**INFLUENCE OF ELECTROCHEMICAL OXIDATION IN THE PURIFICATION OF POLLUTED WATER FROM TEXTILE INDUSTRIES**

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**ABSTRACT**

The textile industries are the most polluting industries, generating large volumes of waste water during cloth dyeing and washing processes. Various chemicals such as wetting agents, dyes surfactants, fixing agents and other additives are used in wet processes (bleaching and dyeing) and as a result, large volumes of highly polluted waste water are produced. Azo dyes (compounds contain at least one – N=N –) are the most widely used colourants (accounting for up to 70% of the overall colourant production) due to their bright colours, excellent colour fastness and ease of application. It has been estimated that more than 700,000 tons of the dyes are used of which over 15-20 % are left in the effluent during the dyeing process. In electrochemical treatments, oxidation is achieved by means of electrodes where a determined difference of potential is applied and dipped in the effluent to treat. The efficiency of this method is due to the method as a function of several parameter differences of potential, the nature of the electrodes and pH. On this principle, several different processes have been developed as cathodic and anodic processes, direct and indirect electrochemical oxidation.

**Keywords:** Textile industries, Polluted water, Electrochemical oxidation, Dyes and intermediates.

* 1. **Introduction**

Water is a limited and a strategically important natural resource. It is impossible to substitute for its uses and is truly a unique gift to mankind from nature. Tirupur, which is located on the bank of the ‘Noyyal River’, though textile industry plays an important role in Indian economy, has been threatening the livelihood by discharging the effluent into the river Noyyal and nearby canals. Water shortage in many developing countries is recognised as one of the most serious political and social issues. Steps should be taken for recycling polluted water of the various industries, as water has now become a key symbol of protest around the world.

A large number of organic substances are nowadays practiced into the water system from various sources such as industrial effluents, agricultural runoff and chemical spills. Their toxicity, stability to natural decomposition and persistence in the environment has been the cause of much concern to societies and regulatory authorities around the world.

Till now, the discharging of waste into the environment has been the way to eliminate them. Dyes, phenols, pesticides, fertilisers, detergents and other chemical products are disposed of directly into the environment, without being treated, controlled or uncontrolled and without an effective treatment strategy. Colour removal from the textile polluted water has become an issue of interest during the last few years because of the toxicity of the dyes and more often the coloured polluted water from the textile industries also decreases the visibility of the receiving water.

Textile industries consume large volumes of water and chemicals for wet processing of textiles (Tim et al., 2001). More than 10,000 dyes are used in the textile industry and 280,000 tons of textile dyes are discharged every year worldwide (Hsueh et al., 2005). Textile dyeing and finishing processes produce large quantities of wastewater that is highly coloured and contains the largest concentration of organic matter (Mass and Chaudhari, 2005) which is difficult to treat via classical methods. Apart from the aesthetic problems created, when the coloured effluents reach the natural water currents, dyes strongly absorb sunlight, thus impeding the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem (Slokar et al., 1998). Tirupur in Tamilnadu state, India is well known for textile industries. There are so many textile dyeing and bleaching units scattered in and around Tirupur.

1. **Dyes and their Intermediates; Environmental Concern**

Water pollution mainly occurs due to discharge of partially or untreated industrial effluents. Textile industry is the second largest employment generator in India and also the third largest polluter in the world. The textile dyes and dye intermediates with high aromaticity and low biodegradability have emerged as major environmental pollutants
(Arslan et al., 2000 and Sauer et al., 2002) and nearly 10-15% of the dye is lost in the dyeing process and it is released in the polluted water which is an important source of environmental contamination. A considerable amount of water is used for dyeing and finishing of fabrics in the textile industries (Sumandeep, 2007).

The polluted water from textile mills causes a serious impact on natural water bodies and land in the surrounding area. High values of COD and BOD5, presence of particular matter, sediments and chemicals which are dark in colour leading to turbidity in the effluents cause depletion of dissolved oxygen which has an adverse effect on the marine ecological system. As dyes are designed to be chemically and electrochemically stable, they are highly persistent in natural environments. The improper handling of hazardous chemicals in textile water also has some serious impact on the health and safety of workers putting them into the high-risk bracket for contacting skin diseases like allergies, irritation and respiratory problems.

1. **Statistics of Discharged Dyes**

An organic colourant classified based on the percentage of Colour Index
(Sumandeep, 2007) is shown in the Table - 1.1.

