1.2 POLLUTION PREVENTION IN TEXTILE DYEING INDUSTRIES

Although water on earth is abundant, 97 percent is salt water, 2 percent is in ice and only 1 percent is available as fresh water in which the groundwater accounts for 0.98 percent. Hence, only 0.02 percent of total amount of water on earth is available in rivers, lakes and streams (Perkins 1999). Therefore, it becomes necessary to conserve, recycle and reuse the limited water resources.

In India, the Water (Prevention and Control of Pollution) Act was enacted in the year 1974 to prevent and control water pollution. Under this act, the tolerance limits have been set for the discharge of industrial wastewater. The textile dyeing industries are placed under the category of highly polluting industries and the removal of colour from the textile dyeing wastewater has been brought under the purview of legal and regulatory requirements (Central Pollution Control Board 1999-2000).

Due to stringent environmental regulations, the textile dyeing industries are switching over from the traditional “end of pipe treatment” to “Pollution Prevention” measures such as process modification and improved operating practices. These measures aim at the maximum reduction of pollutants at the source itself. One such measure is the introduction of cleaner technology namely the use of ‘Low salt / High fixation dyeing’ (Girod 1998). The low salt dyes are getting practiced in the dyeing process in the textile industries in Tirupur, Tamilnadu (Kanmani and Thanasekaran 2000). The low salt dyes require less salt for dye fixation (Janakiraman 1998). Also, an improved operating practice of separation of wastewater into two streams,
namely dye bath wastewater (high salt content) and rinse wastewater (less salt content) is practiced in the industries.

1.3 DECOLOURISATION METHODS

The various physical, chemical and biological processes used for the removal of colour from the wastewater fall into two main categories viz., separation of the colour component and decomposition of the colour component. Chemical coagulation and adsorption fall into the first category and the biological (aerobic and anaerobic) oxidative degradation and reduction techniques fall into the second category (Elliott 1996).

1.3.1 Separation Techniques

In chemical coagulation, coagulants such as alum, lime, ferrous and ferric sulphate are applied at a dose of 300 - 600 mg/L (UNEP 1994). However, it cannot achieve satisfactory removal of soluble dyes. Adsorption has been studied extensively as a decolourisation method for different classes of dyes. Although carbon adsorption of dyes is neither efficient nor economical when used alone, when used with chemical coagulation, it becomes a very useful polishing step for efficient dye removal (Reife and Freeman 1996). However, the separation techniques are not environment friendly since they generate large amount of sludge that require disposal. In addition to the above, membrane-based separation processes have been developed. It can achieve satisfactory colour removal from dye-containing wastewater at source and produce water of reusable quality. It is considered as a waste minimisation or source reduction technique (Elliott 1996). However, the application of this technique is limited by the problem of disposal of the concentrate stream such as evaporation or
ocean discharge that are either economically or environmentally unacceptable (Gravelet et al 1996).

1.3.2 Decomposition Techniques

In the oxidative decolourisation using conventional oxidising agents, chlorine is often used to decolourise the wastewater. It is applied in the form of liquid or gas, chlorine water or hypochlorite. The drawback of this technique is that it has potential for generating chlorinated organics that are harmful to both humans and the environment. At a chlorine level of 150 mg/L, colour was reduced by 77%, but 110 mg/L of total chlorine remained in the wastewater. At chlorine doses below 100 mg/L, no residual chlorine was detected, but only 57% of the colour was removed (Dubrow et al 1996).

Chemical reduction of azo dyes to aromatic amines by sodium hydrosulfite is an effective decolourisation technique. However, there is a possibility of the potential reversal of the reaction upon exposure to oxygen and reappearance of colour. Also, either the reducing agents or aromatic amines generated from the reductive cleavage of azo bonds may be toxic to microorganisms in the biological treatment plant (Dubrow et al 1996).

