The distinct difference between the two is that coagulation requires the use of chemically added coagulants, while in EC the coagulants are generated in-situ by the electrolytic oxidation of the anode material [16]. Table 1 further distinguishes between the coagulation and electrocoagulation processes.

2.2. Electrocoagulation reaction mechanism

As shown in Fig. 1, a simple electrocoagulation cell consists of an anode and cathode arranged in monopolar

Table 1
Differences between coagulation and electrocoagulation

Coagulation	Electrocoagulation
Widely practised in wastewater treatment for economic reasons	Not widely practised as the use of electricity may be expensive in certain places
Charged particles in a colloidal suspension are neutralized by mutual collision with counter ions	Process of creating metallic hydroxide flocs in water by electro-dissolution
Process is highly sensitive to a change in the pH and requires constant monitoring of the pH of the effluent	Process can occur in a wide range of pH values due to the pH neutralization effect
Final process is settled by sedimentation and filtration	Final process can be in the form of sedimentation and/or flotation
Generates a high amount of sludge as a secondary pollutant that is composed of a large quantity of hydroxide flocs	Low production of sludge that is mainly composed of metallic oxides/hydroxides
Requires the use of harmful chemicals, hence is not regarded as an environmentally friendly process	Does not use chemicals, hence is regarded as an environmentally friendly process

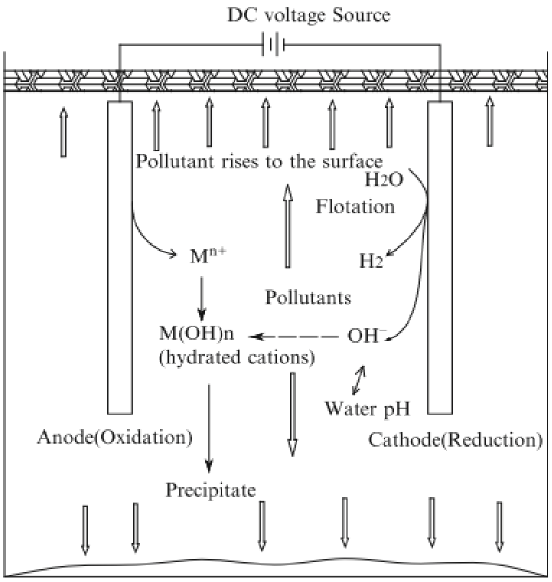

Fig. 1. Schematic diagram of a simple electrocoagulation cell [16].

configuration. When an electric current is applied, the anode will undergo oxidation of the metal species, while the cathode will experience hydrogen gas evolution. If iron is used as the anode material, Fe^{n+} will be released, where the variable n denotes the number of electrons in an iron compound (n = 2 or 3) once it oxidized. Iron hydroxides are produced by two mechanisms depending on the pH of the solution, which will either be basic or acidic, as shown in Eqs. (1)–(6).

2.2.1. Mechanism 1: basic condition

$$\text{Anode: } Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-1} \quad (1)$$

$$\text{Cathode: } 2H_2O(l) + 2e^{-1} \rightarrow H_2(g) + 2OH^-(aq) \quad (2)$$

$$\text{Precipitation: } Fe^{2+}(aq) + 2HO^-(aq) \rightarrow Fe(OH)_2(s) \quad (3)$$

2.2.2. Mechanism 2: acidic condition

$$\text{Anode: } 4Fe(s) \rightarrow 4Fe^{2+}(aq) + 8e^{-1} \quad (4)$$

$$\text{Cathode: } 8H^+(aq) + 8e^-(aq) \rightarrow 4H_2(g) \quad (5)$$

$$\text{Precipitation: } 4Fe^{2+}(s) + 10H_2O + 10O_2 \rightarrow 4Fe(OH)_3(s) + 8H^+(aq) \quad (6)$$

Similarly, Al^{3+} will be oxidized if aluminium is used as the anode. Eqs. (7)–(12) illustrate the anodic aluminium dissolution in both basic and acidic conditions:

2.2.3. Mechanism 1: basic condition

$$\text{Anode: } Al(s) \rightarrow Al^{3+}(aq) + 3e^{-1} \quad (7)$$

$$\text{Cathode: } 3H_2O(l) + 3e^{-1} \rightarrow 1.5H_2(g) + 3OH^-(aq) \quad (8)$$

$$\text{Precipitation: } Al^{3+}(aq) + 3HO^-(aq) \rightarrow Al(OH)_3(s) \quad (9)$$

2.2.4. Mechanism 2: acidic condition

$$\text{Anode: } Al(s) \rightarrow Al^{3+}(aq) + 3e^{-1} \quad (10)$$

$$\text{Cathode: } 3H^+(aq) + 3e^-(aq) \rightarrow 1.5H_2(g) \quad (11)$$

$$\text{Precipitation: } Al^{3+}(aq) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3H^+(aq) \quad (12)$$

While the formation of solid oxides, hydroxides and oxyhydroxides provide active surfaces for the adsorption of pollutants, both the Al and Fe cations, on the other hand, induce decontamination by the following mechanisms [16]:

- Compression of the diffused double layer around the charged species by the interactions of ions generated by the oxidation of the sacrificial anode.
- Neutralization of charges between the ionic species in the wastewater and the counter ions produced from the electrochemical dissolution of the sacrificial anode, which result in a zero net charge outcome.
- Formation of flocs from the sludge blanket that had entrapped and bridged the remaining colloidal particles in the aqueous medium.

