CHAPTER I

Introduction

1. Definition and History

Conventional methods for the removal of suspended particulates in industrial effluents and wastewater treatment frequently involve the bulk addition of inorganic coagulants (e.g. aluminium or ferric salts).[1] The coagulation process involves the charged particles in a colloidal suspension being neutralized by mutual collision with counter ions and agglomerated, followed by sedimentation or filtration.[2] Coagulation processes also remove particulate suspensions, e.g., silt-based turbidity and other associate constituents such as toxic metals and synthetic organic materials.[3] These processes, however, tend to generate large volumes of sludge with a high bound-water content that can be slow to filter and difficult to de-water. These also tend to increase the total dissolved solid content of the effluent.[4] The process of electrocoagulation is a good alternative because it can remove the disadvantages of the classical technique. Electrocoagulation is an electrochemical process that causes basic coagulation.[5] Electrocoagulation causes an effect similar to that produced by the addition of chemical coagulants. The cationic salts produced *in situ* destabilize colloidal suspensions by neutralizing negative charges associated with the colloidal particles at neutral or alkaline pH. This enables the particles to come together closely enough to agglomerate under the influence of van der Waals attractive forces.[5] Although this process resembles traditional coagulation, the characteristics of the electrocoagulated fog differ dramatically from those generated by simple coagulation. The application of the electric field during electrocoagulation can achieve cohesion and coagulation at the same time and causes flow of small particles to the top of the solution where their are easily removed. Electrocoagulation technique is sometime also known as electroprecipitation, electroflotation and electrodecantation.

Electrochemically treating water for purification was reviewed by Vik *et al.*[6] indicating that electrocoagulation techniques were established in Britain in the 1889. Treatment plants built in London and Salford used iron electrodes with the addition of seawater as a chlorine source for disinfection. In 1909, a patent for the purification of wastewater by electrolysis using aluminium and iron corroding electrodes was established in the United States.[6] In 1946, a method of a large scale purification of drinking water was applied.[7,8] This method used aluminium electrodes to produce aluminium hydroxide flocs, which then sedimented rapidly removing colour from the drinking water. Ten years later, Holden[9] reported the treatment of river water in Britain using iron electrodes. More recently electrocoagulation has been revived in a renewed interest in environmental restrictions of effluent wastewater. Electrocoagulation was studied in the treatment of wastewater from the food industry.[10] This study reported the comparison of electrocoagulation to chemical dosing. The flocs formed from electrocoagulation were compacted more quickly. The concept of electrocoagulation has also been applied to microorganism harvesting from cultures[11] and the removal of protein and ether soluble substances from wastewater.[12] In the 1980s, there was a great deal of work preformed by Russian scientists employing electrocoagulation in a variety of ways in the treatment of wastewater[13] and oil-in-water emulsions.[14]

Figure 1a-b[15] shows the effect of wastewater treatment using electrocoagulation technique.

Figure 1a. Chromium Water, before/after electrocoagulation

Figure 1b. Steam Cleaner Wastewater, before/after electrocoagulation

2. Mechanisms and Advantages/Disadvantages

During electrolysis, an electric current applied to electrodes causes the positive electrode to undergo anodic reactions, while at the negative electrode, a cathodic reaction is encountered. Consumable metal plates, such as iron or aluminum, are usually used as sacrificial electrodes to continuously produce ions into the system. The released ions may remove the undesirable contaminants either by chemical reaction and precipitation, or by causing the colloidal materials to coalesce and then be removed by electrolytic flotation. The reaction mechanism of electrocoagulation is highly dependent on the chemistry of the aqueous medium, especially conductivity. In addition, other characteristics such as pH, particle size, and chemical constituent concentrations will also influence the electrocoagulation process. The mechanisms of removal of ions by electrocoagulation will be explained with two specific examples involving aluminium and iron, since these two metals have been extensively used to clarify wastewater.