Aerobic biological degradation, the traditional treatment method is inadequate since most dyes are resistant to biodegradation. It becomes difficult to apply this technique since the dyeing wastewaters require longer period of acclimation and are slow to degrade (Uygur 1997). In the decolourisation by anaerobic treatment, the reduction of azo dyes to aromatic amines takes place. Since the amines are toxic, they may further be treated in aerobic biological treatment (Dubrow et al 1996).
1.3.3 Advanced Oxidation Processes

In recent years, Advanced Oxidation Processes (AOPs) have been proposed as potential alternative decolourisation techniques for the removal of non-biodegradable dyes (EPA 1990, Carey 1992 and Braun and Oliveros 1997). They are based on oxidative degradation initiated by hydroxyl radicals (OH\textsuperscript{•}) that are generated by an oxidant (e.g. hydrogen peroxide, ozone) with or without a source of UV light. The advantages of these systems over conventional chemical oxidation processes is due to the generation of highly reactive free radicals which are 10\textsuperscript{6} - 10\textsuperscript{9} times faster than the strong oxidants such as ozone and hydrogen peroxide (Ince and Tezcanli 1999).

In the oxidative decolourisation techniques, oxidation with hydrogen peroxide requires long reaction time and oxidation with ozone is costly (Uygur 1997). The photooxidative decolourisation techniques using hydrogen peroxide and ozone require high-energy irradiation and hence they are not economical. The semiconductor photocatalysis has emerged as the third in the series of advanced oxidation processes (Ollis and Turchi 1990). It has unique advantages over other advanced oxidation methods.

1.4 SEMICONDUCTOR PHOTOCATALYSIS

Like air and water, light is needed for life. Light is a form of energy characterised by waves and can be classified by wavelength, which is the distance between the crests. Photocatalysis is a technology, which utilises light energy in a completely new and different manner. Scientific studies carried over the past three decades have proved the effective use of this technology to keep our environment clean. Hence 'environmental pollution control and clean up
with light' (called Light Cleaning) is considered to be the most promising application of photocatalysis. The two main factors involved in Light Cleaning are the UV light radiation and a semiconductor that can be activated by light energy. The photoactivity of the semiconductor tends to decompose organic materials that come in contact with it, in the presence of air (Fujishima 1999).

1.4.1 Solar Light as Energy Source

The solar light is the most direct and bountiful source of energy. It emits energy in the form of electromagnetic radiation distributed over a wide range of wavelengths. Wavelengths shorter than 400 nm are described as ultraviolet, whereas wavelengths longer than 700 nm are infrared (Mitra 1996). The visible region lies in between the UV and infrared and it is made up of seven colours. Almost the entire solar spectrum below 300 nm is absorbed by atmospheric ozone and only three to six percent of solar radiation is found to be in the ultraviolet region of 300 – 400 nm. Field studies have proved the potential of solar UV radiation as energy source in photocatalysis (Turchi et al 1993, Goswami et al 1993 and Bahnemann 1999).

The global or total solar radiation is made up of two components viz., direct and diffuse radiations. The direct radiation is received at the earth surface without the change of direction i.e. in line with the sun. The diffuse radiation is received at the earth surface from all parts of the sky’s hemisphere after being subjected to scattering in the atmosphere (Sukhatme 1996). The intensity of global solar radiation varies from 0.55 KWh/m²/day in a northern winter to an average of 55.5 KWh/m²/day in the tropical regions (Viswanathan, 1995).
1.4.2 Titanium Dioxide as Semiconductor

Titanium dioxide (TiO$_2$) is used for many purposes in our daily life. As a ceramic, it is polymorphous occurring as brookite, anatase and rutile forms. It has been used widely as a white pigment in a variety of paints, cosmetics and foodstuffs. Almost 2.2 million tons of rutile TiO$_2$ is used for the white highway paints in a year (Whipple 1999).

About two decades ago, the photocatalytic activity of the anatase TiO$_2$ as a semiconductor was found. The necessary condition for the semiconductor to become photoactive is that the energy of light radiation should exceed the energy of the band gap of the semiconductor. At that condition, holes (h') and electrons (e') are created in the valence and conduction bands respectively of the semiconductor. The holes can react with surface bound hydroxyl groups (OH$^-$) to generate hydroxyl radicals and electrons (e') react with oxygen to generate superoxide ion radicals. The hydroxyl radicals are powerful oxidants and have more oxidation potential than chlorine, hydrogen peroxide and ozone by 2.05, 1.58 and 1.35 times respectively (Zhu et al 1995).

