Fundamentals, present and future perspectives of electrocoagulation

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Abstract

Electrocoagulation is an electrochemical wastewater treatment technology that is currently experiencing both increased popularity and considerable technical improvements. There has been relatively little effort to better understand the fundamental mechanisms of the processes, particularly those that could provide design parameters to optimize the performances of this relatively simple and inexpensive technique. In a research programme to delineate the mechanisms of the fundamental processes involved in, the authors have realized that the technology has been insufficiently reviewed with emphasis on the fundamentals and their relationship to the performance of this technology. This paper presents an in-depth discussion and consideration of the factors that need to be addressed for optimum performance of this technology. Recent improvements of this technique and the theoretical model studies are also reviewed.
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1. Introduction

Water and energy have been identified by Smalley as the two top challenges for the 21st century [1]. Water quality and available quantity are being challenged by increased pollution from point and non-point sources such as industry and agriculture, respectively, and the ever-increasing population. Third-world countries generally have neither the infrastructure nor capital to adequately address the water problem. Although the wastewater treatment process is a well-established engineering science, the need for process incorporation, decentralized treatment and simplified processes have opened new challenges and new opportunities particularly in developing countries [2,3]. Innovative, cheap and effective methods of purifying water for human consumption as well as to clean the wastewater from industrial effluents before discharging into any other water systems are needed. Electrochemical techniques such as, electroflotation (EF), electrodecantation, electrocoagulation (EC), electrokinetic remediation (for contaminated soil) offer the possibility to be easily distributed, require minimum amount and number of chemicals. Robust and compact instrumentation is very easily achievable in above mentioned electrochemical techniques, and hence, they will have the potential to replace sophisticated processes that require large volumes and/or number of chemicals, massive containers that are present in a typical wastewater treatment plant (WWTP), as shown in Fig. 1. As a consequence, a very simple replacement will prevent economically unfeasible capital cost.

According to Rajeshwar et al. [4] benefits from using electrochemical techniques include: environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost effectiveness. In addition to these the following advantages can be added: electrochemical based systems allow controlled and rapid reactions, smaller

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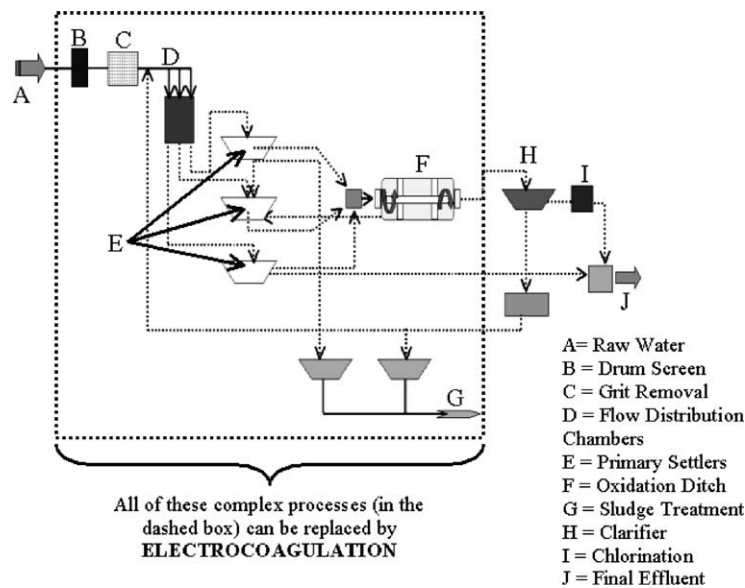*E-mail address:* cockedl@hal.lamar.edu (D.L. Cocke).

Fig. 1. Schematic flow-diagram of a typical wastewater treatment plant and complex processes that can be replaced by EC (section with dashed box).

systems become viable and, instead of using chemicals and micro-organisms, the systems employ only electrons to facilitate water treatment. Of the known electrochemical techniques, there is much interest in using electrocoagulation for treatment of wastewater containing, heavy metals [5–7], foodstuff [8,9], oil wastes [10,11], textile dyes [12–17], fluorine [18], polymeric wastes [19], organic matter from landfill leachate [20], suspended particles [21–24], chemical and mechanical polishing wastes [25], aqueous suspensions of ultrafine particles [26], nitrate [27], phenolic waste [28], arsenic [29], and refractory organic pollutants including lignin and EDTA [30]. Another approach of EC is for drinking water treatment [31,32]. The electrochemical treatment of wastewater has been reported, but only a few authors [33–35] have focused on the variables that are crucial to the improvement of the performance of this application. In a recent review article [36] we have highlighted some of the relevant issues pertaining to this technique. In the present article we are presenting an in-depth discussion of the fundamental principles of this technique, its limitations, areas of improvement, future prospects and surface and near-surface phenomena that control the EC process.

2. Theory of electrocoagulation

Electrocoagulation (EC) is a complicated process involving many chemical and physical phenomena that use consumable electrodes to supply ions into the wastewater stream. In an EC process the coagulating ions are produced 'in situ' and it involves three successive stages: (i) formation of coagulants by electrolytic oxidation of the 'sacrificial electrode', (ii) destabilization of the contaminants, particulate suspension, and breaking of emulsions and (iii) aggregation of the destabilized phases to form flocs. The destabilization mechanism of the contaminants, particulate suspension, and breaking of emulsions have been described in broad steps and may be summarized as follows:

- Compression of the diffuse double layer around the charged species by the interactions of ions generated by oxidation of the sacrificial anode.
- Charge neutralization of the ionic species present in wastewater by counter ions produced by the electrochemical dissolution of the sacrificial anode. These counter ions reduce the electrostatic interparticle repulsion to the extent that the van der Waals attraction predominates, thus causing coagulation. A zero net charge results in the process.
- Floc formation; the floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles still remaining in the aqueous medium.

The solid oxides, hydroxides and oxyhydroxides provide active surfaces for the adsorption of the polluting species.

