CHAPTER 1

INTRODUCTION

1.1 GENERAL

Water is an essential and basic human need for urban, industrial and agricultural use and has to be considered as a limited resource. In this sense, only 1% of the total water can be used for human needs. Inadequate water supply and water quality deterioration represent serious contemporary concerns for municipalities, industries, agriculture and the environment in many parts of the world. Factors contributing to these problems include continued population growth in urban areas, contamination of surface water and groundwater, uneven distribution of water resources and frequent droughts caused by extreme global weather patterns (Asano and Cotruvo 2004). In 2025 nearly one-third of the population of developing countries around 2.5 billion people will live in regions of severe water scarcity (Seckler et al 2000). Our present environmental problems are originated from unplanned utilization of natural sources depending on the especially industrialization. Increase in variation of products, more benefit wishes of industrialists, incorrect applications and deficiencies of regulations are the major reasons of the industrial wastewater pollution. Discharging wastewater without treatment into surface water resources can affect the water quality and aquatic life negatively. Especially the amount and concentration of wastewater determine how they harm the intake habitation. In general, the pulp and paper industry, egg processing industry and rice mills are water intensive industries and it consumes more amount of water than metals and
other chemical industries. The pulp and paper industry, egg processing industry and rice mill effluents are different in nature and its characteristics depend upon the process adopted for manufacturing.

1.2 INDUSTRIAL EFFLUENTS

1.2.1 Pulp and paper industry

Paper is becoming an essential commodity of today’s society. The pulp and paper industry has been growing with demand of paper. The capita consumption has also been steadily increasing over the world. Most of the pulp and paper industries use wood as the major raw material (Singh 2004) and bagasse as an alternative potential raw material for the production of paper because of the limited availability of wood. The pulp and paper making industry is a water intensive industry; it is ranked third based on water consumption after metals and chemical industries. The Indian pulp and paper industry is consuming 100 to 250 m$^3$ freshwater per ton of paper production. The volume of effluent generated by pulping and bleaching operations is approximately in the range of 75 to 225 m$^3$ per ton of product depend on the process and type of raw material used. The volume of effluent generated and its characteristics are normally depended on process used for paper making and the effectiveness of the process. The discharge of highly coloured effluent into the ecosystem involves environmental problems like aesthetic pollution and perturbation of aquatic life. The Pollution Control Board, India has directed the industries to implement suitable treatment facilities before the discharge of effluent into the environment (Ansari 2004).

The characteristics of the effluent generated from the pulp and paper industry vary depending upon the types of raw materials used, types of process technology applied, internal recirculation of the effluent and management practices. In order to design a suitable and economical treatment
technique a complete knowledge of paper making process, usage of raw material and characteristics of the particular industrial effluent is necessary. The nature of the effluent produced from pulp and paper industry at various process stages located in Erode district, Tamilnadu, India is given in Figure 1.1.

![Figure 1.1 Effluent produced from pulp and paper industry at various process stages](image)

In wood preparation section, the raw materials are chopped into small pieces using suitable techniques. Then the pieces are sent to the pulping section where sulfate process method is applied to produce pulp. In pulp bleaching section, pulps are bleached with liquid chlorine and liquid oxygen followed by a second bleaching with chlorine dioxide and third bleaching
with hydrogen peroxide. The bleached pulp is then passed to paper making section.

The wastewater from wood preparation section contains mostly suspended solids, dirt, fibers etc, so this wastewater is filtered and reused again. The effluent from pulping section is called black liquor effluent, which is approximately 20-25 m$^3$/ton of paper production. The black liquor effluent contains the more amounts of cooking chemicals such as sodium hydroxide and sodium sulfate, lignin and other extractives. In industries the effluent from pulping section is sent to chemical recovery plant where chemicals are recovered and reused for process. Effluent from pulp bleaching units (80-100 m$^3$/ton paper production) contains dissolved lignin, carbohydrate, colour, COD, AOX and inorganic chloride compounds. The effluent from paper making section contains particulates, organic compounds, inorganic dyes etc. It is characterized depending on the dyes used and the effluent generation is very low when colour papers are produced. Development of single method for treating effluent from paper making process is more difficult and uneconomical whereas development of new techniques for treatment of effluent from bleaching process is economically feasible because the bleaching effluent having the identical characteristics.