The hydroxyl radical oxidises organic pollutants that come in contact with it. A number of organic compounds e.g. halogenated compounds, alcohols, aldehydes, ketones, carboxylic acids, ethers, esters, amines, nitro compounds, thioethers and mercaptants can be oxidised by the photoactive TiO$_2$. In addition, the TiO$_2$ as a photocatalyst is found to be biologically and chemically inert, nonsoluble, nontoxic, photostable and maintains photoactivity during reuse (Mukherjee and Ray 1999). According to National Institute for Materials and Chemical Research in Japan 'many works which have been devoted to find
a better semiconductor than TiO$_2$ were not successful and only TiO$_2$ is considered practical' (Whipple 1999).

There is a growing interest in the application of TiO$_2$ photocatalysis in areas other than oxidation of organic pollutants. The TiO$_2$ photocatalysis can be used to destroy bacterial contaminants in water and hence it has potential as a photodisinfectant (Dillert et al 1999). It can be used to kill cancer cells and thus it has potential as a ‘photochemical therapy’ in the treatment of cancer. It can also be used as photodeodorant to destroy volatile organics in air (Mills et al 1993). It can be used to keep windshields, mirrors and eyeglasses from being fogged with water vapor and hence it can be used as hydrophilic photocatalyst. The antibacterial, stain-resistant and deodorising functions of TiO$_2$ are being explored in Japan, which uses 1,77,000 tons of TiO$_2$ per year (Whipple 1999).

1.4.3 Solar Photocatalysis

In solar photocatalysis, the solar UV radiation is used as the energy source for activating the semiconductor, TiO$_2$ having a band gap of 3.2 eV. The activated photocatalyst decomposes various organic pollutants such as solvents, alcohols, dyes and fuel oils, which come into contact with it. Solar photocatalysis is considered to be an alternative industrial wastewater treatment method because of various advantages listed below.

- The renewable solar radiation is used as the light source for photoactivation.
- The non-toxic and non-soluble TiO$_2$ is used as the photocatalyst.
- The TiO$_2$ can be recovered and reused.
- There is no transfer of pollutant from one medium to another.
1.5 NEED FOR THE STUDY

Scientific research in the last 30 years has shown great potential for using solar photocatalysis in treating industrial wastewaters (Goswami 1997). Blake (1995) published a bibliography in which he compiled a list of 300 compounds, which can be degraded by photocatalysis. Field studies on a number of concentrating and non-concentrating reactors (e.g. parabolic trough reactor, double skin sheet reactor, tubular flat reactor, trickle down flat reactor and thin film fixed bed reactor) have also proved the potential of solar photocatalysis (Turchi et al 1993, Goswami et al 1993 and Bahnemann 1999). But despite its great potential, there have been only two pilot scale demonstrations reported in literature, one for treating groundwater in US and the other for treating industrial wastewater in Spain (Goswami 1997). Hence, in order to facilitate industrial scale applications of solar photocatalysis, development of a simple, efficient and economic solar photoreactor is considered to be the need of the hour.

In solar photocatalysis, when the solar UV light is absorbed by the photocatalyst, two types of charge carriers viz., electrons (e\textsuperscript{-}) and holes (h\textsuperscript{+}) are generated which can be used for chemical oxidation and reduction (Fujishima 1999). But to ensure efficient conversion of incident solar UV light photons to charge carriers, a solar photoreactor has to be developed scientifically. The scope of the present study was to develop such a solar photoreactor and to demonstrate its applicability for the decolourisation of low salt textile dyeing wastewaters in order to facilitate the possible transfer of technology to the industry.
1.6 OBJECTIVES OF THE STUDY

The present study had the following objectives:

- To conduct laboratory-scale feasibility studies on photocatalytic decolourisation of low salt cotton textile dyeing wastewaters with Degussa P25 and indigenous IS grade TiO$_2$ catalysts under UV and solar light sources.

- To study the effect of various operating variables viz., pH, catalyst concentration, inorganic ions, catalyst reuse and solar UV light intensity on the rate of decolourisation of textile dyeing wastewaters.

- To develop bench-scale solar photoreactors (Water-bell fountain type) of suspended catalyst system and to study the performance of the reactors for decolourisation of textile dyeing wastewaters.

- To study the influence of various operating variables of the reactors in batch and continuous flow modes so as to arrive at the design parameters for a pilot scale reactor.

- To design a pilot scale reactor for solar photocatalytic decolourisation of textile dyeing wastewater and to arrive at the costs.