Where chromium and ammonia present in the effluent are removed through adsorption method. The biochemical methods include biodegradation, bisorption etc. Biological methods of treating industrial effluents are suited for easily degradable organics only. However, these methods become ineffective for the effluents containing refractory (resistant to biological treatment) organic pollutants. Though the conventional methods are traditionally used in tannery industry, these methods have limitation and cannot meet the stringent norms of pollution control board standards. As a result, the industries are forced to look for alternative treatment technologies to treat the tannery effluent effectively. Among them, advanced oxidation processes have already been used for the treatment of industrial effluent containing recalcitrant organics.

1.6 SCOPE OF THE PRESENT STUDY

The objective of the present investigation is to study the feasibility of electro chemical treatment of leather effluent using electro oxidation and electro coagulation methods followed by Reverse osmosis technology. For possible improvement. The specific objectives are

1. To study the electro oxidation of tannery effluent in a batch electrochemical reactor

2. To study the electrocoagulation of tannery effluent in a batch electrochemical reactor


4. Integration of electrochemical method with membrane process (RO Technology).
CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The treatment and reuse of industrial wastewater has gained greater attention among the industries/researchers due to stringent discharge environmental regulations, diminishing water resources and increased wastewater disposal costs (Metcalf and Eddy, 1979; ECSWA, 2003). In India, tannery industry is one of the significant contributors to the economy and provides large scale employment opportunity for people of economically weaker society. The transformation of raw skins into commercial products requires high water consumption and the use of several chemicals. Hence, leather processing industry is classified with high organic loads containing priority pollutants such as sulphite, chromium, synthetic tannins (Syntan), biocides etc. The tanning operation in which, organic or inorganic materials become more chemically bound to the available substance and preserve it from deterioration. The characteristics of effluent from tannery industry vary considerably depending upon the plant size, chemicals and type of final product produced. Wastewater from the tanneries contains high biochemical oxygen demand (BOD), chemical oxygen demand (COD), sodium sulphide and suspended solids (Adel Al-Kdasi et al 1995; Vijayaraghavan & Murthy 1997; Iqbal et al 1998; Lidia et al 2001; Thyagarajan et al 2010) and chromium (Sarkar 1981; Ramasami et al 1995).

2.2 PHYSICO-CHEMICAL TREATMENT SYSTEM

The physico-chemical treatment of organic effluent consists of adsorption, coagulation, precipitation, flocculation, sedimentation, filtration, ion exchange and chemical oxidation (Ramesh et al 2007; Kyung- Sok et al 2004; Lefebvre et al 2006; Metes et al 2004; EPA, 2004; UNEP, 2004; Linda & Peter 1999). Oxidative degradation by chlorine and ozone is the most common chemical processes for color removal. The chlorination however has the disadvantage of producing organochloride byproducts. Coagulation/ flocculation have been tried for leather effluent treatment to reduce COD and suspended solids (Haydar et al 2009; Zhi et al 2009). Some authors attempted both physical and chemical or combination of both for treating leather industrial effluent to reduce organic pollutant and nitrogenous compound
present in the leather effluent (Cassano 1999; Parag et al 2004; Awan 2004, Ramesh et al 2007). The ammonia present in the tanning effluent can be removed using adsorption, chemical precipitation, membrane filtration and reverse osmosis (Metcalf & Eddy, 1979; Seungmoon et al 2006; Sarioglu et al 2005; Metes et al 2004; Kyung- Sok et al 2004; Lidia et al 2005a). The chromium present in the tannery effluent can be reduced by chemical precipitation, adsorption, and ion exchange (Rapoportand Muter 1995; Kurniawan et al 2006; Ramesh et al 2007).

The other contributors on physico-chemical methods of tannery effluent treatment are due to the conventional method which includes membrane filtration (Justina et al 2009), precipitation (Kabdasli et al 1999, 2003; Esmaeili et al 2005) and coagulation (Jing-Wei et al 2007; Haydar et al 2009; Zhi et al 2009; Espinoza-Quinones et al 2009; Sengil et al 2009), adsorption (Santosa et al 2008; Covarrubias et al 2008), ion exchange (Tiravanti et al 1997; Kabir & Ogbeide 2008). Though the physico-chemical methods can be used for removal of both organic and inorganic matter, they are expensive, consume large amount of chemicals and produces secondary solid sludge (Del Pozo & Diez 2003).