Electrocoagulation has been successfully employed in removing metals, suspended particles, clay minerals, organic dyes, and oil and greases from a variety of industrial effluents. In this process, a potential is applied to the metal anodes, typically fabricated from either iron or aluminum, which causes two separate reactions:

- Fe/Al is dissolved from the anode generating corresponding metal ions, which almost immediately hydrolyze to polymeric iron or aluminum hydroxide. These polymeric hydroxides are excellent coagulating agents. The consumable (sacrificial) metal anodes are used to continuously produce polymeric hydroxides in the vicinity of the anode. Coagulation occurs when these metal cations combine with the negative particles carried toward the anode by electrophoretic motion. Contaminants present in the wastewater stream are treated either by chemical reactions

and precipitation or physical and chemical attachment to colloidal materials being generated by the electrode erosion. They are then removed by electroflotation, or sedimentation and filtration. Thus, rather than adding coagulating chemicals as in conventional coagulation process, these coagulating agents are generated in situ.

- Water is also electrolyzed in a parallel reaction, producing small bubbles of oxygen at the anode and hydrogen at the cathode. These bubbles attract the flocculated particles and, through natural buoyancy, float the flocculated pollutants to the surface.

In addition, the following physiochemical reactions may also take place in the EC cell [37]:

- Cathodic reduction of impurities present in wastewater.
- Discharge and coagulation of colloidal particles.
- Electrophoretic migration of the ions in solution.
- Electroflotation of the coagulated particles by O_2 and H_2 bubbles produced at the electrodes.
- Reduction of metal ions at the cathode.
- Other electrochemical and chemical processes.

In an EC experiment the electrode or electrode assembly is usually connected to an external DC source. The amount of metal dissolved or deposited is dependent on the quantity of electricity passed through the electrolytic solution. A simple relationship between current density (A cm^{-2}) and the amount of substances (M) dissolved (g of M cm^{-2}) can be derived from Faraday's law:

$$w = \frac{itM}{nF} \tag{1}$$

where w is the quantity of electrode material dissolved (g of M cm^{-2}), i the current density (A cm^{-2}), t the time in s; M the relative molar mass of the electrode concerned, n the number of electrons in oxidation/reduction reaction, F the Faraday's constant, 96,500 C mol^{-1}.

It is expected that there should be an agreement between the calculated amount of substances dissolved as a result of passing a definite quantity of electricity and the experimental amount determined. Usually a good agreement is obtained [33] although significant error may be introduced if sufficient attention is not given to the geometry of the electrode assembly as well as the optimum conditions of operation of the EC cell. One area of uncertainty is in the measurement of potential of the EC cell. The measured potential is the sum of three components:

$$\eta_{AP} = \eta_\kappa + \eta_{Mt} + \eta_{IR} \tag{2}$$

where η_{AP} is the applied overpotential (V), η_κ the kinetic overpotential (V), η_{Mt} the concentration overpotential (V), η_{IR} the overpotential caused by solution resistance or IR-drop (V).

The IR-drop is related to the distance (d in cm) between the electrodes, surface area (A in m^2) of the cathode and specific conductivity of the solution (κ in mS m^{-1}) and current (I in

A) by the equation [33] shown below

$$\eta_{IR} = \frac{Id}{A\kappa} \tag{3}$$

The IR-drop can be easily minimized by decreasing the distance between the electrodes and increasing the area of cross-section of the electrodes and the specific conductivity of the solution. Concentration overpotential (η_{Mt}, V), also known as mass transfer or diffusion overpotential, is caused by the change in analyte concentration occurring in the proximity of the electrode surface due to electrode reaction. This overpotential is caused by the differences in electroactive species concentration between the bulk solution and the electrode surface. This condition occurs when the electrochemical reaction is sufficiently rapid to lower surface concentration of electroactive species below that of the bulk solution. The concentration overpotential is negligibly small when reaction rate constant is much smaller than the mass transfer coefficient. The mass transport overpotential (η_{Mt}, V) can be reduced by increasing the masses of the metal ions transported from the anode surface to the bulk of the solution and can be achieved by enhancing the turbulence of the solution. It can also be overcome by passing electrolyte solution from anode to cathode at a higher velocity by using some mechanical means. Kinetic overpotential (also called activation potential) has its origin in the activation energy barrier to electron transfer reactions. The activation overpotential is particularly high for evolution of gases on certain electrodes. Both kinetic and concentration overpotential increase as the current increases. However, the effects of these changes need to be investigated for specific types of physical and chemical species in aqueous solution. The detailed effects of the electric field gradient on the relevant surface and solution reactions must also be clearly delineated. A survey of literature indicates that very little work has been done to characterize the deposits on the electrodes. The effect of pH and electrochemical potentials on both solution phase as well as interfacial reactions must also be clearly understood for optimization of the performances of EC techniques.

3. Reactions at the electrodes

A simple electrocoagulating reactor is made up of one anode and one cathode (Fig. 2). When a potential is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals. The electrochemical reactions with metal M as anode may be summarized as follows:
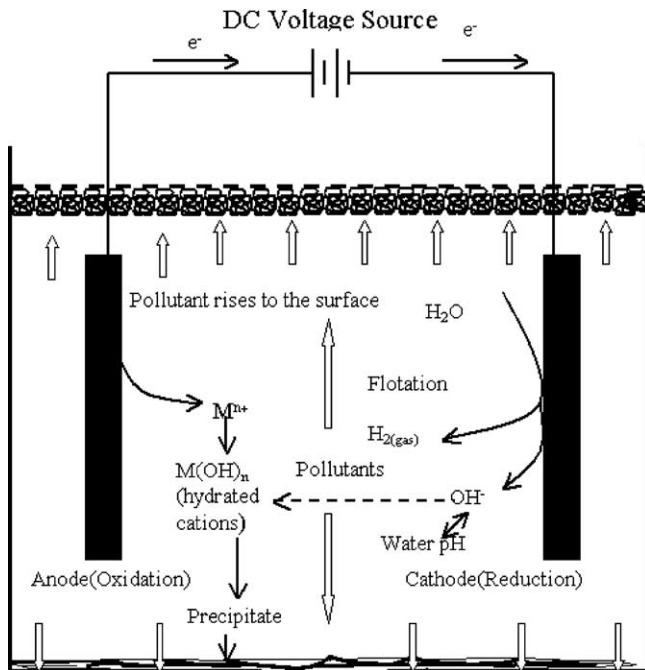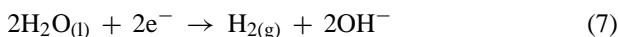
- At the anode:

$$M_{(s)} \rightarrow M_{(aq)}{}^{n+} + ne^- \tag{4}$$

$$2H_2O_{(l)} \rightarrow 4H_{(aq)}^+ + O_{2(g)} + 4e^- \tag{5}$$
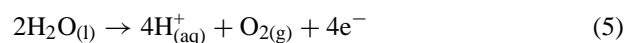
Fig. 2. Schematic diagram of a bench-scale two-electrode electrocoagulation cell.

- At the cathode:

$$M_{(aq)}^{n+} + ne^- \rightarrow M_{(s)} \tag{6}$$

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^- \tag{7}$$

If iron or aluminum electrodes are used, the generated $Fe_{(aq)}^{3+}$ or $Al_{(aq)}^{3+}$ ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. For example, Al^{3+} ions on hydrolysis may generate $Al(H_2O)_6^{3+}$, $Al(H_2O)_5OH^{2+}$, $Al(H_2O)_4(OH)_2^+$ and the hydrolysis products may form many monomeric and polymeric species such as, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^-$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$ [38] over a wide pH range. Similarly, ferric ions generated by electrochemical oxidation of iron electrode may form monomeric ions, $Fe(OH)_3$ and polymeric hydroxy complexes, namely: $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)_2^+$, $Fe_2(H_2O)_8(OH)_2^{4+}$ and $Fe_2(H_2O)_6(OH)_4^{4+}$ depending on the pH of the aqueous medium [39]. These hydroxides/polyhydroxides/polyhydroxymetallic compounds have strong affinity for dispersed particles as well as counter ions to cause coagulation. The gases evolved at the electrodes may impinge on and cause flotation of the coagulated materials.

The EC process is intrinsically associated with electroflotation since bubbles of hydrogen and oxygen are produced at the cathode and anode, respectively. The success of an EC process, and for that matter EF process is determined by the size of the bubbles as well as by the proper mixing of the bubbles with wastewater. It is generally believed that the smaller bubbles provide more surface area for attachment of

the particles in aqueous stream, resulting in better separation efficiency of the EF process [40].

To improve the performances of an EC it may be necessary to interchange the polarity of the electrode intermittently. However, a two-electrode EC cell (Fig. 2) is not suitable for wastewater treatment, because for a workable rate of metal dissolution the use of electrodes with large surface area is required. Performance improvement has been achieved by using EC cells with monopolar electrodes either in parallel or series connections (Figs. 3 and 4). The parallel arrangement essentially consists of pairs of conductive metal plates placed between two parallel electrodes and a DC power source. In a monopolar arrangement, each pair of 'sacrificial electrodes' is internally connected with each other, and has no interconnections with the outer electrodes. This arrangement of monopolar electrodes with cells in series is electrically similar to a single cell with many electrodes and interconnections. The experimental set-up also requires a resistance box to regulate the flow of current and a multimeter to read the current values. The conductive metal plates or rods used in EC fabrication are commonly known as 'sacrificial electrodes'. The 'sacrificial anode' lowers the dissolution potential of the anode and minimizes the reduction or reductive deposition of elemental metals on the cathode. The sacrificial electrode and the cathode may be made up of the same or of different materials.

A higher potential difference is required for a given current to flow in a series arrangement, because the cells connected in series have higher resistance. The same current would, however, flow through all the electrodes. On the other hand, in parallel arrangement the electric current is divided between all the electrodes in relation to the resistance of the individual cells. The readers are referred to an article by Pretorius et al. [41] for discussion of the parallel and series arrangements of monopolar cells.

Bipolar electrodes with cells in parallel have been used by some authors (Fig. 5) [18,31]. In this case, the sacrificial electrodes are placed between the 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 cell arrangement provides a simple set-up, which facilitates easy maintenance during use. 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 to the parallel side beside it. The sacrificial electrodes in this case are also known as bipolar electrodes.