Since water is also electrolyzed as part of the parallel reaction, this will induce the simultaneous production of small oxygen and hydrogen bubbles at the corresponding anode and cathode, as shown in Eqs. (13) and (14), respectively. However, the evolution of oxygen gas at the anode occurs at a low rate since the metal dissolution predominates the reaction. The gases from these electrodes will then attract the flocculated particles and, by means of natural buoyancy, carry the flocculated pollutants to the surface [15].

- At the anode:

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^- \quad (13)$$

- At the cathode:

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \quad (14)$$

2.3. Factors affecting electrocoagulation treatment

2.3.1. Reactor design

The design of the reactor for electrocoagulation treatment depends on its type, water flow direction and mode of operation. Examples of EC reactors include those with cylindrical electrodes or rotating discs, rotating cathode cells, tank cells, plate and frame cells which sometimes called a filter press, and complicated reactors such as fluidized beds, packed beds and porous carbon packing cells, each with its own unique advantages [12,17]. A cylindrical reactor can efficiently separate suspended solids from wastewater, while the filter-press reactor consists of an anode and cathode, which are housed in the same module to allow for easier cleaning and maintenance [17]. The rotating cathode cell is used to enhance the mass transfer from the solution to the electrode surface and also to remove deposited metal powders from the cathode [18]. Of all the reactors, the tank cell reactor is the most popular because it is considered to be one of the simplest reactors.

The electrocoagulation reactor can be horizontal or vertical, depending on the arrangement of the electrode, while the flow of the water through the space between the electrodes can be via multiple channels or a single channel, as shown in Fig. 2. The difference between these channels is the flow velocity, where a high flow rate can be achieved by a single channel flow, which can indirectly reduce electrode passivation. Due to their arrangement, the flow rate through multiple channels is small. The EC reactor can be operated either in a batch or continuous operation. In a batch operation, the working volume of wastewater per treatment is constant throughout, with no feed or product stream. In contrast, a continuous operation consists of a wastewater feed stream, which is pumped into the reactor, and a product stream for the treated output [12].

2.3.2. Electrode material and arrangement

In electrocoagulation, the electrodes play a role in producing adsorbent coagulants depending on the choice of the electrode material such as Al, Ag, As, Ba, Ca, Cd, Cr, Cs, Fe, Mg, Na, Si, Sr, Zn, graphite and lead oxide [19,20]. The most common electrode materials are iron in the form of mild steel or stainless steel, aluminium, zinc, copper and magnesium, where each material has different adsorption capabilities depending on its chemical and physical properties such as oxidation potential, ion size and charge, migration speed in the solution, the polarity of the –OH ion bond, and the structure and size of the hydroxide compound [12]. Apart from their adsorption capabilities, these materials may also differ in terms of their cost, regeneration and toxicity. Hence, the selection of the electrode should be carefully considered for efficient electrocoagulation treatment.

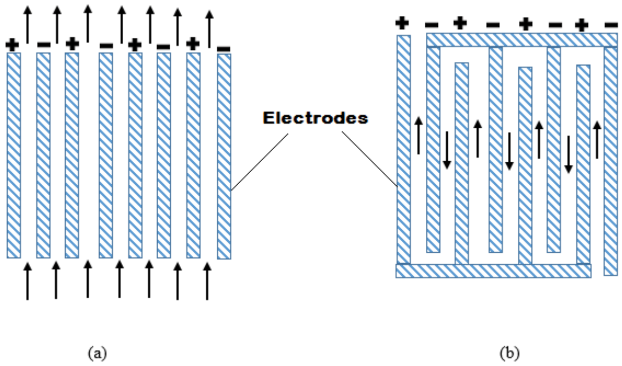

Fig. 2. Flow direction of EC reactor through (a) multiple channels and (b) single channel.

The amount of adsorbent coagulants produced in the EC reactor depends on the surface area of the electrodes. As such, a higher surface area is required for efficient treatment. Hence, to achieve this, the electrodes can be arranged in a monopolar or bipolar manner, in parallel or in series, as shown in Fig. 3. In a parallel arrangement, the electric current is distributed between all the electrodes in proportion to the resistance of the individual cells, while in a series arrangement, the same current flows through the electrodes. However, the electrodes that are connected in a series have a higher resistance, and hence, a higher potential difference is necessary for the required current to flow [21,22]. According to Demirci et al. [22], who studied different electrode connections in electrocoagulation for the removal of colour and turbidity in textile wastewater, monopolar electrodes arranged in parallel are the most cost-effective in reducing colour and turbidity compared with the other two electrode connections, namely, the monopolar-serial and bipolar-parallel electrodes.

2.3.3. Current density

The current density has a strong effect on the efficiency of the EC process because it analyses the coagulant dosage rate, bubble formation rate, size and development of flocs [13]. The current density, which determines the amount of metal ions released from the electrodes, is measured as the current per area of electrode. The coagulant produced by

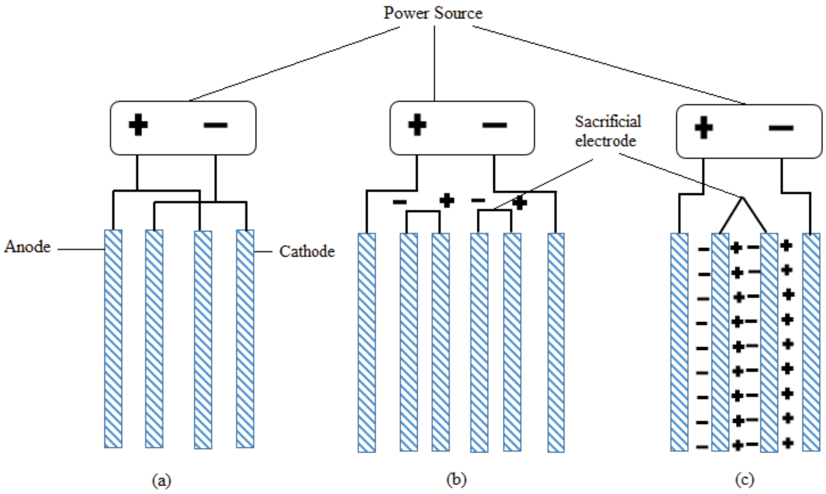

Fig. 3. Arrangement of electrodes in EC reactor (a) monopolar in parallel, (b) monopolar in series, and (c) bipolar electrodes.

