CHAPTER 1

INTRODUCTION

1.1 PETROLEUM INDUSTRY

The petroleum industry is one of the world’s largest industries, and is very important to our everyday activities. The petroleum industry can be divided into four major branches. The first branch is the upstream petroleum industry, which includes oil exploration and extraction activities, responsible for recovering the oil and bringing it to the surface of the oil fields. The transportation sends crude oil from the oil fields to the refineries. The oil refining branch processes crude oil into useful products. While the marketing branch sells and distributes the petroleum products to the consumers (Wong and Hung 2006).

1.1.1 Crude Oil Production

The upstream petroleum industry starts with oil exploration, in which oil geologists study the geological structures and rock formations on and below the earth’s surface to determine where petroleum might be found. In the next step, the petroleum engineers, drill, and complete an oil well, which means bringing the well into production. After that, crude oil is recovered in much the same way as underground water is obtained.
In 2011 more than 30 billion barrels of crude oil were produced in the world. The average worldwide oil production rate is 88 million barrels a day (bpd) according to the U.S. Energy Information Administration. This massive global production of oil requires a huge number of oil refineries, to turn it into useful products.

### 1.1.2 Transportation

Most oil fields are located in desert areas or rugged areas or at sea at a considerable distance from the refineries that convert crude oil into usable products, and therefore, the oil must be transported in pipelines and tankers. Most crude oil needs some form of treatment near the reservoir, before it can be carried considerable distances through the pipelines or in tankers. Due to a decrease in the pressure and temperature of crude oil on the surface after production, gases are liberated from the oil in addition to the associated gases. Therefore, the transportation requires airtight tanks for storage, and leakproof pipes or trucks. Due to the difficulty in transporting the crude oil from each well in separate pipe, the transportation of crude oil is further simplified by blending crude oil from several wells, homogenizing the feedstock to the refinery. Over one-half of the oil produced was moved by tankers on fixed maritime routes. In terms of the volume of oil transit, the Strait of Hormuz leading out of the Arabian Gulf and the Strait of Malacca linking the Indian and Pacific Oceans, are two of the world's most strategic chokepoints. The global oil market is dependent upon reliable transport. The blockage of a choke point, even temporarily, can lead to substantial increases in total oil costs. In addition, chokepoints leave oil tankers vulnerable to theft from pirates, terrorist attacks, and political unrest in the form of wars or hostilities as well as shipping accidents that can lead to disastrous oil spills.
1.1.3 Oil Refining

Once the crude oil is pumped from the oil wells, it is transported through pipes for storage tanks and then to the refineries. Petroleum refining is a complete process involves physical, thermal, and chemical separation, to convert crude oil into useful petroleum products. Petroleum refineries range in size from small plants that process around 150 barrels of crude oil per day to giant complexes with a capacity of more than 600,000 bpd (Wong and Hung 2006). The petroleum products such as liquefied petroleum gas (LPG), gasoline, kerosene, aviation turbine fuels, diesel fuels, fuel oil, lubrication oils, petroleum waxes, and bitumen are very important in our day to day activities. It is used in many industries, and we cannot dispense with the use of petroleum products. Till this date, there is no appropriate alternative to petroleum product and in fact the world economy is based on the crude oil asset.

In petroleum refinery process, each unit operation/process consumes large quantities of water, and about 80-90% of water consumed in refinery process comes out as wastewater. Due to the advancement in science and technology, the major portion of wastewater generated in refining process can be recycled. The wastewater containing a high percentage of crude oil can be reprocessed in the refining, while the wastewater containing a high proportion of hydrocarbons, which resulted after refining can be used in burners and furnaces after being separated from the water. The wastewater containing low levels of soluble hydrocarbons and organic material can be recycled in the cooling towers after a number of treatments. The residuals must be reduced to a minimum in accordance with international regulations before the wastewater can be reused (Prather 1970). Figure 1.1 shows the usage, recycling and reuse of water in a typical petroleum refinery (modified from IPIECA 2010).
Figure 1.1 Schematic diagram of the typical water usage in a petroleum refinery

Every articulation of the oil industry, whether at the stage of production or transportation or refining or even marketing, generate considerable amount of solid, liquid, and gaseous waste, causes global concern. The world has been on the lookout for ways that minimize the environmental impact resulting from the use of oil products. The search began at the beginning of the industrial revolution with the increasing industrial demand for petroleum products.