**Table - 1.1 Classifications of organic colourants**

|  |  |  |
| --- | --- | --- |
| **Sl.No.** | **Nature of dyes** | **Percentage of Colour Index (%)** |
| **1.** | **Azo dyes** | **~ 60% - 70%** |
| **2.** | **Anthraquinone dyes** | **~ 15%** |
| **3.** | **Triarylmethanes** | **~ 3%** |
| **4.** | **Phthalocyanines** | **~ 2%** |
| **5.** | **Unidentified dyes** | **~ 10% - 20%** |

Reactive dyes are known to form a covalent bond with the fiber in the dyeing process. This dyeing process leads to favourable properties such as wash-fastness. However, the dyes unfixed on fiber react with water to form hydrolysed or oxo-dye intermediate. As it has lost its bonding capacity, it cannot be re-used. Therefore, dye recovery is not an option with reactive dyes and the treatment process must lead to final destruction or disposal of these contaminants.

* 1. **Methods for Removal of Dyes and other Organic Compounds from Polluted Water**

Various physical, chemical and biological pre-treatment and post-treatment techniques have been developed over the last two decades to remove colour from dye contaminated polluted water in order to meet environmental regulatory requirements. Chemical and biological treatments have been conventionally followed till now but these treatment methods have their own disadvantages. The aerobic treatment process is associated with the production and disposal of large amounts of biological sludge, while polluted water treated by anaerobic treatment method does not bring down the pollution parameters to the satisfactory level. Activated charcoal adsorption and air stripping methods simply transfer the pollutants from one medium to another. The pollutants either transfer it to the atmosphere which causes air pollution or to a solid which is often disposed of in landfills or must be treated in an
energy-intensive regeneration process. Merely, transferring the toxic materials from one medium to another is not a long term solution to the problem of hazardous waste load on the environment. The recent developments in water decontamination processes are concerned with the oxidation of these bio-recalcitrant organic compounds. These methods rely on the formation of highly reactive chemical species that degrade number of recalcitrant molecules in biodegradable compounds and are called Advanced Oxidation Processes (AOP)
(Poyatos et al., 2010).

* 1. **Advanced Oxidation Processes (AOP)**

Advances in chemical water and wastewater treatment have led to the development of methods termed Advanced Oxidation Processes (AOP) or Advanced Oxidation Technologies (AOT). AOP can broadly be defined as aqueous phase oxidation methods intermediated of highly reactive species such as (primarily but not exclusively) hydroxyl radicals in the mechanisms leading to the destruction of the target pollutants (Comninellis et al., 2008, Poyatos et al., 2010 and Pignatello et al., 2006). With hydroxyl radicals as the main oxidative agents, a complete mineralisation of pollutants to carbon dioxide, water and inorganic compounds can be obtained, or at least a conversion of the organics into highly oxidised more innocuous products can be obtained.

AOP → OH∙ Pollutants CO2 + H2O + Inorganic Compounds (Eq.1.1)

AOP can be classified as homogeneous and heterogeneous processes. Homogenous processes are further subdivided into two processes as with and without energy input
(Fig. 1.1). AOP consists with EO includes heterogeneous photo catalysis based on near ultraviolet (UV) or solar visible irradiation, alkaline ozonation, Fenton’s or modified Fenton’s chemistry and combinations of UV irradiation and chemical oxidants. Another mineralisation process normally considered as an AOP is Wet Air Oxidation (WAO), where the organics are oxidised in an aqueous medium by means of oxygen from air at elevated temperature
(250-300 °C) and high pressure (100-150 bar) with catalysts as Cu2+ present.

Water and polluted water treatments are the most common areas of research and development of AOP. Applications within groundwater treatment, soil remediation, municipal polluted water sludge conditioning, ultrapure water production, volatile organic compound treatment and odour control are also found (Comninellis et al., 2008,
Poyatos et al., 2010 and Pignatello et al., 2006). Within polluted water treatment, the core theme of research covers treatment of industrial effluents of many types including distillery, agrochemical, pulp and paper, textile dye house, oilfield and metal-plating waste. In addition, treatment of hazardous effluents including hospital and slaughterhouse wastes, removal of pathogens and persistent, endocrine disrupting pharmaceutical residues from municipal wastewater treatment effluents (i.e. After secondary treatment), removal of organic micro pollutants such as pesticides and to some extent heavy metals such as arsenic and chromium from water etc., are also major themes of polluted water treatment research
(Comninellis et al., 2008).