electrolysis at the anode can usually be calculated using Faraday's law when the current and treatment times are known, as shown in the following equation [21,23]:

$$m = \frac{ItM_w}{zF} \tag{15}$$

where m is the quantity of metal dissolved (G), I is the current (A), t is the operation time (s), M_w is the molecular weight of the substance (g/mol), F is Faraday's constant (96,485 C/mol), and z is the number of electrons involved in the reactions (2 for Fe^{2+} and 3 for Fe^{3+} and Al^{3+}). From the equation, the quantity of metal dissolved is directly proportional to the current. Hence, the higher the current intensity, the higher will be the quantity of metal dissolved, and consequently, a higher removal efficiency of pollutants can be achieved. This high removal efficiency of pollutants is attributed to the capability of the electrodes to induce several processes such as metal deposition, precipitation and co-precipitation, as well as the high sorption capacity of metal hydroxides generated during the anodic dissolution [24,25]. In addition, with the increase in current density, the rate of bubble generation will increase, while the bubble size will decrease, resulting in the faster removal of pollutants by hydrogen floatation [26].

2.3.4. *Effect of initial pH*

The pH of the wastewater is a significant parameter for the treatment since it has a different effect on the dissolution of aluminium and iron electrodes, and their speciation of hydroxides. The effect of the pH of the wastewater on the removal efficiency of pollutants has been reported in detail in the literature [27–32]. The initial pH at the beginning of the treatment has a substantial influence during electrocoagulation. According to Duan and Gregory [33], aluminium hydroxide precipitate has minimum solubility in the region of pH 6, as shown in Fig. 4, and monomeric ions have a complex chemistry that influences the treatment process significantly. Hence, the acidic properties of wastewater are due to the hydrolysis of the Al^{3+} cations, which explains the acidic condition of the solution. When the pH increases, it is linked to an increase in the bulk concentration of the hydroxide ions (OH^-) formed in the wastewater due to the reduction of water at the cathode [27]. At a pH of between 4 and 9, different aluminium-based polymeric and monomeric species are created and are turned into insoluble amorphous $Al(OH)_{3(s)}$ via complex polymerization processes or precipitation kinetics [34]. Any further increase in the pH will cause the $Al(OH)_4^-$ anions to dominate in the solution and the concentration of $Al(OH)_{3(s)}$ to decrease, hence reducing the removal efficiency.

In contrast, for iron ions, the polarization of the coordinated water molecules is strongly dependant on the charge of the cation (oxidation state 2^+ or 3^+). The ferric complexes are more acidic than the ferrous complexes. Thus, the hydroxylation (substitution of water molecules by hydroxyl anions) in these complexes occurs at different pH values [17]. The ferric hydroxide precipitate shows a much lower solubility over a wide range of pH and this limits the influence of the monomeric species on the treatment results [35]. Fe(II) is a poor coagulant because it tends to oxidize to Fe(III) during the coagulation process to obtain a higher efficiency [13]. In an acidic pH, the dissolution of iron electrodes is higher even without an electric current. However, at pH 5–9, the type of iron released from the anode is Fe^{2+} at a voltage of 3–25 [36]. At a higher pH, the iron dissolution can be significantly lower than the value calculated by Faraday's law. This indicates that at a high pH, the corrosion rate of iron declines in the presence of oxygen due to the formation of an inactive surface layer [37]. Hence, as can be seen from Fig. 4, under a high pH and oxygenated conditions, the ferrous ions and their hydroxyl species are formed into $Fe(OH)_4$.

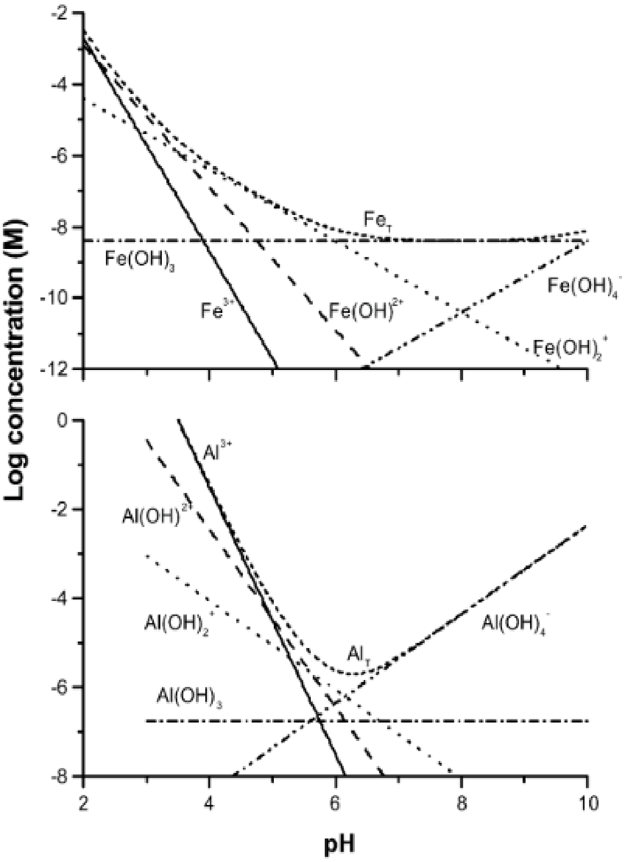

Fig. 4. Concentrations of soluble monomeric hydrolysis products of Fe(III) and Al(III) in equilibrium with amorphous hydroxides at zero ionic strength and 25°C (adapted from the study by Duan and Gregory [33] with permission).

