CHAPTER 2

REVIEW OF LITERATURE

2.1 GENERAL

As for textile industries billions of litres of aqueous waste streams are generated everyday. These effluents usually possess coloured residual dyes and high salt content that can create environmental problems. Due to environmental requirements in recent years, there is increasing interest in innovative treatment of these effluents, which contain toxic and non-biodegradable organic pollutants. To ensure the safe discharge of effluents, proper technologies need to be used by treatment facilities while treating dyeing effluents. Previous research efforts have focused on various biological, chemical, and physical techniques for treating azo dye wastes, which are briefly reviewed in this chapter. Because this research explores the use of electrochemical methods for the treatment of a textile effluent, the main focus of this literature review will be on electrochemical techniques used for treating dyeing effluents.

2.2 TREATMENT METHODS FOR TEXTILE DYEING EFFLUENTS

There are various methods reported for the treatment of textile dyeing effluents including biological (Kandelbauer et al 2004), physical (Al-Malack and Andersen 1997) and chemical processes (Zemataitene et al 2003). Several studies are being carried out on novel, potentially cost
effective treatments, although the developments that have been announced are largely based on, or are variants of these established processes. In practice single process may not give complete, consistent treatment for the effluent. The same criteria also apply to meeting consent conditions. Hence when recycling is the ultimate target, a second stage may be necessary to guarantee complete colour removal and give a final polish to the treated water (Thampi 1998).

The different treatment processes for textile dyeing effluents are reviewed hereunder; wherein it is assumed that the effluents are pretreated with equalisation and are also treated for the removal of any solid matter such as fibre and other detritus present by screening or filtering.

2.2.1 Biological Process

Directly biological treatment of dye wastewater is considered unsatisfactory because of the low efficiency and low reaction rate of the treatment. Consequently, dye wastewater is usually treated using physical and chemical methods before biodegradation (Pala 2002, Chang et al 2003)

2.2.1.1 Aerobic treatment

In aerobic treatment the microorganisms use oxygen present in the air to metabolise a portion of the organic waste to carbon dioxide and water. The microorganisms obtain energy from this oxidation, thus their growth is rapid and a large portion of the organic waste is converted to new cells. The portion converted to biomass is not actually stabilised but is simply biotransformed. Although these cells can be removed from the waste stream, the biological sludge they produce still presents a significant disposal problem (Jiang and Bishop 1994).
Oxidative biodegradation takes place upon action of enzymes such as peroxidases and laccases. The involvement of fungal peroxidases and laccases for the oxidation of sulfonated azo dyes has been reported earlier (Kandelbauer et al 2004). Jane et al 2005 reported the use of azo-degrading bacteria (Aeromonas hydrophila, Comamonas testosteroni and Acinetobacter baumannii) entrapped into a phosphorylated gel that was used to study azo dye biodegradation in a fluidised bed reactor (FBR). Experimentally, it was confirmed that fluidised bed reactor with an immobilised cell beads system could achieve a color removal efficiency of 90% at initial dye concentration < 2200 mg/L under a continuous-flow condition, but the removal efficiency dropped dramatically after the dye concentration was over 2200 mg/L.

Conventional activated sludge treatment of wastes is often an effective and highly economic system for reducing organic pollutants in wastewater. A fair amount of research has been conducted assessing the viability of using activated sludge to treat textile effluents (Zissi et al 1997, Loyd 1992, Shaul et al 1991, Pagga and Brown 1986). However, aerobic treatment of azo dye wastes has proven ineffective in most but is often the typical method of treatment used today. Because aerobic microbes cannot reduce azo linkages, their ability to destroy dye chromogens is less. However, aerobic sludges have been successfully used to stabilise dye metabolites. On the other hand the portion converted to biomass is not actually stabilised but is simply biotransformed. Although these cells can be removed from the waste stream, the biological sludge they produce still presents a significant disposal problem (Brown et al 1981).

The presence of high total dissolved solids is one of the factors that is reported to affect the efficiency of activated sludge process. This fact was confirmed by the study conducted by Pophali et al (2003) who reported that
the presence of high TDS concentration in the range of 20,000 mg/L in the wastewater reduced oxygen transfer efficiency in the aeration tank and affected biological metabolism.

2.2.1.2 Anaerobic treatment

Anaerobic bioremediation allows azo and other water-soluble dyes to be decolourised. This decolourisation involves an oxidation/reduction reaction with hydrogen rather than free molecular oxygen in aerobic systems. Typically, anaerobic breakdown yields methane and hydrogen sulphide. Azo dye acts as an oxidising agent for the reduced flavin nucleotides of the microbial electron chain and is reduced and decolourised concurrently with reoxidation of the reduced flavin nucleotides. In order for this to occur, additional carbon is required for decolourisation to proceed at a viable rate. This additional carbon is converted to methane and carbon dioxide, releasing electrons. These electrons cascade down the electron transport chain to a final electron acceptor, in this case, the azo-reactive dye. The electrons react with the dye reducing the azo bonds, and ultimately causing decolourisation (Carliell et al. 1996).

Most azo dyes are reduced anaerobically to the corresponding amines with cleavage of azo bonds by bacterial azo reductase. Anaerobic degradation of azo dyes yields only azo reduction and decolourisation (Manu and Chaudhari 2002). Although this effectively alters the chromogen and destroys the observed color of the dye, many aromatic groups are not susceptible to anaerobic reduction. However, there is evidence that some azo dye metabolites may be fully stabilised in anaerobic environments (Razo et al. 1997).
2.2.1.3 Combined aerobic and anaerobic methods

Since conventional biological wastewater treatment plants were not effective in the treatment of dye effluents, investigations have been carried out on aerobic and anaerobic treatment methods using sequential batch reactor (Panswald et al 2001). During the study on treatment of wastewater containing polyvinyl alcohol from desizing and an azo dye (Remazol Black) 66% TOC removal was reported of the applied TOC. Colour removal was 94% but dye metabolites caused reactor instability. Aromatic amines from the anaerobic breakdown of the azo dyes were not completely mineralised by the aerobic phase. Breakdown of polyvinyl alcohol by the reactor was reported to be poor with 20–30% degradation (Shaw et al 2002). However the biological treatments, which are considered as the most economical and environmentally friendly ones, are not a suitable alternative while working with toxic and/or non biodegradable wastewater of textile dyeing industries (Robinson et al 2001).

2.2.2 Coagulation and Flocculation Process

Coagulation–flocculation treatments are generally used to eliminate many organic and inorganic substances. Inorganic coagulants based on aluminum and iron salts, that produce voluminous alkaline precipitates have been established to remove soluble anionic dyes, at least in part, from coloured effluent, together with a portion of the anionic colourless organic chemical axillaries present. Recently, certain aids like polyelectrolytes are used in combination with chemical coagulants (Nasiman 1996). Water soluble polymeric organic flocculants are used to aid the separation of the insoluble flocs containing the complex dyes. These flocs which are formed are separated from water by gravitational settling of the particles that are heavier than water (Georgiou et al 2003). Golob et al (2005) studied the
decolourisation of residual dyebath effluents after dyeing cotton/polyamide blends using reactive and acid dyes employing coagulation/flocculation method. They observed that a combination of aluminium sulphate and a cationic organic flocculant yielded an effective treatment for residual dyebath wastewater since almost complete decolourisation was achieved. Similarly Zemaitaitiene et al (2003) postulated active participation of various anionic textile wastewater contaminants in dye removal using a cationic flocculant (polyquaternary ammonium salt). The limitations of these methods are reported to be large area required by the plant, with its associated separation and sludge disposal facilities (Slokar and Le Marechal 1978, Vandevivere et al 1998).

2.2.3 Adsorption

Adsorption treatment process can be classified as mass transfer operation in which the contaminant is transferred from water phase, to the surface of active solid phase, where it is accumulated for its subsequent extraction or destruction. Adsorption processes using activated carbon and ion exchange resins have been applied for concentrating organic compounds from industrial effluents for years. The most widely used adsorbent is granular activated carbon (GAC). GAC has been proven to be effective for the removal of color from textile and also pulp and paper industrial effluents (Tunay et al 1996, Basibuyuk and Forster 1997, Bergna et al 1999, Walker and Weatherley 2001). Due to the high capital, regeneration, and disposal costs, full scale GAC adsorption systems for effluent decolourisation have yet to be accepted by the industry. Various other (mostly low-cost) adsorbents have therefore been investigated as an alternative to activated carbon. Those adsorbents include: wood chips (Nigam et al 2000), sawdust (Garg et al 2004), coirpith (Namasivayam and Kavitha 2002), bagasse fly ash (Vinod et al 2000), peat (Poots 1976) and biosorbents like bacterial biomass
(Hu 1992), fungal biomass (Nawar and Doma 1989), yeast biomass (Bustard et al 1998). Sorption techniques yield spent sorbent, i.e. dye-saturated material, which should be disposed off or regenerated. As there are nonionic, anionic and cationic dyes, most adsorbents do not remove all different dye types. Further, high pH and salt concentrations may have an adverse effect on the adsorption (Karcher et al 1999).

### 2.2.4 Ion Exchange

Ion exchange has not been widely used for the treatment of dye-containing effluents, mainly due to the opinion that ion exchangers cannot accommodate a wide range of dyes (Slokar and Le Marechal 1997). Wastewater is passed over the ion exchange resin until the available exchange sites are saturated. Both cation and anion dyes can be removed from dye-containing effluent this way. Advantages of this method include no loss of adsorbent on regeneration, reclamation of solvent after use and the removal of soluble dyes. A major disadvantage is the cost. Organic solvents are expensive, and the ion exchange method is not very effective for disperse dyes (Mishra and Tripathy 1993).

### 2.2.5 Advanced Oxidative Process

Advanced oxidation processes (AOPs) were defined by Glaze (1987) as near ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals (specially hydroxyl radicals) in sufficient quantity to effect water purification. Also via AOP’s complete organic matter mineralisation could be achieved. Hydroxyl radical is special oxidation agent that attacks majority of organic matters. The kinetic of these reactions is first order for (\(^{\cdot}\)OH) radical concentration, and to the species to be oxidised. Rate constant in general are in order \(10^{-8}-10^{-10}\) m/s, where the hydroxyl radical concentration lies between \(10^{-12}-10^{-10}\) m/s.
The hydroxyl radical is an attractive oxidant that can be used in the wastewater treatment. Several organic compounds can be eliminated or degraded immediately by hydroxyl radicals. However, some organics are not attacked by this action like the acetic acid, oxalic acid, chlorine derivatives such as chloroforms and tetrachloroethane (Oussi et al 1997). The AOPs that have been most widely studied are ozonation, UV/H₂O₂, Fenton’s reagent (Fe²⁺/H₂O₂), UV/TiO₂ and electrolysis.

Ozonation is a new technique that has been suggested in the literature as a potential alternative for decolourisation purpose. Widely used in the water treatment, ozone is now used (either alone or in combination with other treatments, such as O₃-UV or O₃-H₂O₂) in the treatment of industrial effluents. The ozone dosage applied to the dye-containing effluent is dependent on the total colour and residual COD to be removed with no residue or sludge formation. Ozone especially attacks the double bonds which are responsible for coloration. For this reason, decolourisation of wastewater by ozone alone is not always accompanied by a significant reduction of the COD (Adams et al 1995). A disadvantage of ozonation is its short half-life, typically being 20 min. One of the major drawbacks with ozonation is cost, continuous ozonation is required due to its short half-life. In alkaline conditions, ozone decomposition is accelerated, and so careful monitoring of the effluent pH is required (Scott and Ollis 1995).