**Fig. 1.1 Classification of Advanced Oxidation Processes (AOP)**

**ADVANCED OXIDATION PROCESSES (AOP)**

The EO method for full mineralisation or partly conversion of organic pollutants is a technology considered very interesting for the treatment of particularly dilute wastewater (COD < 5 g/L) (Comninellis et al., 2008,) which is in competition with the processes of chemical oxidation with mixtures of strong oxidants, photo catalysis etc. (Fig. 1.1). However, some authors claim it to be feasible up to COD levels of 30 g/L (Serikawa et al., 2009) or even 100 g/L (Fryda et al., 2003). The main advantage of the EO technology is that chemicals are not used. In fact, only electrical energy is consumed in the oxidation of organic pollutants and electrochemistry is often referred to as an environmentally friendly approach, since the electron itself is considered a “clean”, safe and very effective reagent. The main processes as often stressed in the literature are (Comninellis et al., 2008 and Rajeshwar and Ibanez, 1997).

* **Versatilit*y*:** EO is generally not selective and can deal with many pollutants and treat from micro liters to millions of liters
* **Energy efficiency:** the electrochemical processes generally require lower temperature with respect to equivalent non-electrochemical counterparts (e.g. Thermal incineration), the potential can be easily controlled and operational parameters can be designed to minimise power loss
* **Amenability to automation:** the electrical parameters are used in the process and well suited for data acquisition, process automation and control

The purification by chemical procedures usually is multi-staged and gives poor result. Apart from these, many of the present chemical procedures lead to pollution. Electrochemical process remains unique, because of the nature of specific products formed and their mode of formation, in which current is a reactive input in place of redox reagents. By designing and optimising the electrolysis conditions, the desired result is obtained. Oxidation is also achieved by electrochemical method, by controlling the potential, temperature, and pH (Anthuvan et al., 2011).

For these reasons, electrochemistry and EO is a very interesting and promising alternative technology in environmental engineering for the prevention of pollution problems, especially within water treatment but the other fields of application as e.g. soil remediation does exist.

* 1. **Direct and Indirect Electrochemical Oxidation of Organic Pollutants from Textile Polluted Water**

Dye pollutants from the textile industry are important elements of environmental contamination. In a rapidly growing world population and increasing number of reports on harmful effects on the environment, protection of environment has become a major issue and a crucial factor for future technological progress which will have to meet the requirements for sustainable development. The strategies for environmental protection in industry generally include processes for polluted water treatment as well as development of new processes or products which have no or less harmful effects on the environment (Simond, 1997).

Industrial polluted water is usually treated by conventional methods such as biological oxidation (Raghukumar et al., 2008), adsorption (Gutierrez and Crespi, 1999 and
Vlyssides et al., 2002), ozonation (Sanjay et al., 2012), photochemical oxidation
(Schrank et al., 2004 and Shen et al., 2006), Ultrasonic method(Lorimer et al 2000 and Lorimer et al., 2001) and electrochemical technology (Vlyssides et al., 2004
 Szpyrkowicz et al., 2005, Rajkumar et al., 2003 and Tunay et al., 1995, Kotz et al., 1991 and Panizza and Cerisola, 2004). In recent years, there has been increasing interest in the use of electrochemical methods for the treatment of polluted water. Electrochemical methods have been successfully applied in the purification of several industrial polluted water such as textile (Mohan et al 2001), tannery phenol solution (Vaghela et al., 2005). Poly aromatic organic pollutants (Tunay et al., 1995), textile dye and finishing process in textiles are among the major industrial water users; in many areas, this industry has the pollutants which are most difficult to treat satisfactorily. The major problem in the polluted water from the finishing process in textiles is strong colour and high COD (Karlis and Zorpas, 2000). The organic and toxic pollutants present in treating polluted water such as dyes are usually destroyed by a direct anodic process or by an indirect anodic oxidation. The time of oxidation depends upon the stability and concentration of compounds, concentration of NaCl, solution pH and applied voltage (Szpyrkowicz et al., 2005).

The direct electro-oxidation rate of organic pollutants is dependent on the catalytic activity of the anode, diffusion rates of organic compounds in the active points of the anode and the applied current density Fig.1.2.