2.3 BIOCHEMICAL METHOD

In this treatment technique, micro-organisms utilize the organic matter for metabolism processes as they can uptake organic matter and nutrients (nitrogen and phosphorus) for energy source (Pittier & Chudoba 1990; Ahn et al 1996; Chandra et al 1997; Bashaar 2004). The biological treatment methods have following advantages (Durai et al 2010):

(i) Low capital and operating costs

(ii) Relatively less secondary sludge compared chemical method
(iii) Eco friendly

(iv) Oxidation of a wide variety of organic compounds

(v) Removal of reduced inorganic

(vi) Operational flexibility to handle a wide range of flows and wastewater characteristics

(vii) Reduction of aquatic toxicity

Typical biological treatment processes make use of trickling filters, activated sludge, Sequencing Batch Reactor (SBR) and wetland as polishing system. Organic pollutants and colloidal organics from wastewater can successfully be removed by biological treatments (Benefield & Randall 1985. Biodegradation of organic matter during wastewater treatments occur either in the presence of oxygen (aerobically) or in anoxic conditions (Ahn et al 1996; Metcalf & Eddy 1979; EPA 1990). Several studies focused on bio-remediation of tannery effluents (Jayaseelan 1997; Haydar et al 2009). Carbon dioxide is generated along with solid sludge when soluble organics are oxidized biochemically. However, the oxidation of organic matter in anoxic environment by denitrification of nitrate or nitrite yields carbon dioxide, water, nitrogen and sludge (Nicholas 1996; Scabloom & Buchanan 2005; Boari et al 1997).

Puvanakrishnan & Dhar (1986) experimentally proved the possibilities of treating tannery effluent using enzymes. They used the combination of hydrolytic enzymes, viz. proteases, carbohydrases, and lipases for treating tanning effluent and suggested that the protein by-product are utilized for animal feed as well as energy conservation and fat recovery. Removal of organic pollutant from tannery effluents is clearly favored by the
combination of processes with and without oxygen (Delpozo & Diez 2003). Microorganisms such as *A. fumigate* and species of *Pseudomonas* can reduce the chromium presence in the tanning effluent and *P. aeruginosa* could be used successfully to degrade pentachlorophenol (Venkat Rao & Puvanakrishnan 1993). Many investigators have reported the use of biological treatments, specifically, sequencing batch reactors (SBR) in tannery wastewater as an efficient way for the removal of organic matter (Ganesh & Ramanujam 2009; Farabegoli et al 2004; Murat et al 2002; Lefebvre et al 2006). The presence of higher concentration hinders the performance of aerobic biological treatment (Thorsten & Petruzelli 1997; Sekaran et al 1996; Ganesh & Ramanujam 2009).

Even though the conventional methodologies are technically feasible, on lab scale operations they are questionable for their technical and economic feasibility in large scale operations. Thus, it can be observed that the problem involving the proper management of the tannery effluent has not been solved.

2.4 MEMBRANE PROCESS

The development of cellulose acetate membranes in the early 1960's, started gaining attention among researchers/industries in 70's. Today the importance of membrane is felt beyond reverse osmosis (desalination) to wide variety of wastewater treatment applications (Krishnanamoorthi et al 2009; Jain et al 2006). Membrane based processes offer a cleaner technology in the treatment of various industrial processes for separation, purification, concentration, and fractionation of the solutes (Jonsson et al 1990; Afonso & Pinho 1991; Cassano 2001; Marcucci et al 2002; Brans et al 2004). Several
advantages of the RO process that make it particularly attractive for dilute aqueous wastewater treatment include:

- Simple in design and operation, low maintenance
- RO can be used to remove inorganic and organic pollutants simultaneously
- The RO treated effluent can be reused

RO process considerably reduces the volume of waste streams so that the stream can be further treated effectively by other processes such as incineration (Cartwright 1985, 1991; Sinisgalli & McNutt 1986; McCray et al 1990; Cartwright 1991; Williams et al 1990). In addition, RO systems can replace or be used in conjunction with other treatment processes such as oxidation, adsorption, stripping, or biological treatment (as well as many others) to produce high quality treated water which can be reused or discharged. Sourirajan & Matsuura (1985) have compiled separation and flux data of cellulose acetate membranes for a large number of organic compounds, including many organic pollutants.

