CHAPTER 1

Introduction and Literature Review

1.1 Definition and history of electrocoagulation

Electrocoagulation (EC) is a process of destabilizing suspended, emulsified or dissolved contaminants in an aqueous medium by introducing an electrical current via parallel plates constructed of various metals that are selected to optimize the removal process. The two most common plate materials are iron and aluminum. The electrical current provides the electromotive force to drive the chemical reactions. When reactions are driven the elements or compounds will approach the most stable state. Generally, this state of stability produces a solid that is either less colloidal and less emulsified (or soluble) than the compound at equilibrium values. As this occurs, the contaminants form hydrophobic entities that precipitate and can easily be removed by a number of secondary separation techniques.[1]

Using electricity to treat water was first proposed in UK in 1889.[2] The application of electrolysis in mineral beneficiation was patented by Elmore in 1904.[3] EC with aluminum and iron electrodes was patented in the US in 1909. The electrocoagulation of drinking water was first applied on a large scale in the US in 1946. [4,5] Because of the relatively large capital investment and the expensive electricity supply, electrochemical water or wastewater technologies did not find wide application worldwide then. Extensive research, however, in the US and the former USSR during the following half century has accumulated abundant amounts of knowledge. With the ever increasing standard of drinking water supply and the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades. There are companies supplying facilities for metal recoveries, for treating drinking water or process water, treating various wastewaters resulting from tannery, electroplating, diary, textile processing, oil and oil-in-water emulsion, etc. Nowadays, electrochemical technologies have reached such a state that they are not only comparable with other technologies in terms of cost but also are more efficient and more compact.[6]

The advantages of this technique are requirement of simple equipment, easiness of operation, production of effluent with less total dissolved solids content, avoidance of uses of chemicals. Additionally the process of EC is controlled electrically with no moving parts thus requiring less maintenance. [7]

EC in normally used for removing undesirable particles such as heavy metal ions, inorganic anions, colloidal suspensions, oil and grease aquatic humus etc. from various types of wastewater. However, nowadays the process of EC has also been applied to the isolation of various organic compounds, especially natural products.[8-11] The technique may also be of potential use in selectively coagulating certain desired organic substances from solution.[12,13]

1.2 Instrumental setup and reaction

1.2.1 Instrumental setup for electrocoagulation

In its simplest form, an electrocoagulating reactor may be made up of an electrolytic cell with one anode and one cathode. [7] A pair of conducive metal plates is connected to a power supply as shown in Figure 1.1 and dipped into the solution.

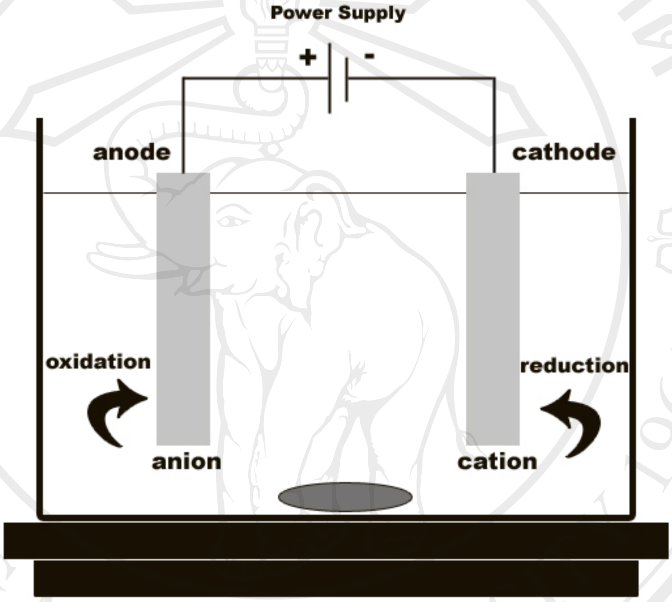


Figure 1.1 Bench-scale electrocoagulation reactor with electrodes.