Fenton reaction is widely used in many fields such as degradation of pollutants. More than one century ago, Fenton discovered that the mixture of ferrous ion and hydrogen peroxide can oxidise many organic compounds that was called Fenton reaction later on. The active species can be generated by the inter-reaction of hydrogen peroxide with ferrous and ferric ions as shown below in equations (2.1) – (2.3).
\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{H}_2\text{O} \quad (2.1)
\]
\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \cdot \text{OOH} + \text{H}^+ \quad (2.2)
\]

Illumination of \(\text{Fe}^{2+/\text{H}_2\text{O}_2}\) or \(\text{Fe}^{3+/\text{H}_2\text{O}_2}\) system increased significantly the Fenton degradation rate of many organic substances (Xie et al 2000). The effect of UV light is attributed to the direct \(\cdot \text{OH}\) radical formation and regeneration of \(\text{Fe}^{2+}\) from photolysis of the complex \([\text{Fe(OH)}]^2+\) in solution as per the following mechanism (equation (2.3)).

\[
[\text{Fe(OH)}]^2+ \xrightarrow{hv} \cdot \text{OH} + \text{Fe}^{2+} \quad (2.3)
\]

Results on decolourisation and dearomatisation of dyes by Fenton’s process revealed that pH 3 was the optimum pH for achieving degradation of dye. More than 95% of color was removed with Fenton’s oxidation process in all studied dyes. In overall treatment train 81.95%, 85.57% and 77.83% of COD reduction was achieved in Reactive black 5, Reactive blue B13, and Acid orange 7 dyes, respectively (Nilesh and Chaudhari 2006). Drawback of application of Fenton or Fenton-like oxidation for the treatment of usually highly alkaline- textile-processing wastewater is that the process requires low pH. At higher pH, large volumes of waste sludge are generated by the precipitation of ferric iron salts and the process loses effectiveness, as \(\text{H}_2\text{O}_2\) is catalytically decomposed to oxygen. Fenton or Fenton-like oxidation will furthermore be negatively affected by the presence of radical scavengers and strong chelating agents in the wastewater. Though AOPs are capable of dearomatisation of dye stuff the main handicap lies in the high cost of reagent, energy and formation of sludge which contain high amount of \(\text{Fe}\) (III), which needs to be managed by safe disposal methods (Azbar et al 2004).

Photocatalytic oxidation processes using UV/\(\text{H}_2\text{O}_2\) (Behnajady and Modirshahla 2006), UV/TiO\(_2\) (Bizani et al 2006), UV/ Fenton’s reagent
(Arslan et al 2000), UV/O\textsubscript{3} (Arslan and Balcioglu 2001) are all based on the formation of free radicals due to UV irradiation. Faster, cheaper and more effective photocatalytic processes receive therefore increasing attention, especially those based on catalysis by solid semiconductor materials, mostly TiO\textsubscript{2} particles (Bizani et al 2006). With TiO\textsubscript{2} catalysed UV treatment, a wide range of dyes can be oxidised. The dyes are generally not only decolourised but also mineralised (Muruganandham and Swaminathan 2006). Methylene blue was successfully decolourised and degraded by titania-based photocatalysis at room temperature, during which the final products were identified as CO\textsubscript{2}, SO\textsubscript{4}\textsuperscript{2−}, NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{3}− (Ammar et al 2001). During the treatment of Acid orange 7 using UV radiation in the presence of H\textsubscript{2}O\textsubscript{2} in a tubular continuous-flow photoreactor, the effects of oxidant, dye concentrations, reactor length and volumetric flow rate were studied. The removal efficiency of AO7 was found to be dependant on the operational parameters where the degradation efficiency increased with initial concentration of H\textsubscript{2}O\textsubscript{2} but decreased when the flow rate and initial concentration of AO7 are increased. The decolourisation rate followed pseudo-first order kinetic with respect to the dye concentration (Behnajady and Modirshahla 2006).

2.2.6 Membrane Technologies

Membrane based separation processes have gradually become an attractive alternative to the conventional separation processes in the treatment of wastewater. The application of membrane filtration processes not only enables high removal efficiencies, but also allows reuse of water and some of the valuable waste constituents (Fersi et al 2005).

Microfiltration (MF) is suitable for treating dye baths containing pigment dyes (Al-Malack and Anderson 1997) as well as subsequent rinsing baths. The auxiliaries remain in the retentate. MF can also be used as a
pretreatment for nanofiltration (NF) or reverse osmosis (Ghayeni et al 1998).
Buckley (1992) proposed the use of MF to remove colloidal species from
exhausted dye-baths and the subsequent rinses, and reverse osmosis (RO) to
concentrate exhausted dye-bath (after pretreatment), or the rinse effluent for
dyeing recipes with a high electrolytes content. Pilot-scale membrane
treatment (MF followed by NF or RO) has been also used in centralised
treatment plants, which are fed with mixed industrial and domestic waste-
water. The results which have been obtained seem to allow for permeate reuse
in textile factories (Rozzi et al 1999).

Nanofiltration membranes retain organic compounds of low
molecular weight, divalent ions or large monovalent ions, such as hydrolysed
investigated the initial performance of commercially available NF membranes
in treating the effluents consisting of reactive dye and salt. For the feed
containing salt and dye, the effects of transmembrane osmotic pressure and
concentration polarisation were superimposed, resulting in the substantial flux
decline. The presence of dye in the effluent significantly affected the salt
removal effectiveness with the tested membranes. It was probable that the
concentration build-up of dye near the membrane surface involved increased
salt retention of the membranes. They reported that the tested membranes
(ES20 and LES90) could effectively retain colour, producing the permeate
with reuse possibility. In-depth evaluation of those membranes is required
prior to the implementation in industry.

Ultrafiltration enables the elimination of macromolecules and
particles, but the elimination of polluting substances, such as color is never
complete which is usually between 31% and 76% (Watters et al 1991).
Results obtained from a small membrane test cell indicated that the reuse of
reactive dye liquors was technically feasible using ultrafiltration (UF)
Ultrafiltration can only be used as a pretreatment for reverse osmosis (Ciardelli and Ranieri 2001) or in combination with a biological reactor (Mignani et al 1999).

Reverse osmosis (RO) is one of the membrane process applied for desalination purposes. In order to desalinate water, a flow through a membrane is created, causing the water to leave the salty side of the membrane, to flow into the unsalted side. This is achieved by creating the pressure upon the water column on the salt side of the membrane; firstly, to remove the natural osmotic pressure and secondly, to create extra pressure on the water column, in order to push the water through the membrane. It is reported that removal of all mineral salts, hydrolysed reactive dyes and chemical auxiliaries (Suksaroj et al 2005) can be achieved using RO. The problem involved is that the higher the concentration of salt, the more important the osmotic pressure becomes and therefore the greater the energy required (Ghayeni et al 1998). The experiments conducted by Al-Bastaki (2004) showed that increasing the dye concentration from 500 to 1000 ppm resulted in a decrease in the salt rejection for all of the operating pressures and for both feed salt concentrations of 5000 and 10,000 ppm.

2.3 ELECTROCHEMICAL TREATMENT OF WASTEWATER

Electrochemistry, a branch of physical chemistry, plays an important role in the 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. The
scale of electrochemical technology beyond nano amperes to mega amperes is given in Figure 2.1, which shows the contribution of electrochemical technology in many ways to a cleaner technology (Walsh 2001). In case of laboratory studies with emphasis on the removal of contaminants from (and the regeneration of) aqueous solutions, total cell current can vary in the general range 0.0001 to 1000 m² (involving currents of <10⁻² A to >100 kA).

**Figure 2.1 The scale of electrochemical technology: beyond nanoamperes to mega amperes**

Electrochemistry offers promising approaches for the prevention of pollution problems in the process industry. The inherent advantage is its environmental compatibility, due to the fact that the main reagent, the electron, is a ‘clean reagent’. The strategies include both the treatment of effluents and waste and the development of new processes or products with less harmful effects, often denoted as process-integrated environmental protection (Juttner et al 2000). Attractive advantages of electrochemical processes are generally:

- **Versatility** - direct or indirect oxidation and reduction, phase separation, concentration or dilution, biocide functionality, applicability to a variety of media and pollutants in gases,
liquids, and solids, and treatment of small to large volumes from microlitres up to millions of litres.

- **Energy efficiency** - electrochemical processes generally have lower temperature requirements than their equivalent non-electrochemical counterparts, e.g. thermal incineration. Electrodes and cells can be designed to minimise power losses caused by inhomogeneous current distribution, voltage drop and side reactions.

- **Amenability to automation** - the system inherent variables of electrochemical processes, e.g. electrode potential and cell current are particularly suitable for facilitating process automation.

- **Cost effectiveness** - cell constructions and peripheral equipment are generally simple and, if properly designed, also inexpensive.

2.4 **TYPES OF ELECTROCHEMICAL WASTEWATER TREATMENT**

Different types of electrochemical technologies exist which have been widely used in water and wastewater treatment and several applications have been studied. The various electrochemical treatment methods include,

- Cathodic metal deposition
- Electro-coagulation
- Electro-floatation
- Electro-flocculation
- Anodic electrooxidation
- Electro membrane process
2.5 CATHODIC METAL DEPOSITION

Since most of the metal ions can be removed by cathodic deposition, electrochemical processes have been developed, some of which are already commercialized and being now used in the industry. The removal of metal ions $\text{Me}^{z+}$ from wastewater is based on the cathodic metal deposition.

$$\text{Me}^{z+}_{\text{sol}} + \text{ze}^- \leftrightarrow \text{Me} \quad (2.4)$$

From a thermodynamic point of view, the Nernst equation predicts that it should be possible to decrease the $\text{Me}^{z+}$ concentration in solution to an arbitrarily low level, if the potential $E$ of the $\text{Me/Me}^{z+}$ electrode is maintained sufficiently negative with respect to the standard potential $E^0_{\text{Me/Me}^{z+}}$ (Pletcher and Walsh, 1993).