 **Pollutants**

 **Electron**

 **Destroyed Pollutants**

 **Anode**

**Fig. 1.2 Direct oxidation on anode**

The indirect electro-oxidation rate depends on the diffusion rate of secondary oxidants into solution, temperature and pH. The effective pollutant degradation is based on the direct electrochemical process because the secondary oxidants are able to completely convert all organics into water and carbon dioxide Fig.1.3**.**

 **Pollutants Pollutants**

 **Oxidation in the bulk**

 **Oxidant**

 **Destroyed pollutants**

**Anode**

**Fig. 1.3 Indirect oxidation mechanism in bulk solution**

In acid solution, oxygen, free chlorine, some amounts of ozone and chlorine oxides are the secondary main oxidants as by-products of the direct oxidation process. In moderate alkaline solution, a cycle of chloride-chlorine-hypochlorite-chloride takes place. This cycle produces OCl–, oxygen, some amounts of hydrogen peroxide and ozone. In the strong alkaline solutions, the cycle of chloride-chlorine-chloride is reduced, owing to the production of ClO-3, which is a chlorate anion. Therefore, in low pH, the chlorides are reduced during the electrolysis process to produce free chlorine, while at high pH values, the chlorides are reduced producing chlorates (Szpyrkowicz et al., 2005 and Panizza and Cerisola, 2004).

Water has a number of unique characteristics that are essential for life and that determine its environmental and chemical behavior. Many of these characters are due to the polar nature and the ability to form hydrogen bonds in water molecules. Water has the highest di-electric constant of any common liquid, a more density as a liquid at 400C and a higher heat capacity than any other liquid except ammonia. But most of the important chemical phenomena associated with water do not occur in solution, rather through the interaction of solutes in water with other phases. For example, the redox reactions catalysed by bacteria occur in bacterial cells. Many organic hazardous wastes are carried through the water as emissions of very small particles suspended in water. Some hazardous wastes are deposited as sediments in water bodies from which they may later enter into water through chemical or physical processes and cause severe pollution and need to be eliminated as much as possible.

The Electrochemical method of de-pollution presents many important advantages, (Anthuvan et al., 2012).

* It does not need auxiliary chemicals,
* It is applicable on a large range of pollutants,
* It does not need high pressure and temperature.

There is a new research on the electrochemical oxidation of organic compounds from the polluted water, due to its greater efficiency and the excellent control. The EO of pollutants from polluted water was studied using anodes made from different materials.

1. **Benefits of Electrochemical Oxidation over Others**

Different treatments to decolourise and degrade dyeing polluted water have been attracted increasing interest since the majority of the dyes are not degradable in conventional wastewater treatment plants (Martínez-Huitle and Brillas, 2008). Then, a wide range of methods have been developed for this purpose. Ozonation (Wang et al., 2003), advanced oxidation (Neamtu et al., 2003; Swaminathan et al., 2003; Lucas et al., 2007; Nuñez et al., 2007), enzymatic (Peralta-Zamora et al., 1999) or adsorption processes (Dávila-Jiménez et al., 2005) have been studied recently for the removal of different dyes. Over the past 10 years, the electrochemical techniques have been found of special interest for polluted water remediation. Among all their advantages, it is interesting to notice that there is a high yield of colour removal and COD reduction of polluting substances with maximum energy resource management.

Moreover, these techniques show facility and precision of control of the electrochemical process (since the electron is the main reagent) and a compact design (Genders and Weinberg, 1992). To improve electrochemical treatment efficiency, many researchers have focused on the electrode development.

* 1. **Electrochemical Oxidation of Textile Polluted Water and Its Reuse**

The day-to-day human activities and industrial revolution have affected the flow and storage of water and the quality of available fresh water. Many industries like textile, refineries, chemical, plastic and food-processing plants produce polluted water characterised by a perceptible content of organics (e.g. phenolic compounds) with strong colour. For example, a typical textile dyeing process consists of desizing, scouring, bleaching, dyeing, finishing and drying operations. Except the last two stages, each operation is associated with rinsing step which requires large amount of water. In general, textile industries generate effluent at an average of 100–170 L/kg of cloth processed, which is characterised by strong colour, high COD with wide variation in pH (Rajagopalan, 1989 and Panchiao, 1994).

Conventionally effluents containing organics are treated by adsorption, biological oxidation, coagulation, etc. Though the conventional methods have individual advantages, they are lacking effectiveness if applied individually. For example, biological treatment is the most efficient and economical way of reducing the environmental impact of the industrial effluents containing organic pollutants, but this technique is time consuming and cannot be employed in textile effluent, as textile effluent is recalcitrant to biodegradation. On the other hand, the physical adsorption is expensive and difficult for adsorbent regeneration. Further, biological and chemical methods generate a considerable quantity of sludge which itself requires treatment. Due to the large variability of the composition of textile polluted water, most of the traditional methods are becoming inadequate (Hao et al., 2000 and
Sakalis et al., 2005).