Apart from the electrodes, the evolution of gas at the cathode is also influenced by the pH of the solution. In electrocoagulation, the pH plays an important role in determining the size of the gas bubbles. Gas bubbles that are produced at the cathode help the process by providing a surface area for the particles to be attached and allow the formation of flocs. As such, smaller gas bubbles are favourable since they provide a high surface area. The smallest hydrogen bubbles are produced at a neutral or acidic pH [13]. According to Liu and Wu [32], changes to the pH in an acidic environment are due to the evolution of oxygen and hydrogen, as shown in reactions (6) and (7), respectively.

2.3.5. Type and concentration of electrolyte

The ability of a solution to conduct an electrical current between two electrodes is referred to as electrical conductivity. A substance whose aqueous solution conducts electricity is referred to as an electrolyte [38]. The electrical conductivity of a solution depends greatly on the type and concentration of the electrolyte used during electrocoagulation. Several studies have been conducted to determine the effect of the type of electrolyte such as chloride, nitrate, phosphate and sulphate anions on electrocoagulation [31,32,37,39,40]. It has been found that sodium chloride (NaCl), which is commonly used as an electrolyte, helps to improve the pollutant removal efficiency. This is because increasing the concentration of NaCl in the solution may increase the conductivity, so the current passing through the electrodes will be increased. Thus, the cell resistance and voltage will be reduced, thereby facilitating the efficient transfer of metal hydroxides between the electrodes [32].

2.3.6. Residual metal after EC treatment

While very few studies have been carried out to investigate the residual metals after the EC treatment, it is important to conduct a detailed study to determine the composition of the sludge produced after the electrocoagulation treatment as it can reveal the chemical constituents of the sludge and lead to the possibility of sludge recycling, that is, the extraction or regeneration of residual elements such as aluminium and iron in sludge to avoid wastage or to reduce the cost incurred for sludge treatment. The residual concentration of aluminium or iron varies with respect to the quality of the wastewater and other parameters involved in the EC treatment. It has been reported that for electrocoagulation using aluminium electrodes, the residue after EC treatment contains amorphous aluminium hydroxide and/or aluminium oxyhydroxide, while iron electrodes produce crystalline phases such as magnetite, iron oxyhydroxides and lepidocrocite [13].

In a study on the removal of trace metal contaminants from potable water using aluminium and iron electrodes, Heffron et al. [41] highlighted that the residual aluminium and iron were affected by the pH and conductivity of the solution, respectively. They reported that the concentration of the residual aluminium was lowest at pH 6.5, while the concentration of the residual iron was lowest in low ionic strength water. Since the solubility of aluminium changed more drastically than the solubility of iron (III) between pH 6.5 and 8.5, hence, the higher concentration of soluble iron was probably due to the speciation of iron with the background ions in high ionic strength water. For both the residual aluminium and iron, they recommended electrocoagulation with post-treatment filtration to reduce their content in order to meet drinking water standards.

The analysis of residual metals is possible using various analytical instruments such as fourier-transform infrared spectroscopy, X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy, Scanning electron microscopy with energy dispersive spectroscopy, and energy-dispersive X-ray spectroscopy (EDX) [40,42,45,46]. For example, Vasudevan et al. [39] studied the sludge produced during fluoride removal by EC with aluminium electrodes using XRD and EDX. The identified components using XRD were aluminium coagulants in an amorphous crystalline state, while through the use of EDX they were able to identify the presence of fluoride, aluminium and oxygen, which proved that fluoride was adsorbed onto the aluminium oxide.

2.3.7. Energy consumption

The amount of energy that is consumed during treatment is an important economic parameter since it accounts for the bulk of the operating costs in the EC process. Energy or power consumption can be calculated using the following equation.

$$W = \frac{v \times i \times t}{1000 \times V} \tag{16}$$

where W is the power consumption (kWh m^{-3}), v is the voltage supplied in volts, i is the electric current (Amperes), V is the volume of the sample (m^3), and t is the residence time (h). From the equation, the power consumption is directly proportional to the voltage, electric current and time. Hence, increasing these parameters will result in higher electrical consumption.

The relationship between these parameters can be seen in Table 2. In a study on the removal of suspended solids and metals from synthetic water, the results showed that when the current density was increased from 0.15 to 0.6 A, and the time was increased from 10 to 40 min, there was a slight increase in the energy consumption [44]. According to the authors, this was due to the polarization and increase in the number of aluminium compounds in the solution, which indirectly enhanced the removal of suspended solids and metals from the solution. The evaluation of both the data on the percentage removal and electrical energy consumption is necessary when determining the optimum current density.

Apart from the current density, the energy consumption is also dependant on the type of electrode materials used. For example, Demirci et al. [22], in a study to determine the energy consumption between aluminium and iron electrodes, found that the power consumption of the aluminium electrode was higher compared with the iron electrode. The amount of energy consumed was in agreement with the high removal efficiencies of turbidity, colour and COD obtained in the study by using aluminium electrodes. Nevertheless, the impact of electrode passivation on the efficiency of the EC process is another important consideration due to the fact that the passivation layer hinders the ionic transfer between electrodes, this being another cause

Table 2
Consumption of electrical energy at different time conditions [44]

Voltage (V)	Current (A)	Electrical energy consumption, (kWh m^3)			
		10 min	20 min	30 min	40 min
6.3	0.150	0.0216	0.0445	0.067	0.089
8.6	0.300	0.058	0.121	0.184	0.243
14.3	0.450	0.141	0.303	0.459	0.606
16.6	0.600	0.227	0.469	0.711	0.939

of high electrical consumption which requires that the passivation phenomenon be overcome.