1.2 PETROLEUM REFINERY

The petroleum refinery is the third branch (downstream) of the petroleum industry after oil exploration, production (upstream), and transportation, as mentioned in chapter one. India, one of the countries interested in oil refineries, tries to exploit crude oil to the maximum, generating poor quality products at cheaper prices, thereby leading to
environmental problems. The recent industrial revolution, change in lifestyle in India has led to an increased demand for petroleum products to five times. The gross import of crude oil and petroleum products in India was 121.672 million tons 2007-2008. India imports three-quarters of the crude it refines, at an estimated 2.6 million barrels per day (Rajesh et al 2009), and exports refinery products of roughly ten percent of its production (Desai et al 2009). This huge use of crude oil, has made India occupy the sixth place, in terms of the global consumption of crude oil, and is projected to replace South Korea and emerge as the fourth largest consumer of energy after the United States, China and Japan. The petroleum refinery industry is one of the largest and the core industrial sector in India. It requires highly capitalized and huge amounts of water. On the other hand, refinery is a highly polluting process for land, air, and water, requires substantial investments in pollution control equipments (Ali and Sreekrishnan 2001).

The main goal of typical petroleum refineries is to convert crude oil into useful and profitable products. The quality of crude oils processed by petroleum refineries is expected to decrease gradually with an increase in the sulfur contents and densities, due to increasing oil production to meet the demand, especially with increasing prices (Gary and Handwerk 2001). The increase in the poor quality of crude oil increases the amount of heavy products, and reflects on the quality of wastewater generated. Hence, the quality of wastewater generated by the petroleum refinery is heavily loaded with organic matter, acute toxicity and poor biodegradability (Wei et al 2010).

The recent environmental regulations, which are more stringent, encompass a broader range of chemical constituents and processes. More than 124 regulations were laid down according to the federal regulations relevant to petroleum refineries. Refineries are generally considered a major source of pollutants in areas where they are located, and are regulated by a number of
environmental laws related to air, land, and water. In general, the waste from the petroleum refinery can be hazardous as (Speight 2007):

1. The material has a flash point less than 140-F, and is ignitable;

2. The waste has a pH of less than 2.0 or above 12.5, and is corrosive in nature;

3. The waste is unstable and produces toxic materials, and is considered reactive; and

4. The waste is found to be toxic.

Many researchers and companies dealings with the oil refining industry are working on various aspects to raise its status to a remarkable level, which is one of the most important industries in the world. Ford et al (1971) studied the analytical parameters of refinery wastewaters. The degree of biological treatment depends on the BOD: TOC or BOD: COD ratios of wastewater. Higher levels of biological treatment efficiency in terms of organic removal were noted with increasing BOD: TOC or BOD: COD values. Wigren and Burton (1972) which suggested designing the overall collection and treatment facilities to enable the refinery to meet water quality control requirements. Use of a large stripping unit, and dissolved air flotation facility reduced the volume of wastewater and contaminants level at the source. Hoffman et al (1973) suggested simulation to achieve a fundamental understanding of the operation of the processing units and the analyses of the components of the input and output streams. A combination of plant testing and experimental work is required to provide a good understanding of the various units in the refinery. Lindsay and Prather (1977) defined and evaluated the petroleum refinery wastewater problems. A successful solution to these problems is attested to design a plant that could operate with high
automatic facility. Gealer et al (1980) suggested using electrolytic method to remove emulsified oil from dilute oily wastewater streams. The results of the electrolytic pilot unit study indicate that the process is capable of rendering the wastewater suitable for direct discharge to municipal sewers. Skinner (1984) suggested three criteria to regulate oil/water/solids separation sludges generated in the wastewater treatment system prior to biological treatment. Environmental protection agency (EPA) is planning to bear the burden of proof on the demonstration of the application of the scouring argument. Walters et al (1988, 1989) presented all innovative processes of physical and chemical methods used for wastewater treatment. Butseva et al (1997) introduced a progressive technology for treatment of oily wastewater. The major part of the particulate matter, oil, and dissolved organic compounds are removed by pressurized flocculation-flotation and flocculation-impeller flotation. The reagents used are high-molecular-weight cationic flocculants with good foaming properties. Nikanorov and Stradomskaya (2009) identified the petroleum pollution sources of water bodies and streams. The scheme is based on an optimal complex of simple methods for the identification of the integral group composition of oil product samples, taken from an oil spill, and standards, as well as on highly informative methods for the examination of their component and composition. Koytsoykos (2009) determined the range of contaminants present in some typical effluent streams and described the methods used to treat these effluents, and the costs of constructing and operating such treatment processes. In 2011 team of United Arab Emirates University (UAEU) introduced a new option to develop, design and evaluate of advanced refinery wastewater treatment processes through using electrochemical technology.
1.3 PETROLEUM REFINERY PRODUCTS

The crude oil is an extremely complex mixture of hydrocarbon compounds, sulfur, nitrogen, oxygen, salts, metals, and other elements, which may vary widely in volatility, specific gravity, and viscosity. In addition, the properties of crude oil vary widely as do its color, from colorless to black. Thus, petroleum is not used in its raw state (Speight 2007). A wide variety of processing steps are required to convert petroleum from its raw state to products that have well-defined properties. The major products of oil refineries are asphalt, diesel fuel, fuel oils, gasoline, jet fuel, kerosene, liquefied petroleum gas (LPG), lubricating oils, paraffin wax, tar, petrochemicals. Figure 1.2 shows the breakdown of the products from one barrel of crude oil.