1.2.2 Egg processing industry

The egg processing industry is a water intensive industry and it generates more than 10 billion liters of effluent annually which contains very high organic loads (Carawan et al 1979, Xu et al 2001). The volume of effluent generated and its characteristics normally depend on the process used for egg processing. High concentrations of organic components in effluent streams involve a serious problem for the egg processing industry in terms of water pollution concerns and product losses and must be needed to discharge
after treatment due to legal restrictions in organized industrial zone and environment conservation.

**Figure 1.2 Effluent produced from egg processing industry at various process stages**

The characteristics of the effluent generated from egg processing are depending upon the types of process technology applied, internal recirculation of the effluent and management practices. In order to design a suitable technique for treatment of effluent in the process application, a complete
knowledge of the characteristics of the particular industrial effluent is necessary. The nature of the effluent produced from egg processing industry at various process stages located in Erode district, Tamilnadu, India is given in Figure 1.2.

In egg breaking section, the egg liquids such as albumen and yolk are separated from raw eggs using suitable techniques. The albumen is passed through the centrifugation unit to remove chalazae and major precipitate. The fermentation process is carried out to avoid Maillard browning of the final product when heated. Then ultrafiltration unit is used to remove as much water as possible. Then albumen power is produced using spray dryer and stored at 21°C. The yolk liquid is sent to the pasteurization unit followed by spray drier to produce yolk power. Then the yolk powder is stored at 21°C. The effluent which is generated from all the process stages mainly contains detergent solution, chemicals, egg proteins and fats. High concentrations of these organic components in effluent streams remain a serious problem for the egg industry in terms of water pollution.

1.2.3 Rice mill

Rice is a major crop and staple food in India. It contains fats, carbohydrates, starch and vitamins (B and C). Rice with husk is called paddy. Rice milling is the process of removing the husk and part of the bran from paddy. In order to avoid rice breaking and improve the quality of rice, the parboiling process is used (Manogari et al 2008). Parboiling process is practiced in different methods in the world today and it varies industries to industries. Most of the methods follow the basic steps namely soaking (hydration), steaming (thermal treatment), drying and milling. Effluent generation in parboiling rice mill is mainly due to soaking operation. The water consumption for parboiling process differs from mill to mill depending on the soaking method. The nature of the effluent produced from rice mill at
various process stages located in Erode district, Tamilnadu, India is given in Figure 1.3.

Figure 1.3 Effluent produced from rice mill at various process stages

The quantity of water required for soaking of paddy is about 1.3 times the weight of paddy parboiled. The effluent yield is about 1.0–1.2 l/kg of paddy (Rajesh et al 1999) and it contains considerable amount of organic matter. The effluent discharged from rice mill does not contain toxic compounds or pathogenic bacteria but the continuous discharge into soil or surrounding water bodies can cause adverse environmental effects. Off-odours during soaking can be developed due to fermentative changes. Impact on public health due to soak effluent discharged into land and water bodies is another issue. The growth of natural flora can also get affected by this effluent.
when discharged into land. Aquatic lives also get affected by water quality and deficit of dissolved oxygen. Due to the colour and turbidity of effluent, low penetration of sunlight into waterways affects the photosynthesis process. Hence, it is necessary to reduce the organic load of rice mill effluent prior to disposal.