### 2.5 ADVANCE OXIDATION PROCESS

Biological methods of treating industrial effluents are suited for easily degradable organics only. However, these methods become ineffective for the effluents containing refractory (resistant to biological treatment) organic pollutants. Advanced oxidation processes (AOPs) have been developed to overcome this problem (Rameshraja & Suresh 2011). In AOP, high powerful oxidants such as ozone, hydrogen peroxide, fenton oxygen are generated through different techniques. The oxidant radicals are very reactive and attack the organic molecules with very high rate constants (Hoigne et al 1997). Further, the oxidants are characterized by a low selectivity which is a
useful attribute for an oxidant used in wastewater treatment and to solve pollution problems. The versatility of AOP is also enhanced by the fact that they offer different possible ways for oxidant production thus allowing a better compliance with the specific treatment requirements. Advanced oxidation processes (AOPs) are emerging and promising technology both as an alternative treatment to conventional wastewater treatment methods and enhancement of current biological treatment methods especially dealing with highly toxic and low biodegradable wastes (Chamarro et al 2001; Lidia et al 2005a; Stanislaw et al 2001; Tzitzi et al 1994). The AOPs are attractive alternative for the treatment of refractive organic effluents such as aromatics, tanneries, pesticides, petroleum constituents and volatile organics etc. (Metcalf & Eddy 1979; Legrini et al 1993; Hoffmann et al 1995; Robertson et al 1996; Mohan et al 2007; Durai et al 2010). The higher molecule pollutants are reduced to water, carbon dioxide and salts.

The oxidation of organic pollutants with strong oxidants (H₂O₂, O₃ etc.) takes place generally at room temperature. In order to increase the efficiency of mineralization, the oxidation takes place in the presence of catalyst and UV radiation. This technology is interesting for the treatment of dilute wastewater with COD < 5,000 ppm. Many phenolic compounds are thought to be highly toxic and carcinogenic and considered to be priority pollutants (Rao et al 2001). Because of their high environmental impact, the removal process of phenolic compounds from wastewaters was widely investigated by means of different technologies and many papers are reported in the literature. Some of them include Posada et al (2006), Meng et al (2006), Beltran et al (2005), Yermakova et al (2006) etc. Although AOP use different reacting systems, but they are characterized by the same chemical feature: production of OH radicals. These radicals are extraordinarily reactive species, they attach the most part of organic molecules with very high rate (Hoigne et al 1997).
OH radicals are also characterized by a low selectivity of attach which is a useful attribute for an oxidant used in wastewater treatment and to solve pollution problems. The versatility of AOP is also enhanced by the fact that they offer different possible ways for OH radical production thus allowing a better compliance with the specific treatment requirements. AOP are usually classified according to the reaction phase (homogeneous or heterogeneous) or to the OH radical generation method (chemical, electrochemical, sonochemical or photochemical).

2.5.1 Wet Air Oxidation Process (WAO)

Wet oxidation is the oxidation of dissolved or suspended components in wastewater using oxygen as the oxidizer. It is referred as ‘wet air oxidation’ (WAO), when air is used. In WAO, reaction occurs by means of oxygen from air at elevated temperature (250–300°C) and high pressure (100–150 bar). Sekaran et al (1996) reported more than 90% removal of sulphide in limeyard wastewater by wet air oxidation in the presence of manganese sulfate as a catalyst. The efficiency of the mineralization is more than 99% and the main by-products formed in the aqueous phase after the treatment are acetone, methanol, ethanol, pyridine, and methane sulfonic acid.

2.5.2 Photochemical Processes

The photochemical degradation process is gaining importance in wastewater treatment as the photochemical process results in complete mineralization at mild conditions (Petersen et al 1988; Parag et al 2004). The photochemical chemical reactions are characterized by a free radical mechanism initiated by the interaction of photons of a proper energy level with the molecules of chemical species present in the solution, with or without the presence of the catalyst. The radicals can be easily produced using UV radiation by the homogenous photochemical degradation of oxidizing
compounds like hydrogen peroxide and ozone. The advantage of photochemical oxidation is based on effective utility of sun/UV light (Bauer 1999; Guillard et al 1999; Dillert et al 1999; Yawalkar et al 2001). Various chalcogenides such as TiO$_2$, ZnO, ZrO$_2$, CeO$_2$ etc. have been used as photocatalysts. Good amount of work (Legrini et al 1993) has been reported on the degradation of organic pollutant using Hg emission at 253.7 nm produced by low-pressure mercury lamps.