In addition, as water containing colloidal particulates, oils, or other contaminants moves through the applied electric field, there may be ionization, electrolysis, hydrolysis, and free-radical formation that may alter the physical and chemical properties of water and contaminants [42]. As a result, the reactive and excited state causes contaminants to be released from water and destroyed or made less soluble. Inert (non-sacrificial) electrodes, such as titanium and the passage
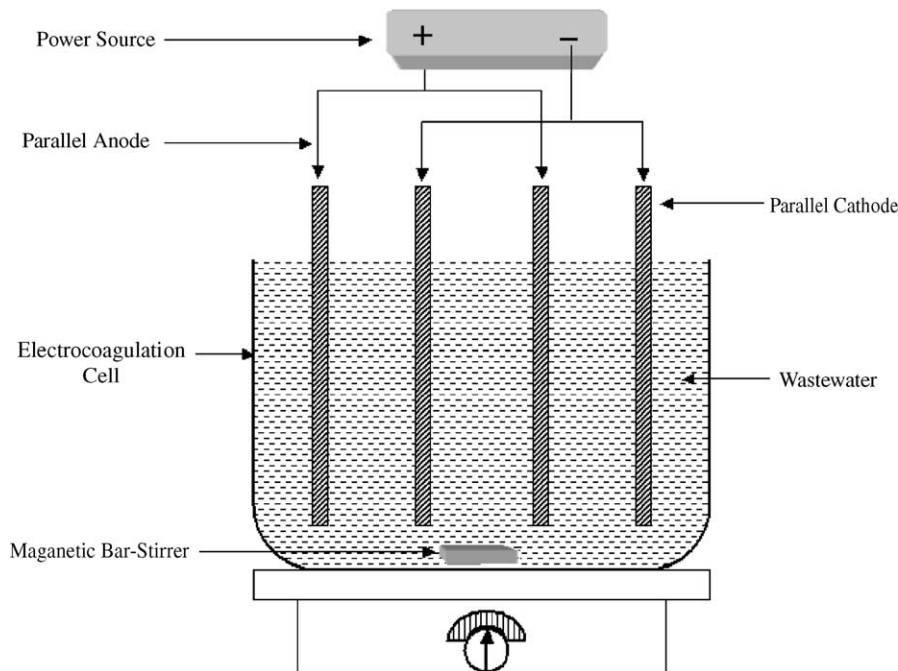
Fig. 3. Schematic diagram of a bench-scale EC reactor with monopolar electrodes in parallel connections (based on Ref. [41]).

of alternating current have been observed to remove metal ions from solution and to initiate coagulation of suspended solids. Direct and indirect oxidation of organics present in the wastewater [43] and removal of oil, grease, suspended solids and COD from restaurant water [44] were found very effective using different metal/metal oxide-coated titanium electrodes. But the high cost and the large consumption of these electrodes limit their wide application [32]. To ensure more effective removal of the undesirable ions, wastewater can be passed through a series of cells containing electrodes made up of various metals. In such cases, the contaminated wastewater is passed through the annular spaces between the electrodes and is exposed to sequential positive and negative electrical fields. To optimize the removal efficiencies, the water characteristics such as, pH, oxidation–reduction potential, and conductivity can be adjusted for specific contaminants.
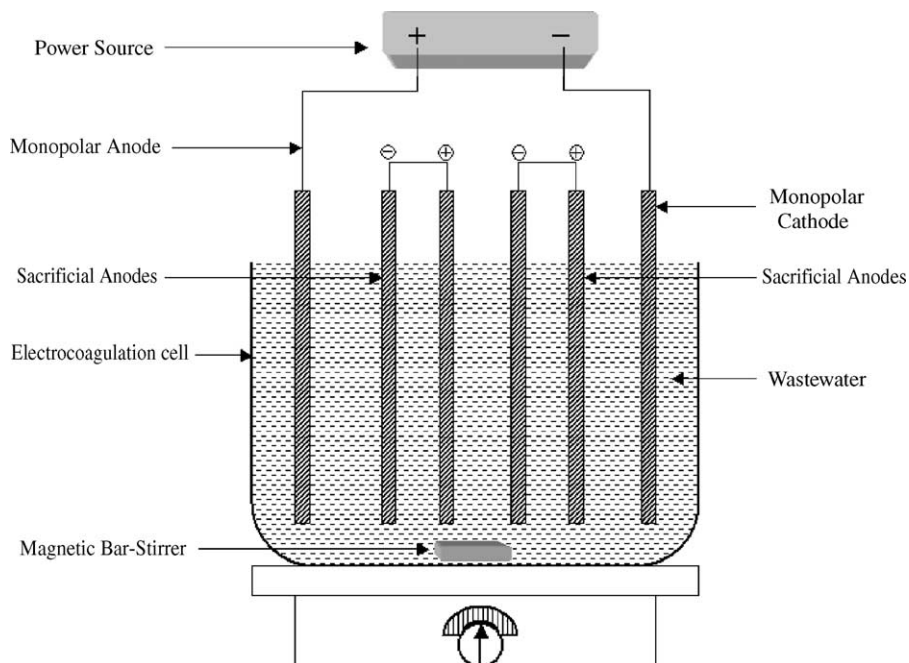
Fig. 4. Schematic diagram of a bench-scale EC reactor with monopolar electrodes in series connections (based on Ref. [41]).
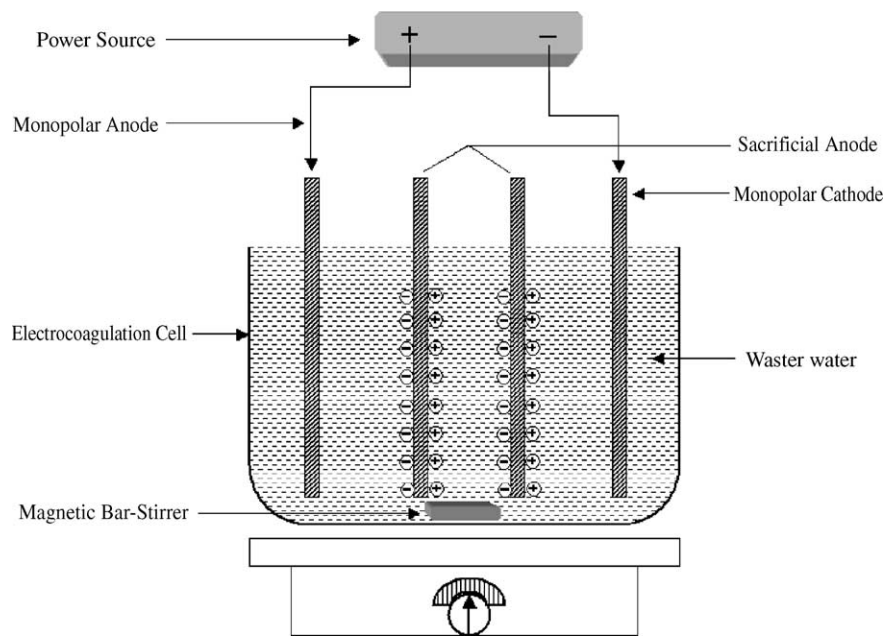
Fig. 5. Schematic diagram of a bench-scale EC reactor with dipolar electrodes in parallel connections (based on Ref. [41]).