1.2.4 Treatment techniques

Conventionally, wastewaters coming from different industrial operations contain high concentration of organic and inorganic substances are treated by many different techniques such as adsorption, membrane filtration, coagulation–flocculation, advanced oxidation processes such as ozone, photochemical and Fenton's method etc. (Zhang et al 2006, Minhalma et al 2006, Akyol et al 2004, Blanc and Navia 1991). These technologies take considerable time and require an extensive setup for treatment of effluents. Moreover, each step takes place in a separate tank and the entire treatment requires several pH adjustments as well as the addition of chemicals. These conventional processes generate a considerable quantity of secondary pollutants and large volumes of sludge which it needs further treatment. The biological treatment processes are more suitable for treatment of high strength organic effluent and the high organic effluent requires a two-stage (anaerobic + aerobic) treatment system to degrade the organic components (Kalyuzhnyi et al 2005). However, the two-stage is still not optimal as the total treatment efficiency in terms of COD is only about 80% (Thompson et al 2001).

The electrocoagulation is a simple and efficient method for the treatment of many types of water and wastewaters. In recent years, many investigations have been particularly focused on the use of electrocoagulation due to the increase in environmental restrictions on effluent (Kobya et al 2003). According to Abuzaid et al (2002), electrocoagulation method is expected to be economically more feasible than conventional coagulation
which involves cost of purchasing, transportation, storage and handling of chemical coagulants.

In recent years, the electrocoagulation method was used for the treatment of different effluents such as olive mill (Un et al 2006), distillery industry (Yusuf Yavuz 2007), dairy industry (Blanc and Navia 1991), pulp and paper industry (Mahesh et al 2006, Parama Kalyani et al 2009, Soloman et al 2009), textile industry (Arash Dalvand et al 2011), poultry slaughterhouse (Bayramoglu et al 2006), yeast industry (Koby et al 2008) etc., Electrocoagulation process is a simple, reliable and cost effective method for the treatment of effluents with short reaction time and low sludge formation. This technique needs no additional chemicals and therefore does not produce secondary pollution (Holt et al 2005).

Electro coagulation technology offers an alternative to conventional coagulation process, where the metal ions directly from sacrificial electrodes 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 iron, aluminum and other metals (e.g. stainless steel and titanium), 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. The technology removes metals, colloids particles and soluble organics pollutants from aqueous media by introducing highly charged polymeric hydroxide species. The process occurs in steps during electrocoagulation; (i) anode dissolution, (ii) formation of OH ions and H2 at the cathode, (iii) electrolytic reactions at electrode surfaces, (iv) adsorption of coagulant on colloidal pollutants and (v) removal by sedimentation or flotation (Can et al 2006).
A metallic element employed in the anode is oxidized to yield its ions. The metal ions hydrolyze to some extent in water. When aluminum is used, $\text{Al}^{3+}$ ions are produced in water, which forms soluble monomeric and polymeric hydroxo-metal complexes. The main reactions occurring at electrodes during electrolysis are as follows:

At the anode, aluminum oxidation occurs,

$$\text{Al}_{(s)} \rightarrow \text{Al}_{(aq)}^{3+} + 3e^- \quad (1.1)$$

At the cathode, water reduction occurs,

$$3\text{H}_2\text{O} + 3e^- \rightarrow \frac{3}{2}\text{H}_2 + 3\text{OH}^- \quad (1.2)$$

At alkaline conditions,

$$\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \quad (1.3)$$

At acidic conditions,

$$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ \quad (1.4)$$

The standard potential of aluminum dissolution is lower (-1.662 V), than the standard potential of hydrogen evolution, -0.828 V. The dissolution of aluminum is thermodynamically favored ($E^\circ_2 >> E^\circ_1$) and it should proceed spontaneously (Szymkarczuk et al 1994). Aluminum ions (Al$^{3+}$) are produced by electrolytic dissolution of the anode which generates various monomeric and polymeric species. $\text{Al}_{(aq)}^{3+}$ and OH$^-$ ions generated by electrode reactions (1.1) and (1.2) react to form various monomeric species such as $\text{Al(OH)}^{2-}$, $\text{Al(OH)}_2^-$, $\text{Al(OH)}_3^-$, and polymeric species such as $\text{Al}_6(\text{OH})_{15}^{3-}$, $\text{Al}_7(\text{OH})_{17}^{4-}$, $\text{Al}_8(\text{OH})_{20}^4$, $\text{Al}_{13}O_4(\text{OH})_{24}^7$, $\text{Al}_{13}(\text{OH})_{34}^5$ (Can et al 2006, Gurses et al 2002).
The adsorption of monomeric and polymeric hydrolysis species on particle surfaces leads to electrical double layer compression and surface charge neutralization. In addition, another coagulation mechanism, i.e. sweep flocculation, is observed at sufficiently high electrolyte dosage (Lu et al 2005). During the removal of hydroxide precipitate, impurity particles are enmeshed, and they are effectively removed from the suspension. In sweep flocculation, particles are swept out of the medium by an amorphous hydroxide precipitate (Duan and Gregory 2003). Also, interactions between the colloidal particles and the precipitated polymeric hydroxides become significant.