2.5.3 O$_3$/UV

The conventional ozonation of organic pollutants does not completely oxidize organics to CO$_2$ and H$_2$O. The intermediates after ozonation may be as toxic as or even more toxic than initial compound (Rein, 2001). Ozone coupled with UV radiation could complete the oxidation reaction by supplementing the reaction with it. The O$_3$/UV process makes use of UV photons to activate ozone molecules, thereby facilitating the formation of hydroxyl radicals (Metcalf and Eddy 1979). Hung-Yee and Ching-Rong (1995) documented O$_3$/UV as the most effective method for decolorizing of organic comparing with UV oxidation by UV or ozonation alone. Azbar et al (2004) documented that using O$_3$/UV process high COD removal would be achieved under basic conditions (Crittenden et al 1999).

2.5.4 O$_3$/H$_2$O$_2$

The addition of hydrogen peroxide in ozonation process accelerates the decomposition of ozone and enhances production of the hydroxyl radical. In acidic condition, H$_2$O$_2$ reacts only very slowly with O$_3$ whereas hydrogen peroxide accelerates O$_3$ effectively in basic condition (Staehlin & Hoigne 1982; Stanisław et al 2001; Tanja et al 2003; Schrank et al 2005) demonstrated effective removal of organic pollutant using O$_3$/H$_2$O$_2$. 
2.5.5 Fenton and Photo-Fenton Oxidation

The Fenton reaction was discovered by Fenton (1894). The Fenton mechanism revealed that the effective oxidative agent in the Fenton reaction was the hydroxyl radical. The Fenton reaction can be outlined as follows:

\[ M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + HO^- + HO^* \]  \hspace{1cm} (2.1)

where M is a transition metal as Fe or Cu. Fenton reaction rates are strongly increased by irradiation with UV/visible light (Ruppert et al 1994; Sun & Pignatello 1993; Torrades et al 2004). The Fenton process has been adopted successfully to treat various industrial effluents (Andreozzi et al 2000; Benitez et al 2000). This oxidation method is based on the use of a mixture of hydrogen peroxide and iron salts (Fe\(^{+2}\)) which produces hydroxyl radicals ('OH) at acidic pH in ambient conditions. Both, H\(_2\)O\(_2\) and Fe\(^{+2}\) can react with 'OH and therefore both can inhibit the oxidation reactions if either of them is not in the optimal dosage (Tang & Huang 1996). Fenton and photo-Fenton reaction depend not only on H\(_2\)O\(_2\) concentration and iron added, but also on the operating pH value. An improvement of photoassisted Fenton processes is the UV-vis/ferrioxalate/H\(_2\)O\(_2\) system, which has been recently demonstrated to be more efficient than photo-Fenton for the abatement of organic pollutants (Zepp et al 1992; Safarzadeh-Amiri et al 1996). The H\(_2\)O\(_2\)/UV or Fenton process is successful in removing COD from oil containing wastewaters. The peroxide dose is important in order to obtain better degradation efficiency, while the iron concentration is important for the reaction kinetics. Chamarro et al (2001) have used the Fenton process for the degradation of phenol, 4-chlorophenol, 2,4-dichlorophenol and nitrobenzene and reported more than 90% removal efficiency. The process was found to eliminate the toxic substances and increased the biodegradability of the treated water.
2.6 ELECTROCHEMICAL TREATMENT