In the EC process, an electric field is applied to the medium for a short time, and the treated dispersion transferred to an integrated clarifier system where the water-contaminant mixture separates into a floating layer, a mineral-rich sediment, and clear water. The aggregated mass eventually settles down due to gravitational force. The clear water can be extracted by conventional methods.

4. Design of the EC cell

It is important to design the EC cell so that maximum efficiency can be achieved. In dealing with this problem, the following factors must be taken into consideration [37]:

- the IR-drop between the electrodes must be minimized;
- accumulation of O_2 and H_2 gas bubble nucleates at the electrode surfaces must be minimized;
- impediment to mass transfer through the spaces between the electrodes must be minimum.

The IR-drop depends on [45]:

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

The magnitude of the error due to IR-drop can be minimized in three different ways:

- use of highly conducting solution;
- decreasing the distance between the electrodes;
- devising an electronic means to compensate for IR-drop (feedback action of a potentiostat).

The mass transport can be enhanced by increasing the turbulence level in the flow through a EC reactor. Turbulence can be increased by increasing the flow rate inside the EC reactor. The increase in turbulence level also reduces the passivation layer near the electrode plates.

Oxygen and hydrogen gases are evolved at the anode and the cathode in the form of gas bubble nucleates. These gas bubbles are insulating spheres, and if allowed to accumulate at the electrode surfaces will increase the electrical resistance of the cell and, as a result, more electric energy must be used to achieve optimum removal efficiency. To minimize the accumulation of the gas bubbles the electrolyte flow around the electrodes must be increased to sweep out the bubbles.

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. In the following section, we discuss several types. The terms 'plates' or 'tubes' are used to refer to the anodic and cathodic surfaces, since the polarity is commonly reversed on a periodic basis in all reactors.

4.1. Tall vertical-plate reactor

The tall vertical-plate EC reactor [18] uses electrodes made of flat steel plates whose vertical dimension significantly exceeds the horizontal dimension (Fig. 6). The plates are typically arranged in a non-conductive case that may be open or closed at the top. The open case allows electrical contact above the solution level, while a closed case requires submerged contacts. Submerged contacts typically erode at a rate faster than the plates unless they are coated with an insulating material. This problem complicates the assembly.
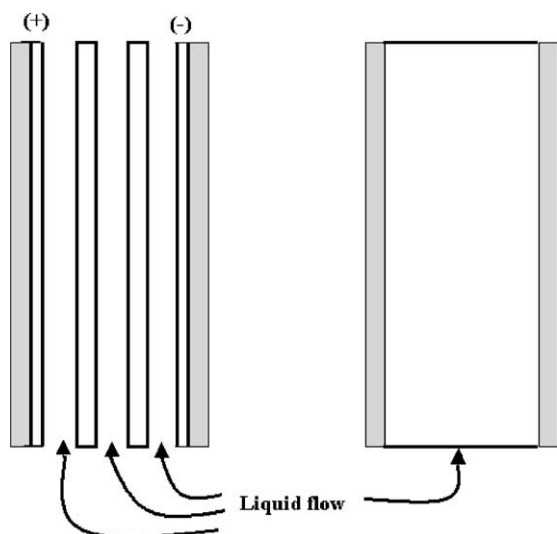
Fig. 6. Schematic flow-diagram of EC reactor with tall, vertical-plate electrodes.

Fig. 7. Schematic flow-diagram of EC reactor with long horizontal plate electrodes on edge.

A number of attempts have been made using non-conductive (typically PVC) pipe or tubing as the outer case. These reactors use plates of various widths to fill the tube, as all must be equally spaced and parallel. The narrower plates near the inner tangent can offer more flow restriction, so that the flow in the reactor is not uniform. The narrower plates also have less surface area than adjacent plates closer to the center of the tubular case, causing uneven erosion and shortened plate life unless the plate thickness is varied. Flow must be from bottom to top to allow gas bubbles to move with the solution. These reactors typically use a plate spacing of 1/8 to 1/4 in. and are subject to shorting as scale falling from the plates fills the void and collects at the bottom of the reactor within the plate field. The design usually includes an acid-wash step performed frequently to dissolve the scale, generating additional waste.

Since plate spacing is not conducive to the additional bulk of bolts or connectors, assembly of the plates is typically done by welding. The welding operation results in an extended downtime during reactor rebuild unless a spare reactor is used. Some manufacturers have used a 'disposable' reactor cell that is scrapped when the plates are exhausted by erosion, adding to the cost of operation. Corrosion will sometimes lock the plates to the case if the plates are contained in slots within the case to maintain their spacing.

An open reactor with a wider plate gap and with all plates the same dimensions within a rectangular case has also been used. The plates use a vertical to horizontal ratio of less than 2 so that the plates are removable even if corroded within the plate grooves in the case. The plates use contacts above the solution level so that welding and insulation are not required. The reactor itself contains the plates within a removable cartridge so that downtime is minimized when plate replacement is required. The reactor also has a large annular space below the plates to prevent shorting if sheets of scale occur. This reacto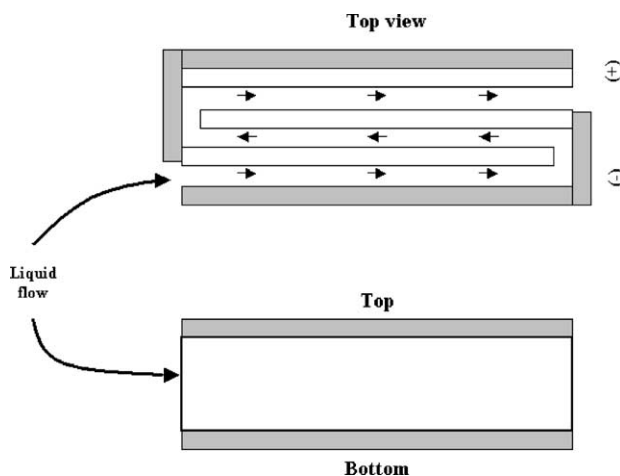r is capable of treatment to a degree far exceeding other vertical-plate reactors and can process water at a wide range of flow rates.