The electrodeposition method was employed for the treatment of electroplating rinse wastewater containing copper cyanides. During treatment at alkaline conditions ($\text{pH} \ 13$) with a current density of 2 A/dm$^2$ it was observed that a copper oxide catalyst formed at the anode was composed totally of CuO and copper was electrodeposited on the cathode in its metallic form. Within treatment time of 1.5 h it was possible to destroy 78% of cyanides and eliminate 79% of copper from the solution, 90.3% of which was recovered as electro deposited metallic copper. Under these conditions no sludge was produced, which offers a great advantage in comparison with the conventional treatment (Szpyrkowicz et al 1998). Successive results on copper ion removal from copper metal pickling wastewater was also reported by Watanabe et al (2001) using carbon electrodes in bio–electrochemical reactor. Hunsom et al (2005) have reported the treatment of industrial effluent containing heavy metals such as copper, nickel and chromium in a membrane flow reactor where more than 99% of metal reduction was achieved. Ruotolo et al (2006) investigated the electrochemical reduction of Cr (VI) using three-
dimensional electrodes, such as reticulated vitreous carbon (RVC) and polyaniline-modified RVC, and reported that RVC/PANI electrode showed the best reaction rates as a result of the polyaniline electrocatalytic effect. Another study demonstrated the removal of copper from metallophthalocyanine reactive dye (turquoise blue 15) using a Ti/TiO$_2$ thin film photoanode and platinum cathode using photoelectrocatalytic treatment. After 4 h of potential controlled electrolysis at $-1.2\text{V}$ on a cathode of platinum followed by 6 h of photoelectrocatalytic oxidation, 100% of color removal was achieved accompanied by 83% of TOC decay and electrodeposition of 69% of the released copper originally presented as copper phthalocyanine complex, by electrodeposition on the cathode (Osugi et al 2005).

### 2.6 ELECTRO-COAGULATION

Electro-coagulation is a process consisting of creating metallic hydroxide flocs within the wastewater by electrodissolution of soluble anodes, usually constituted by iron or aluminium (Chen et al 2000, Zaroal 2006).

When wastewater is treated with direct current, a number of physicochemical processes take place. Three main processes occur during electro-coagulation; (i) electrolytic reactions at electrode surfaces, (ii) formation of coagulants in the aqueous phase, (iii) adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation or flotation. The main pathway for removing colorant from aqueous solutions is coagulation. At large cathodic potentials, local hydroxyl ions (OH$^-$) can be generated due to water and oxygen reduction as in equations (2.5) – (2.6).

\[
2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2 \\
2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-
\]
With cast iron sheets as consumable electrodes, ferrous (Fe$^{2+}$) and ferric (Fe$^{3+}$) ions are produced on the anodes (equations (2.7) – (2.9)).

Anode:

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- \\
\text{Fe} & \rightarrow \text{Fe}^{3+} + 3e^- 
\end{align*}
\]

Cathode:

\[
\begin{align*}
2\text{H}_2\text{O} + 2 \, e^- & \rightarrow \text{H}_2 + 2\text{OH}^- 
\end{align*}
\]

With aluminium sheets as consumable electrodes, Al$^{3+}$ ions are produced on the anodes (equations (2.10)).

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e^- 
\]

And on the cathode (equation (2.11)),

\[
\begin{align*}
2\text{H}_2\text{O} + 2e^- & \rightarrow \text{H}_2 + 2\text{OH}^- 
\end{align*}
\]

During the process, an increase in pH is expected. As a result of high pH, precipitates of Fe(OH)$_2$, Fe(OH)$_3$, and Al(OH)$_3$ are formed and remain in the solution. The gelatinous suspension removes colorants by adsorption and electrostatic attraction followed by coagulation. The cathode may also be chemically attacked by OH$^-$ ions generated during H$_2$ evolution at high pH (Picard et al 2000). Electro-coagulation has some significant advantages namely; simple equipment, easy operation, automation, a shorter retention time, high sedimentation velocities, more easily dewatered and reduced amount of sludge due to the lower water content (Mollah et al 2001). Indeed, electro-coagulation has been tested successfully to treat textile wastewater (Dhaneshwar 2004, Can et al 2006, Zaroul 2006).
Can et al (2006) studied the application of chemical and electrocoagulation methods for the treatment of textile wastewater. For an operating time of 5 min, the treatment yielded a COD removal of 23% for electrocoagulation, which improved effectively to 78% on addition of polyaluminium chloride. Though the technique was efficient in COD removal the limitations associated with the process are sludge formation, which requires sludge dewatering and disposal (Can et al 2006, Yang and MacGarrahan 2005). For the process to be applied to an industrial scale, a sludge separation mechanism needs to be considered and examined thoroughly.

2.7 ELECTRO-FLOATATION

Electro-floatation is a simple process that floats pollutants to the surface of a water body by tiny bubbles of hydrogen and oxygen gases generated from water electrolysis. Therefore, the electrochemical reactions at the cathode and anode are hydrogen evolution and oxygen evolution reactions, respectively (Balmer and Foulds 1985). It is reported that the hydrogen bubbles are smallest at neutral pH. For oxygen bubbles, their sizes increase with pH. The gas bubbles depend also on the current density. This method has been used to remove oil emulsions and surfactants from effluents (Fukui and Yuu 1980).

2.8 ELECTRO-FLOCCULATION

Electro-flocculation is a combination of the processes of electrofloatation and electroprecipitation. Electroflocculation is a new technology for separation of oil-in-water emulsions. By use of the electroflocculation method it is possible to remove a high degree of finely dispersed particles (e.g. oil, heavy metals, and organic substances) from polluted water (Balmer and Foulds 1985). Separation of oil from seawater is
favorable. The technology can be used for effluents from industrial processes, for instance wastewater from paper mills, food processing, metallurgical industry and municipal sewage with a high content of organic and inorganic matters in the form of dispersed particles (Rajeshwar et al 1997, McClung et al 1994).

2.9 ANODIC OXIDATION OF ORGANICS

By electrochemical oxidation treatment of wastes either a partial (reduction of toxicity) or a complete decomposition of the pollutants can be achieved. Complete decomposition of organic material means the oxidation of organic compounds to carbon dioxide and water. As a consequence it results in relatively high energy consumption for large organic molecules. The types of anodic oxidation (direct and indirect), anode materials used for this purpose, effect of operating parameters on the process and the types of wastewater treated using this method are presented in detail hereunder.

2.9.1 Direct Oxidation at the Anode

The direct electrochemical oxidation of organic compounds could generally occur via a mechanism in which the first step is the oxidation of water molecules on the electrode surface (MOx), giving rise to formation of hydroxyl radicals according to equation (2.12) (Comninellis  1994, Panizza and Cerisola 2003)

\[ \text{MO}_x + \text{H}_2\text{O} \Rightarrow \text{MO}_x[\text{OH}^+] + \text{H}^+ + e^- \]  

(2.12)

The produced hydroxyl radicals can, if possible, oxidise the underlying oxide lattice to a higher state forming the so-called higher oxide (equation (2.13)):  

\[ \text{MO}_x[\text{OH}^+] \Rightarrow \text{MO}_x[\text{O}] + \text{H}^+ + e^- \]  

(2.13)
The only role of the formed higher oxide is its participation in the formation of selective oxidation of the organic pollutants (R) without complete incineration as shown in equation (2.14):

\[
\text{MO}_x\text{[O]} + R \rightarrow \text{RO} + \text{MO}_x
\]  

(2.14)

It is to be noted that the above route can take place only if the transition of the underlying oxide to a higher oxidation state is possible and the electrodes of this class are called “active electrodes”. However, if this is not possible, the electrogenerated hydroxyl radicals could directly oxidise the organic compound to carbon dioxide and water; predominantly causing the combustion of the organic compound (equation (2.15)):

\[
\text{MO}_x\text{[OH]}^+ + R \rightarrow \text{M} + \text{MCO}_2 + n\text{H}_2\text{O} + \text{H}^+ + e^-
\]  

(2.15)

and this class of electrodes are called “non-active electrodes”.

In direct anodic oxidation where the pollutants are adsorbed on the anode surface (M) and destroyed by the anodic electron transfer reaction, the rate of oxidation depends on the electrode activity, pollutant diffusion rate and current density. On the other hand, temperature, pH and diffusion rate of generated oxidants determine the rate of oxidation in indirect electrolysis (Israelides 1997).

2.9.2 Indirect Oxidation at the Anode

Indirect electrochemical oxidation of organic pollutants occurs via “in situ” electrogeneration of catalytic species with powerful oxidising property capable of eliminating the detrimental pollutants from their solutions by converting them into harmless compounds. Indirect electrochemical oxidation can be further classified into two types based on its reaction type which may be reversible or irreversible. In the reversible type of the process
the chemical oxidation of organic molecules is carried out by metal ion. The metal which is the oxidising species can be generated at the anode in the electrochemical cell in aqueous solution. Radical species initiated by metal ion, attack the organic substrate progressively converting it in a series of steps irreversibly to CO₂, water and residual salts. During the oxidation step, the metal ion is reduced back. This is then regenerated by oxidation again at the electrochemical anode. This “catalytic” use of metals makes a mediated electrochemical oxidation process. The typical mediators include Ag²⁺, Co³⁺, Fe³⁺, Ce⁴⁺ and Ni²⁺. Though redox reagents are successful in treating the pollutants, the following are the drawbacks of the process. Silver ions are hazardous in nature, if chloride ions are present in the wastewater, they react with silver and precipitate as silver chloride. This leads to the reduction of overall efficiency of the treatment process, silver is relatively expensive, the efficient operation of Fe(II)/Fe(III) system requires low current density and high temperature (~100°C) (Rajeshwar et al 1997).

In irreversible indirect oxidation, oxidants such as hypochlorite, ozone and hydrogen peroxide are generated. Among these, hypochlorite is the most commonly employed oxidant in wastewater treatment as chlorides are a common constituent of several industrial wastewater. Anodic water discharge results in the formation of hydroxyl radicals that are adsorbed on the anode surface and can then oxidise the organic matter. In the presence of NaCl, chlorohydroxyl radicals are also formed on the anode surface and then oxidise the organic matter (equations (2.16) – (2.19)).

\[
\begin{align*}
H_2O + M & \rightarrow M[OH^\cdot] + H^+ + e^- \quad (2.16) \\
R + M[OH^\cdot] & \rightarrow M + RO + H^+ + e^- \quad (2.17) \\
H_2O + M + Cl^- & \rightarrow M[ClOH^\cdot] + H^+ + 2e^- \quad (2.18) \\
R + M[ClOH^\cdot] & \rightarrow M + RO + H^+ + Cl^- \quad (2.19)
\end{align*}
\]
Reactions between water and radicals near the anode can yield molecular oxygen, free chlorine and hydrogen peroxide (equations (2.20) – (2.23)).

\[
\begin{align*}
\text{H}_2\text{O} + \text{M}[^{\cdot}\text{OH}] & \rightarrow \text{M} + \text{O}_2 + 3\text{H}^{+} + 3\text{e}^{-} \quad (2.20) \\
\text{H}_2\text{O} + \text{M}[^{\cdot}\text{ClOH}] + \text{Cl}^{-} & \rightarrow \text{M} + \text{O}_2 + \text{Cl}_2 + 3\text{H}^{+} + 4\text{e}^{-} \quad (2.21) \\
\text{H}_2\text{O} + \text{M}[^{\cdot}\text{OH}] & \rightarrow \text{M} + \text{H}_2\text{O}_2 + \text{H}^{+} + \text{e}^{-} \quad (2.22)
\end{align*}
\]

Furthermore, hypochlorite can be formed as follows:

\[
\text{H}_2\text{O} + \text{Cl}^{-} \rightarrow \text{HOCl} + \text{H}^{+} + 2\text{e}^{-} \quad (2.23)
\]

Therefore, direct anodic oxidation through reactions (2.20) and (2.22) results in reduction of COD as well as the formation of primary oxidants such as oxygen, chlorine, hypochlorite and hydrogen peroxide. Therefore in the experiments NaCl, Cl\textsubscript{2} and OH\textsuperscript{-} are electrochemically produced on the surface of the anode and the cathode respectively. In an undivided cell, the mixing of these species within the interelectrode gap results in hypochlorite formation. The oxidation of the dye by hypochlorite often implies the regeneration of the Cl\textsuperscript{-} that can be recycled back at the anode surface for further production of Cl\textsubscript{2}. In this regard, the overall process is cyclical although the anode reaction is irreversible in the electrochemical sense. Free chlorine and oxygen can further react on the anode yielding secondary oxidants such as chlorine dioxide and ozone, respectively as in equations (2.24) and (2.25) (Gotsi et al 2005, Israilides et al 1997).

\[
\begin{align*}
\text{H}_2\text{O} + \text{M}[^{\cdot}\text{OH}] + \text{Cl}_2 & \rightarrow \text{M} + \text{ClO}_2 + 3\text{H}^{+} + 2\text{Cl}^{-} + \text{e}^{-} \quad (2.24) \\
\text{O}_2 + \text{M}[^{\cdot}\text{OH}] & \rightarrow \text{M} + \text{O}_3 + \text{H}^{+} + \text{e}^{-} \quad (2.25)
\end{align*}
\]
Several reports are available on the electrochemical oxidation of organic compounds using chloride as electrolyte, but the process using hypochlorite are undesirable due to possible evolution of organochlorinated compounds which are considered to be toxic (Panizza and Cerisola 2003, Chatzisymeon et al 2006). The efficiency of indirect oxidation is reported to be dependent on the diffusion rate of oxidants in the solution and the pH value (Israelides et al 1997).