Many hydrolysis products are cationic and they can interact strongly with negative colloids, giving destabilization, under the correct conditions of coagulant dosage and pH. Excess dosage can give charge reversal and restabilization of colloids. Positively charged precipitate particles may deposit on impurity particles, again giving the possibility of charge neutralization and destabilization. Aluminum additives remove the colloidal particles either by charge neutralization to give insoluble forms, or by adsorption on precipitated metal hydroxide (Duan and Gregory 2003).

The factors such as voltage and current applied, conductivity, pH, electrode materials and reactor design are influencing the electrocoagulation process. The supply of current to the electrocoagulation system according to Faraday’s Law determines the amount of metal ions released from the respective electrodes. The ability of water to conduct electricity is affected by the substances dissolved in it. If the water or wastewater to be treated does not have sufficient conductivity then electrolytes such as NaCl are in some cases employed to increase it. The effect of pH of the water or wastewater on electrocoagulation is mainly reflected in the solubility of metal hydroxides and other compounds. In some cases pH has to be adjusted before the
electrocoagulation process. The materials employed in electrocoagulation are usually Al or Fe, but they might yield completely different results. Many different designs have been used with electrocoagulation, for example monopolar, bipolar and concentric electrodes, solid, solid with holes and scrap electrodes and each may also provide different results.

The advantages of electrocoagulation method include; high particulate removal efficiency, possibility of complete automation, production of less sludge, large and stable flocs etc., (Mollah et al 2001, Chen 2004). The amount of chemicals which has to be transported is lower than conventional coagulation treatment (approx. 1/10 of the amount) as previously reported by Vik et al (1984). Chemical precipitants mean further cost since they require the purchase and installation of dosing equipment and operating cost for power, disposal of additional sludge, manpower, and of course, the chemicals used (Bektaş et al 2004). The handling and disposal of the sludge stemming from chemical precipitation is one of the greatest difficulties associated with chemical treatment. Most chemical precipitation operations produce great volumes of sludge. Coagulation plants show that there are considerable operational difficulties involved pH control, chemical mixing and aluminum sulfate dosing (Vik et al 1984). Besides the obvious advantage that the electrocoagulation process has over these factors in coagulation, electrocoagulation also has some disadvantages; namely expensive electricity, high conductivity of wastewater and the necessity to replace the electrodes.

The reduction of dissolved lignin, carbohydrate, colour, COD, AOX and inorganic chloride compounds from bleaching effluent and high concentration of organic load from egg processing effluent and rice mill effluent is important prior to disposal. The treatment of bleaching, egg processing and rice mill effluent using physico-chemical methods generate a considerable quantity of secondary pollutants and large volumes of sludge
which it needs further treatment. The biological treatment processes are more suitable for treatment of high strength organic effluent when two-stage (anaerobic + aerobic) treatment technique is used to degrade the organic components. The biological treatment process can be used in combination with other processes such as physico-chemical and electrochemical methods because of low removal efficiency. The drawbacks associated with the conventional and biological techniques forced the effective treatment method for complete degradation of pollutants. Hence, in this present research an attempt has been made to study the efficiency of electrocoagulation process for treatment of bleaching, egg processing and rice mill effluent as a function of operating parameters on colour, turbidity, COD and BOD reduction. A detailed review of literature was carried out to explore the current research work carried out globally and a brief report is presented in the next chapter.