![Figure 1.2 A breakdown of the products delivered from a barrel of crude oil (US EPA 2008)](image-url)
The growing demand for products such as liquid fuels is a major driving force behind the petroleum industry. The demand for products started long back. It started in the eighth century, since the Babylonians used asphalt to construct the city’s walls, towers and roads (Desai et al 2009) and in approximately 865 A.D naphtha was used in lamps (Veenstra and Sanders 1998). The widespread use of petroleum has led to enormous releases of gases into the environment. Considering the composition of petroleum and petroleum products (Speight 2007), it is not surprising that petroleum and petroleum-derived chemicals are environmental pollutants. The National Oceanic and Atmospheric Administration (NOAA) identified cleanup options by the following categories (API 1994):

1. Gasoline products: are very volatile, highly flammable and have high evaporation rates. It has narrow cut fractions with no residue, specific gravity of less than 0.80 and low viscosity, which spreads rapidly as a thin sheet on water or on land. It has high acute toxicity to biota, will penetrate the substrate, and is non adhesive.

2. Diesel-like products and light crude oils (No. 2 fuel oil, jet fuels, kerosene): are moderately volatile; the refined products can evaporate with no residue. Diesel has a specific gravity of 0.80-0.85; API gravity of 35-45. It has low-to-moderate viscosity, spreads rapidly into thin slicks, and forms stable emulsions. It has moderate-to-high toxicity to biota, and the specific toxicity is often related to the type and concentration of aromatic compounds. These products tend to penetrate the substrate, but fresh spills are not adhered.

3. Intermediate products (No. 4 fuel oil, lube oil) are moderately volatile products and up to one-third will evaporate within 24
hours. This fuel has a moderate-to-high viscosity, specific gravity of 0.85-0.95, API gravity of 17.5-35 and a variable toxicity that depends on the amount of light fraction components. These products can form stable emulsions and may penetrate the substrate.

4. Heavy Crude Oils and Residual Products (No. 6 fuel oil, bunker C oil) are slightly volatile, and there is very little product loss by evaporation. It has high viscosity and may become less viscous when warmed. It has a specific gravity of 0.95-1.00, and API gravity of 10-17.5. It is highly adhesive to the soil. It has low acute toxicity relative to other oil types and can form stable emulsions.

1.4 PETROLEUM REFINERY WASTEWATER

1.4.1 Global Volume of Wastewater Discharge

The health and environmental risks posed by high-volume waste stream and the currently available treatment and disposal methods are inadequate to protect human health and the environment. The most significant changes needed now are (a) closing the loophole that exempts hazardous oil and gas waste from treatment, storage, and disposal requirements applicable to other hazardous waste, and (b) improving regulatory standards for wastewater treatment facilities and the level of treatment required before discharge to water bodies. There has been a significant increase in the volume of the global discharge of wastewater. Nearly 50 gallons of wastewater generated for every barrel of crude oil processed (Manning and Snider 1983). Figure 1.3 shows the volume of wastewater generated and expected by oil refineries from 1980 to 2020. It can be noticed from the figure that more than 15.4 million m$^3$/day of wastewater discharged into the water bodies in 2010
and it is expected to reach 17.5 million m$^3$ in the year 2020, i.e. nearly 30% increase in the volume of wastewater discharge from 1990-2010. It is due to the increased global energy and fuel demand, which in turn increased the production in oil refineries.

![Statistical data on the volume of wastewater generated from refineries (1980-2020)](image)

Figure 1.3  Statistical data on the volume of wastewater generated from refineries (1980-2020)

1.4.2 Sources of Refinery Wastewater

Petroleum refining is a complete process involving several unit operations to convert raw crude oil into useful petroleum products. Considerable amounts of wastewaters are generated at every stage of refinery process such as tank farm drainage, rainwater, cooling tower blowdown, intake water treatment, blowdown from the steam regenerated boilers, miscellaneous discharge as leaks in some of the equipments, the wastewater generated in the refinery laboratories, and the spill from the pumps and the trucks during loading and unloading of raw materials (Wigren and Burton 1972, Hoffman et al 1973, Diya’uddeen et al 2011). Cooling unit accounts for
about 90% of the total refinery water requirements. In many refineries, approximately cooling tower requirements of water is about 55% which can be estimated as a function of refinery complexity and about 85% of the makeup demand of the cooling tower is rejected as water blow down (Parkash 2003).

