Chapter VII

Electrochemistry and Water Treatment
7.1 Introduction

Wastewater is a real challenge for many of the industries. Treatment provided to the wastewater should be feasible, cost effective and should ensure consistence compliance with prescribed effluent standards. Very often feasible treatment technologies may not be available for some of the wastewaters. These wastewaters are often known as difficult wastewaters. Treatment of these wastewaters may require segregation of the culprit wastewater streams at source and pretreatment prior to addition to other wastewater for treatment and disposal. Electrochemistry is a clean, versatile and powerful tool for the destruction of organic pollutants in water. Electrochemical oxidation of organic compounds in aqueous solution is an anodic process occurring in the potential region of water discharge to produce oxygen. Electrocoagulation is an emerging water treatment technology that has been applied successfully to treat various wastewaters. It has been applied for treatment of potable water (Holt et al. 2002), heavy metal laden wastewater (Mills 2000), restaurant wastewater (Chen et al. 2000), and colored water (Jiang et al. 2002).

7.1.2 Wastewater Treatment using Electrochemical Methods

The field of electrochemistry concerns either utilization of energy from spontaneous chemical reactions in the form of electricity or the other way around, to supply energy in order to get non spontaneous chemical reactions running. Electrochemistry is redox chemistry, where electrons are transferred from one species to another. A species is in this terminology said to be oxidized when it lose electrons and reduced when it gains electrons. When chemical reactants capable of spontaneous redox reaction are physically separated and the electrons from the reaction flow through an electric circuit by means of electrodes and wires, it produces a current which can be utilized as an energy source (battery or fuel cell). The electric current is proportional to the reaction rate, and the cell voltage is proportional to the free energy change for the electrochemical reaction.
In electrolysis, non-spontaneous chemical reactions can be forced to occur at the surface of an electrode by an imposed potential difference (energy) high enough to overcome the activation energy for a reaction at the specific electrode and the resistance in the reagent media. Two electrodes, most commonly solid materials, are connected via a power supply and submerged in a solution containing the chemical reagents, termed the electrolyte. If the supplied energy is sufficient, electrons will be removed from the compounds in the electrolyte (they become oxidized) at the positive electrode (anode), while electrons will be delivered to compounds in the electrolyte (they become reduced) at the negative electrode (cathode). Electrons cannot travel freely in solutions, so the charge passed through an electrochemical cell originates from continuous simultaneous oxidation and reduction of chemical species and electrostatic and hydrodynamic transport of ions and molecules. This system of electrodes and electrolyte, where electrochemical reactions can happen, is termed the electrochemical cell. In order to avoid reduction of the oxidized species at the cathode, the anode compartment (anolyte) and cathode compartment (catholyte) are normally separated by a membrane, but just as frequently undivided cells are used due to their more simple construction and maintenance. At the electrodes both organic and inorganic molecules and ions can be involved in electron transfer in the electrolysis process.

7.1.3 Advantages and Disadvantages of Electrochemical Treatment

7.1.3.1 Advantages:

Wastewater treated by electrochemical treatment gives palatable, clear, colourless and odorless water. Sludge formed by electro-chemical treatment tends to be readily settleable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Above all, it is a low sludge producing technique. Flocs formed by this process are similar to chemical floc, except that the flocs tend to be much larger, contain less bound water, are acid-resistant and more stable, and therefore,
can be separated faster by filtration. This process produces effluent with less total dissolved solid (TDS) contents as compared with chemical treatments. If this water is reused, the low TDS level contributes to a lower water recovery cost. The electro-chemical treatment process has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation. This process avoids uses of chemicals, and so there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemical substances added at high concentration as when chemical coagulation of wastewater is used. The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed. The electrolytic processes in the electro-chemical cell are controlled electrically with no moving parts, thus requiring less maintenance.

The electrochemical technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

7.1.3.2: Disadvantages

The ‘sacrificial electrodes’ are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced. The use of electricity may be expensive in many places. An impermeable oxide film may be formed on the cathode leading to loss of efficiency of this unit. High conductivity of the wastewater suspension is required. Gelatinous hydroxide may tend to solubilize in some cases.