As environmental regulations have become stringent, new and novel processes for efficient treatment of various kinds of polluted water at a relatively low operating cost are needed. For this, scientists are trying the electrochemical technique method for the degradation of organic compounds. Among the advanced oxidation processes (Fig. 1.1), the electrochemical treatment has received greater attention in recent years, due to its unique features, such as versatility, energy efficiency, automation and cost effectiveness (Gutierrez and Crespi, 1999 and Lorimer et al., 2001).

Comninellis, 1994 experimented anodic oxidation of phenol in the presence of NaCl using tin oxide coated titanium anode and reported second order kinetics for the degradation of phenol at the electrode surface. Fernandes et al., 2004 studied the degradation of C.I for Acid Orange 7 using boron-doped diamond electrode and reported that more than 90% of COD reduction. Anastasios et al., 2005 demonstrated 94% dye removal using a pilot plant electrochemical reactor for textile polluted water treatment.

The use of new anodic materials like Boron-doped diamond (BDD) has also been reported in recent years as BDD electrodes present additional properties including high resistance to corrosion, high thermal stability, hardness, good electrical conductivity, etc., Panizza et al., 2001 demonstrated 2-naphthol oxidation in acid media using synthetic BDD thin film electrodes and reported complete incineration of 2- naphthol.

Bellagamba et al., 2002 reported on electro combustion of Polyacrylates [PA], under galvanostatic conditions using BDD anode at various current densities and in a wide range of PA concentrations. Canizares et al., 2005 studied the electrochemical oxidation of several phenolic aqueous pollutants using bench-scale electrochemical flow cell with boron-doped diamond anode. Complete mineralisation of the waste is obtained in the treatment of phenols when chlorine or nitrogen was not present in the phenols. The authors reported that the efficiencies of the process depend strongly on the concentration of organic pollutants and on their nature and not on the current density, at least in the operation range studied.

The above cited works are intended to treat the textile polluted water to a level which meets the discharge standards of TNPCB. However, due to dwindling water supplies, increasing demand of the textile industries and stringent pollution control board regulations, a better alternative is to further elevate the quality of treated polluted water to a standard where it can be reused.

**1.9 The Principles and Mechanisms in Electrochemical Oxidation (EO)**

The mechanism of electrochemical oxidation of polluted water is a complex phenomenon involving the coupling of electron transfer reaction with a dissociate chemisorptions step. Basically two different processes occur at the anode; on anode having high electro-catalytic activity, oxidation occurs at the electrode surface (direct electrolysis); on metal oxide electrode, oxidation occurs via surface mediator on the anodic surface where they are generated continuously [indirect electrolysis]. In direct electrolysis, the rate of oxidation is depending on electrode activity, pollutants diffusion rate and current density. On the other hand, temperature, pH and diffusion rate of generating oxidants determine the rate of oxidation in indirect electrolysis. In indirect electro-oxidation, chloride salts of sodium or potassium are added to the wastewater for better conductivity and generation of hypochlorite ions (Rajeshwar and Ibanez, 1997). The reaction of anodic oxidation of chloride ions to form chlorine is given as

 *k1*

2Cl −   Cl2 + 2e− (Eq. 1.2)

The liberated chlorine forms hypochlorous acid (Eq.1.2)

 *k2*

Cl2 + H2O H++ Cl−+ HOCl(Eq. 1.3)

Which is further dissociated to give hypochlorite ion (Eq.1.3)

 *k3*

HOCl H+ + OCl−  (Eq.1.4)

 *k13*

The generated hypochlorite ions act as main oxidising agent in the pollutant degradation. The direct electro-oxidation rate of organic pollutants depends on the activity of the anode, on the diffusion rate of the organic compounds in the active points of anode and applied current density. A generalised scheme of the electrochemical conversion or combustion of organics of pollutant (Panizza and Cerisola, 2004)on anode (MO*x*) is given below. In the first step, H2O is discharged at the anode to produce adsorbed hydroxyl radicals according to the reaction.

MO*x* + H2O MO*x*(•OH) + H+ + e− (Eq.1.5)

In the second step, generally, the adsorbed hydroxyl radicals interact with the oxygen which is already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the oxide forming the higher oxide MO*x*+1.