2.3.8. Economic analysis

Although high removal efficiency is the main target in every EC process, it is, however, limited by the high operating cost due to the high electrical consumption required during treatment. Apart from the cost of energy consumption, other operating costs include the cost of the electrode consumption, the cost of sludge disposal and the cost of external chemicals (used for increasing the solution conductivity and varying the pH). These costs vary, depending on the price of the materials and energy, which changes over the course of time. Therefore, an economic analysis of the EC process is necessary, especially when evaluating the large-scale feasibility of the process.

Eyvaz [45] investigated the economic feasibility of the electrocoagulation process on the treatment of effluents from the brewing industry using both a direct current (DC) and alternating pulse current (APC). Interestingly, the operating costs, energy and electrode consumption, and sludge formation were evaluated for each parameter that was studied such as the effect of the initial pH, current density, electrode type, operating time and current type. As expected, each of these parameters was highly dependent on the current density, and exhibited an increasing trend with an increase in the current density [45]. Consequently, the optimum condition for each parameter was deduced based on the highest pollutant removal efficiency at a low current density, and hence, minimum energy consumption and lower operating costs.

3. Electrode passivation

3.1. Factors affecting electrode passivation

One of the major deficiencies in the electrocoagulation process is the formation of an oxide layer on the electrode or electrode passivation. Electrode passivation is important for the longevity of the EC process. It has been reported that electrode passivation at the sacrificial aluminium anode is due to the precipitation of aluminium oxide (Al_2O_3) [46]. Meanwhile, in the investigations into iron electrodes, calcium carbonate and magnesium hydroxide were observed at the cathode, and an oxide layer at the anode [47]. This resulted in an increase in the resistance of the electrolytic cell and a decrease in the ionic transfer rate between the electrodes [45]. Despite the higher pollutant removal efficiency that was achieved from the application of an increasing current density using a DC, the increase in the current density beyond the optimal value had no effect on the contaminant removal efficiency [21,48]. In their study, Singh and Mishra [44] pointed out that the TSS removal increased with an increase in the current density from 1.3 to 5.3 mA/cm^2, with removal percentages of 46.6% and 76.6%, respectively. However, beyond 5.3 mA/cm^2, no further TSS removal was observed. The current density that was applied beyond the optimum condition could have resulted in the enhancement of the secondary reaction, whereby the charge of the flocs could be reversed, thereby leading to their re-dispersal and re-stabilization [12]. Consequently, this process reduced the lifetime of the electrode and affected the efficiency of the coagulant, which hindered the dissolved metal from forming metal hydroxides, and also led to a reduced removal.

On the other hand, the purity of the electrode material used during electrocoagulation may also impact the passivation. While different types of aluminium alloys may contain different percentages of metals such as Cu, Fe, Mg, Mn, Si, Zn and Cr, pure aluminium consists of impurities (i.e., Si, Fe, Cu, Ti, Mn, Zn) but at a lower percentage compared with aluminium alloy [49]. In a neutral electrolyte solution, the passivation of pure aluminium causes very small dissolution current densities over a wide range of potentials. Hence, increasing the positive electrode potential will lead to an increase in the thickness of the passive layers [50]. This concept was further confirmed by an electrocoagulation study using aluminium alloy and pure aluminium. In his research into the remediation of phosphate-contaminated water, Vasudevan et al. [51] highlighted that the lower and non-uniform dissolution was caused by the formation of a passive film at the pure aluminium anode. This resulted in a lower pollutant removal efficiency and a higher operating voltage over time compared with using aluminium alloy [51].

On the same note, the O_2 and H_2 gas bubbles that are generated during the process will also accumulate at the surface of the electrodes and increase the electrical resistance between the electrodes, thereby resulting in a less than optimum ionic transfer. Due to passivation, the electrodes have a rough surface, which provides a larger adhering force to the bubbles compared with a smooth surface [44]. As such, an uneven formation of gas bubbles on the electrode surface can lead to a concentration of gas bubbles in the specific zone of flotation. As a result, a high electrolytic flow is required to minimize the accumulation and detach the bubbles from the surface of the electrode.

3.2. Recent enhancement to reduce electrode passivation

Studies have been conducted on the prevention of electrode passivation in EC cells such as through the use of an alternating current (AC) instead of a DC [39,52] and adjustable time relays from an APC [14,53]. The prevention of the formation of a passive film was also found to be significant when using an aluminium alloy since it was reported that the aluminium alloy produced a higher Al(III) species during electrocoagulation compared with pure aluminium, which favoured the removal of pollutants in the solution. In addition, the copper content in the aluminium alloy electrode made it more prone to pitting corrosion, thereby reducing the impact of passivation [49]. Mechelhoff et al. [50] encountered a 'spontaneous de-passivation' effect when using the rough surface of an aluminium electrode. This was attributed to the precipitation of dissolved aluminium (III), which released H^+ ions, leading to an acidic pH that dissolved the passive layer and enhanced the dissolution rate [50].

Other than the aluminium electrodes, iron electrodes have also been enhanced, specifically in a combined electrocoagulation process. For example, in a study of a combined electrodisinfection/electrocoagulation process using iron bipolar electrodes, it was found that the electrodes worked efficiently at a low current density during the process since the formation of a passive layer was avoided, which apparently occurred when Al bipolar electrodes were used [54].