1.2.2 Reaction mechanism

Electrocoagulation involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from respectively aluminum or iron electrodes. The metal ions generation takes place at the anode while hydrogen gas is released from the cathode. The hydrogen gas also helps to float the flocculated particles out of the water. This process sometimes is called electrofloculation. The chemical reactions taking place at the anode are given as follows.[6,7]

For aluminum anode:

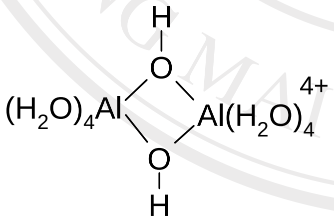
$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \quad (1)$$

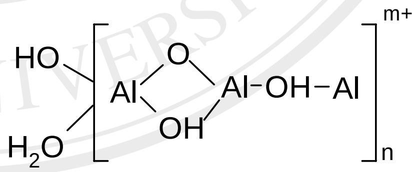
at alkaline conditions $$Al^{3+}_{(aq)} + 3OH^- \rightarrow Al(OH)_3 \quad (2)$$

at acidic conditions $$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (3)$$

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \quad (4)$$

The mechanism proposed was that the dissolution of the aluminium anode produces Al^{3+} ions which at the appropriate pH are transformed in a first step to aluminium hydroxide $Al(OH)_3$ which is finally polymerized (equations (1)-(4)). However, depending on the pH of the aqueous medium other ionic species, such as $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$ and $Al(OH)_4^-$ may also be present in the system. Examination of the pE-pH equilibrium diagram reveals that under appropriate conditions various forms of charged multimeric hydroxo Al^{3+} species may be formed. For example, the structures of dimeric and polymeric Al^{3+} hydroxo complexes are shown below: [14]





These highly charged polymeric metal hydroxide species can effectively remove metals, colloidal solids and particles, and soluble inorganic pollutants by neutralizing the electrostatic charges on suspended solids and oil droplets to facilitate agglomeration or coagulation and final separation from the aqueous phase. This treatment promotes the precipitation of certain metals and salts. In addition, as colloidal particulates, oils, or other contaminants move through the applied electric field, they may be ionized, electrolysed, hydrolysed, or form free-radicals which may alter the physical and chemical properties of the water and the contaminants. As a result of these processes, contaminants may be released from water and decomposed or made less soluble.

For Iron anode upon oxidation in an electrolytic system it produces iron hydroxide, $Fe(OH)_n$, where n = 2 or 3. Two mechanisms have been proposed for the production of $Fe(OH)_n$. [15-17]

Mechanism 1

$$\text{Anode:}\quad 4Fe_{(s)} \rightarrow 4Fe^{2+}_{(aq)} + 8e^- \tag{5}$$

$$4Fe^{2+}_{(aq)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+_{(aq)} \tag{6}$$

$$\text{Cathode:}\quad 8H^+_{(aq)} + 8e^- \rightarrow 4H_{2(g)} \tag{7}$$

$$\text{Overall:}\quad 4Fe_{(s)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \tag{8}$$

Mechanism 2

$$\text{Anode:}\quad Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \tag{9}$$

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)} \tag{10}$$

$$\text{Cathode:}\quad 2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \tag{11}$$

$$\text{Overall:}\quad Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)} \tag{12}$$

The $Fe(OH)_{n(s)}$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the unwanted particles form water either by complexation or by electrostatic attraction, followed by coagulation.

1.2.3 Factors affecting electrocoagulation[6]

(1) Current density or charge loading

The supply of current to the electrocoagulation system determines the amount of Al^{3+} or Fe^{2+} ions released from the respective electrodes. For aluminum, the electrochemical equivalent mass is 335.6 mg/(Ah). For iron, the value is 1041 mg/(Ah). A large current means a small electrocoagulation unit. However, when too large current is used, there is a high chance of wasting electrical energy in heating up the water. More importantly, a too large current density would result in a significant decrease in current efficiency. The current density selection should be made in accordance with other operating parameters such as pH, temperature, as well as flow rate to ensure a high current efficiency. The current efficiency for aluminum electrode can be 120–140% while that for iron is around 100%. The over 100% current efficiency for aluminum is attributed to the pitting corrosion effect especially when there are chlorine ions present. The current efficiency depends on the current density as well as the types of the anions. The operating current density or charge loading can be determined experimentally if there are no reported values available.