Several authors (Do and Chen 1993, Oturan and Pinson 1995, Ponce de Leon and Pletcher 1995) have treated some pollutants with electrogenerated $\text{H}_2\text{O}_2$ in a two-compartment cell. In this technique, hydrogen peroxide is continuously supplied to the cathodic compartment from the two-electron reduction of sparged oxygen on graphite or RVC cathodes (equations (2.26)):

$$\text{O}_2 + 2\text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2 \quad (2.26)$$

and its oxidising power was enhanced in acidic medium by addition of $\text{Fe}^{2+}$ to produce electrogenerated Fenton's reagent.

In the electro Fenton process, $\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$ can be generated onsite electrochemically, either separately or concurrently. $\text{H}_2\text{O}_2$ can be electro-generated by the reduction of dissolved oxygen, or by water oxidation at anode (Katsuki et al 1998), and $\text{Fe}^{2+}$ by the reduction of $\text{Fe}^{3+}$ or the oxidation of a sacrificial Fe anode. The electro Fenton simplifies field application and thereby enhances process efficiency. However, most electro Fenton studies primarily focus on the electro-generation of $\text{H}_2\text{O}_2$ whereas the electro-regeneration of $\text{Fe}^{2+}$ is largely neglected. However generation of iron sludge limits the applicability of Fenton oxidation processes. The potential of electrochemical oxidative process using sodium sulphate was explored by Saracco et al (2000) for the degradation of coumaric acid over Pt-Ti anodes.
The study showed that the in situ generated hydrogen peroxide acted as an oxidant through reaction mechanisms parallel to those occurring at the anode. It was also observed that the kinetics of the process was enhanced by dissolving \( \text{Fe}^{3+} \) ions in the anolyte. The results also indicated that both the bulk and electrode oxidation pathways co-existed; which lead to high pollutant abatement efficiencies.

Previous investigators have verified that during anodic polarisation on diamond electrodes, ozone gas can also be generated *in situ* by water oxidation as per equation (2.27), which can be used for effective treatment of organic pollutants (Katsuki et al 1998).

\[
3\text{H}_2\text{O} \rightarrow \text{O}_3 + 6\text{e}^- + 6\text{H}^+ \quad (2.27)
\]

### 2.9.3 Anode Materials for the Oxidation of Organic Pollutant

The main objective of electrochemical treatment is the complete oxidation of organics to \( \text{CO}_2 \) or atleast their conversion to biodegradable compounds. In this frame several anodic materials have been investigated for the degradation of model substrates. The choice of the anode material for wastewater treatment depends upon the type of the electrochemical treatment to be employed and the nature of the wastewater to be treated.

Treatment processes using electrochemical coagulation or electro flocculation may employ consumable anodes such as iron anodes. Similarly electrochemical oxidation involving *in situ* generation of Fenton’s reagent may also employ iron anodes for generating \( \text{Fe}^{2+} \) ion.

In case where direct anodic oxidation is used, dimensionally stable anodes (DSA) are employed. The electrode material chosen for such treatment process should be resistant to corrosion that could be caused by wastewater of
corrosive nature or due to application of high potential. It is also important to note that the durability of electrodes depends inversely on the current density (Lozanzo et al 1996). The most commonly used anode materials for direct oxidation of wastewater include graphite, lead/lead di oxide, nickel, graphite, platinum and titanium. Anodes with high O_2 evolution over potentials are favorable for the oxidation of organic compounds. Therefore noble metal oxides have better performance than those of the corresponding noble metals. Therefore oxides such as PbO_2, SnO_2, TiO_2, RuO_2, IrO_2 etc, and coated electrodes are more in preference (Tahar and Savall 1998, Zhou 2002, Comninellis and Pulgarin 1993, Comninellis 1994, Chen 2004). These oxides can be coated on to a DSA in combination with one another to make a binary, ternary or quaternary oxide coated electrodes. These oxide coatings confer electro-catalytic properties to the electrodes, making it desirable in terms of exchange current density and treatment time. But the draw back of these electrocatalytic coatings includes high cost and poor instability. The superiority of oxide coated electrodes over the metal electrodes have been evidenced by the study conducted by Naumczyk et al (1996). They reported that the efficiency of organic removal during indirect oxidation followed the order Ti/RuO_2 > Ti/Pt > Ti/Pt/Ir during the treatment of textile wastewater. Another study conducted on treatment of domestic wastewater showed that hydroxyl radicals detected with Ti/RuO_2–TiO_2 anode was larger when compared to Pt anode (Feng et al 2003).

The use of electrocatalytic anodes have also been demonstrated by many researchers for the treatment of organic pollutants. Li et al (2003) reported the electrocatalytic degradation of aniline to CO_2 using SnO_2–Sb_2O_3–PtO anode, and have proposed the reaction pathway for aniline degradation and intermediates production by electrocatalysis. Many workers have found PbO_2 to be catalytic in the oxidation of organic compounds including phenol (Baizer and Lund 1983, Fleszar and Ploszynska 1985). Phenol oxidation by
using the packed bed of lead dioxide was reported as an efficient electrode material (Chettiar and Watkinson 1983, Sharifian and Krik 1986). But the main problem with PbO\textsubscript{2} is the removal of dissolved lead from the treated solution (Oloman 1981). Tahar and Savall (1999) reported that Ta/PbO\textsubscript{2} and Pb/PbO\textsubscript{2} are corroded during the electrolysis of acidified phenol solution. The Ti/Fe-PbO\textsubscript{2} anode was not stable during the degradation of benzoquinone and the presence of dissolved lead in the solution was reported (Feng et al 1995). Brillas et al (1996) reported that during the electro-Fenton degradation of aniline using Ti/Pt/PbO\textsubscript{2}, appreciable amount of lead was released into the treated solution. It should also be noted that the release of lead ion was dependent upon current density, type of electrolyte and type of substrate (Iniesta et al 2001).

Shen et al (2006), have reported the use of nanophase catalysts for the treatment of dye effluents. It was revealed that either nanophase catalyst, TiO\textsubscript{2} or DSA, Co–Bi–PbO\textsubscript{2}/Ti anode lead to some 0.15 times higher color removal than graphite anode. If DSA anode and nanophase catalyst are used together for the electrocatalytic degradation of dye, they could bring forth higher color removal without increased electric current. The application potential of electrochemical oxidation will be great if more effective catalysts or electrodes are invented.

Ti/Pt anodes are also widely used in the electrooxidation of pollutants. Platinum is a material with rather good characteristics, but it is very expensive to use as anode. Instead, the much cheaper platinised titanium can be used, presenting similar effectiveness, stability, easy cleaning and storage. Platinised titanium anodes exhibit great anodic stability and resistance to redox and acidic/basic environments (Sakalis et al 2005). However previous investigators have reported that even these electrodes are known to suffer passivation during oxidation of some organics (Szpyrkowicz et al 2000, Vlyssides et al 1998). The film causing electrode passivation
interferes with the supply of fresh reactant, and the removal of products from the reaction zone, meanwhile decreasing the available potential to drive the reaction. During phenol degradation using Ti/Pt anode, surface passivation of the electrode was observed due to quinone formation and irreversible adsorption onto the electrode (Gattrell and Kirk 1993).

Graphite is one of the cheapest anode material available, but it undergoes disintegration leading to weakening of inter crystalline bonds causing graphite to peel off. Glassy carbon electrodes, inspite of electrocatalytic activity suffer from rapid loss of activity due to surface fouling. The electrode was found to be ineffective for decolorisation of dye solutions (Gatrell et al 1990).

Boron-doped diamond (BDD) electrodes are gaining much interest in recent studies (Chen et al 2003, Fernandes et al 2004, Carniero et al 2005) since it demonstrates very good chemical, mechanical and thermal resistance, wide electrochemical potential window in aqueous solutions, very low voltammetric background current, high resistance to deactivation via fouling, extreme electrochemical stability and no significant corrosion even under high current densities. Studies conducted by Martinez-Huitle et al (2004) on the electrochemical oxidation of chloranilic acid in acidic media at Pb/PbO2, boron-doped diamond (Si/BDD) and Ti/IrO2 electrodes by bulk electrolysis experiments under galvanostatic control where the results showed faster chloranilic acid elimination was obtained at the BDD electrode.

In a recent study by Maluleke et al (2003) a novel ceramic – based membrane was investigated as the anode material for the degradation of phenol. The ceramic-based membranes were modified to exhibit electrocatalytic activities by depositing nano-sized carbon black-supported antimony doped tin oxide on membrane surface.
In addition to the material of the electrode its physical structure is also very important. Electrodes constructed from meshes (Figure 2.2) are presently used in order to promote turbulence, maximise surface area to reduce cost and weight and to enhance the release of gaseous products from the surface. One of the recent types of porous, three dimensional materials to receive attention is reticulated (foam) metal (e.g. Ni, stainless steel, Cu) carbon, e.g. reticulated vitreous carbon (RVC). The open cell alveoli like porous structure of these materials possess a range of interesting properties such as reasonable isotropy of electrical conductivity, porosity and hence low pressure drop, low effective density, possibility of coating the material to provide a surface modified electrode. Possible drawbacks include the brittle–fragile nature of RVC, difficulties in making the feeder connections, relatively high cost, restricted range and availability of materials (Pletcher and Walsh 1993, Ralph 1996).

2.9.4 Effect of Operating Variables on Anodic Oxidation Treatment

There are several operating factors that influence the performance of the process with respect to pollutant removal. The various operating parameters that have been reported to influence the treatment process include pH, electrolyte concentration, current density and initial pollutant concentration. The effect of these operating variables on the performance of anodic oxidation are presented below with respect to the treatment of textile dyeing effluent which is the focus of the study.
2.9.4.1 Effect of pH

The pH can affect the electrochemistry of the conducting electrode (Huang et al 1986). The effect of pH on the electrochemical oxidation is variable depending upon the type of electrochemical treatment and pollutant tested.