The integration of electrocoagulation and electrodisinfection also resulted in the complete disinfection of the effluent, and a high percentage of turbidity removal was also reported. Another use of iron electrodes in coupling electrocoagulation technology is for photo-electrocoagulation, which utilizes UV irradiation [55]. It was found that the higher effect of the combined photo-electrocoagulation could be explained by the light irradiation, which was able to promote the production of hydroxyl and chlorine radicals by means of hypochlorite decomposition. These radicals contributed to the chemical dissolution of the iron electrodes, hence removing the passive layers.

It has been reported that the addition of a supporting electrolyte in the electrocoagulation process is useful for slowing down the electrode passivation. The order for the use of the best electrolytes is $Cl^- > Br^- > I^- > F^- > ClO_4^- > OH^-$ and SO_4^{2-} [38]. Chloride ions are well known as depassivation agents since they can remove the passivating oxide layer formed on an electrode due to their catalytic action [38,53]. This was proven by Li et al. [31], who studied the effect of the addition of NaCl for leachate treatment using electrocoagulation at an effective concentration ranging from 819 to 2,500 mg/L. It was found that the percentage removal of COD and NH_3–N increased from 29.8% to 38.9% and 23.5% to 32.6%, respectively. Hence, by adjusting the conductivity of the wastewater through the addition of chloride ions, passivation can be relieved and, at the same time, the electrical conductivity can be improved [56].

A renewed interest in mitigating electrode passivation in the EC process has led to the recent developments with regard to the EC reactor, specifically focusing on modifications to the reactor and electrodes in order to improve the mass transfer in the EC process. Table 3 shows the recent changes that have been made to the EC reactor from 2013 to 2019.

Most of the recent approaches highlighted in Table 3 focused on the enhancement of mass transport in EC cells as a way of increasing the efficiency of pollutant removal and the indirect improvement of film passivation. According to Szpyrkowicz [67], the mixing and stirring intensity, which have a strong influence on the mass transfer and hydrolysis reactions, are essential for electrocoagulation to operate in a batch process. Technically, this can be achieved by increasing the turbulence and the flow velocity of the solution by mechanical agitation, the use of a filter-press reactor and by mixing with the evolved gas.

Table 3
Recent modifications to the EC reactor

Pollutants	Enhancement made on EC	Removal efficiency	Year	Investigators
Fluoride and arsenic from groundwater	Electrocoagulation with filter-press flow reactor with a three-cell stack	Satisfied World Health Organization (WHO) standard with fluoride ($C_F \leq 1.5$ mgL^{-1}) Arsenic ($C_{As} \leq 10$ μgL^{-1})	2019	[57]
Synthetic effluents containing kaolin	Oscillating anode	>95% turbidity removal	2018	[58]
Synthetic effluents containing methylene blue	Periodic electrode reversal (PerevEC)	97% colour removal	2018	[59]
Heavy metals from electroplating wastewater	Use of chitosan as corrosion inhibitor on steel anode	94% zinc removal	2018	[60]
Fresh leachate from municipal solid waste	Ultrasonic electrocoagulation	98% COD removal	2018	[7]
Synthetic effluent containing red dye	3-D Rotating anode in EC reactor	96% COD removal	2017	[61,62]
Textile wastewater	Rotated anode	Removal of 97% COD, 96% BOD, 98% TSS, 96% turbidity, 99% colour, 99% phenol	2016	[63]
Synthetic wastewater containing Reactive Blue 19 dye (RB19)	Ultrasonic electrocoagulation	97% of RB19 removal	2016	[64]
Smelting wastewater	Coupling of electrocoagulation, fluidized bed and micro-electrolysis	Removal of 100% Cu, 82% F, 100% Pb and 99.7% As	2014	[65]
Methylene blue (MB) wastewater	Nanocoated electrode coupled with sono-electrochemical catalytic oxidation	Removal efficiency of 92% total organic compounds	2014	[66]
Arsenic from groundwater	Electrocoagulation in a pre-pilot scale continuous filter press	Removal efficiency of <60%	2013	[46]

4. Enhancing mass transfer in ECs by mechanical agitation and filter-press reactor

One of the operating parameters that affect the EC treatment is the agitation speed. In the electrocoagulation treatment, the flow velocity between the electrodes greatly affects the transportation of ions from the surface of the electrode to the bulk solution. As such, an increase in the flow velocity can be achieved by increasing the agitation speed near the surface of the electrode. In bench-scale electrocoagulation, the agitation is generally performed using a magnetic stirrer bar with fixed or variable rotations. A few studies have been conducted on the effects of the mixing rate on the electrocoagulation performance by varying the agitation speed [56,58], and these showed the contribution of electrocoagulation with induced agitation in the elimination of pollutants. The rotational speed, however, was fixed between low to moderate mixing as a high agitation speed may cause the flocs to break up.

4.1. Rotating anode

Other than the flow velocity, the overall efficiency of the agitation by mechanical stirring also depends on the intensity of the turbulence. In this case, a high agitation speed may promote a state of turbulence that cannot be achieved through the use of a conventional stirrer bar. For this reason, the inclusion of turbulence in a flow field is seen as important in enhancing the mass transfer between electrodes [68]. In their research, Naje et al. [63] showed the feasibility of inducing a turbulent flow in the removal of the chemical oxygen demand (COD) in textile wastewater through the use of a novel rotating aluminium (Al) anode. The rotating anode consisted of 10 impellers attached to an adjustable speed motor. In the study, the researchers measured the Reynolds number, as described in Eq. (17), at various rotational speeds of the anode, and found the flow inside the reactor to be turbulent for all the tested rotational speeds ($Re > 10^4$). During the turbulent mixing, the homogenization of the reactor was achieved, which corresponded to a higher removal of the COD compared with a stationary anode. The increase in the turbulence also led to a decrease in the passivation at the electrode plates. In another study conducted on rotating anodes, the researchers discovered that there was an improvement of 10%–15% in the COD removal efficiency compared with non-rotating anodes [24,25], which indicated that the modification made on the electrode had enhanced the electrocoagulation process.

$$\mathrm{Re} = \frac{\rho N D^2}{\mu} \tag{17}$$

ρ = density (kg/m^3); N = impeller revolutions (per second); D = impeller bar length (cm); μ = viscosity (Pa s).