(2) Presence of NaCl

Table salt is usually employed to increase the conductivity of the water or wastewater to be treated. Besides its ionic contribution in carrying the electric charge, it was found that chloride ions could significantly reduce the adverse effect of other anions such as HCO^{3-}, SO_4^{2-}. The existence of carbonate or sulfate ions would lead to the precipitation of Ca^{2+} or Mg^{2+} ions that forms an insulating layer on the surface of the electrodes. This insulating layer would sharply increase the potential between electrodes and result in a significant decrease in the current efficiency. It is therefore recommended that among the anions present, there should be 20% Cl^- to ensure a normal operation of electrocoagulation in water treatment.

The addition of NaCl would also lead to the decrease in power consumption because of the increase in conductivity. Moreover, the electrochemically generated chlorine was found to be effective in water disinfections.

(3) pH effect

The effects of pH of water or wastewater on electrocoagulation are reflected by the current efficiency as well as the solubility of metal hydroxides. When there are chloride ions present, the release of chlorine also would be affected. It is generally found that the aluminum current efficiencies are higher at either acidic or alkaline condition than at neutral. The treatment performance depends on the nature of the pollutants with the best pollutant removal found near pH of 7. The power consumption is, however, higher at neutral pH due to the variation of conductivity. When conductivity is high, pH effect is not significant. The pollutant removal efficiency was found to be the best near neutral pH using aluminum electrode. When iron electrode was used in textile printing and dying wastewater treatment, alkaline influence was found to give better color as well as COD removal.

(4) Temperature

The effect of temperature on this technique was not very much investigated. For water treatment, some literature show that the current efficiency of aluminum increases initially with temperature until about 60 °C where a maximum current efficiency was found. Further increase in temperature results in a decrease in current efficiency. The increase of current efficiency with temperature was attributed to the increased activity of destruction of the aluminum oxide film on the electrode surface. When the temperature is too high, there is a shrink of the large pores of the $Al(OH)_3$ gel resulting in more compact flocks that are more likely to deposit on the surface of the electrode. Similar to the current efficiency, the power consumption also gives a maximum at slightly lower value of temperature, 35 °C, for treating oil-containing wastewater. This was explained by the inverse effect of temperature on current efficiency and conductivity of the wastewater. Higher temperature gives higher conductivity hence lower energy consumption.

(5) Power supply

When current passes through an electrochemical reactor, it must overcome the equilibrium potential difference, anode overpotential, cathode overpotential and ohmic potential drop of the solution. The anode overpotential includes the activation overpotential and concentration overpotential, as well as the possible passive overpotential resulting from the passive film at the anode surface, while the cathode overpotential is principally composed of the activation overpotential and concentration overpotential.

It should be noted that the passive overpotential highly depends on the electrode surface state. Usually, DC power supply is employed. In order to minimize the electrode surface oxidation and passivation, the direction of power supply is changed at a certain time interval. Fifteen minutes were found to be optimal for water treatment using aluminum electrodes.

1.3 Applications

1.3.1 Wastewater treatment

Treatment of wastewater by EC has been practiced during most of the 20th century with limited success and popularity. In the last decade, this technology has been increasingly used in South America and Europe for treatment of industrial wastewater containing metals. It has also been noted that in North America EC has been used primarily to treat wastewater from pulp and paper industries, mining and metal-processing industries. In addition, EC has been applied to treat water containing foodstuff wastes, oil wastes, dyes, suspended particles, chemical and mechanical polishing waste, organic matter from landfill leachates, defluorination of water, synthetic detergent effluents, mine wastes and heavy metal-containing solution. Typically, empirical studies are done on EC to define major operating parameters for broad classes of contaminated water or waste streams. The technology has been optimized to minimize electrical power consumption and maximize effluent throughput rates. This approach, which provides little insight into the fundamental chemical and physical mechanisms, does not allow modeling of the process or the design of improved systems, process control and optimization from fundamental physico-chemical principles.[7]