All these wastewaters are runoff into streams of rain and sewers, and move into the wastewater holding basins. The petroleum refinery wastewater has different types of pollutants as explained in the next section.

1.4.3 Pollutants and their Effects

The term "Pollution" is defined as the undesirable alteration of our surroundings partly or wholly or largely, as a byproduct of human activities. According to “the Indian environmental Act 1986”, “a pollutant has been defined as any solid, liquid or gaseous substance present in such concentration as may be or tend to be injurious to the environment”. Pollution problems are not new; but their effects began to worsen during the last three decades. Rapid industrialization for sustaining economic stability is leading to the pollution of the environment. There are different types of pollution such as Air, Water, Solid waste, Land, Noise, Thermal, Marine, and Radiation pollution. Among these types of pollution, water pollution is the release of undesirable materials into water sources-including drinking water sources- (Raghu and Ahmed Basha 2007). If concentrations of contaminants in the discharge are too high, the pollution can seriously harm ecosystems and human health. Some contaminants (e.g., benzene, toluene, ethylbenzene, and xylenes) are directly toxic to people; others interact in the environment to produce unwanted effects (e.g., ammonia that can encourage harmful algal blooms). Some are of great concern because of their toxicity to aquatic life and the reduction of the normal oxygen level of the water. Depending upon the nature of the contaminates in the effluent, and its relative quantities from different
operations, the extent of pollution in any wastewater is characterized by the following factors: colour and odour, suspended and dissolved solids, pH, acidity, alkalinity, hardness, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and toxic ions. Industrial wastewater requires specialized treatment to monitor one or more of these factors.

The generated wastewater from a petroleum refinery contains free hydrocarbons, suspended solids, phenol, benzene, sulphides, ammonia, heavy metals, cyanide, mercaptans, solvents, inorganic elements having high concentration of salts, and organic carbon (IPIECA, 2010; Diya’uddeen et al 2011). Further, the chemicals used within the refinery for controlling scaling, corrosion in cooling towers, reducing frothing in desalters, and others are also coming out along with the refinery wastewater (Burks 1982). The concentrations of various pollutants present at the upstream of an API separator in refinery wastewater are given in Table 1.1 (Parkash 2003; Yavuz et al 2010). The current regulation of discharge limits for petroleum refinery effluents prior to discharge into water bodies in accordance with the Presidency of Meteorology and Environment (PME) are shown in Table 1.2.
Table 1.1  Pollutants present in petroleum refinery wastewater

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>Concentration mg/L</th>
<th>Load Kg/Day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total oil</td>
<td>50000</td>
<td>240000</td>
</tr>
<tr>
<td>Free oil</td>
<td>49500</td>
<td>237600</td>
</tr>
<tr>
<td>Emulsified oil</td>
<td>500</td>
<td>2400</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>375</td>
<td>1320</td>
</tr>
<tr>
<td>BOD</td>
<td>625</td>
<td>3000</td>
</tr>
<tr>
<td>COD</td>
<td>1250</td>
<td>6000</td>
</tr>
<tr>
<td>Sulphides</td>
<td>180</td>
<td>864</td>
</tr>
<tr>
<td>Phenols</td>
<td>20</td>
<td>96</td>
</tr>
<tr>
<td>Cyanides</td>
<td>2</td>
<td>9.6</td>
</tr>
<tr>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>55</td>
<td>264</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>100</td>
<td>480</td>
</tr>
<tr>
<td>Acid oils</td>
<td>75</td>
<td>360</td>
</tr>
</tbody>
</table>

Table 1.2  Discharge limits for petroleum effluents

<table>
<thead>
<tr>
<th>Chemical Constituent</th>
<th>Discharge Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH units</td>
<td>6-9</td>
</tr>
<tr>
<td>TSS mg/L</td>
<td>15</td>
</tr>
<tr>
<td>BOD/5 mg/L</td>
<td>25</td>
</tr>
<tr>
<td>COD mg/L</td>
<td>150</td>
</tr>
<tr>
<td>Total Oil &amp; Grease mg/L</td>
<td>5</td>
</tr>
<tr>
<td>Ammonia (as NH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>1</td>
</tr>
<tr>
<td>Sulfide mg/L</td>
<td>0.2</td>
</tr>
<tr>
<td>Benzene mg/L</td>
<td>0.05</td>
</tr>
<tr>
<td>Cyanide (free) mg/L</td>
<td>0.05</td>
</tr>
<tr>
<td>Phenols mg/L</td>
<td>0.1</td>
</tr>
</tbody>
</table>
The most toxic compounds presented in the petroleum effluent, according to the cooperative survey by the Environmental Protection Agency (EPA) and the American Petroleum Institute (API), are: methylene chloride, benzene, carbon tetrachloride, trichloroethane, phenol, toluene, chloroform, trichloroethylene, ethyl benzene, pyrene, di-n-butyl phthalate, and bis (2-ethylhexyl) phthalate (Burks 1982). These compounds cause major environmental impacts such as oxygen depletion and toxic effect on aquatic life tainting the water, and making it unsuitable for human use. Also, many studies have shown that oil refinery effluents often have an impact on the fauna, fish, crustaceans, plankton, and algae, especially in the areas around the oil refinery outfalls (Wake 2005).