7.1.4 Mechanisms and Role of Electrodes in Electrochemical Waste Water Treatment

Electro-chemical treatment is actually a combination of many processes like; 1) electro-oxidation 2) electro-coagulation and 3) electro-flocculation. Electro-oxidation deals with the generation of the ions from the electrodes by the process of oxidation. Electro-coagulation is the
process in which neutralization of charges occurs by electrochemical treatment. Electro-flocculation is the process where metal ions released from the metal electrodes combine with hydroxide to form insoluble precipitate along with which the pollutant particles are co-precipitated. In electrofloatation process, the gas bubbles (because of the generation of the hydrogen gas) are produced on the electrodes in the electrochemical reactor. The EC technology offers an alternative to the use of metal salts or polymers and polyelectrolyte addition for breaking stable emulsions and suspensions.

7.1.4.1 Electrochemical Oxidation

Electro-oxidation is a process in which the pollutants are destroyed or oxidized and converted into simpler forms like carbon dioxide and water. This oxidation process can be either direct oxidation or indirect oxidation. Direct oxidation is an anodic oxidation process. Here the pollutants are first adsorbed on the anode surface and then destroyed by anodic electron transfer reaction. In the indirect oxidation process, strong oxidants like hypochlorite, chlorine, ozone, hydrogen per-oxide, hydroxyl ions (OH-) are electrochemically generated at the anode. In the first step, $\text{H}_2\text{O}$ in acid or OH- in alkali solution is discharged at the anode to produce adsorbed hydroxyl radical. In the second step, the adsorbed hydroxyl radicals may interact with the oxygen already present in the metal oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the lattice of the metal oxide anode forming the so-called higher oxide. Thus, we can consider that at the anode surface, two states of active oxygen can be presented as physically sorbed active oxygen (adsorbed hydroxyl radicals, •OH) and chemisorbed active oxygen (oxygen in the oxide lattice,) In the absence of any oxidizable organics, the physisorbed and chemisorbed active oxygen produce dioxygen. In the presence of oxidizable organics, it is speculated that the physisorbed active oxygen (•OH) should cause predominantly the complete combustion of organics, and chemisorbed active oxygen participate in the formation of selective oxidation products.
7.1.4.2 Electro Coagulation

They neutralize the electrostatic charges on colloidal particles and facilitate coagulation and then separation from the solution. This treatment also prompts precipitation of some of the metals and salts. Electrocoagulation involves the in situ generation of coagulants by dissolving electrically either aluminum or iron ions from aluminum or iron electrodes, respectively. The metal ions generation takes place at the anode, hydrogen gas is released from the cathode. The hydrogen gas would also help to float the flocculated particles out of the water. This process sometimes is called electroflocculation. The electrodes can be arranged in a mono-polar or bi-polar mode. Application of electric current to sacrificial electrodes, usually aluminum or iron generates aluminum and ferrous ions. These ions act as coagulating agents.

The chemical reactions taking place at the anode are given as follows.

For aluminum anode:
\[
\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^{-}
\]
At alkaline conditions
\[
\text{Al}^{3+} + 3\text{OH}^{-} \rightarrow \text{Al(OH)}_3
\]
At acidic conditions
\[
\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^{+}
\]
For iron anode:
\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^{-}
\]
At alkaline conditions
\[
\text{Fe}^{2+} + 2\text{OH}^{-} \rightarrow \text{Fe(OH)}_2
\]
At acidic conditions
\[
4\text{Fe}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}^{3+} + 4\text{OH}^{-}
\]
In addition, there is oxygen evolution reaction
\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-}
\]
The reaction at the cathode is
\[
2\text{H}_2\text{O} + 2\text{e}^{-} \rightarrow \text{H}_2 + 2\text{OH}^{-}
\]
The $\text{Al}^{3+}$ or $\text{Fe}^{2+}$ ions are very efficient coagulants for particulates flocculating. The hydrolyzed aluminum ions can form large networks of $\text{Al}–\text{O}–\text{Al}–\text{OH}$ that can chemically adsorb pollutants such as $\text{F}^–$. Aluminum is usually used for water treatment and iron for wastewater treatment (Comninellis 1994). The advantages of electrocoagulation include high particulate removal efficiency, compact treatment facility, relatively low cost and possibility of complete automation.