1.3.2 Isolation of organic substances

Phutdhawong *et al.*[8]. studied the electrocoagulation of certain phenolic compounds in a systematic manner. The results showed that it was selective to a certain degree, i.e. phenolic compounds with 2 adjacent hydroxyl groups (1,2-dihydroxy and 1,2,3-trihydroxy) almost completely precipitated from the solution. Otherwise, phenol itself and phenols with 1,3-dihydoxyl, 1,3,5-trihydroxyl and 1,4-dihydroxyl substitution patterns stay quite unaffected (not more than 25% precipitation). Two years later, the electrocoagulation of other organic compounds namely, flavonoids, monosaccharides, disaccharides, starch, polyols, and proteins were studied by Chowwanapoonpohn and Buddhasukh.[9] The results showed that three flavonoids samples (fisetin, quercetin, and myricetin) with adjacent hydroxyl groups were completely coagulated, while two flavonoids with non-adjacent hydroxyl groups (naringenin and morin) were essentially uncoagulated even after 2 hours of electrolysis. This result was in greement with those from the first report.

The studies of other major natural compounds with hydroxyl groups, i.e. monosaccharides and disaccharides, showed that they are generally unresponsive to electrocoagulation and so were glycerol and sorbitol whereas starch and proteins were completely coagulated. Another work of electrocoagulation application was continued by Chowwanapoonpohn *et al*.[10], in studying the electrocoagulation and recovering of tannin from tree barks. The result showed that phenolic substances from selected tree barks were coagulated electrolytically and subsequently recovered as concentrated phenolic extracts with overall increase in antioxidant activity.

Phutdhawong and Buddhasukh [11,12] studied the isolation of glycyrrhizic acid (a sweet-tasting glycoside) from *Glycyrrhiza radix.* and D-Pinitol (1D-3-O-methyl-chiro-inositol) from *Cassia siamea.* by a simple process in three main steps, namely hot water extraction, decolorization by electrolysis, and simultaneous decolorization and demineralization by ion exchange.

Phutthawong and coworker [13] applied electrocoagulation to the isolation of seven known alkaloids. The result showed that they could be extracted successfully with a yield comparable to that obtained by conventional methods.

1.3.3 Decolorization

Yang and McGarrahan[18] studied the decolorization of textile effluent by electrocoagulation. In this work, the group of dyestuffs C.I. Reactive Blue-19, C.I.Acid Red-266, and C.I.Disperse Yellow-218 was chosen for study of the feasibility of coagulation for color removal. The dyes used in these experiments were chosen to represent the two major structural features; anthraquinone and azo dyes. Reactive blue is an anthraquinone-based dye, and Acid Red and Disperse Yellow represent azo-based dyes. Removal efficiencies on these dyes were obtained by measuring absorbance of a sample at appropriate wavelength. Removal efficiencies of more than 98%, in term of absorbance were observed. In 2004 electrocoagulation for decolorization of dye (C.I. reactive red 124) was studied by Sengil *et al.*[13] The results showed that the dye in aqueous phase were effectively removed when iron was used as sacrificial anode. The optimum current, pH and electrolysis time for 100 mg L^{-1} initial dye mass concentration were 1.351 mA cm^{-2}, 8 and 5 min.

1.4 Research Objectives

This research work is presented in two main parts. The first one is a model study of electrocoagulation using synthetic dyes, viz anthraquinones and flavonoids, with attempt on the recovering of substances from the coagulation sludge. The selectivity of electrocoagulation technique for coagulation of substance was investigated. Electrocoagulation of natural phenolic dyes, notetably those from black sticky rice, seedlac, jackfruit wood, turmeric, betel nut, roselle, black bean, beet root and gardenia are reported in the second part.