1.5 MANAGEMENT AND TREATMENT OF REFINERY WASTE

Eliminating the effluent generated from chemical process industries is practically not possible. However, by adopting a new technology can improve water management and can potentially reduce the volume and cost of raw water used in refinery operations. Furthermore, it may also reduce the mass of contaminants in the treated effluent, thus improving the quality of a wastewater discharge and ultimately the environmental impact of a refinery. The management of wastes from refineries includes three stages (Wong and Hung 2006); in-plant source control, pretreatment, and end-of-pipe treatment. In-plant source control includes reducing the overall pollutant load, water-based utilities, and recycling/reusing. The pretreatment approach addresses reduction/elimination of the particular pollutant before it is diluted in the main wastewater stream, and providing an opportunity for material recovery. While the end-of-pipe treatment is the final stage for meeting the regulatory discharge requirements and protection of stream water quality.
1.6 REFINERY WASTEWATER TREATMENT TECHNIQUES

The traditional treatment of the wastewater originating from the petroleum refineries, typically involves a combination of primary, intermediate, secondary and tertiary treatment processes. Primary processes include the American Petroleum Institute separator (API), and parallel or Corrugated Plate Interceptor (CPI). Intermediate processes include Dissolved Air Flotation (DAF) /or Induced Air Flotation (IAF), and equalization. Secondary processes include biological treatment processes in their different forms or combinations. This includes activated sludge, trickling filters, aerated lagoons, stabilization, and Rotating Biological Contactors (RBC). While tertiary treatment processes include filtration, ozonation and Granular Activated Carbon (GAC) adsorption.

The Chennai Petroleum Corporation Limited (CPCL) Chennai, India is the largest refinery cooperation in south India, with an installed refining capacity of 10.5 MMTPA or 28760 m$^3$/day, generating 12500 m$^3$/day of wastewater. The segregated effluent from (CPCL) refinery are routed to an effluent treatment plant and treated to meet the standards received from the Tamilnadu Pollution Control Board (TNPCB) for disposal into inland surface waters. The main treatment chains primarily consist of three stages of treatment, namely primary treatment, secondary treatment and polishing treatment. The primary treatment facilities include the effluent equalization for the combined effluent, free oil separation in API separator followed by Tilted Plate Interceptor (TPI) separator. The emulsified oil removal along with sulphide removal is done by chemical precipitation by dosing FeCl$_3$ to improve the secondary oil removal system by dissolved air flotation unit. Alternatively, H$_2$O$_2$ is dosed when the sulphide levels are low. The spent caustic from different units are combined together and regeneration effluent from hydrocracker unit, is collected in two equalization tanks separately and fed at a controlled rate to the main treatment chain. The secondary treatment
facilities include the biological treatment system consisting of two stages conventional biological treatment system comprising random fill plastic media bio-tower as the first stage followed by activated sludge extended aeration tank and a clarifier as the second stage. The clarified effluent after the bio-treatment is routed to polishing treatment section, which comprise of pressure sand filter and granular activated carbon adsorption in fixed bed, resulting in the effluent quality which meets the discharge standards. The effluent from the activated carbon filter is routed to a compartment, dedicated to treated process effluent.

The suspended solids, immiscible liquids, and oil and grease components of the effluent are removed in primary processes, while emulsion and organic constituents are reduced in secondary treatment. Tertiary treatment is an advanced stage of the treatment process, in this step removes stubborn contaminants that secondary treatment was not able to clean up and contaminants are reduced in value which meet the applicable discharge limits. The stages of a refinery treatment process are given in Figure 1.4.
Since 1990, the new stringent discharge requirements for specific toxic constituents as well as whole-effluent toxicity, specific advanced treatment processes are becoming a necessity for refineries. The removal of petroleum contaminants to allowable global limits, can be accomplished by means of well-known and accepted techniques, such as electrochemical methods (Dimoglo et al. 2004, Yavuz et al. 2010, biodegradation (Jou and Huang 2003, Plaza et al. 2008), membrane process (Rahimpour et al. 2011), photo degradation (Santos et al. 2006), advanced oxidation processes (Dincer et al. 2008, Coelho et al. 2006), and fluidized bioreactor (Kuyukina et al. 2009). However, the performance of any given technique will depend entirely on the condition of the wastewater mixture.