MO*x*(•OH) MO*x*+1 + H+ + e− (Eq.1.6)

At the anode surface, the “active oxygen” can be found in two states: either as physisorbed (adsorbed hydroxyl radicals (• OH)) or as chemisorbed (oxygen in the lattice (MO*x*+1)). In the absence of any oxidisable organics, the “active oxygen” produces dioxygen according to the following reactions:

MO*x*(•OH) MO*x* + ½ O2 + H+ + e−  (Eq.1.7)

MO*x*+1 MO*x* + ½ O2 (Eq.1.8)

When NaCl is used as supporting electrolyte Cl- ions react with MO*x*(•OH) to form adsorbed •OCl radicals according to the following (Raghu and Ahmed, 2007),

MO*x*(•OH) + Cl− MO*x*(•OCl) + H+ + 2e− (Eq.1.9)

Further, in the presence of Cl- ion, the adsorbed hypochlorite radicals interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hypochlorite radical to the oxide forming the higher oxideMO*x*+1 according to the following reaction and also MO*x*(•OCl) simultaneously react with chloride ion to generate active oxygen (dioxygen) and chlorine according to the following reactions:

MO*x*(•OCl) + Cl− MO*x*+1 + Cl2 + e− (Eq.1.10)

MO*x*(•OCl) + Cl− MO*x* + ½ O2 + ½ Cl2 + e− (Eq.1.11)

In the presence of oxidisable organics, the physisorbed “active oxygen” (•OH) should be a cause predominantly for the complete combustion of organics and chemisorbed will participate in the formation of selective oxidation products (Vlyssides et al., 2004) according to the following reactions:

½ R + MO*x*(•OH) ½ ROO + H+ + e− + MO*x* (Eq.1.12)

R + MO*x*+1 RO + MO*x* (Eq.1.13)

The physisorbed route of oxidation is the preferable way for polluted water treatment.

It is probable that the dioxygen participates in the combustion of organics also according to the reactions, such as formation of organic radicals by a hydrogen abstraction mechanism: RH + •OH → R + H2O; reaction of organic radical with dioxygen formed at the anode: R• + O2 → ROO• and further abstraction of a hydrogen atom with formation of an organic hydrogen peroxide (ROOH) and other radical; ROO• + R’H → ROOH + R’. Since, the organic hydrogen peroxide formed is relatively unstable, decomposition of such intermediates leads to molecular breakdown and formation of subsequent intermediates with lower carbon numbers. These sequential reactions continue, until the formation of carbon dioxide and water. In this case, the diffusion rate of organics on the anode area controls the combustion rate (Panizza et al., 2001 and Vlyssides et al., 2004). In the same way, indirect electrochemical oxidation mechanism has been proposed for metal oxide with chloride as supporting electrolyte for wastewater treatment (Buso et al., 2000 and Rajkumar et al., 2003). The role of hypochlorite in the electrochemical treatment of dye effluent via chlorine generation is

 *k4*

Dye + OCl−  CO2 + H2O + Cl− + P (Eq.1.14)

Since dye molecules of the effluent are electrochemically inactive, the reaction occurs at the anodes is chloride ion oxidation with the liberation of Cl2 which is a robust oxidising agent. As regards to the reactions in the bulk, gaseous Cl2 dissolves in the aqueous solutions due to ionisation as indicated in Eq.1.3. The rate reaction is less in acidic solution due to OH− instability and considerably more in basic solution due to ready formation of OCl− (p*K*a 7.44) ion in Eq.1.4 implying that the basic or neutral pH conditions are more favourable for conducting reactions involving Cl2. A cycle of chloride–chlorine–hypochlorite–chloride takes place, which produces OCl−. The Pseudo Steady State Theory will be applied to each of the intermediate products (HOCl and OCl−) taking part in the bulk solution. Taking all other reactions as irreversible processes, the rates of reactions *ri* specific for the sequence are
(Eqs. (1.1) – (1.4) and (1.14))

−*r*Cl2 = *k*2[Cl2] (Eq.1.15)

*r*HOCl = *k*2[Cl2] − *k*3[HOCl] + *k’*3 [H+][OCl−] = 0 (Eq.1.16)

*r*OCl− = *k*3[HOCl] – *k’*3 [H+][OCl−] − *k*4[Dye][OCl−] = 0 (Eq.1.17)

−*r*Dye = *k*4[Dye][OCl−] (Eq.1.18)

Then using Eqs. (1.15) and (1.18)

−*r*Cl2 = −*r*Dye = *k*4[Dye][OCl−] (Eq.1.19)

Finally, as regards to bulk solution, it is also to be noted that −*r*Cl2 = *r*Cl− from material balance of Eq. (1.14), that is,