Electrochemistry is a branch of physical chemistry plays an important role in most areas of science and technology. Furthermore, it is increasingly acknowledged as a significant means for handling environmental and energy problems facing us today and in the near future. Briefly, electrochemistry deals with the charge transfer at the interface between an electrically conductive (or semi-conductive) material and an ionic conductor (e.g. liquids, melts or solid electrolytes) as well as with the reactions within the electrolytes and the resulting equilibrium. Use of electricity to treat water was first proposed in UK in 1889. The first application of electrochemical technique for water purification The electro coagulation of drinking water was first applied on a large scale in the US in 1946 (Stuart et al 1946, Bonilla et al 1947). Because of the relatively large capital investment and the expensive power supply, electrochemical treatment of water or wastewater technologies did not find wide application worldwide then (Koby et al 2003). However, due to extensive research in US and USSR during the following half century, the process has gained large amount of knowledge. With the ever-increasing stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide (Lin et al 1998). At present, the electrochemical technologies have reached a state that they are not only comparable with other technologies in terms of cost but also potentially more efficient, and for some situations, electrochemical technologies may be the indispensable step in treating wastewaters containing refractory pollutants (Chen et al 2004; Genders & Weinberg 1992). Electrochemical technologies offer various treatment processes such as electro oxidation, electro coagulation, electro disinfection, and electro deposition. An extensive research has been done by many researchers in treating various wastewaters by using electrochemical technologies.
Electrochemical technique offers several advantages (Rajeshwar et al 1994) such as

(i) **Versatility** - direct or indirect oxidations and reductions, phase separations, concentrations or dilutions, biocide functions, ability to deal with many pollutants: gases, liquids and solids, and can be treated from micro litres to millions of litres

(ii) **Energy efficiency** – electrochemical processes generally have lower temperature. Potentials can be controlled and electrodes and cells can be designed to minimize power losses.

(iii) **Amenability to automation** - the electrical variables used in electrochemical processes are suited for facilitating data acquisition, process automation and control.

(iv) **Environmental compatibility** - the main reagent here, the electron, is a 'clean reagent' and there often is no need for adding extra reagents.

(v) **Cost effectiveness** - the required equipment and operations are generally simple and, if properly designed, are also inexpensive.

Electrochemical waste destruction shows several benefits in terms of costs and safety. The process runs at very high electrochemical efficiency and operates essentially under the same conditions for a wide variety of wastes. Operation at room temperature and atmospheric pressure reduces the possibility of volatilization and the discharge of unreacted waste. The waste
treatment can be terminated within seconds by simply cutting off power to the 
electrodes. The viability of such methods for sterilization, disinfection, 
deodorization and similar microbiological applications is also considered. 
Environmental applications of electrochemistry have been the topic of several 
recent books and reviews (Bockris 1975; Genders & Weinberg 1992; 
The electrochemical method for the mineralization of organic pollutants is a 
relatively new technology and has attracted a great deal of attention recently. 
This technology is of interest for the treatment of dilute wastewater (COD 
< 5,000 ppm) and it is in competition with the process of chemical oxidation 
using strong oxidants. The electrochemical technique has been successfully 
tested for various industrial effluents: electroplating (Praveen et al 2010); oil 
mill wastewater (Apostolos et al 2007); heavy metal (Lai et al 2003; 
Balasubramanian et al 2009a, b); nitrite effluent (Koparal et al 2002); de-
fluoridation (Zhu et al 2007); textile (Mohan et al 2007); Phenol compounds 
(Canizares et al 2004 & 2005); landfill leachate (Tsai et al 1997); restaurant 
wastewater (Chen et al 2004); laundry wastewater (Ge et al 2004); surfactants 
(Ebru et al 2007); agro industry wastewater (Patrick et al 2008).

A typical electrochemical treatment process consists of electrolytic 
cell. The electrolytic cell consists of two electrodes; anode and cathode 
immersed in an electrical conducting solution and are connected together via 
an electrical circuit. The electrochemical techniques such as electro oxidation, 
electro coagulation, electro flotation, electro deposition are increasingly tried 
for environmental applications. In electrochemical process, the electrolyte has 
significant effect on formation of oxidizing species during the process. For 
example, if HCl is used as the electrolyte, H⁺ moves toward the negatively 
charged electrode (cathode) in order to accept electrons and get reduced to 
hydrogen according to the following reaction.
\[ \text{H}^+ + e^- \rightarrow \frac{1}{2} \text{H}_2 \]  \hspace{1cm} (2.2)

At the same time, Cl\(^-\) moves toward the positively charged electrode (anode) to discharge electrons and gets oxidized to chlorine as the following:

\[ \text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 + e^- \]  \hspace{1cm} (2.3)

The species H\(^+\) and Cl are called the principal charged species, which are responsible for current flow in the solutions.