Aluminium[2,16]

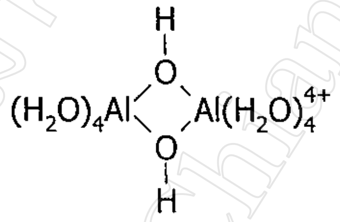
The mechanism proposed was that dissolution of the aluminium anode produces Al^{3+} ions which at the appropriate pH are transformed in a first step, to aluminium hydroxide $Al(OH)_3$ which is finally polymerised to $Al_n(OH)_{3n}$ (equations (1) - (3)).

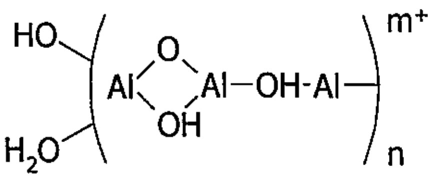
$$Al \rightarrow Al^{3+}{}_{(aq)} + 3e^- \qquad (1)$$

$$Al^{3+}{}_{(aq)} + 3H_2O \rightarrow Al(OH)_3 + 3H^+{}_{(aq)} \qquad (2)$$

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

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:





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.[4] As a result of these processes, contaminants may be released from water and decomposed or made less soluble. The examples of removing phenol and quinone using the electrocoagulation technique are shown in Figures 2 and 3. The quinone which may be reduced to phenol, can then form insoluble complexes with Al^{3+} that precipitate out of the solution.[17]

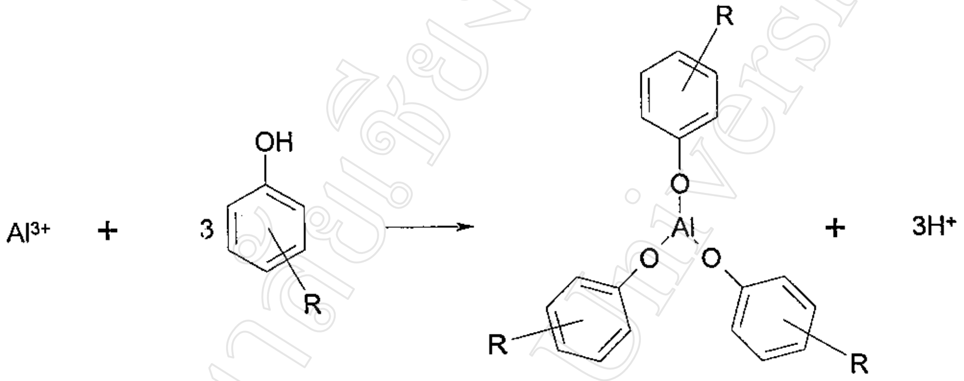


Figure 2. Complexation of phenols with Al^{3+}

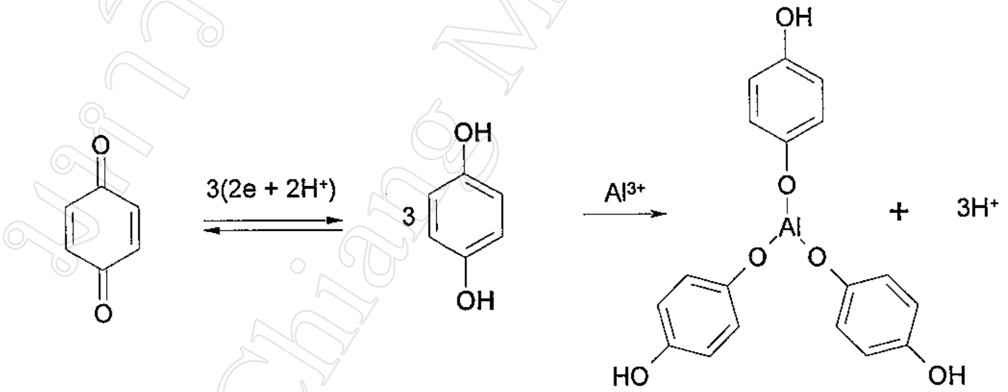


Figure 3. Reduction of quinones to phenols, followed by complexation with Al^{3+}

Iron[1,2]

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

Mechanism 1

Anode:

$4Fe_{(s)} \rightarrow 4Fe^{2+}{}_{(aq)} + 8e^-$ (6)

$4Fe^{2+}{}_{(aq)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+{}_{(aq)}$ (7)

Cathode:

$8H^+{}_{(aq)} + 8e^- \rightarrow 4H_2(g)$ (8)

Overall:

$4Fe_{(s)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)}$ (9)

Mechanism 2

Anode:

$Fe_{(s)} \rightarrow Fe^{2+}(aq) + 2e^-$ (10)

$Fe^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Fe(OH)_{2(s)}$ (11)

Cathode:

$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-(aq)$ (12)

Overall:

$Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)}$ (13)

The $Fe(OH)_{n(s)}$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the unwanted particles from water either by complexation or by electrostatic attraction, followed by coagulation.[18] The prehydrolysis of Fe^{3+} cation also leads to the formation of reactive clusters for water treatment. Structural models for these oxyhydroxy iron cations have been extensively reported in the literature.[19]

Wastewater containing Cr^{6+} (CrO_4^{2-}) ions can be removed by the electrocoagulation technique using iron as electrodes.[20,21] The ferrous ion (Fe^{2+}) generated at the iron anode can reduce Cr^{6+} to Cr^{3+} under alkaline conditions and is itself oxidized to ferric (Fe^{3+}) ion according to equations (14) or (15).

$$CrO_4^{2-}{}_{(aq)} + 3Fe^{2+}{}_{(aq)} + 4H_2O_{(l)} \rightarrow 3Fe^{3+}{}_{(aq)} + Cr^{3+}{}_{(aq)} + 8OH^-{}_{(aq)} \quad (14)$$

or

$$CrO_4^{2-}{}_{(aq)} + 3Fe^{2+}{}_{(aq)} + 4H_2O_{(l)} + 4OH^-{}_{(aq)} \rightarrow 3Fe(OH)_{3\,(s)} + Cr(OH)_{3\,(s)} \quad (15)$$

The $Cr^{3+}{}_{(aq)}$ ion is then precipitated as $Cr(OH)_{3\,(s)}$. The $Fe^{2+}{}_{(aq)}$ ions can also reduce $Cr_2O_7^{2-}{}_{(aq)}$ under acidic conditions according to the following reaction:

$$Cr_2O_7^{2-}{}_{(aq)} + 6Fe^{2+}{}_{(aq)} + 14H^+{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 6Fe^{3+}{}_{(aq)} + 7H_2O_{(l)} \quad (16)$$

The adsorption and absorption of heavy metals by polymeric Fe^{3+} and Al^{3+} hydroxo complexes has been extensively reported[22] which is beyond the scope of the current review. It should, however, be pointed out that the use of Fe^{3+} as flocculation agent in water treatment has considerable advantage because of its innocuity compared to Al^{3+} ions, which exhibits some toxic effects.[23]

3. Applications

In the last decade, electrocoagulation has been increasingly and successfully used for wastewater treatment and pretreatment.[2] One of the most extensive articles of the electrocoagulation process is a review of the treatment of natural water and wastewater.[24]

Electrocoagulation and electroflotation can be used for effective removal of dispersion and emulsion admixtures, dissolved molecules (humic and fulvic acids, dyestuff, anionic surface-active substances and others), dissolves ions in natural water or wastewater which specifically interact with electrogenerated Al or Fe hydroxides. Moreover, the removal of dissolved organic substances such as pesticides and herbicides are reported.[24] In addition, a review concerning electrochemical environmental protection has also been reported.[25] Energy consumption and efficiency was also mentioned.

Wastewater containing food and protein has been treated using electrocoagulation.[26] This technique was claimed to allow by-product recovery, surface the floc and keep it together for easy skimming, lower the water content of the floc, handle both light and heavy waste water, have a very short detention time, and reduce COD, BOD, suspended solids, fats, oils, and greases. In addition, electrocoagulation has also been reported in the separation of fats, oil and grease.[27-29] High oil and grease wastewater was treated using electrocoagulation with different electrode materials and operational conditions.[27] The results showed that aluminium electrodes are preferred for this application. The influences of pH, conductivity and electrical current density do not affect the pollutant removal efficiency significantly.

