CHAPTER 1

INTRODUCTION

1.1 GENERAL

Reclamation of wastewater has been practised in many parts of the world. In the developing countries, particularly those in the arid parts of the world, there is an urgent need to develop low cost methods for generating new water supplies and protecting the existing water sources from pollution. These methods should include measures to encourage conservation of water, conjunctive use of surface and ground water, wastewater reclamation and reuse. As the demand for water increases, so does the importance of wastewater reclamation and reuse. While the estimation of most of the parameters of pollution requires careful analysis, it is easy to detect the colour present in water. It has been observed that the visible pollution caused by textile dyeing wastewater draw public attention immediately. Hence, colour in water is a major environmental concern.

The colour, if not properly dealt with would have a strong negative impact on the aquatic environment. Discharge of coloured wastewater into natural water bodies is not desirable as they are not only aesthetically displeasing, but also prevent re-oxygenation in receiving water by cutting off penetration of sunlight, and upset the biological activity in natural water.

The presence of colour in water may be due to the wastes discharge from distillery, pulp and paper and textile industries. The wastes from dyeing operations in the textile industries may contain dyes of various
intense colours. Most of the dyes have been found to be low biodegradable in nature (Dubrow et al 1996). Recent studies show that some dyes can be carcinogenic (Smith 1996). Colour render water unfit even for secondary uses like washing, since it is a primary criterion for water quality. Hence, there is a necessity for removal of colour from water.

1.2 SILK DYEING WASTEWATER RECLAMATION

Silk fibre, because of its natural beauty, lustre and charm, is called the queen of textiles. Silk is a valuable fibre. Inspite of the advent of many synthetic fibres resembling, silk is still preferred particularly by women for their dress wear. Many traditional small scale silk dyeing cottage industries have been in existence for generations all over India. Typical cottage silk dyeing units located in Kanchipuram (Tamilnadu, India), process about 5 to 20 kgs of yarn per day and use about 100 litres of drinking water for every kg of yarn processed. The wastewater discharge from a typical silk dyeing cottage industry is in the order of about 500 to 2000 litres per day. Frequent changes of dye stuffs employed in the dyeing process cause considerable variations in the wastewater characteristics.

Since 70 to 80% of the wastewater from silk dyeing industries is from the rinse operations and less coloured, there is ample scope for reclamation of such wastewater by decolourisation. Besides, the batch process adopted in cottage industries does not pose operational problems for segregation of such wastewater for reclamation. While high quality water can be preserved for primary uses like drinking, cooking and bathing, the decolourised wastewater can be used for flushing, washing etc., which results in saving of high quality water. Hence, there is a vast scope for reclamation of wastewater by decolourisation in cottage silk dyeing industries.
1.3 WASTEWATER DECOLOURISATION METHODS

The decolourisation methods employed for treating textile dyeing wastewater include various combinations of physical, chemical and biological processes (Reife and Freeman 1996). The various techniques adopted are:

i) Adsorption
ii) Chemical coagulation cum precipitation
iii) Chemical oxidation including chlorination
iv) Electrochemical oxidation
v) Biological oxidation
vi) Membrane separation
vii) Ozonation and
viii) Reduction by bisulphite catalysed borohydride.

Among the above, chemical coagulation cum precipitation by alum, adsorption by activated carbon and chemical oxidation by chlorination are the conventional decolourisation methods practised in Indian cottage dyeing industries. While these conventional techniques are quite effective in decolourisation, they are not environment friendly. The first two methods do not result in any actual degradation of dyes but result in simple phase transfer of dye from wastewater in the form of either sludge or spent carbon. This create sludge management and disposal problems besides the recurring cost for consumables. Though chlorination is an effective decolourisation method, it generates chlorinated organics, which are suspected to be carcinogenic. The increasing global awareness for environmental protection, demands clean, environment friendly methods for decolourisation.

Photocatalytic oxidation (PCO) has emerged as a potentially powerful, environment friendly decolourisation method. It is capable of transforming the hazardous pollutants like dyes into harmless end products such as carbon dioxide and water by highly reactive hydroxyl radicals.
generated using semiconductors like titanium dioxide in the presence of ultraviolet radiation (Matthews 1989). Hence, photocatalytic oxidation can be an alternative to the conventional decolourisation methods.