### 2.6.1 Electro-Oxidation

In electro-oxidation, the pollutants are destroyed by either the direct or indirect oxidation process. In direct anodic oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction. In indirect oxidation process, strong oxidants such as hypochlorite/chlorine, ozone, and hydrogen peroxide are electrochemically generated. The pollutants are then destroyed in the bulk solution by oxidation reaction of the generated oxidant. All the oxidants are generated in situ and are utilized immediately (Rajeshwar et al 1994; Comninellis & Pulgarin 1993; Comninellis 1994). Among the oxidants, generation of hypochlorite is cheaper and most of the effluents have a certain amount of chloride. Though, direct electrolysis of organic compounds at the anode surface is also possible, a major portion of oxidation is mediated by active chloro species when conducting electrochemical oxidation in the presence of chloride using an undivided cell. The application of indirect electrochemical oxidation mediated by chlorine/hypochlorite has been attempted for treating organic effluents by several investigators.
Mohan et al (2006) experimented electrochemical oxidation of textile dye wastewater using RuO$_2$/Ti anode in batch electrochemical reactor. The authors reported more than 90% COD removal under optimum conditions. The authors later (2007) attempted to reuse the electrochemically treated textile effluent for dyeing application and reported that the electrochemically treated wastewater can be effectively reused for industrial application. Canizares et al (2009) electrochemically treated ink-manufacturing process wastewater containing organic, solvents and surfactants using boron doped diamond electrode and reported complete removal of COD. The electrochemical oxidation of phenolic compounds has been reported by several authors (Comminellis and Pulgarin 1993, Saracco et al 2000, 2001, Canizares et al 2004, 2005, 2009; Lidia et al 2001, 2005a,b).

Mohan et al (2006) reported the influence of anode material on electro oxidation process. The authors compared the performance of SnO$_2$/Ti, PbO$_2$/Ti and RuO$_2$/Ti anodes for degradation of textile effluent and reported better performance of RuO$_2$/Ti than other anodes. Application of noble metals and metal oxides electrodes for treatment of tannery wastewater has been reported by Lidia et al (2005b); Rao et al (2002); Vijayalakshmi et al (2009). The order of efficiency of anodes for tannery effluent was found to be Pt/Ti followed by PbO$_2$Ti, MnO$_2$/Ti (Rao et al 2001). Ouejhani et al (2008). Used Doehlert matrix to optimize the significant experimental variables such as temperature, pH, current intensity and time for tanning effluents and reported that the current intensity and the electrolysis time were the main influent parameters on the removal ratio of COD, TOC and electrochemical oxidation of trivalent chromium. Upendra & Sumathi (2008) studied the removal of pentachlorophenol (PCP) as a model AOX compound in pulp bleaching effluent of a bamboo based mill by electrochemical treatment in batch mode and reported that 10 ppm of PCP in water removed almost completely in less
than 10 min at a current density of 0.6 A/dm$^2$ in the presence of 1000 ppm NaCl serving as an electrolyte and source of chloride ions.

Dominguez et al (2008) described the electrochemical oxidation using boron-doped diamond electrodes as an efficient alternative in the treatment of biorefractory effluents. Total organic carbon (TOC) removal was reported higher than 80% under the selected experimental conditions. Anna et al (1997) investigated the electrochemical removal of 2-chlorophenol and 2, 6-dichlorophenol from aqueous solutions using porous carbon felt anodes and reduced 2-chlorophenol below the prescribed level. The experimental results showed a satisfactory detoxification, consisting of removal of cyclic chlorinated compounds, could be accomplished by means of this electrochemical method. They developed a mathematical model based on the reaction between chlorophenols adsorbed on the carbon fibers of the electrode and hydroxyl radicals produced by anodic oxidation of water has been proposed to interpret the experimental behavior of the system under different operating conditions.

Marinerc & Lectz (1978) attempted to remove ammonia present in the tannery effluent through electrooxidation and recorded more than 90% ammonia removal. Rao et al (2001) studied electrooxidation of tannery effluent and reported more than 90% removal efficiency under optimum conditions. Min et al (2004) studied electrochemical method for tannery effluent treatment and reported that the electrochemical method can be an alternative for conventional chemical and biochemical method for tannery effluent treatment.