Where *ri* (*i* = 2, 3 and 4),is the rate of reactionand the rate constants *ki* (*i* = 2, 3 and 4) are defined with respect to the bulk and the rate expression for the main electrode reaction as per the Eq. (1.2) can be written as,

−*r*Cl2 = *r*Cl− = *k*2[Cl2] = −*r*Dye = *k*4[Dye][OCl−] (Eq.1.20)

−*r*Cl− = −*r’*Cl2 = *k*1[Cl−] (Eq.1.21)

Where, *k*1 is the heterogeneous electrochemical rate constant. Hence, in the following section, an attempt has been made to establish a relationship between the reacting species in bulk and at the electrode surfaces. The basic relationship applies to all electrochemical reactions. Faraday’s law that relates to the amount of substance reacted at the surface of the charge (*I*A*t*) passed is’ (*M*A*I*A) *t)* /(*NF*) (assuming 100% current efficiency) and the characteristic measurable parameter is the current density, *I*A, which is *I*A/*A*e. Thus, the electrochemical reaction rate (for the disappearance of reactant A) can be expressed as,

- (*V*R/ *A*e ) d[*A*] /d*t* = *i*A / *nF* (Eq.1.22)

Where,

*I*A is the current passed in time *t*

*n* isthe number of electrons transferred per mole of reaction

*A*e the electrode area

*V*R the reactor volume and

*F* is the Faraday (96,500 C or As/Mol).

It has to be noted −*r*A = −d[*A*]/d*t* = *i*A *a*/*nF*, where *a* is specific electrode area (*A*e/*V*R). Assuming the main electrode reaction is governed by a simple Tafel type expression, then

- (*V*R /*A*e ) d[*A*] /d*t* = *i*A /*zF* = *k’*[*A*]exp(*bE*) (Eq.1.23)

or

−*r’*Cl = *r’*Cl2 = *k*1[Cl−] = *k*1*’a*[Cl−]sexp(*bE*) (Eq.1.24)

The reaction is assumed to be under diffusion control as the reacting species, Cl− in the electrolyte is diluted. The reactant Cl− is transported for the bulk to electrode surface, where, it undergoes electrochemical oxidation to Cl2 and it will be transported back to bulk by diffusion reaction in the bulk. Then,

*i*A/ *zF* = *k*1([Cl−] − [Cl−]s) (Eq.1.25)

Elimination of [Cl−]s using Eqs. (1.24) and (1.25) results can be written as,

*i*A /*zF* = *k*1[Cl−] (Eq.1.26)

Where,

1/*k*1 = 1/*k*1 + 1/*k’a* exp(*bE*) (Eq.1.27)

From a material balance of species Cl− by taking note of Eqs. (1.13) and (1.14)

*i*A/*zF* = *k’*[Cl2] (Eq.1.28)

*i*A/*zF* = *k”*[Dye][OCl−] (Eq.1.29)

During electrolysis, since the constant current is applied, the rate of generation of [OCl−] will remain constant under a given set of experimental condition, but it varies as the applied current is altered. Then,

*i*A/*zF* = *k*obs[Dye] = *k*[COD] (Eq.1.30)

Adopting the same classification for the reactors as of conventional reactors, thus the electrochemical reaction rate (for reduction of COD) can be expressed as,

- (*V*R/ *A*e ) d[COD] /d*t* = *i*A *nF* = *k*[COD] (Eq.1.31)

or

ln([COD]o [COD] ) = *kat* (Eq.1.32)

In electrochemical conversion, the high molecular weight aromatic compounds and aliphatic chains are broken to intermediate products for further processing. In electrochemical combustion, the organics are completely oxidised to CO2 and H2O. The progress of the destruction of the organic pollutant has been monitored by COD estimation. The COD has been estimated for all the experimental runs in the present investigation and critically examined (Anthuvan et al., 2012).

The textile industry is one of the oldest and largest sectors in India. At present it is amongst the top foreign exchange earning industries in India (Naik, 2001). The textile units are scattered all over India; out of 21,076 units, Tamilnadu alone has 5285 units (Bal, 1999). The textile industry involves processing or converting raw material into finished cloth employing various operations. It consumes large quantities of water and produces polluting waste effluents (Karthikeyan and Venkatamohan, 1999).