7.1.4.3 Electro Flotation

Electroflotation is a simple process that floats pollutants to the surface of a water body by tiny bubbles of hydrogen and oxygen gases generated from water electrolysis. Therefore, the electrochemical reactions at the cathode and anode are hydrogen evolution and oxygen evolution reactions, respectively. The bubbles generated by electrochemistry are smaller than those generated by gases bubbling and help to remove the aggregate generated by electrocoagulation. Electroflotation is a continuous process. In these process uniform size small bubbles of hydrogen gas is generated at the cathode surface during the electrolysis of water. This process mainly consists of four steps: (1) gas bubble generation (2) contact between gas bubble and oil drop (3) gas bubble adsorption on the surface of the particle (4) gas bubble and oil drops rising on to the surface. In electrochemical process, it is easy to adjust the gas bubble flux, by varying the current across the electrodes. Distributions of gas bubbles occur (initially) because the bubbles are produced at whole of the surface of the electrode. At the top surface foam comprising of gas bubbles as well as floating particles is formed and these are removed by skimming. The rate of flotation depend on many factors like: (1)surface tension of solution, (2) gas bubble diameter, (3) size of the particle, (4) water residence time in the electrolytic cell, (5) particle and gas bubble zeta potential, (6) temperature, (7) pH and (8) pollutant particle concentration.
7.2 Materials and Method

7.2.1 Experimental Set Up

The studies were exercised in a lab-scale reactor, which was composed of an electrolysis cell, a power supply, a magnetic stirrer. An electrolysis cell was made of plexiglass having working volume 1L and two electrodes (cathode and anode) each of length 15cm, width 5cm and 2mm thickness are housed inside the reactor as shown in Fig: 7.1 With the help of grooves in the reactor, spacing between the electrodes was maintained at 1cm. Aluminum and stainless steel sheets were used alternatively as electrodes in the present study. Synthetic mercury solution and two wastewater namely, dairy effluent and wastewater from electroplating industry were used in the studied.

Fig: 7.1 Set up of laboratory scale electrochemical reactor
7.2.2 Treatment of Dairy Effluents

The dairy industry wastewaters are primarily generated from the cleaning and washing operations in the milk processing plants. It is estimated that about 2% of the total milk processed is wasted into drains (Munavalli and Saler, 2009). Dairy wastewaters are characterized by high biological-oxygen demand (BOD) and chemical-oxygen demand (COD) concentrations, and generally contain fats, nutrients, lactose, as well as detergents and sanitizing agents (Kushwaha et al. 2011). Due to the high pollution load of dairy wastewater, the milk-processing industries discharge untreated wastewater which may cause many environmental problems. Effluent samples were collected from dairy industry plant in Kozhikode and its physico chemical and biological characteristics were analyzed and then the treatment was done within the reactor.

7.2.3 Treatment of Effluents from Electroplating Industry

The wastewater used in this study was collected from the outlet of glossy metal plating plant, Calicut. The wastewater was characterized for pH, conductivity, Cu, Cr and Ni and the data is presented in Table 7.2. The effluent was filtered using a screen filter to remove suspended solids before it was used for the subsequent studies. The amounts of heavy metals were determined from the filtrate with the help of atomic absorption spectrophotometer (AAS, Thermo Scientific M-Series).

7.2.4 Treatment of Synthetic Mercury Solution

The discharge of heavy metals into aquatic system has a matter of worldwide concern over last few decades. Among all the metals present in the pollutants, treatment of mercury is most important because it is considered to be one of the most toxic metals in wastewater (Dong et al. 2008). Mercury is considered as carcinogenic, teratogenic and promotes tyrosinemia. If a high amount has been taken, it can create impairment of pulmonary and kidney function, chest pain and
dyspnoea (Zhang et al. 2005). Synthetic solution of mercury was prepared from reagent grade chemical without any further purification. The mercury measurements were performed using solid state electrode Rotating Gold Electrode (Au-RDE) in differential pulse mode in 797 VA Computrace (Metrohm, Schweiz-Suisse- Switzerland).