1.7 ELECTROCHEMICAL TECHNOLOGY

Rigorous environmental pollution control and legislation in many countries resulted in an intensive research to increase the efficiency of water treatment technologies and access to technology-friendly environment. Among the available treatment methods, electrochemical technology is regarded as a clean and powerful technology for the destruction of organic pollutants in water. Electrochemical technology has reached a state when they are not only compared with other technologies in terms of cost, but in term of efficiency, and in some situations, may be an indispensable method for treating refractory pollutants (Chen 2004). Electrochemical technologies offer various treatment processes, such as electrooxidation, electrocoagulation, electroflotation, and electrodeposition. The electroflotation and electrodeposition technologies will not be explained, as electrooxidation, and electrocoagulation technologies are our central points. The following references explain electroflotation, and electrodeposition (Mansour and Chalbi 2006, Chen et al. 2011).
1.7.1 Electrocoagulation

Electrocoagulation is a physicochemical process, which uses sacrificial electrodes for the generation of coagulants. The generation of metallic hydroxide by electro-dissolution takes place at the anode, usually constituted by iron or aluminium, while H\(_2\) production occurs at the cathode (Balasubramanian and Srinivasakannan 2010). Electrocoagulation allows in situ production of a coagulating agent during the electrolysis process. The metal salts or polymers or ions added, have the ability to break the stable suspensions of the colloidal particles. The electrocoagulation technique is used to remove undesirable contaminants without adding chemicals, produces less sludge volume, and promotes the flocculation process caused by the destabilization of colloidal particles into microfloc, and later into bulky flocules which can be settled. In addition, the formed oxygen and hydrogen bubbles increase the efficiency of the separation process through electroflotation (Balasubramanian and Srinivasakannan 2010). Electrocoagulation technique has been adopted for the treatment of wastewater since the early 19th century. Recently, there has been renewed interest in the use of electrocoagulation, owing to the increase in the environmental restrictions on effluent wastewater. Indeed, electrocoagulation has been tested successfully to treat urban wastewater, restaurant wastewater and oil–water emulsion. The electrocoagulation process depends on the response of the water contaminant to strong electric fields, and electrically induced oxidation and reduction reactions. The electrocoagulation technique utilizes direct current to cause sacrificial electrode ions to remove undesirable contaminants, either by chemical reaction and precipitation or by causing colloidal materials to coalesce, and then they are removed by electrolytic floatation. In this process, the coagulation of ions is produced in situ, and it involves three successive stages:
• Formation of coagulants by the electrolytic oxidation of the sacrificial electrode.

• Destabilization of the contaminants, particulate suspensions and breaking of emulsions.

• Aggregation of the destabilized phases to form flocs.

When a potential is applied from the external power source, the anode material undergoes oxidation, while the cathode is subjected to reduction or reductive deposition of the elemental metals. The electrochemical reactions with metal M as the electrode may be summarized as follows,

• At the anode

\[ M(s) \rightarrow M^{n+}(aq.) + ne^- \quad (1.1) \]

\[ M^{n+}(aq.) + nOH^-(aq.) \rightarrow M(OH)_n(s) \quad (1.2) \]

• At the cathode

\[ nH_2O(l) + ne^- \rightarrow H_2(g) + n(OH)^-(aq.) \quad (1.3) \]

• Overall:

\[ M(s) + nH_2O \rightarrow M(OH)_2(s) + H_2(g) \quad (1.4) \]

The bulk reactions of the electrocoagulation of aluminium and mild steel anodes can be written as (Mollah et al. 2001, Balasubramanian and Srinivasakannan 2010):

For the aluminium electrode

• Anode

\[ Al(s) \rightarrow Al^{+3}(aq.)+3e^- \quad (1.5) \]
\[
\text{Al}^{3+}_{(aq)} + 3\text{H}_2\text{O}_{(l)} \rightarrow \text{Al(OH)}_3(s) + 3\text{H}^+_{(aq)}
\] (1.6)

- Cathode

\[
3\text{H}_2\text{O}_{(l)} + 3\text{e}^- \rightarrow \frac{3}{2}\text{H}_2(g) + 3(\text{OH})^-_{(aq.)}
\] (1.7)

- Overall

\[
\text{Al}_(s) + 3\text{H}_2\text{O}_{(l)} \rightarrow \text{Al(OH)}_3(s) + \frac{3}{2}\text{H}_2(g)
\] (1.8)

The electrolytic dissolution of the aluminium anode produces the monomeric and polymeric species during the above reaction, such as \(\text{Al}^{3+}\) and \(\text{OH}^-\), which are transformed into \(\text{Al(OH)}_3\). The \(\text{Al(OH)}_3\) flocs capture the pollutant molecules present in the wastewater, to form sludge as shown in the following reaction:

Organic Pollutant + flocs \([\text{Al(OH)}_3(s)]\) \(\rightarrow\) Stable Sludge

For the mild steel electrode, two mechanisms for the production of metal hydroxides, \(\text{Fe(OH)}_n\) (where \(n=2\) or \(3\)), have been proposed during the dissolution in an electrolytic system (Balasubramanian and Srinivasakannan 2010).