4.2. Oscillating anode

The concept of mass transfer has also been applied on another mechanical enhancement of the EC process. Panikulam et al. [58] introduced a new agitation mechanism in the EC reactor through an oscillating anode along with the current pulsation at the electrode surface as a way of reducing turbidity in a kaolin solution. In this study, the mass transport was controlled by the oscillating anode that created the turbulent flow. As the anode moved closer to the cathode, the current on each side of the anode caused it to oscillate from a maximum value at a constant total current to a minimum when it was at its maximum, thus resulting in an earlier onset of sweep coagulation. The application of current pulsation caused the metal ions to be added periodically at a higher concentration level compared with the constant current. From the results obtained, an oscillating anode was found to enhance the contaminant removal performance as a result of the combined improved mass transfer of dissolved coagulants into the bulk solution and the pulsation of the current at the surface of the electrode [58].

4.3. Filter-press reactor

The mass transfer can also be enhanced by the reactor design without mechanical agitation. As such, the turbulent flow of the solution is induced by the use of a filter-press reactor, as shown in Fig. 5, which is commonly used for the removal of arsenic and fluoride in groundwater [46,57,69]. According to Flores et al. [46], the inlet and outlet distributors of each channel in the reactor can induce fluid turbulence, thus improving the mass transfer of the coagulant from the anode to the bulk solution. In addition, the turbulent regime inside the filter-press reactor allows fast mixing to occur simultaneously, thus avoiding alumina precipitation and anode passivation. It has been reported that the removal of arsenic and fluoride was successfully accomplished by electrocoagulation through the use of a filter-press flow reactor, whereby the final concentration of arsenic and fluoride in the treated groundwater met the standard requirements of the World Health Organization (WHO) [57].

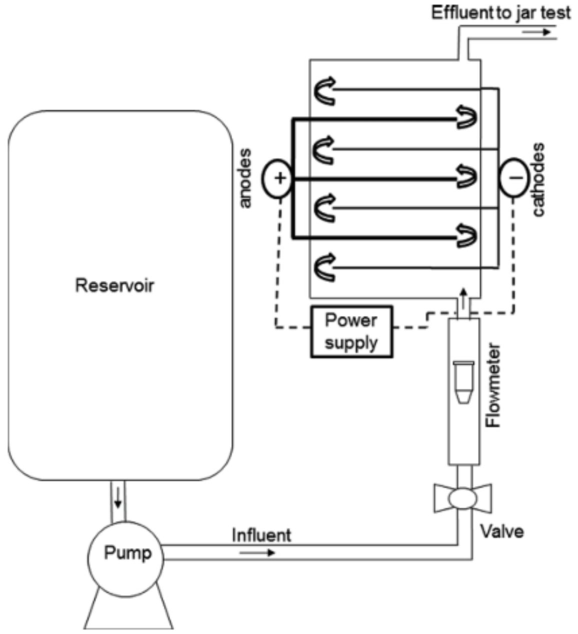

Fig. 5. Electrocoagulation in a filter-press reactor [46].

5. Enhancing mass transfer in EC by evolved gas

Depending on the current density applied in EC, the flocs are removed either by sedimentation or flotation through the hydrogen gas that is released from the cathode. In accordance with Faraday's law, the mass of the gas (M) released at the electrode in time t can be represented as in Eq. (18) [70]:

$$M = j\,I\,g\,S\,t \tag{18}$$

where M is the mass of gas released at the electrode in time t, j is the electrochemical equivalent of the gas (for hydrogen $j = 1.0 \times 10^{-7}$ kg/A s; for oxygen $j = 8.29 \times 10^{-8}$ kg/A s), I is the current density (A/m^2), g = 90%, 95% of current output (the ratio of actual gas mass transfer to the theoretical gas mass transfer calculated in terms of percentages) and S is the square of the upper electrode (m^2). From Eq. (10), it can be deduced that the mass of the gas released at time t is directly proportional to the value of the current density.

Since the current density determines the electrolytic gas production rate and bubble density, an increase in the current density can, therefore, lead to a higher bubble density and a greater upward momentum flux for carrying the pollutant to the top of the solution, where it can be easily clustered, collected and removed. Likewise, a low-current density will produce relatively fewer bubbles with a low upward momentum flux resulting in a gentle agitation [16]. According to Ge et al. [71], the hydrogen gas that is produced at the aluminium cathode has the capability of carrying about 60% of the total pollutants. This finding indirectly implies the influence of the current density in EC as a contributing factor to an effective pollutant removal since it has been demonstrated that it has a significant effect on the solution mixing and mass transfer of the electrodes.

5.1. Generation of gas bubbles

The success of an EC process is also determined by the size of the bubbles as well as by the proper mixing of the bubbles with wastewater. Generally, smaller bubbles are believed to contribute to a better separation efficiency of the EC process as they offer a wider surface area for the attachment of the particles in the aqueous stream. As such, microbubbles with a size of less than 50 µm and with a higher surface area per unit volume are seen to be most appropriate for effective attachment with the particles in the bulk solution [15]. According to Zimmerman et al. [72], these microbubbles can be generated in three different ways:

- *Method 1*: Compression of the air stream to dissolve air into the liquid.
- *Method 2*: The use of power ultrasound to induce cavitation locally at points of extreme rarefaction in the standing ultrasonic waves.
- *Method 3*: The use of an air stream delivered under low offset pressure and air to break off the bubbles due to an additional feature such as mechanical vibration, flow focusing or fluidic oscillation.