Ceron-Rivera et al (2004) reported that the rate of electrochemical degradation of Reactive Black 5 over an iron anode at pH 5.5 was as much as four times faster than that at pH 7.5, while Awad and Galwa (2005) found that the electrochemical oxidation of Acid Blue and Basic Brown over a lead/lead oxide anode was favored at pH 2–3 but strongly suppressed at pH 12. Rajkumar et al (2007) during their study on indirect anodic oxidation of Reactive Blue 19, reported that acidic pH conditions are favourable for dye degradation.
On the contrary, few studies on degradation of textile dyes have reported that alkaline pH are more favourable for dye degradation. Mohan and Balasubramanian (2006) reported that the electrochemical oxidation treatment was favorable at neutral and alkaline conditions. The results indicated that the rate of COD reduction increased significantly when the electrolyte pH increased to 7 from 4 during their study on treatment of textile dye effluent containing chloride when Ruthenium/lead/tin oxide coated titanium and stainless steel were used as anode and cathode. They explained that the increase in electrolyte pH increases the •OH radicals that favor the hydrolysis reaction and consequently the rate of oxidation. Coulometric results obtained by controlled potential electrolysis of the dye Reactive blue 4 at reticulated glassy carbon electrode revealed that at pH 10, 18% colour removal was obtained whereas at pH 2 only 2% colour removal was obtained during dye effluent treatment (Carniero et al 2005).

Some studies have reported that pH has only minor or negligible effect on the degradation of organic pollutants. Direct oxidation studies conducted by Jia et al (1999) using carbon fibre anode demonstrated that the effect of pH was not very significant within the range of 3.0 - 11.0 during their studies on textile dyeing effluents. They reported that the process can work effectively within a broad pH range. It was also concluded that if the sample’s pH is within 7.0 - 11.0, the result will be more satisfactory. Lopez-Grimau and Gutierrez (2006) also studied the influence of pH in the range of 5-11 and verified that the decolourisation results were almost not dependent on the pH. Furthermore, Fernandez et al. (2004) have also observed little influence of the pH on the electrochemical degradation rate of textile dyeing effluents.

Hence from the existing literature it may be seen that there are variable results with respect to effect of pH on the dye degradation using
anodic oxidation method. Therefore, it is suggested that for application of this method for dye effluent treatment, optimisation of pH is essential with respect to the particular system.

2.9.4.2 Type of electrolytes used

Electrolytes are added to the medium to increase the conductivity and in return current density. The enhancement of electrolytic current can improve not only the degradation of pollutant in wastewater but also some side reactions such as production of H₂O at cathode (Jia et al 1999).

In electrochemical processes, the type and the concentration of the electrolyte are of crucial importance. Different types of electrolytes have been tested for the electrochemical treatment of pollutants among which the most commonly used electrolyte was found to be sodium sulphate, sulphuric acid and sodium chloride. Other electrolytes that are tested include potassium chloride, magnesium chloride, sodium carbonate, sodium nitrate followed by sodium chloride. Several studies have shown the superiority of sodium chloride over sodium sulphate and other electrolytes (e.g. sodium hydroxide and sulphuric acid) for the treatment of organic pollutants. The previous investigators have reported that faster and higher degree of mineralisation have been achieved only in the presence of sodium chloride containing effluents where the reactions are driven by indirect oxidation (Rajkumar and Kim 2006, Awad and Galwa 2005, Fernandes et al 2004, Panizza et al 2000, Panizza and Cerisola 2003). Chatzisymeon et al (2006) during treatment of textile dyeing effluents reported that at acidic conditions, free chlorine was the dominant oxidising agent, while at slightly alkaline conditions hypochlorite and hydroxyl radicals were prevalent. Their study was performed at ambient pH, which was alkaline and they observed that pH typically varied throughout the course of the reaction between 7.5 and 8.5 for the runs with the synthetic effluent and 9 and 9.5 for the runs with the actual
one. This implied that indirect oxidation might have preceded through various oxidants such as such as free chlorine (Cl₂) and hypochlorite anions (ClO⁻). During oxidation with chloride it was reported that although the ecotoxicity of the untreated actual effluent to *V. fischeri* was weak, it sharply increased after electrochemical oxidation, which was ascribed to the formation of organo chlorinated and other toxic by-products that are usually persistent to further oxidation. Similar observations have been documented during treatment with chloride containing effluents that have proved to release toxic organo chlorine compounds, which limit their application (Naumczyk et al 1996, Panizza et al 2000, Panizza and Cerisola 2003, Canizares et al 2004).

Therefore recently researchers are focusing on the treatment of organic pollutants in the presence of non-halide electrolytes such as sulphuric acid and sodium sulphate (Panizza et al 2001, Chen et al 2003, Jia et al 1999, Shen et al 2006). In case these electrolytes are employed, direct electro oxidation takes place which are reported to be dependant on the anode activity, the diffusion rate of organics on the anode surface and the applied current density. On the other hand, the efficiency of indirect oxidation depends on the diffusion rate of oxidants in the solution and the pH value (Israilides et al 1997). It is reported that in the presence of Na₂SO₄ and other sulfate-containing electrolytes in the reaction mixture formation of SO₂ (especially in acidic media) which is a moderate reductant is observed.

Few researchers have investigated the production of peroxodisulphuric acid from the oxidation of sulphuric acid on a Si–BDD (equation (2.28)):

\[
2\text{HSO}_4^- \rightarrow \text{S}_2\text{O}_8^{5-} + 2\text{H}^+ + 2\text{e}^- \quad (2.28)
\]

They reported that during electrolysis at very high potentials the main side reaction is oxygen evolution, however small amounts of
peroxomonosulphuric acid (H$_2$SO$_5$, Caro’s acid) were also detected. In particular, the current efficiency for peroxodisulphuric acid production increased with the H$_2$SO$_4$ concentration and current density, while it decreased with temperature due to the chemical decomposition of peroxodisulphate to oxygen according to equation (2.29) (Serrano et al 2002).

$$S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + \frac{1}{2}O_2$$  (2.29)

They also proposed a reaction mechanism for peroxodisulphate production involving a primary formation of hydroxyl radicals from the water discharge (equation (2.30)) followed by a reaction with HSO$_4^-$ to give peroxodisulphate (equation (2.31)):

$$H_2O \rightarrow OH^* + H^+ + e^-$$  (2.30)

$$2HSO_4^- + 2OH^* \rightarrow S_2O_8^{2-} + 2H_2O$$  (2.31)

Direct oxidation using sodium sulphate as electrolyte was employed for the treatment of various dye solutions using Ti/B- diamond electrodes (Chen et al 2003). The results showed that on treatment the COD of the solutions reduced from 402 - 980 mg/L to 8-93 mg/L with current efficiency being 51.0 - 90.2%. Shen et al (2006) during their studies on electrolytic colour removal using sodium sulphate as electrolyte reported that high salt concentration can improve the color removal effect. However, colour removal was not proportional to the electric current and salt concentration. At low salt concentration, colour removal was improved quickly with salt added in the solution. At high salt concentration, it increased slightly.

However in case of real effluents addition of electrolyte to the solutions may not be necessary because considerable amount of electrolytes may already be present in the effluents (Chatzisymeon et al 2006, Sakalis et al
This provides an additional advantage in the application of the electrochemical process for the treatment of wastewater.

### 2.9.4.3 Effect of current density

The amount and the type of the electrolyte is strictly coupled with the applied voltage. High concentration of electrolyte needs low voltage, while low concentration requires higher voltage for the same result. In any case, the lowest possible potential value was achieved to satisfactory level of decolourisation within a relatively short period of treatment should be applied. Higher values of voltage lead to energy loss, high temperatures and electrode damage. Concerning the real wastewater treatment, the applied potential should complete the whole process satisfactorily, without any further addition of electrolyte (Sakalis et al 2006).

The effect of changing current on color removal and COD conversion during the electrochemical treatment of synthetic and actual effluents was studied. Increasing current from 5 A to 14 A improved decolourisation from 39 to 68–87%, respectively, after 5 min with the synthetic effluent. Other than the initial stages of the reaction, the applied current, at the conditions employed did not seem to be critical to decolourisation since quantitative removal was achieved within 10 – 15 min of reaction; for instance, over 98% color removal occurred after 15 min with the actual effluent regardless the applied current. Conversely, COD conversion appreciably increased with increasing current and this was more pronounced for the run with the synthetic effluent. For instance, the final COD reduction for the synthetic effluent was 55, 65 and 86% at 5, 10 and 14 A, respectively; these values for the actual effluent became 29, 34 and 39% at 5, 10 and 20 A, respectively (Chatzisymeon et al 2006). Similarly Mohan and Balasubramanian (2006) reported that the rate of degradation increased significantly when the current density increased from 1
Adm$^{-2}$ to 3 Adm$^{-2}$ and becomes insignificant beyond 3 Adm$^{-2}$ for a given supporting electrolyte concentration. They reported that a pseudo steady state between the generation of hypochlorite ion and the degradation of pollutant may be arrived when the current density increased from the lower value.

2.9.4.4 Effect of initial concentration of the organic pollutant

One of the parameters that influence the performance of the electrochemical oxidation of the pollutants is the initial pollutant concentration.

Several studies had been conducted in this regard to find out the effect of initial concentration of pollutant on treatment efficiency. The information on this part may be useful to determine the amount of pollutant load that can be subjected to the treatment and also evaluation of time required for the treatment specific pollutant or pollutants.

Mohan and Balasubramanian (2006) reported that during indirect electrochemical oxidation the rate of degradation decreased with increase in effluent initial concentration. This was due to the ratio of OCl$^-$ to the effluent concentration which decreased with increase in effluent initial concentration. Similar results were reported by Allen et al (1995) during their treatment on textile dyeing effluents.

On the contrary Fernandes et al (2004) during the treatment of textile effluent in the presence of sodium sulphate reported that the colour removal efficiency increased with initial dye concentration. They explained that the rate of degradation of the dye was controlled by mass transfer limitations; in that situation, the dye concentration at the interface becomes
zero because the electrochemical reaction rate is higher than the diffusion rate, thus making the degradation rate proportional to the bulk concentration.

2.9.5 Application of Anodic Oxidation to Wastewater Treatment

Electrochemical techniques are becoming more reliable and are gaining popularity for the treatment of industrial wastewater. The electrochemical methods have proved efficient in destroying a variety of pollutants: ammonia (Marinere and Lectz 1978), nitrites (Lin and Wu 1996), benzoquinone (Feng et al 1995), benzene (Fleszar and Ploszynska 1985), phenols (Canizares et al 2004), chlorophenols (Polcaro and Palmas 1997), dyes (Szpyrkowicz et al 2000), formaldehyde (Do and Yeh 1996), cyanides (Szpyrkowicz et al 1998), alcohols (Kowal et al 1997, Burstein et al 1997) and hydrocarbons (Otsuka and Yamanaka 1998).