Electrocoagulation has also been reported in the decolourization of dye-containing wastewater.[30-31] The experimental results showed that the aqueous dye colour was effectively removed when Fe and Al were used as sacrificial anodes. The suitability of a sacrificial anode depends on the concentrations of dyes and their properties.[31]

Electrocoagulation was shown to effectively destabilize and clarify high conductivity, producing aggregates several-fold larger that the primary particle size, which subsequently sedimented from suspensions.[32] Therefore, the ultrafine and submicron-sized particles can be removed from wastewater. The concentration of ultrafine kaolin particles in an aqueous suspension decreased when subjected to electrocoagulation with Fe electrodes.[1] The submicron-sized silica or alumina particles can also be removed from the suspensions when treated with platinum-coated glass electrode electrocoagulation.[32]

The applications of electrocoagulation in removing chemically contaminated wastes have been reported in many literatures. Phosphate was more effectively removed by electrocoagulation using Al electrodes rather than Fe electrodes.[33-34] A low-frequency sonic field was used in order to improve the process of obtaining colloidal iron hydroxides by electrocoagulation and electroflotation in model solutions containing sulphates and chlorides in wastewater.[35] It was established that the low-frequency acoustic treatment increases significantly the quantity of the obtained iron hydroxides, and correspondingly the quantity of contaminations removed from the wastewater. An investigatation of chromium (Cr^{6+}) removal from an electroplating wastewater using the electrochemical precipitation process (ECP) has been studied.[36] Using steel plates representing anode and cathode, the concentration of Cr^{6+} decreases from 215-3860 mg/l to less than 0.2 mg/l. The X-ray fluorescence analysis of the sludge revealed formation of Fe_2O_3 and $FeCr_2O_4$ as the main products. Using electrocoagulation, nitrate removal has been accomplished accompanyed by the precipitation of $Fe(OH)_3$ produced by the soluble anode.[37]

The electrocoagulation process with aluminum bipolar electrodes permitted the defluorination of Sahara water and could also be utilized for the defluorination of industrial wastewater.[38] The electrocoagulation has also proved to be an effective method in removing heavy metal-containing solutions.[39-41] For example, molybdenum is removed as an Fe-Mo precipitation from mining-milling wastewater by $Fe_2(SO_4)_3$. Solid-liquid separation is achieved in both cases by electrocoagulation-electroflotation. The feasibility of the sludge recycling for Fe and Mo recovery is also described.[41] The electrocoagulation can be used to remove organic matter from landfill leachates.[42] The COD removal range, 30 to 50% were obtained using two different electrodes pairs, Fe-Cu or Al-Cu. There are only few reports on the applications of electrocoagutation to natural product purification. For example, the decolorization of crude aqueous plant extracts[43-46] have been reported. Werner *et al.*[47] reported the extraction of naturally occurring organic acids from plants using the electrochemical process. However, the method has not been revealed as it is a patent. Shomer *et al.*[48] have studied protein coagulation in citrus fruit extracts. Pectin was obtained from a aqueous plant extract by the electrochemical method.[49] A natural quinone was electrochemically polymerised and its properties were investigated.[50]

4. Purpose of Research

The main objective of this research is to investigate the utility of the electrocoagulation process as a general method of decolourizing and purifying aqueous plant extracts. Specifically, it is of interest to study the isolation of glycosides from natural sources using this technique. Because of the relatively few studies on the decolourization of plant extracts using electrocoagulation, this investigation might be useful for the isolation of natural products in the future.

The results of this part of the project are described in two chapters. The first chapter is concerned with model studies of electrocoagulation in relation to the isolation of glycosides. The efficiencies of electrocoagulation in removing unwanted chemicals in aqueous solution are reported. The electrocoagulation conditions developed were then applied to the isolation of glycosides and other natural compounds from plants. The compounds obtained were identified using spectroscopic techniques. This work is reported in the second chapter.

5. References

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