7.3 Results and Discussion

7.3.1 Treatment of Synthetic Hg Solution

7.3.1.1 Effect of Initial pH

It is well known that pH influences the electrocoagulation process and the pollutant removal efficiencies were best found near neutral pH (Chen & Hung 2007). In the present work, the effect of pH from 3 to 8 has been studied. HCl (0.1 N) and NaOH (0.1 N) solutions were used to increase and decrease pH, respectively. It can be observed from Fig 7.2 (a) that pH has an effect on the percent removal of Hg (II). The percent removal has increased up to a pH value of 7; this is because of evolution of hydrogen at cathode would be higher in the acidic pH (Chen & Hung 2007) and thereafter it started to decrease with both the electrodes. The reason for this downward trend may be that at higher pH values results in less generation of H\(^+\) ions which will lead to decreased rate of generation of metal hydroxides. In acidic range percent removal remains more than 99%. But there has been a drastic change in percent removal for a pH value higher than 7.

7.3.1.2 Effect of Time of Electrocoagulation

Time of electrocoagulation is one of the most important parameters. Optimization of time of electrocoagulation is essential because finding the minimum required time for desired removal is necessary. In the present work, it can be observed from Fig 7.3(b) that the removal of Hg(II) increased drastically at the initial stage of the process up to 10 min (99% removal) in the case of SS electrodes and 15 min (98% removal) in the case of Al electrodes. In the case of SS electrodes after
15 min electrolysis time the observed removal percent is 99.7%. At the end of 30 min process time SS electrodes removed 99.83% Hg(II) and Al electrodes removed 99.37% Hg(II). Hence, 15 min process time has been taken as optimum time for further experiments.

7.3.1.3 Effect of Hg (II) Concentration

Effect of Hg (II) concentration from 5 to 20 mg/L on the removal efficiency has been shown in Fig 7.3(a). It can be observed that increase in concentration for same electrocoagulation time and voltage results in decrease in removal efficiency.

7.3.1.4 Effect of Applied Voltage

Applied voltage has to be optimized because higher current density does not mean higher removal after certain limit. From Fig 7.2(b), it can be observed that an increase in voltage results in increased Hg(II) removal. Here, optimum voltage is considered to 4, as after this value the percent separation of Hg(II) was marginal.

![Fig. 7.2(a) Effect of pH](image1)
![Fig. 7.2 (b) Effect of applied voltages](image2)
7.3.2 Treatment of Dairy Effluent

Table 7.1 Physico chemical and biological characteristics of dairy effluent

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Before treatment</th>
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<tbody>
<tr>
<td>pH</td>
<td>9.15</td>
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<tr>
<td>Electrical conductivity μs/cm</td>
<td>906.8</td>
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<tr>
<td>TDS mg/l</td>
<td>643.82</td>
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<tr>
<td>Turbidity NTU</td>
<td>146.6</td>
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<tr>
<td>BOD mg/l</td>
<td>266.66</td>
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<tr>
<td>COD mg/l</td>
<td>1400</td>
</tr>
<tr>
<td>Oil and grease mg/l</td>
<td>1251.8</td>
</tr>
<tr>
<td>Nitrate mg/l</td>
<td>0.8</td>
</tr>
<tr>
<td>Total coliform MPN/100ml</td>
<td>≥2400</td>
</tr>
<tr>
<td>Fecal coliform MPN/100ml</td>
<td>150</td>
</tr>
<tr>
<td>E coli MPN/100ml</td>
<td>Present</td>
</tr>
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In case of dairy effluent, maximum removal efficiency was found with Stainless steel electrodes. Effluent pH of 7, voltage of 4 V, an electrolysis time of 60 minutes and electrolyte dose (NaCl) of 0.8 g/l gave best results when stainless steel electrodes were used. Under optimal conditions, COD and oil and grease of the effluent were removed by 85%, and 60% respectively.