In the EC process, the microbubbles are generated through an external air supply system. Since Method 1 and Method 2 are commonly integrated into the EC process for the generation of gas bubbles, these two methods will be further discussed in the following sections.

5.2. Electrocoagulation–dissolved air flotation (EC-DAF)

DAF is an example of the technology that falls under Method 1. The bubbles in DAF are produced by the reduction in pressure of a water stream saturated with air. When the pressure is released into the flotation basin, small bubbles will nucleate from the supersaturated solution and adhere to the suspended colloids as they float upward, causing the colloids to coalesce on the surface [73]. This coupling process displayed excellent particle removal efficiency, as demonstrated in the experiment conducted by Shammas et al. [74], where the combined EC-DAF process was shown to have effectively removed 80% of the fine particles as compared with 65% when only EC was used.

5.3. Electrocoagulation–electroflotation (EC-EF)

Electrocoagulation has also been used together with electroflotation to efficiently separate solids during the treatment process. In EC-EF, the electroflotation process utilizes electrodes of a separate electrochemical cell for the generation of oxygen or hydrogen gas bubbles by water oxidation–reduction. When the tiny air bubbles collide and get attached to the pollutant particles, the particle-bubble density will fall below that of water, thereby causing them to rise to the surface of the liquid. The efficiency of the electrocoagulation–electroflotation process has been studied with regard three different types of wastewater with three parameters, namely, the current density, residence time and pollutant concentration, and the ratio of the floated/settled solids was optimized in the study using the response surface methodology [75]. It was found that the use of a combined EC-EF reactor produces good results in the separation of solids through electroflotation, especially for pollutants that form low-density solids, as these types of solids can be easily dragged to the surface of the reactor by the hydrogen bubbles produced during electroflotation [75]. Meanwhile, high-density solids are better separated from the coagulated dispersion by sedimentation.

5.4. Sono-electrocoagulation

Another way of generating bubbles is through the application of sound energy or ultrasound [76], where the energy is applied either by the use of an ultrasonic probe or water bath [77,78]. The combination of ultrasound with EC, commonly known as sono-electrocoagulation, can have a synergistic effect in terms of improving the kinetics and effectiveness of the electrode processes [79]. It is expected that the ultrasound will be able to improve the removal efficiency of pollutants and the coagulation of the flocs since it promotes turbulence and the formation of radicals during the treatment [80]. This process is based on the use of hydrodynamic cavitation to aid in the mass transfer.

Hydrodynamic cavitation is the process of the growth, formation and unexpected collapse of microbubbles. When the cavitation of bubbles undergoes an asymmetrical implosion at the critical size, bubbles of a certain size can become unstable and collapse, causing a forceful micro-jet of liquid. The ultrasonic cavitation micro-jet then produces a strong stirring action in the solution that not only cleans the surface of the electrodes, but also facilitates mass transfer and improves the elimination of gas bubbles from the surface of the electrodes, which in turn, keeps the electrodes active during the process [66].

Sono-electrocoagulation was successfully applied for the treatment of water polluted with Rhodamine 6G using a bench-scale installation with aluminium or iron electrodes as the anode and cathode [80]. The results showed that ultrasound irradiation enhanced the effectiveness of the electrocoagulation treatment from 60% to 95%, which indirectly allowed the promotion of the floc enmeshment mechanism when the initial pH wastewater was alkaline. Nevertheless, similar to EC-DAF and EC-EF, the use of a combination of electrocoagulation with ultrasound or sono-electrocoagulation is highly dependent on high power densities and power consumption to generate gas bubbles, which can lead to high operating costs. This could be one of the challenges to having an effective electrocoagulation process that is efficient in terms of energy and cost, yet is still able to achieve the targeted pollutant removal, especially when operated on an industrial scale.

6. Conclusions

The electrocoagulation process and technology have indeed gained considerable interest over time, as evidenced by the many past and recent researches. Recent studies, which focused on enhancing the mass transfer in EC as a way to reduce the impact of electrode passivation, have shown promising results. This was done by modifying the current operational functions of the EC electrodes to one of mechanical agitation such as rotating and oscillating electrodes, and the incorporation of EC with a filter-press reactor in order to generate a turbulent flow during treatment. Although the formation of bubbles from the hybrid electrocoagulation–DAF and sono-electrocoagulation methods have been shown to have enhanced the mass transfer in EC, these two processes, however, are dependent on an external source of air supply and are not cost-effective. As such, the following studies are necessary to further establish a more effective EC performance relating to mass transfer:

- The EC process should be combined with lower power microfluidic devices (Method 3) to form microbubbles, since the DAF (Method 1) utilizes the high-power nucleation of microbubbles.
- The effects of other forms of mechanical agitation in the enhancement of mass transfer, for instance, the use of mechanically controlled vibration-induced electrodes in reducing passivation, while simultaneously eliminating the accumulated gas bubbles at the electrode.
- A comprehensive study on the behaviour of gas bubbles in the EC process that is operated with mechanically controlled vibration-induced electrodes or a controlled vibration-induced liquid flow.
- Modelling the bubble hydrodynamics in the EC reactor to further comprehend the main hydrodynamic parameters affecting mass transfer in the EC process.
- To optimize the use of the evolved gases from the EC for the flotation process rather than as an external air supply system.

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