The electrochemical treatment was also applied to the treatment of various wastewater such as landfill leachate (Chiang et al 1995, Cossu et al 1998), tannery waste liquors (Szpyrkowicz et al 1995, Vlyssides and Israelides 1997, Panizza and Cerisola 2004), car wash wastewater (Panizza et al 2005) and industrial effluent containing naphthalene sulfonated acids (Panizza et al 2000, Panizza and Cerisola 2001), which have demonstrated successful results.

2.9.6 Combined Electrochemical Methods with Other Treatment Methods for Removal of Organic Pollutants

Nowadays single process alone may not be adequate for the treatment of bio-refractory organic compounds. Hence, researchers are attempting for a combination of two or more treatment methods for the complete and successful removal of pollutants. Table 2.1 presents some of the studies conducted on the electrochemical treatment methods combined with
other methods such as biological, physical and chemical methods. Kim et al (2002) have studied the performance of pilot scale combined process of fluidised biofilm process, chemical coagulation and electrochemical oxidation for textile wastewater. They concluded that the combined process was successfully employed which effectively decreased pollutant loading on post-treatment for textile wastewater treatment at pilot scale. Combination of electrochemical treatment and chemical coagulation (Lin and Peng 1994), combined chemical coagulation, electrochemical oxidation and activated sludge process (Lin and Peng 1996), combination of electrochemical method, chemical coagulation and ion exchange (Lin and Chen 1997), electrocoagulation and electro oxidation with γ-irradiation (Barrera-Diaz et al 2003) have been successful in the effluent treatment to meet out the legal requirements or for reuse standards. Similarly, combination of electro-Fenton oxidation and biological treatment for landfill leachate was reported as an effective treatment to meet out the discharge standards (Lin and Chang 2000). The treatment performance of a coupled bio-electrochemical/adsorption process for denitrification and pesticide removal showed promising results in the removal of nitrate and isoprothiolane (Feleke and Sakakibara 2002).

Recent studies have demonstrated that the external electric field could greatly enhance photocatalytic efficiency, which is well known as an electric field enhancement effect. This is familiarly known as photoelectrocatalysis and is nowadays gaining interest (Zainal et al 2004). During investigations on photo electrochemical processes a composite photo-electrochemical reactor was prepared and studied for the degradation of organic pollutants in wastewater. In the reactor, a UV lamp was installed to provide energy to excite nano TiO\(_2\), that served as photo catalyst and a three-
### Table 2.1 Combined electrochemical treatment methods for the treatment of pollutants

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Compound/Nature of wastewater</th>
<th>Electrode</th>
<th>Supporting electrolyte</th>
<th>Operating conditions / Observations</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td><strong>PHOTO ELECTROCHEMICAL OXIDATION</strong></td>
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</tr>
<tr>
<td>1.</td>
<td>Textile Dye Reactive blue –19</td>
<td>Anode; Ti/RuO₂</td>
<td>Sulphate and chloride</td>
<td>Degradation was studied using quartz tube. Decolourisation obtained was higher than 95% and TOC reduction of about 52% during period of 120 min. The observed synergic effect of both the process was compared and proved to be better than the single application of these processes. The electrochemical process was conducted at 28 °C at pH 11 at 1-8 V with mean current of 23 mA.</td>
<td>Pelegrini et al (1999)</td>
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<tr>
<td>2.</td>
<td>Naphthol Blue Black (NBB)</td>
<td>Anode; Pt /WO₃</td>
<td>Sulphate and chloride</td>
<td>Photoelectrochemical degradation of NBB in aqueous solutions was investigated. Higher rate of NBB degradation was observed in Cl⁻ containing media than in sulphate solutions. pH was found to influence the degradation on Cl⁻ media and NBB degradation was found to be slower in acidic media.</td>
<td>Hepel and Luo (2001)</td>
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<td><strong>SONO ELECTROLYSIS</strong></td>
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<tr>
<td>3.</td>
<td>Textile dyes</td>
<td>Platinum and carbon electrodes</td>
<td>NaCl</td>
<td>Solutions of both basic and acidic dyes were subject to sonolysis, electrolysis and sonoelectrolysis. Only basic dyes were decolorized by ultrasound alone. Removal of acidic dye required the use of electrooxidation and needed to be performed in a sealed cell to minimize the effects of ultrasonic degassing.</td>
<td>Lorimer (2001)</td>
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<tr>
<td>Sl. No.</td>
<td>Compound/Nature of wastewater</td>
<td>Electrode</td>
<td>Supporting electrolyte</td>
<td>Operating conditions / Observations</td>
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<td></td>
<td><strong>BIO ELECTROCHEMICAL TREATMENT</strong></td>
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<tr>
<td>4.</td>
<td>Textile wastewater</td>
<td>Cast iron plates</td>
<td>Mixture of salts</td>
<td>Electrochemical oxidation achieved maximum treatment efficiency at pH 7 with addition of 40 mg/L polyaluminum chloride. A current density of 53.4 mA/cm² was considered as optimum during the electrolysis. Increase in the electrode number did not have significant improvement in the COD removal.</td>
<td>Lin and Peng (1996)</td>
</tr>
<tr>
<td>99.</td>
<td>Textile wastewater</td>
<td>Steel</td>
<td>Mixture of salts</td>
<td>Combined treatment of electrochemical, chemical coagulation and ion exchange processes were proposed for reuse. Addition of small amount of hydrogen peroxide at pH of 3.0 enhanced the treatment efficiency up to 100 %. The formation of large amount of small flocs led to settling problem.</td>
<td>Lin and Chen (1997)</td>
</tr>
<tr>
<td>119</td>
<td>Textile wastewater</td>
<td>Anode Titanium plates with RuO₂- Cathode Stainless steel Plate</td>
<td>NaCl</td>
<td>The performance of pilot scale combined process of fluidised biofilm process, chemical coagulation and electrochemical oxidation for textile wastewater treatment was studied. Two species of microbes which can degrade textile wastewater pollutants were applied to the system with supporting media, with optimal FeCl₃ dosage at pH 6 at 3.5 × 10⁻³ mol/L con was used with 2.1 mA/cm² current density and 0.71 min flow rate. The obtained COD and colour removal was 95.4% and 98.5% with the combined process.</td>
<td>Kim et al (2002)</td>
</tr>
</tbody>
</table>
electrode electrolysis system was used to accumulate \( \text{H}_2\text{O}_2 \) which plays an important role in the degradation process (Chen et al 2003). An et al (2004), during their studies on synergetic photoelectrocatalytic degradation of quinoline reported that the synergetic effect have more efficiency in pollutant degradation than with the individual processes. Degradation of oxalic acid, has also been successfully demonstrated using photoelectrocatalysis (An et al 2005). A combined process based on photoelectrocatalytic oxidation and electrolysis was also tested for the treatment of solution containing high metallo phthalocyanine dye which yielded successive results. The mineralisation process for 2,4-dichlorophenoxyacetic acid (2,4-D) at pH 3 has been studied by advanced electrochemical oxidation processes (AEOPs), such as electro-Fenton and photoelectro-Fenton processes, in which a Pt anode and a carbon -polytetrafluoroethylene \( \text{O}_2 \)-fed cathode, for in situ production of \( \text{H}_2\text{O}_2 \) were used. A solution of 230 ppm 2, 4-D with a low salt content was completely mineralised by the photoelectro-Fenton process at low current, whereas the electro-Fenton process lead to 90% of mineralisation. In both methods, 2, 4-D was quickly destroyed at the same rate (Brillas 2000).

Electrolysis in combination with ultrasound also offers promising solutions in the treatment of pollutants. Ultrasound improves the electrochemical degradation by two mechanisms: a physical and a chemical one. The propagation of acoustic waves in a liquid medium induces cavitation, which leads to the formation, growth and vibration of bubbles and even their violent collapse at high acoustic pressure. Among the physical effects of these collapses are the high rates of micro mixing, the cleaning of the electrodes' surfaces by dissolving or pitting the inhibiting layers. These effects result mainly in an enhancement of the solid-liquid mass transfer between the electrodes and the solution. The chemical effects are also a consequence of the violent collapses. The "hot spot" theory (Suslick 1988) predicts temperatures of many thousands of Kelvin and pressures of hundreds
of atmospheres inside the bubble during the final compression. Under such drastic conditions oxidising species are generated by the homolitic cleavage of molecules (gases and solvent). In aqueous media and in the presence of oxygen, radicals such as \(\text{HO}^\cdot\), \(\text{HOO}^\cdot\), and \(\text{O}^\cdot\) are produced. Some mechanisms involving these radicals may considerably enhance the electrochemical processes for the destruction of hazardous waste (Trabelsit et al 1996). Yasman et al (2004) have recently addressed the detoxification of hydrophilic chloroorganic pollutants in effluent water, using a combination of ultrasound waves, electrochemistry and Fenton’s reagent with almost 50% oxidation of pollutant at quite a small current density in just 60 s.

Thus the electrochemical method proves to be versatile and flexible that is easily integratable with other existing treatment technologies.

2.10 ELECTROMEMBRANE PROCESS

Electrodialysis (ED), one of the oldest membrane techniques, is an isothermal separation process based on charge transfer by using an electric field as the driving force. The electric potential is established between two faces of the ion-exchange membranes that are permeable to either anions or cations, but not to both. The electrochemical processes are mainly used in industries for solution demineralisation. Recently, EDBPM has been used to produce acids and bases from a salt stream (Gnieste et al 1996) or for the recovery of concentrated acids (Cattoir et al 1999).

2.10.1 Ion-Exchange Membranes

A membrane is defined as a permselective barrier separating two phases. Under the influence of a driving force certain components can
permeate the membrane while others are retained. Thus a membrane is capable of selectively transporting components from one phase to the other (Bazinet 1998).

Ion-exchange (or ionic) membranes are made of a macromolecular material (skeleton) having ionizable groups. Once impregnated with a dissociable solvent such as water, the membrane fixed ions are electrically neutralised by mobile charges of the opposite sign, called compensator ions or counter-ions. Counter-ions are positive in the case of a cationic membrane, negative for anionic membranes. They exchange by diffusion between the membrane and the surrounding solution.

2.10.1.1 Monopolar membrane

Membranes are available based on the nature of the functional groups attached to the matrix: cation-permeable membranes, called cation-exchange (or cationic) membranes (CEM) and anion-permeable membranes, called anion-exchange (or anionic) membranes (AEM) are depicted in Figure 2.3. Both of these membranes are monopolar; this means that they are permeable to only one type of ion (Visser 2001).

The main functional groups used are sulfonic groups (-SO$_3^-$) for cationic membranes and alkyl ammonium groups (-NR$_3^+$, -NHR$_2^+$), (-NH$_2R^+$) for anionic membranes. Under the influence of an electric field, cations (in a cationic membrane) move from one side to another in the network of anionic functional groups fixed on the skeleton and cross the membrane. In an anionic membrane, the transport of anions from one side to another takes place in the network of cationic functional groups (Gartner et al 2005).
2.10.1.2 Bipolar membrane

A bipolar membrane (BPM) is a combination of anion and cation exchange membrane. Bipolar membrane electrodialysis (EDBPM) technology, which uses the property of BPM to dissociate water (water splitting), has greatly extended the potential of electrodialysis in the last years. It has been mainly used to generate acids and bases from salts without the production of oxygen and hydrogen gases (Gnieste et al 1996).