**Mechanism 1**

Anode

\[
\text{Fe}_(s) \rightarrow \text{Fe}^{2+}_{(aq.)} + 2\text{e}^-
\] (1.9)

\[
\text{Fe}^{2+}_{(aq.)} + 2\text{OH}^-_{(aq.)} \rightarrow \text{Fe(OH)}_2(s)
\] (1.10)

Cathode:

\[
2\text{H}_2\text{O}_{(l)} + 2\text{e}^- \rightarrow \text{H}_2(g) + 2(\text{OH})^-_{(aq.)}
\] (1.11)

Overall:
\[
\text{Fe}(s) + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2(s) + \text{H}_2(\text{g}) \quad (1.12)
\]

**Mechanism 2**

**Anode:**

\[
4\text{Fe}(s) \rightarrow 4\text{Fe}^{2+}_{(\text{aq.})} + 8\text{e}^- 
\]

\[
4\text{Fe}^{2+}_{(\text{aq.})} + 10\text{H}_2\text{O}(l) + \text{O}_2(\text{g}) \rightarrow 4\text{Fe(OH)}_3(s) + 8\text{H}^+_{(\text{aq.})} \quad (1.14)
\]

**Cathode:**

\[
8\text{H}^+_{(\text{aq.})} + 8\text{e}^- \rightarrow 4\text{H}_2(\text{g}) \quad (1.15)
\]

**Overall:**

\[
4\text{Fe}(s) + 10\text{H}_2\text{O}(l) + \text{O}_2(\text{g}) \rightarrow 4\text{Fe(OH)}_3(s) + 4\text{H}_2(\text{g}) \quad (1.16)
\]

The electro generation of \(\text{Fe(OH)}_{n(s)}\) remains in the aqueous stream as a gelatinous suspension, which can remove the waste matter from wastewater, either by complexation or by electrostatic attraction followed by coagulation depending on the pH range (Chen 2004). The complexes (i.e., hydrolysis products) have a pronounced tendency to polymerize at pH 3.5–7.0. The generated ferric ions form monomeric, ferric hydroxo complexes with hydroxide ions and polymeric species, depending on the pH range. These are \(\text{FeOH}^{2+}, \text{Fe(OH)}_2^+, \text{Fe}_2(\text{OH})_2^{4+}, \text{Fe(OH)}_4^-, \text{Fe(H}_2\text{O})_2^+, \text{Fe(H}_2\text{O})_6^{3+}, \text{Fe(H}_2\text{O})_5\text{OH}^{2+}, \text{Fe(H}_2\text{O})_4(\text{OH})_2^+, \text{Fe(H}_2\text{O})_8(\text{OH})_2^{4+}\), and \(\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{2+}\), which transform finally into \(\text{Fe(OH)}_3\) at pH around 3.5-8 (Kobyta et al 2003, Benefield et al 1982). The \(\text{Fe(OH)}_3\) flocs capture the pollutant molecule present in the wastewater to form sludge as shown in the following reaction:

\[
\text{Organic Pollutant} + \text{flocs [Fe(OH)}_3(s)] \rightarrow \text{Stable Sludge}
\]
The mechanism of EC is highly dependent on the chemistry of the aqueous medium, especially the conductivity. The other characteristics, such as pH, particle size, and chemical constituent concentrations, also influence the EC process. The electrolyte pH plays an important role in the separation of suspended particles; at low pH the separation is dominated by precipitation, while adsorption dominates at high electrolyte pH.

Electrocoagulation technique has attracted the interest of many industries such as petrochemical industry (El-Naas et al. 2009, Martínez-Delgadillo et al. 2010a), dairy industry (Şengil and Özacar 2006), oil and gas industry (Nordin and Chatwin 1990), textile industry (Raju et al. 2008), petrochemical industry (Dimoglo et al. 2004), pulp and paper industry (Kalyani et al. 2009), and the tannery industry (Jing-wei et al. 2007), as a potential tool for the reduction of numerous organic and inorganic pollutants, suspended solids, oil and greases. It removes metals, colloidal solids/particles, and soluble inorganic pollutants from aqueous solutions. The electrocoagulation process is a potential alternative technique for treating organic effluent. It is generally characterized by a simple equipment, easy operation, and brief retention time to attain high removal efficiency of the pollutants (Balasubramanian and Srinivasakannnan 2010).