2.6.2 Electro-Coagulation

Electrocoagulation is a process involving chemical and physical phenomena, which uses sacrificial electrodes for generation of coagulants.
The generation of metallic cations takes place at the anode, while H₂ production occurs at the cathode (Mollah et al 2001; Balasubramanian & Srinivasakannan 2010). Electro coagulation technology offers an alternative to conventional coagulation process, where the metal salts or polymers are added to break the stable suspensions of the colloidal particles. In electro coagulation, coagulants are produced in situ within the reactor without direct addition of any chemicals. Coagulants are produced by the electrolytic oxidation of appropriate anode materials, such as mild steel or aluminium, which result in formation of highly charged polymeric metal hydroxyl species. These species neutralize the electrostatic charges on the suspended solids and facilitate agglomeration resulting in separation from the aqueous phase. This technique removes metals, colloidal particle, and soluble organic pollutants from aqueous media by introducing highly charged polymeric hydroxide species. The treatment prompts the precipitation of certain metals and salts.

The advantage of electrocoagulation is effective removal of smallest colloidal particles with generation of low amount of sludge (Ignacio et al 1995; Mollah et al 2004). It has been reported that the adsorption on metal hydroxide generated “in situ” by electrocoagulation is more powerful than the metal hydroxides formed chemically in conventional coagulation. When chemical coagulation is used for treating industrial effluent, secondary pollution is caused by chemical substance. Whereas in electrocoagulation, the metal hydroxide is generated “in situ” and the chances of excess coagulants is strictly eliminated (Balasubramanian & Srinivasakannan 2010).

Generally mild steel and aluminium are used as sacrificial anode in electrocoagulation process. When mild steel is used as an anode, it generates iron hydroxide, Fe(OH)ₙ, where n=2 or 3. In addition to the above hydroxyl species, the electro generated ferric ions form monomeric, ferric hydroxo
complexes with hydroxide ions and polymeric species, depending on electrolyte pH, i.e., FeOH$^{2+}$; Fe(OH)$_2^+$; Fe$_2$(OH)$_2^{4+}$; Fe(OH)$_4^-$; Fe(H$_2$O)$_2^+$; Fe(H$_2$O)$_5$OH$^{2+}$; Fe(H$_2$O)$_4$(OH)$_2^+$; Fe(H$_2$O)$_8$(OH)$_2^{4+}$ and Fe$_2$(H$_2$O)$_6$(OH)$_4^{2+}$; which transform into Fe(OH)$_3$ (Koby et al 2003, Benefield et al 1982, Rubin et al 1974). These metallic hydroxides have a strong affinity to disperse particles. The charged hydrolyzed hydroxyl can reduce the net surface charge of the colloidal particles that are in suspension due to the reduction of repulsive potential of electrical double layer. As a result of this, the repulsive forces between the colloidal particles decrease, and bring the particles close to such an extent where the van der Waals force predominate and facilitate agglomeration. Hydrolyzed metal species can be adsorbed on the colloids and creates bridges between the particles. In addition to that, the amorphous solid ferric hydroxide flocs that forms at elevated pH, settle down causing sweep flocculation (Lofrano et al 2006; Balasubramanian & Srinivasakannan 2010).

Electrocoagulation has been successfully applied on various wastewater treatment, and found to be the promising method for solids/liquids separation (Vik et al 1984, Donnini et al 1994). Khansorthong et al (2009) attempted to find the optimum condition for colour and total COD reduction from the pulp and paper industry effluent by electrocoagulation and reported more than 97% colour and 77% COD removal under optimum conditions. Parama Kalyani et al (2009) attempted to study the influence of electrolysis time, applied charge density, electrolyte pH and supporting electrolyte concentration on electrocoagulation efficiency for the treatment of pulp and paper industry effluent. The maximum color removal efficiencies were reported as 92 % and 84 % for mild steel and aluminium electrode respectively. The corresponding maximum COD reduction has been recorded as 95 % and 89 %. Beata et al (2008) experimented electrocoagulation of pulp and paper industry effluent using aluminium anode. The authors observed more than 60% COD removal and 90% color removal. The other contributors
on electrocoagulation for environmental application are Mahesh et al (2006 a,b); Yuan et al (2007); Ugurlu et al (2006, 2008).

From the above discussion, it has been clearly proved beyond doubt that electrochemical technique can be an alternative for treatment of organic effluent with the unique features such as complete mineralization, less energy consumption, no generation of solid sludge etc (Rajeshwer et al 1994). The stringent environmental regulations of pollution control board overtake the growing energy and electrode cost and makes the process economically viable soon.