Serpentine flow is not practical with any of these vertical-plate designs. Thus the fluid will be proximate to either an anode or cathode during most of its residence. The reactions necessary for treatment usually require exposure to both anodic and cathodic conditions, so that with the typical design the fluid is only partially reacted in a single pass through the reactor.

4.2. Long horizontal plate reactor

These reactors use horizontal plates lying either flat or on edge (Fig. 7). The plates are mounted within a rectangular non-conductive case with slots to maintain their spacing. The plates are nearly impossible to remove once corrosion occurs.

When the plates are installed flat, the gas bubbles rise within the stream causing resistance at the bottom of the upper plate soon after the solution begins to move between the plates and continues down the long axis. The produced gases include oxygen, which causes rapid corrosion and scaling. When the scale falls, it causes short circuits between the plates.

When the plates are installed vertically (on edge), the three phases of the solution (solid, liquid, and gas) can separate, so that only the central part of the plate is effective while the bottom is shorted with solids and the top is insulated by gas. The presence of solids at the base edge of each plate locks the plates to the case and complicates reactor service.

4.3. Short horizontal plate reactor

These reactors use plates that are roughly square, parallel, horizontal, and set apart by spacers or grooves within a non-conductive case (Fig. 8) [46]. Flow is serpentine, so that the solution must pass between all spaces between the plates. The configuration allows the use of multiple changes in polarity along the path. The water will have an opportunity to
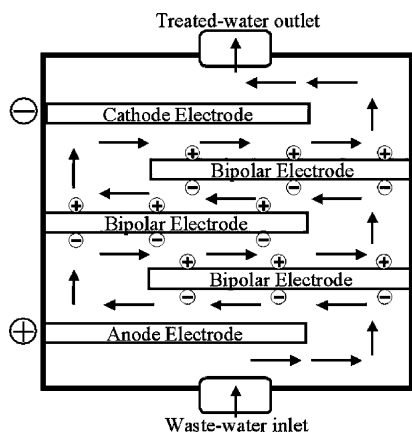
Fig. 8. Schematic flow-diagram of EC reactor with short horizontal parallel plate electrodes.

Fig. 9. Schematic diagram of EC reactor with perforated, flat and horizontal parallel plate electrodes.

approach both anode and cathode, allowing complete treatment in a single pass. The contacts are made within the case, requiring either difficult assembly or innovative methods of case design that allow electrical contacts without welding and insulation. The short contact area between the plates and the sides of the reactor case allows easy removal of corroded plates. Reactors of this type are considered to be most effective and are capable of treating high concentrations of waste.

Some attempts with these reactors have used a low flow velocity to maximize residence time of the solution. A high fluid velocity ensures that there is no phase separation and removes scale in smaller pieces that do not foul the reactor.

This configuration can be difficult to stop fluid leaks. Some attempts have used drip basins to capture leaks and shields to prevent spray rather than attempting to thoroughly seal the case.

4.4. Perforated plate reactor

Even though perforated plate reactor is not so commercialized due to the drawbacks mentioned below, it is worth to mention it here. Reactors with perforated, flat, horizontal, parallel plates within a non-conductive case can also be used (Fig. 9). The flow of wastewater passes through the plates rather than between them. This configuration allows solids to collect rapidly between the plates in the dead space be-
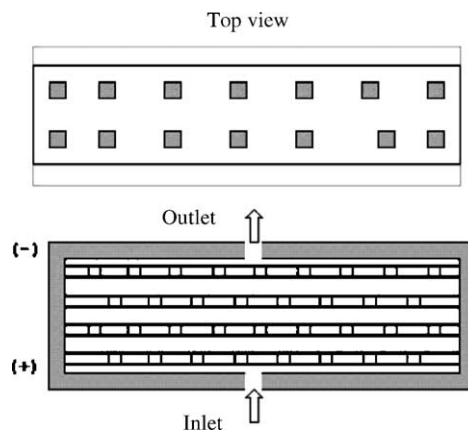
tween adjacent perforations, causing electrical short circuits that can only be cleared with acid washing or disassembly. The perforations erode with the plates, so that fluid velocity through the perforations changes with time. If any foreign matter is present the perforations can be plugged. A plugged perforation will accelerate fouling, as solids will build in that area. Since the many perforations amount to parallel flow there is no way to ensure uniform flow between all perforations. These reactors are effective if they are processing drinking water and do not use consumable plates, but they are difficult to assemble without leakage and usually operate at high pressure.

4.5. Solid tube reactor

A successful reactor with two concentric tubes employed as the sacrificial surfaces are usually contained within a third, non-conductive tube can also be fabricated (Fig. 10). The tubes are held apart by wrapping with non-conductive cord or other, more complex fixtures. The annular space is minimized, keeping reaction voltage low and fluid velocity high. There is no opportunity to vary the current density by using non-charged surfaces, as one tube must always be the anode and the other the cathode. Since the inner and outer tubes have different surface areas, current reversal (switching anode and cathode electrically) requires differing forward and
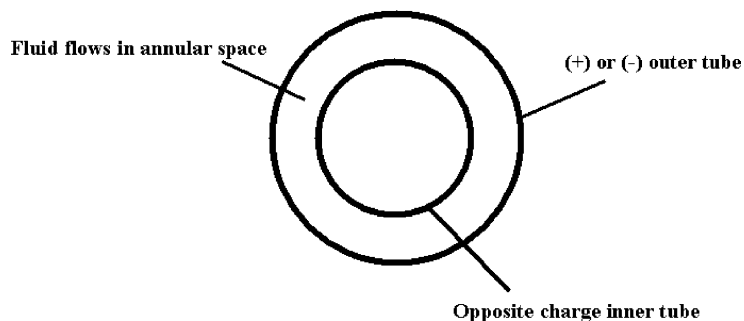

Fig. 10. Schematic diagram of EC reactor with two concentric tubes as sacrificial electrodes.

reverse times that vary with the amount of plate erosion. The current density at each reactive surface also varies depending on the direction of the current.