**Fig. 1.4 Polluted water at Kasipalayam, downstream of the Noyyal river in Tirupur**

Tirupur is a fast growing industrial District in Tamilnadu, also known as the
‘Banian City’ of India. It is located on the bank of the Noyyal River, a tributary of the River Cauvery. The hosiery industry in Tirupur provides a substantial contribution to the economy in the form of income, employment and foreign exchange generation (Geetha et al., 2008). However, the rapid growth of the industry has resulted in serious environmental problems, especially from the bleaching and dyeing units. Hence, there is evidence to suggest that these units extract a considerable quantity of ground water from the peripheral areas and discharge the effluents of TDS and various salts due to industrial pollution. Environmental pollution is an ‘externality’ which is present in welfare economics. According to Xia Guangs’ view, when the individuals’ values are chosen by others (as persons, corporations and governments), it must include the relationship of the individuals’ utility and production.

The tolerance limit of textile industry effluents in Tirupur District is governed by TNPCB. According to TNPCB norms, the textile dye effluent discharge into natural water systems is shown in Table - 1.2.

**Table – 1.2 Tamil Nadu Pollution Control Board (TNPCB) norms for Textile dye effluent discharge into natural water systems**

|  |  |  |  |
| --- | --- | --- | --- |
| **S.No.** | **Characteristics** | **Unit** | **Tolerance Limit** |
| **1.** | **pH** |  | **5.5 – 9.0** |
| **2.** | **Temperature** | **0C** | **40 0C** |
| **3.** | **TSS** | **mg/L** | **100** |
| **4.** | **TDS** | **mg/L** | **2100** |
| **5.** | **BOD; 5days @20 0C** | **mg/L** | **30** |
| **6.** | **COD** | **mg/L** | **250** |
| **7.** | **Chloride (as Cl)** | **mg/L** | **1000** |
| **8.** | **Fluoride (as F)** | **mg/L** | **2** |
| **9.** | **Phenolic compounds** | **mg/L** | **1** |
| **10.** | **Oil and grease** | **mg/L** | **10** |
| **11.** | **Total residual chlorine** | **mg/L** | **1** |

* 1. **The Objectives of the Work Undertaken**
1. The main objective is the effluent purification from its dyes in an economically affordable method and efficiently higher method. It will be useful for the textile industries.
2. Optimisation of the electrochemical degradation process by varying operational parameters like anode, pH, supporting electrolyte and current density etc., for improving effectiveness of the process.
3. Electrochemical degradation studies of various dyes and their intermediates.
4. **Approach Adopted**
5. Control experiments are done with electrochemical degradation process.
6. Mainly water-soluble reactive dyes, dye intermediates and textile effluent are electrochemically degraded by varying the initial concentration of dye, current density, concentration of supporting electrolyte and pH (adding HCl or NaOH) by electrochemical oxidation.
7. Different anodes like Graphite, Pt, Stainless steel (304) and Pb/PbO2 are tried for the above mentioned compounds to find the most effective anode.
8. Synthetic and real polluted water are decolourised electrochemically.
9. Influence of supporting electrolyte and substituent on the electrochemical oxidation of synthetic dye in aqueous solution are studied.
10. Since harmful chemicals are not used for this purification of effluent by the electrochemical oxidation method. It is considered that, this method is one of the best pretreatment methods for effluent treatment.

The effluents from various textile industries in Tirupur District were collected and
pre-treated by an electrochemical degradation method. The change in the water quality parameters was repeatedly done for various samples and analysed. The dyes present in the effluents were analysed.

**The Main Scope of Polluted Water Treatment is,**

1. To treat the effluents from textile industries in Tirupur.
2. To improve the various water quality parameters.
3. To treat all the impurities present in the effluents before it has been disposed outside i.e. into the ground. Thus the pollution of soil as well as ground water can be prevented.
4. The biodegradability of the effluents can be improved. The treated water can be converted into good water through biodegradation.
5. The fully treated water can also be reused in the industries for various purposes. (Irrigation, plants, domestic usages, Industrial needs, etc.,)

**CONCLUSION**

In Tirupur District, most of the textile industry effluents contain organic dyes as the major pollutant. The conventional polluted water treatment methods such as biological treatment (Chatezisymeon et al., 2009), chemical precipitation, adsorption by activated carbon (Konstantinos, 2010), photocatalytic oxidation (Yousuf et al., 2010), ozonation
(Ahmed et al., 2010) etc. could not remove the organic dye pollutants effectively compared to other water quality parameters such as TDS, TSS, Chloride, Fluoride etc. So, indirect electrochemical degradation method was used for converting the organic dye pollutants into inorganic substances as shown in Equation. The inorganic substances that one got from conversion could be removed by conventional polluted water treatments easily.

 EOP → OCl-  Dye pollutants  CO2 + H2O + Inorganic substances

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