1.7.2 Electrochemical Oxidation

There are a number of promising techniques based on electrochemical technology being developed, and use in process industries. Principal among the techniques is electrochemical oxidation. Electrochemical oxidation of wastewater is a complex phenomenon, in which the electrical energy is used to generate an oxidizing reagent. The main reagent is the electron, called the ‘Clean Reagent’ which degrades all the organics present in the effluent. The electrooxidation have the ability to treat the effluents without generating any secondary pollutant or by-product/sludge. The electrochemical
oxidation technique offers high removal efficiencies, and has lower temperature requirements, compared to non-electrochemical treatment. In addition to the operating parameters, the rate of pollutant degradation depends on the anode material and cell potential (Mohan et al 2007). The electrochemical oxidation of organic and inorganic compounds takes place via two principal mechanisms, direct and indirect oxidation. Direct oxidation occurs at the anode surface in which the pollutants discharge their electrons to the anode in order to maintain the flow of current in the bulk solution. Indirect oxidation occurs as a result of the production of powerful oxidizing agents in the electrolyte, such as chlorine, hydrogen peroxide and ozone.

The energy supplied to an electrochemical reactor plays an important role in any electrolysis process. The following steps are involved in an electrolysis process.

- The electro active solid phase is transferred to the electrode surface of the bulk solution
- The electro active particle is adsorbed on the surface of the electrode
- Electron transfer occurs between the bulk and the electrode
- The reacted particle is either transported to the bulk solution [desorption] or deposited on the electrode surface.

Among the above four steps, the transfer of electrons between the solution and the electrode surface plays an important role in electrochemical processes as the electrical energy is converted to chemical energy at the interface of the electrode. A generalized reaction scheme of the electrochemical oxidation (Conversion/ combustion) of organic compounds
on the metal oxide coated catalytic anode (MO<br>) is given in the following equations:

\[ MO_x + H_2O \rightarrow MO_x(\cdot OH) + H^+ + e^- \] (1.17)

\[ MO_x(\cdot OH) \rightarrow MO_{x+1} + H^+ + e^- \] (1.18)

\[ MO_x(\cdot OH) \rightarrow \frac{1}{2}O_2 + MO_x + H^+ + e^- \] (1.19)

\[ MO_{x+1} \rightarrow \frac{1}{2}O_2 + MO_x \] (1.20)

A water molecule is hydrolysed to generate the adsorbed hydroxyl radical at the electrode surface (equation 1.17), called physisorbed active oxygen. The generated adsorbed hydroxyl radical reacts with the oxygen already present in the oxide anode, with the possible transition of oxygen from the radical to the electrode to form a higher oxide MO_{x+1} (equation 1.18) called chemisorbed active oxygen. The \( \cdot OH \) plays a vital role in the oxidation of the organics in the electrode processes. Both physisorbed and chemisorbed oxygen will be liberated if there is no oxidisable organic compound in the effluent (equations 1.19 and 1.20).

According to Comninellis (1994), adsorbed oxygen participates in the formation of selective oxidation products as shown in the following equations (1.21-1.23).

\[ MO_{x-1} + R \rightarrow RO + MO_x \] (1.21)

\[ (p - 1)MO_{x-1} + RO \rightarrow R_2 + (p - 1)MO_x \] (1.22)

\[ R \rightarrow R_2 + CO_2 + nH^- + ne^- \] (1.23)
Where \( R \) is the organic species, \( RO \) is the organic oxide, \( MO_{x+1} \) is the higher oxide, \( p \) is the number of adsorbed oxygen necessary to covert \((R)\) to stable compound \((R_2)\) or carbon dioxide.

1.8 ADVANTAGES OF ELECTROCHEMICAL TECHNIQUES IN ENVIRONMENTAL PROTECTION

The electrochemical technique offers several options for alleviating the pollution problems faced in the chemical process industry with the best protection to the environment. Among the options that make this technique attractive are the following features (Huitle 2004):

- **Versatility**- It can deal with different processes (oxidation, reduction, phase separation, and etc.); different range of pollutant volumes (micro liters to millions of liters); and different pollutant matter (gases, liquids, and solids).

- **Energy efficiency**- This technique gives the user the flexibility to design the cell and electrodes, to minimize the power consumption, and to control the potentials, because it has lower temperature requirements than non-electrochemical processes.

- **Amenability to automation**- The electrical variables used, and the potential and current, are particularly suited for data acquisition, process automation and control.

- **Environmental compatibility**- The electron as a clean reagent is used; hence, no unwanted intermediate product is produced during the process, because high selectivity is used to degrade the pollutant.
• **Cost effectiveness** - Generally simple equipment is used in construction, involving less cost.