These reactors are difficult to seal from leakage. They are also subject to massive shorting near the end of the tubing's useful life as stresses deform the tubes and short circuits occur. A short circuit commonly results in external leakage. The tubes are usually set in banks to increase residence time. In EC, the greatest erosion occurs near the solution inlet where the pH is at its lowest. With the tube-in-tube reactor there can be considerable waste if all tubes are replaced when the first set in a bank suffers breakthrough or frequent downtime if they are not.

4.6. Perforated tube reactor

The perforated tube reactor [47] is a variation of the tube-in-tube that uses perforated inner or outer tubes or both (Fig. 10). These reactors suffer the same sealing problems as the solid tubes but have a shorter life. This is partially overcome by placing all the tubes in a case that becomes a manifold for the treated solution. This configuration results in attempting parallel flow through a number of tubes with resultant variations in flow and erosion. The tubes also suffer plugging and other disadvantages common with perforated plate reactors.

5. Benefits and drawbacks of EC technique

Electrocoagulation has the potential to be the distinct economical and environmental choice for treatment of wastewater and other related water management issues. EC is an efficient technique since adsorption of hydroxide on mineral surfaces are a 100 times greater on 'in situ' rather than on pre-precipitated hydroxides when metal hydroxides are used as coagulant. EC needs simple equipments, designable for virtually any size. It is cost-effective, and easily operable. The start-up and operating costs are relatively low. It requires low maintenance cost with no moving parts. Since practically no chemical addition is required in this process, it brings minimum chance of secondary pollution. It needs low current, and it can be run even by green processes, such as, solar, windmills and fuel cells. Electrocoagulation process can effectively destabilize small colloidal particles. It produces minimal sludge. Gas bubbles produced during electrolysis can enhance flotation. It removes the smallest colloidal particles efficiently in compared with the conventional chemical and biological techniques, because the smallest charged particles have greater probability of being coagulated by the electric field that sets them in motion.

Although EC has numerous advantages, it has some drawbacks as discussed below. The 'sacrificial anodes' need to be replaced periodically. It requires a minimum conductivity depending on reactor design, limiting its use with water containing low dissolved solids. In case of the removal of organic compounds, some toxic chlorinated organic compound may be formed in situ if chlorides are also present. Wastewater with high humic and fluvic acid content may be amenable to the formation of trihalomethanes. If phenols and algal metabolic and decomposition products are present, chlorine may lead to bad taste and odor. An impermeable oxide film may be formed on the cathode that may interfere with the performance of the EC cell. However, changing polarity may help reduce this interference. The cost of operating EC may be high in those are as where the cost of electricity is high.

6. Recent improvements of electrocoagulation

The EC phenomenon has been known as an electrochemical technique for the last century. It has been used with varying degrees of success for treatment of water and wastewater obtained from various sources. However, there has been very little discussion regarding the improvement of the design and performance of EC reactors with respect to power consumption or to understanding the actual mechanisms to help delineate the physical and chemical parameters involved in EC process.

In a recent article Jiang et al. [35] reported the treatment of wastewater by a hybrid electrocoagulation–flotation technique using aluminum electrodes. The authors designed two different EC reactors to evaluate their water treatment performance and found out the best configurations to maximize the treatment efficiency. The EC reactors were configured with water up-flow or cross-flow arrangements. The bipolar electrodes were connected in series via the water, and the monopolar electrodes connected in parallel via copper connectors. The current efficiency (Φ) required for the production of dissolved Al^{3+} due to the passage of electrical charge Q (C) in a volume V (m^3) of water was calculated using Faraday's law:

$$\Phi = \frac{3FV[\text{Al(III)}]}{Q} \tag{8}$$

where F is the Faraday constant. The specific electrical energy consumption (SEEC) was calculated as a function of the applied cell voltage (U):

$$\text{SEEC}\,[\text{kWh}\,(\text{kg Al}^{3+})^{-1}] = \frac{nFU}{3.6 \times 10^3 M_{\text{Al}}\Phi} \tag{9}$$

where n is the number of moles of electrons per mole of the aluminum dissolved. It was concluded that an up-flow configuration of the electrocoagulator performed better than a horizontal flow configuration, with both bipolar and monopolar electrodes. Also, the performance of the EC process was found to be superior to that of conventional chemical coagulation with aluminum sulphate.

Kovatcheva and Parlapanski [48] applied low frequency (25–75 Hz) sonic field at current densities of 0.1–$0.4\,\text{A m}^{-2}$ to improve the performance of the EC cell with carbon steel electrodes. It has been reported to increase the quantity of iron

hydroxides, and thereby enhance coagulation. It was assumed that the applied sonic field:

- Enhanced the rates of mass transport.
- Decreased the thickness of the diffuse double layer at the electrode surface.
- Activated the electrode surface by generating defects at the crystal lattices of the electrodes.
- Activated the ions in the reaction zone at the electrodes by ultra-sound waves.
- Increased the temperature at the electrode surface due to friction between the liquid and the surfaces.

However, the authors also mentioned the disadvantages of applying the sonic field. Among other things the acoustic waves may destroy part of the colloidal iron hydroxides as well as the adsorption layer at the surface of the colloidal particles.