The principle of the electrodialytic water-dissociation process employing BPM is represented in Figure 2.4. If a direct electrical potential (DC) is established between a bipolar membrane which consists of a layer of an anion exchange membrane and a layer of a cation exchange membrane, water dissociation occurs at the interphase and a current is sustained through the membrane by the migration of hydrogen and hydroxyl ions to the
respective compartments under the fluency of applied DC electric field (Tongwen and Weihua 2002a, Trivedi et al 1997).

When a BPM is introduced in an ED stack, the fluxes of H\(^+\) and OH\(^-\) ions enable the salt M\(^+\)X \(^-\) to be transformed into both acid HX and base MOH. The feed and the two product streams are circulated separately through the membrane stack between the membranes. With each passage, the salt feed stream is diluted by the transport of anions and cations across the anion- and cation-permeable membranes, respectively. These salt ions, together with the hydroxide and hydronium ions that are formed in the bipolar membrane, increase the concentration of the products, i.e. the alkali and the acid, respectively. So one can see that the bipolar membrane acts as both an acid source and a alkali source. The separation or better, production of acid and alkali is possible with only one pair of working electrodes and many repeat units in between, reducing the cost of electrodes and reducing the influence of the electrode reactions on the energy efficiency and membrane transport compared to electrolysis (Wilhelm et al 2001).
However, ion exchange membranes are not perfectly selective due to the incomplete exclusion of co-ions, i.e. the ions that carry the same charge as the membrane fixed charge. In the CEM and AEM, the co-ions are mainly hydroxide ions and protons, respectively. Their transport limits the overall current efficiency and the maximum alkali or acid concentration. However, the product purity is mainly influenced by the salt ion transport across the BPM (Gnieste et al 1996).

In general, a good membrane yields low energy consumption, low electrical resistance and high current density, high current efficiency or product purity, high water dissociation rate, low co-ion transport rate, high ion selectivity and a good long-term stability. The economical advantages of the EDBPM are based on several criteria: the electrical energy consumption, the current efficiency, the purity of the produced acid and base, and their maximum concentration level (Gnieste et al 1996).

### 2.10.2 Application of Electrodialysis for the Production of Acid and Alkali from Salt Streams

It has been increasingly acknowledged today that ED conducted with BPM has the property of being an energy efficient process for the conversion of salts into their corresponding acids and bases (e.g. HX, MOH). Infact a simple configuration using monopolar membranes can also be used for the generation of acid and alkali from salt solutions (Visser 2001). Though it offers advantages like simple design and avoidance of using expensive bipolar membranes, insertion of repetitive units as in case of bipolar membranes within the cell is not possible, since it will lead to the production of concentrated salt solutions rather than the production of acids and bases.

By using bipolar membranes two major types of membrane combinations are employed to produce acids and bases from salts. The
two-compartment unit is simple in structure, but the base produced from the cathode has a tendency to be transported to the acid compartment through the anion membrane and neutralise the acid produced from water dissociation and thus decrease the current efficiency. Another disadvantage of the two-compartment BP configuration as well as any other two-compartment electromembrane systems is the generation of acid within the feed compartment. The concentration of acid in this compartment leads to a reduction in current efficiencies for both the production of base and acid (Jorissen and Simmrock 1991, Paleologou et al 1996, Paleologou et al 1997). These disadvantages are overcome by a three-compartment unit. Moreover, in a three compartment configuration, there are no direct contacts of cation layer with acid and anion layer with base, and thus the duration of a membrane is significantly increased (Tongwen 2001). In fact, concentration of the produced acid and base can be attained as high as 6 mol/ L by using three compartment configuration (Gnieste et al 1996).

Schaffner et al (2003) reported that EDBPM has been successful for its capability to both demineralise solutions and to produce alkali and acid solutions from diester wastes containing glycerine. Demineralisation rates above 80% were achieved with glycerin loss below 2%. Alkali and acid solutions were obtained with a final concentration of about 2 N and an energy cost of about 0.5 kWh/kg of pure glycerin. The EDBPM process had been used to convert sodium acetate solution to sodium hydroxide and acetic acid (Trivedy et al 1997). Similarly Tongwen and Weihua (2002b), conducted the recovery of citric acid from sodium citrate and sodium sulphate solutions sing EDBPM. The reported the technical feasibility of generation of citric acid from sodium citrate using BPM.

The technology had also been reported for the recovery of acids and alkali from etching solutions. It enabled the recovery and further
concentration of hydrochloric and sulphuric acids from the acid and iron salt concentrates produced in the course of conventional electrodialysis. Bipolar electrodialysis, in combination with a two-stage monopolar electro-dialysis process, yielded the recovery of two valuable components of etching rinse: high-quality water and acid. The study also involved the recovery of sodium hydroxide from the solution of sodium hydroxide and sodium nitrate formed during alkaline absorption of nitrogen oxides from flue gas. The process yielded an acid solution concentrated 51-fold (in the case of hydrochloric acid) and 63-fold (in the case of sulphuric acid) as compared to the feeding solution for conventional electrodialysis (Wisniewski et al 2004).

Thus it can be seen that EDBPM has been widely studied for the recovery and concentration of acid and alkali solutions from organic/inorganic salt containing solutions.

Despite higher desalting degrees, several investigators have observed the losses of acid through anion exchange membrane. Hence the concentration of acid is limited attributed by the proton leakage through the AEM (Schaffner et al 2003, Wisniewski et al 2004, Cauwenberg et al 2001). It was also noted that at high base concentration in the concentrate the Faradic yield for the recovered base was also lower. This could be attributed by the leakage of OH⁻ ions across the CEM to the diluate stream (Wisniewski et al 2004).

2.10.3 Effect of Operating Variables on the Process

2.10.3.1 Effect of current density

As is known, ED is an electrochemical separation process in which mineral salts and other ionic species are transported through ion-selective membranes from one solution into another under the driving force of a DC
electrical potential. When a DC voltage is applied, the electrical potential created becomes the driving force to move ions, with the membranes forming barriers to ions of opposite charge (Yazicigil and Oztekin 2006). At a certain value of the current density the water dissociation occurs so fast that the transport of water into the BPM transition region cannot keep up and limits the water dissociation process and the limiting current density is reached (Krol et al 1998). Thus the limiting current is a current, which corresponds to the minimum concentration electrolyte in the vicinity of the membrane/solution interface. At current close to the limiting current and exceeding it, there arise concentration polarisation coupled effects: water splitting, exaltation effect and gravitational convection (Valerdi and Mengual 2001).

The effect of current density on the electrodialytic process has been investigated by several researchers who have reported that the mobility of ions increased rapidly with applied current density. Nevertheless, it was also reported that the mobility of ions plotted as a function of the total number of electrical charges transferred through the cell does not depend on the current density (Basta et al 1998). During the demineralisation of sodium acetate solutions, the concentration of salt decreased and both the concentrations of acid and alkali increased with the increase in applied voltage. Though the demineralisation was faster at higher current density the final demineralisation rate was the same for an equivalent electrical quantity (Trivedi et al 1997).

Increasing the current density gives the opportunity to decrease the membrane area since the production is faster (Schaffner et al 2003). Frenzel et al (2005) reported that increased current density (greater than 20 mA/cm²) considerably improved the chromate transport (the chromate flux was around 30% higher at 30 mA/cm² in accordance to Faraday’s law) but also resulted in
a steadily growing high voltage drop over the electrodialysis system. Additionally, processing with increased voltage leads to high power consumptions. Trivedi et al (1997) have reported similar observations during their study on demineralisation of sodium acetate solutions, where the energy consumed per kg salt removed also increased with applied voltage.

Current density is therefore a key factor acting on the membrane area needed to treat the salt solutions. Hence establishment of limiting current density and operating the process at an optimal point of current density will allow for effective application of the process.

2.10.3.2 Effect of flow rate

The effect of flow rate often show counteracting results and may be rather different for different applications, e.g., increasing the flow rate in a given stack design will decrease the residence time of the solutions in the stack and thus reduce the amount of salt ions removed. On the other hand, an increased flow rate allows for a higher current density, which leads to an increase of the ion removal (Lee et al 2002).

Al-Madani (2003) during his study on water desalination reported that increasing the flow rate of solutions resulted in lower product quality given in terms of percent salt removal. He also explained that it was attributed by a lower residence time and hence availability of less time available for mass transfer at the higher flow rates.

On the contrary, Frenzel et al (2005) reported that high flow rates are required for the successful scaling up of the ED process. They explained that high initial membrane resistance could be reduced when using high flow rates. Concentration polarisation is estimated to be influenced by the solution flow in a desalting cell. In an experiment carried out by Tanaka et al (2003) it
was shown that the boundary layer thickness was more in case of membranes with unforced solution as when compared to forced flow solution in a desalting cell. At less flow rate of the solutions concentration polarisation occurs which is highly undesired in electro dialysis since it drastically decreases the process efficiency due to the increasing electrical resistance of the solution (Visser 2001).

2.10.3.3 Effect of initial concentration of feed solutions

Electrodialysis for salt removal and acid/alkali recovery is not suitable to treat low concentrated solutions.

Ali et al (2004) reported that no effect on acid or base current efficiency was observed when varying the salt concentration in the central compartment. However, the cell voltage increased when the salt concentration decreased. This implied that higher energy consumption and higher cost unless salt concentration is maintained at higher value. Thus it was suggested that solutions with very low concentration should be coupled with a concentration/ demineralisation technique. Furthermore, concentration polarisation limits the intensity of the current density that can be applied. This makes the electrodialysis process unsuitable for treatment of solutions of low conductivity (Ali et al 2004).

During the production of citric acid from sodium citrate using EDBP, it was observed that the concentrations of the salts had some effect on the magnitude of acid concentration. The acid concentration increased with Na$_3$Cit concentration until the concentration of Na$_3$Cit was 0.5 M and then kept approximately unchanged, in the considered concentration range. It was also suggested better operations may be obtained by optimising the membranes configurations and improving the cell structure (Tongwen and Weihua 2002a).
2.10.4 Membrane Fouling and Mitigation Measures

Fouling of the membrane surface is the bane of membrane operations. Membrane fouling in ED is typically characterised by an increase in the membrane resistance and can also cause a loss in the perm selectivity of the membranes. Due to increase in resistance the energy consumption of the process increases. These changes in membrane properties often continue throughout the ED process and sometimes require extensive cleaning or replacement of the membranes. This has economic detrimental effects on the process (Bazinet and Farias 2005).

The concentration of calcium in the form of carbonate and sulfate and hardness in effluents in reasonable high concentrations are reported to cause scale formation on the membrane surface, thereby causing subsequent fouling. There are two types, colloidal floculation or inorganic scaling above the membrane surface, and adsorption of organics to the membrane. In case of organic pollutants present in the effluents anionic membranes are found to be affected more, since solutions containing organic pollutants are mostly negatively charged (Kotrappanavar et al 2006, Bouhidel and Rumeau 2004).