Addition of electrolytes to solutions will increase the conductivity of the medium. Electrolytes like NaCl, KCl, Na₂SO₄, K₂SO₄, NaNO₃, etc. can be used for this purpose. Since, NaCl is the most commonly and cheaply available electrolyte, researchers have widely used it to increase the conductivity of the system solution. In the present work, without adding electrolyte only 54% COD removal by SS electrodes and 51.7% removal by Al electrodes were observed. It was observed that the percent removal is more than 99% with both the electrodes at 5% NaCl concentration, and thereafter the percent increment rate was negligible. Hence, 5% NaCl was used as optimum electrolyte concentration in further experiments.

![Graph](image)

**Fig. 7.4(a) Effect of time on removal of COD  Fig. 7.4(b) Effect of time on removal of Oil & Grease**

### 7.3.3 Treatment of Plating Industry Effluent

#### 7.3.3.1 Effects of Operating Parameters

The electrocoagulation process is affected by several operating parameters, such as initial
pH, pollutants concentrations, current density, COD and contact time. In the present study contact time have been explored in order to evaluate a treatment technology for nickel and zinc removal from actual electroplating wastewaters.

**Table: 7.2 Characteristics of plating industry effluent**

<table>
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<tbody>
<tr>
<td>pH</td>
<td>5.32</td>
</tr>
<tr>
<td>Electrical conductivity μs/cm</td>
<td>36100</td>
</tr>
<tr>
<td>Ni mg/l</td>
<td>584.60</td>
</tr>
<tr>
<td>Zn mg/l</td>
<td>632.70</td>
</tr>
<tr>
<td>COD mg/l</td>
<td>1580</td>
</tr>
</tbody>
</table>

The relatively high COD content of the wastewater indicates the presence of organic compounds added to the electroplating baths as brighteners, levelers, complexing and wetting agents. At a constant voltage of 4V and an electrolysis time of 60 minutes the concentrations of metals such as Ni and Zn at a concentration of permissible limit for discharge (Fig. 7.5). The initial COD of 1580 mg/L was decreased to less than 120 mg/L after 120 minutes showing a removal efficiency of about 75 % when Al electrodes were used (Fig.7.6 (b)) and reaches an efficiency of 51% in the case of SS electrodes (Fig.7.6 (a)). The removal efficiency reached a maximum value after a particular time beyond which no change was observed.
7.4 Summary

The electro-coagulation and flocculation process was used to treat the wastewater from electroplating industry and dairy effluent from a milk processing unit. Treatment was optimized for the operational variables such as electrode type, influent pH, electrolyte dose and treatment time. Treatment efficiencies were assessed on the basis of removal of color, turbidity, chemical oxygen demand (COD), and heavy metals.
demand (COD), oil and grease and metals from the effluents. In case of dairy effluent, maximum removal efficiency was found with stainless steel electrodes. Effluent with pH of 7, voltage of 4 V, an electrolysis time of 60 minutes and electrolyte dose (NaCl) of 0.8 g/l gave best results when stainless steel electrodes were used. Under optimal conditions 85% COD and 60% of the oil and grease of the effluent were removed.

Removal of Hg(II) from synthetic aqueous solutions by electrocoagulation, with SS and Al electrodes, was studied. Effects of various parameters, viz, electrocoagulation time, initial pH, applied voltage, presence of electrolyte in the on Hg(II) removal efficiency was attempted. SS electrodes (99.7% Hg (II) removal) was found to be a better than the Al electrodes (98% Hg( II) removal) in the present case. The optimum operating parameters are electrocoagulation time of 15 min, current voltage 4, pH 7 and distance between electrodes 1 cm.

In case of electroplating effluent, maximum removal efficiencies were found with Aluminum electrodes. Best results were obtained with aluminum electrodes at the voltage of 5V and at the pH of 2, for the electrolysis time of 60 minutes. Color, turbidity and COD of the first extraction stage effluent were removed by 98%, 76% and 86% respectively. Power consumed was found to be high in both the cases of wastewaters. In respect to power consumption, it was concluded that this technology is costly for wastewater treatment but for some of the difficult wastewaters for which the alternative technologies are not feasible, this technology may proves to be appropriate for treatment. It is also concluded that if this technology is used in large scale, then it would be cost effective in comparison to the lab scale observations. Another alternative is to use solar energy or solar powered photovoltaic devices.