One of the most important considerations in lowering the cost of the EC process is to minimize the IR-drop to enhance current efficiency. Evolution of oxygen at the anode represents an unwanted leakage of current, which reduces the overall current efficiency. This problem can be minimized through the choice of an anodic material that presents a high overpotential for the oxygen evolution reaction near the anode. This high overpotential permits the realization of anodic reactions, which are not possible with other materials, and in particular the oxidation of organic compounds with a very high current efficiency. In order to achieve this goal, a number of authors have used binary [49–51] and ternary [52] alloys as well as carbon electrodes and titanium sheets coated with certain active oxides [53] as anodes for electrochemical treatment of wastewater, in particular those containing organic dyes, phenols, chloro-substituted phenols, and tannery wastes.

Matteson et al. [26] investigated the electrocoagulation of aqueous suspensions of ultrafine kaoline particles in a single stirred cell apparatus and in a continuously flowing system consisting of three cells in series. The coagulation rate was described by a second-order rate equation:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -k_1 c^2 (1 - \mathrm{e}^{-k_2 t})^2 \tag{10}$$

where c is the concentration at time t, u the electrophoretic velocity of the particles, $k_2 = u/x$ (x being the geometric parameter of the electrode size), and $k_1 = 4kT/3\mu$ (k is the Boltzmann's constant and μ the viscosity of the continuous medium). This second-order rate equation incorporates the electrophoretic migration of particles, and subsequent release of discharged particles into the bulk. The constant terms in this equation were derived from the basic electrophoretic and coagulation phenomenon, which is dependent on the zeta potential of the suspended particles, the applied voltage, the initial concentration of the particles and the electrode geometry. The authors conducted a number of EC experiments with ultrafine kaoline particles in a single stirred cell with electrodes in parallel connections and found reasonably good agreement with the theoretically predicted fraction coagulated.

Chen et al. [34] reported a theoretical model involving the electrolysis voltage required in an EC process, the current density, conductivity of the water/wastewater, the inter-electrode distance, and the surface of the electrodes. Experiments were carried out with aluminum electrodes to verify and confirm the theoretical model and determine the constant terms used in the model. Two mathematical models, one applicable to non-passivated aluminum electrode and the other to passivated aluminum electrodes were proposed and experimentally verified.

The theoretical model is based on the fact that when current passes through the electrochemical reactor, it must overcome the equilibrium potential difference, anode overpotential, cathode overpotential and IR-drop of the solution [54]. The electrolysis voltage U_0 (V) between electrodes may, therefore, be considered to consists of the following terms:

$$U_0 = E_{\mathrm{eq}} + \eta_{\mathrm{a,a}} + \eta_{\mathrm{a,c}} + \eta_{\mathrm{a,p}} + |\eta_{\mathrm{c,a}}| + |\eta_{\mathrm{c,a}}| + \frac{d}{\kappa} j \tag{11}$$

where E_{eq} is the equilibrium potential difference between the electrodes (V), $\eta_{\mathrm{a,a}}$ the activation overpotential at the anode, $\eta_{\mathrm{a,c}}$ the concentration overpotential at the anode, $\eta_{\mathrm{a,p}}$ the passive overpotential at the anode, $\eta_{\mathrm{a,a}}$ the activation overpotential, $|\eta_{\mathrm{c,a}}|$ the activation overpotential at the cathode, $|\eta_{\mathrm{c,c}}|$ the concentration overpotential at the cathode, j the current density ($\mathrm{A\,m^{-2}}$), d the net distance between the electrodes (m), and κ the conductivity of the wastewater ($\Omega^{-1}\,\mathrm{m^{-1}}$). However, the authors then considered the oxidation at the anode, reduction at the cathode and hydrolysis reaction in the medium to evaluate different potential terms by using Tafel equation [45] and Nernst–Planck equation [55] and finally propose the following mathematical relationships for calculations of U_0 values:

$$U_0 = A + \eta_{\mathrm{a,p}} + \frac{d}{\kappa} j + K_1 \ln j \tag{12}$$

where U_0 is the potential, A and K_1 are the constant terms, j the current density ($\mathrm{A\,m^{-2}}$), d the net distance between the electrodes (m), $\eta_{\mathrm{a,p}}$ the anode passive potential (V) and κ the conductivity of the wastewater ($\Omega^{-1}\,\mathrm{m^{-1}}$). For a non-passivated electrode, the passive overpotential can be neglected. For a passivated electrode the relationship can be rearranged to

$$U_0 = A + \frac{d}{\kappa} j + K_1 \ln j + \frac{K_2 j^n}{\kappa^m} \tag{13}$$

where K_2 is the constant term. It should, however, be mentioned that the values of A, K_1, K_2, m and n need to be experimentally determined. Theoretical analysis and experiments demonstrated that pH and flow rate had little effect on the electrolysis voltage of the EC process. However, the models can be used to calculate the total electrolysis voltage required for an EC process.

In an earlier article, Vik et al. [33] proposed a model involving terms of, activation potential, concentration overpotential, and IR-drop due to solution resistance. However, this

model cannot directly predict the electrolysis voltage since it contains unknown terms, which include the activation overpotential and the concentration overpotential.

7. Conclusions

The full potential of EC technique as a wastewater treatment alternative is yet to be fully realized. It is still an empirically optimized process that requires more fundamental understanding for improved engineering design. The EC comprises complex chemical and physical processes involving many surface and interfacial phenomena. There is, however, a paucity of scientific understanding of these phenomena, which limits the engineering design of EC reactor for optimum performance and future progress of this novel and innovative technology. Literature survey indicates that up-flow configuration of the electrocoagulator is better than a horizontal flow configuration. In addition, the use of sonic field, stirrer and hybrid EC-EF technique increases the efficiency and provides better control of this process. In this review, a comprehensive discussion of the fundamental electrochemical factors is presented. This technology will continue to make inroads into the water treatment arena because of numerous advantages and the nature of the changing strategic water needs in the world.

Acknowledgements

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