2.7 COMBINED APPROACH

Many organic compounds present in the chemical process industries such as leather, textile, petroleum refractory organics and are resistant to conventional chemical and/or biological treatment (Saracco et al 2000, 2001; Schrank et al 2004, 2005; ParamaKalyani 2009). The degradation of inhibitor substance such as tannin during the anaerobic digestion was investigated by Banu & Kaliappan (2007). Due to non availability of alternative treatment technique, even today, industries are using conventional treatment methods. Biochemical oxidation are employed where the treatment of complex industrial effluents are not amenable to conventional biochemical methods. On the other hand, chemical methods are employed knowingly that this method generates considerable secondary pollutants such as solid sludge. Further, chemical oxidation method aiming at complete mineralization might become extremely cost-intensive since the highly oxidized end-products that are formed during chemical oxidation tend to be refractory to total oxidation by chemical means. Many times, the chemical oxidations vary from partial remediation to complete mineralization. In the case of partial treatment, chemical oxidation aims at the selective removal of the bioresistant fractions and their conversion to readily biodegradable intermediates that can
subsequently be treated biologically. Coupling chemical pre-oxidation with biological post-treatment is conceptually beneficial as it can lead to increased overall treatment efficiencies compared with the efficiency of each individual stage (Dionissios & Psillakis, 2004). Suthantharajan et al (2004) proposed an exhaustive tertiary treatment for the biological treated waste water from a tanning industry consisting of a sand filter, a photochemical oxidation step, a softener, chemical dosage cartridge filter NF and RO.

A potentially attractive alternative to complete oxidation through chemical means is the use of advanced oxidation pre-treatment step to convert biorecalcitrant organics to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biogas, biomass and water. For example, organic macromolecules such as soluble polymers may simply be too large to permeate cell walls, which preclude their effective biological oxidation. Advanced oxidation process breaks these molecules into smaller compounds (eg short-chain organic acids) that can easily enter cells and may be more readily biodegradable, since the rate of biological oxidation is generally thought to increase with decreasing molecular size. Conversely, total chemical oxidation of these intermediates to carbon dioxide and water may be difficult and require severe oxidative conditions, since the rate of chemical C–C bond scission seems to decrease with decreasing molecular size. Combination of biochemical with chemical/advanced oxidation process results in an integrated approach for effective treatment process to handle the present environmental crisis.

2.7.1 **Biodegradability Index (BI)**

Biodegradability index, defined as the ratio of BOD/COD is an important indicator to assess whether the effluent can be biologically degradable or not. The BI can be measured by respirometric test (Amat et al 2005); oxygen uptake rate (OUR); Zahn-Wellens test (Sarria et al 2002) and,
toxicity (EC_{50}) measurement (Scott & Ollis 1995). The earlier investigators used different techniques to enhance BI (Arslan et al 2004, Chamarro et al 2001, Yeber et al 1999). Thus BI ranges from zero to unity. The effluent BI should be above 0.4 for effective treatment by conventional biochemical methods (Metcalf & Eddy 1979; Morais et al 2005). The BI of industrial effluent has been improved through various treatment methods (Dionisiossia & Psillakis, 2004)

Paramakalyani et al (2009) improved BI for pulp and paper industrial effluent using electrocoagulation method. The biodegradability was increased to more than 0.4 from the original value of 0.2 within 10 minutes of process time. The authors compared the performance of percentage COD removal for the effluent treated directly (without improving BI) by SBR (without pre treatment by electro-coagulation) with the BI improved (BI improved through electrocoagulation) effluent by SBR and reported very significant improvement on percentage COD removal for the effluent pretreated for BI improvement. While Preethi et al (2009a, b) improved the bio-degradability index of tannery effluent from 0.18 to 0.4 by ozonation.

2.8 RESPONSE SURFACE METHODOLOGY

In conventional experimentation, the experiments are conducted keeping all the variables constant except the parameter whose influence is being studied. This type of experiment reveals the effect of the chosen parameters under set conditions, assuming that variables are independent and that the effect will be the same at other values of the remaining variables. However, it does not show what would happen if other variables are changed. Experimental design is an effective and efficient optimization strategy to overcome this drawback, which has gained wide application in chemical engineering optimization (Myers et al 1989; Saravanathamizhan et al 2008). The combined effect of variables can be predicted and optimization can be