Farias and Bazinet (2006) reported that no fouling was found on the anionic membranes treated without calcium chloride in presence of sodium carbonate, while during ED process of solutions containing calcium chloride and sodium carbonate the membranes were slightly fouled. A thin layer of precipitates was observed on the anionic membrane surface. The appearance of precipitates was typical of a crystalline substance. The size and form of crystal increased in proportion to the concentration of calcium chloride in solution. Large and cubic crystals were the best defined on the membrane treated at 1600 mg/L of CaCl₂. The precipitate was identified as calcium hydroxide. However, this fouling was not found to affect significantly the electrical conductivity and the thickness of the membranes. Furthermore, the
fouling formed was reversible. Similarly ED membrane fouling was also observed by Bouhidel and Rumeau (2004) during nickel salts electrodialysis. They reported that an acidification or an increase of temperature of the diluate solution almost instantaneously eliminated membrane fouling.

Many approaches, including pretreatment of the feed solution, filtration, increase in the flow rate, and optimisation of process conditions, have been considered to minimise and mitigate membrane fouling potentials during electrodialysis (Lee et al 2002, Park et al 2003, Sheikholeslami 1999).

In order to prevent fouling by organics on anion-exchange membrane, it is suggested that the feed solution must be pretreated by acidification to pH 2.0 and filtration (Mavrov et al 1999). In Eurodia pilot plant which used electrodialysis, the pH in the concentrate was maintained at a neutral value by the addition of hydrochloric acid in order to avoid the precipitation of CaCO₃ (Wisniewski et al 2002). It is also reported that the fouling or scaling of the membranes can also be reduced by creating a turbulent environment by vigorously stirring the solutions or increasing the flow rate (Lee et al 2002, Park et al 2003). To prevent scaling, frequent polarity reversal of the electric field were also suggested. This process is called electrodialysis reversal (Lindstrand et al 2000, Wisniewski et al 2002, Al-Madani 2003).

Fouling layers are removed by using appropriate cleaning procedures. The most common procedures are by using caustic detergent for the removal of dirt, oils and colloidal material, acids for metal hydroxides, and oxidising agents for adsorbed organics (Kotrappanavar et al 2006).

Recent studies are also being focused on the modification of membrane characteristics to possess antifouling properties. Nagarale et al (2004) have modified the surface of the membrane by radiation grafting of
urathane acrylates in order to introduce antifouling characteristics so that these membranes be very useful for the separation of different electrolytes by electro-driven membrane technology.

Therefore, it appears that it should be possible to prevent membrane fouling by using appropriately pretreated feed solution and also control fouling with mechanical cleaning, polarity reversal and chemical cleaning.

2.10.5 Basic Parameters to be taken into Consideration

For optimal operation of an ED unit several basic parameters should be taken into account during its design and construction phase. These parameters are highly related fact, that makes the optimisation a difficult task (Korngold 1982).

An ED unit should

- Have the diluate and concentrate cells as thin as possible.
- Maintain low pressure difference between diluate and concentrate cells so to minimise the stress on the membranes.
- Avoid leakages due to sealing and mechanical deficiencies of the membranes or the spacers used.
- Select the optimal cell-pair configuration so that the pressure drops within the cell is minimal but the material transfer coefficients remain high by obtaining a good water distribution.

2.10.6 Advantages of EDBPM Process

The electrodialysis and its related technologies offer several advantages that have made them attractive in applications for industries and in
daily life, such as chemical production and separation, environmental conservation, etc. (Tongwen 2001)

- Low initial cost and space-saving (no electrode is needed in the repeating cell).
- Low running costs
- No oxidation and/or reduction species that may produce undesirable products (no electrochemical reaction).
- The process is simple in concept. The only pretreatment needed is filtration to remove insoluble materials, etc.
- It generates only the desired product into the purified and concentrated form.
- It can do the job which cannot be done by conventional methods such as separation of ions with the same valence and sign.
- The recovery process of acid eliminates the costs associated with the purchase and utilisation of neutralisation chemicals.
- The process significantly reduces the amount of waste disposal while recovering valuable chemicals etc.
- Additionally, bipolar membrane water splitting does not generate any gases such as, O₂ and Cl₂, and thus there is no corrosion to both cathode and anode.

2.10.7 Limitations of EDBPM

However, and as for all the processes, ED has its limitations which are presented below (Tongwen 2002, Tongwen and Weihua 2001a).

- Due to the leakage of the individual membrane, the undesired diffusion processes such as cations through anion membrane and anions through cation membranes reduce the current
efficiency. If the final product is not the strong acid or base, the concentration of strong acid or base is also not so important.

- A pre-treat of solutions is necessary to remove organic pollution in case of membrane swelling and metallic hydroxides precipitation.
- Nevertheless, some limits can be overcome by improving membrane quality or the cell configurations

2.11 USE OF RENEWABLE ENERGY SOURCES FOR WASTEWATER TREATMENT

Renewable energy is important because of the benefits it provides. They are clean sources of energy that have a much lower environmental impact than conventional energy technologies and hence have a flourishing future. Renewable energy will not run out ever, whereas the other sources of energy are finite and will some day be depleted. By using renewable energy and energy-efficient technologies in waste treatment practices, one can help the environment and typically save more money in the long run.

Consumer demand for clean renewable energy and the regulation of the utilities industry have spurred growth in green power - solar, wind, geothermal steam, biomass, and small-scale hydroelectric sources of power.

2.11.1 Solar Energy in Wastewater Treatment

Solar technologies use the sun's energy and light to provide heat, light, hot water, electricity, and even cooling, for homes, businesses, and industry. Photovoltaic solar cells, which directly convert sunlight into electricity, are made of semiconducting materials. The simplest cells power watches and calculators and the like, while more complex systems can light houses and provide power to the electric grid.
India is endowed with very good solar energy resource. Considering the ever increasing energy demands of the country, this resource can be gainfully utilised, especially for meeting the electrical needs of domestic, industrial, and commercial sectors.

The utilisation of solar energy for pollution abatement has long been recognised. Solar energy had been used to drive chemical reactions in treatment of pollutants. Studies on solar photo-catalysis and solar photo Fenton had been reported in the degradation of variety of environmental pollutants like pesticides (Peyton and Burry 1981), phenol (Kavitha and Palanivelu 2004), dyestuffs (Reeves et al 1997 and Muszkat et al 1995). Since the direct use of concentrated solar energy to supply the energy needed to drive the chemical reactions is possible, a study to establish an efficient and practical method for using highly concentrated sunlight to completely mineralise several organic dyestuffs was indicated by Reeves et al (1997). Dhodapkar et al (2002) has demonstrated the degradation of reactive dyes in presence of TiO\textsubscript{2} and ZnO catalysts under sunlight.

Another form of solar energy which is most widespread and studied is the photovoltaic power. The photovoltaic (PV) process converts sunlight, the most abundant energy source on the planet, directly into electricity. PV equipment has no moving parts and as a result requires minimal maintenance and has a long life. It generates electricity without producing emissions of greenhouse or any other gases, and its operation is virtually silent (Kazmerski 1997).

A PV cell consists of two or more thin layers of semiconducting material, most commonly silicon. Other materials used are cadmium sulphide (CdS), cuprous sulphide (Cu\textsubscript{2}S), and gallium arsenide (GaAs). When the silicon is exposed to light, electrical charges are generated and this can be conducted away by metal contacts as direct current. The electrical output from
a single cell is small, so multiple cells are connected together and encapsulated (usually glass covered) to form a module (also called a ‘panel’). The PV panel is the principle building block of a PV system and any number of panels can be connected together to give the desired electrical output. This modular structure is a considerable advantage of the PV system, where further panels can be added to an existing system as required. Photovoltaic (PV) cells are made of various semiconductors, which are materials that are only moderately good conductors of electricity (Kalogirou et al 2005).

Solar, or photovoltaic (PV), panels are an excellent choice for remote water treatment applications due several advantages that are presented as follows (Al-Madani 2003).

- Long life: solar panels have a warranty of up to 20 years, contain no moving parts, and withstand harsh environments,
- Modularity: like membrane modules, more solar panels can be added at a later stage to meet increased demand;
- Low maintenance: solar systems that do not include batteries, an inverter (to convert from DC to AC electricity), and a tracker (to make the panels follow the path of the sun across the sky) rarely break down and require very little maintenance.
- Well-matched to load: solar panels produce more power in areas that receive more sunshine, where the people are likely to face more water scarcity.
- Storage: it is possible to store energy in batteries, enabling a water treatment system to run on cloudy days or at night.
- In a tropical country like India where solar radiation/ intensity is high almost throughout the year, the energy can be efficiently utilised to make an economically feasible and sustainable treatment process.
2.11.2 Application of Some Renewable Energy Sources in Water/Wastewater Treatment Practices

Nowadays, the social concern about the environment is growing in the developed countries, and laws demanding environmental protection are being approved. This fact has led to the research and development of new forms of renewable energy and applications. Table 2.2 presents the application of renewable energy sources in wastewater treatment.

Table 2.2 Application of renewable energy sources in wastewater treatment

<table>
<thead>
<tr>
<th>Renewable energy resources</th>
<th>Mode of utilisation</th>
<th>Treatment Method</th>
<th>Water/Waste treated</th>
<th>References</th>
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<tr>
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<td>(pilot plant scale)</td>
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<td>Solar Energy</td>
<td>Direct utilisation</td>
<td>Photocatalysis</td>
<td>4-hydroxybenzoic acid (4-HBz) and benzamide (Bz)</td>
<td>Robert et al (2004)</td>
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<td></td>
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<td>(semi-pilot plant scale)</td>
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<tr>
<td>Solar energy</td>
<td>Photovoltaic cells</td>
<td>Electrodialysis</td>
<td>Reverse osmosis</td>
<td>Richards and Schiifer (2002)</td>
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<td>(pilot plant)</td>
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<td>(small scale commercial type)</td>
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<td>(lab scale)</td>
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<td>Wind energy</td>
<td>Multi blade wind mill</td>
<td>Reverse osmosis</td>
<td>Aqua culture wastewater</td>
<td>Qin et al (2005)</td>
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<td>(pilot plant study)</td>
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2.12 CONCLUSION

Textile dyeing effluents, which are highly coloured and contain high TDS needs to be treated using suitable methods prior to discharge/reuse. Based on the available literature, it could be understood that a single method may not be sufficient for complete treatment of textile effluents, hence necessitating a combination of different treatment techniques. From the literature survey it can be seen that the chemical methods such as coagulation/flocculation require large amount of chemicals and lead to production of sludge. Both the chemical and physical methods involving RO, filtration techniques etc., do not treat the pollutants but transfer them from one media to the other. On the other hand biological methods seem to be inefficient when high concentrations of dyes and salts are present. Electrochemical methods namely anodic oxidation and electrodialysis appear as a potential choice for the removal of colour and TDS respectively from the textile dyeing effluents. But the limitation associated with these processes is the formation of toxic chloroorganic compounds when anodic oxidation processes are conducted in the presence of chlorides. Other limitation associated with these processes is high energy consumption. Hence there is a need that a treatment method be identified which can overcome these limitations. Thus in our study it was aimed to avoid the evolution of chloro organics, by using sodium sulphate as electrolyte and also recover the TDS by using ED process. The limitation of high energy consumption was planned to overcome by the utilisation of abundantly available solar energy through solar panels.