1.4 SOLAR PHOTOCATALYTIC PROCESS

Photocatalytic oxidation (PCO) is the oxidation of a substrate by means of a series of chemical reactions involving light energy. In semiconductor solid particles, the electrons occupy energy bands as consequence of extended bonding network; and the highest occupied and the lowest unoccupied energy bands are separated by a band-gap. When semiconductor particles are illuminated by light having sufficient photonic energy ($h\nu$), the electrons ($e^-_a$) will be excited to the conduction band while leaving an electronic vacancy, called hole ($h^+_b$) in the valence band. The minimum photonic energy required for such activation is known as band-gap energy. Semiconductor particles like titanium dioxide ($\text{TiO}_2$), have a band gap energy of 3 to 3.3 eV which is equivalent to the wavelength of light between 388 and 413 nm. Hence, titanium dioxide ($\text{TiO}_2$) can be excited either by artificial UV radiation sources like mercury/xenon lamps or UV component of solar radiation with wavelength less than 380 nm (Davis 1994).

It has been reported that hydroxyl radicals formed by such PCO process are powerful oxidants and have more oxidation power than chlorine, $\text{H}_2\text{O}_2$ and ozone, respectively, by 2.05 times, 1.58 times and 1.35 times (Zhu et al. 1995). The mechanism and kinetics of photodegradation of pollutants including dyes using UV radiation have been reported by several authors (Chen and Ray 1998; Stangroom et al. 1998; Chazzed and Thacker 1997; Halmann 1996; Rajeshwar 1995; Wise and Trantol 1994; Rao et al. 1993; Davis et al. 1994; Das et al. 1994; Ollis and Al-Ekabi 1993; Mills et al. 1993; Davis 1994; Manilal et al. 1992; Muneer et al. 1992).
According to World Meteorological Organisation report, solar insolation has about 5% UV radiation with wavelength less than 380 nm (1981). Hence, the same can be utilised for solar photocatalytic (SPC) process application in principle.

1.5 NEED FOR THE STUDY

In most of the photocatalytic oxidation studies reported, titanium dioxide of Degussa make of Germany has been used. It has been reported that titanium dioxide of Degussa P-25 grade has an unique efficiency which is derived from a synergy of many characteristics like particle size, morphology etc., (Nargiello and Herz 1993). Hence, there is a need to assess the feasibility of using the locally available TiO$_2$ as photocatalyst.

Further, most of the studies reported have used artificial UV radiation source for PCO (Halmann 1996; Davis 1994). Since solar energy is inexhaustible and available throughout the year, except for a few weeks, SPC process is ideal for tropical Indian conditions. Hence, there is a vast scope for application of solar energy based SPC technology in Indian cottage industries.

Cottage silk dyeing industries in Kanchipuram discharge about 500 to 2000 litres of wastewater per day. Since, major portion of silk dyeing wastewater is less coloured, there is a vast scope for reclamation of such wastewater by decolourisation. Though, literature on photocatalytic degradation of synthetic dyes is available, no studies have been reported on SPC decolourisation of wastewater for cottage silk dyeing industrial applications (Reeves et al 1992; Matthews 1989 and 1991). Hence, there is a need for detailed study on the application of solar photocatalytic technology (SPC) for reclamation of cottage silk dyeing industrial wastewater by decolourisation. Further, the economics of SPC process has to be studied in order to recommend the same for field applications, in lieu

Though, many reports are available on slurry photocatalyst system, studies on photocatalytic media system (PCMS), which eliminates separation of catalyst particles after treatment, are scanty (Halmann 1996). Since any appropriate technology for cottage industrial application has to be simple, there is a need for studies on the feasibility of developing solar photocatalytic media system for such decolourisation process.

Chemical and biological oxidation processes have been used individually for treatment of textile dyeing wastewater. On several occasions, biological oxidation is preferred over chemical oxidation due to economic consideration. Though, kinetically faster, chemical oxidation application is often limited due to the production of intermediates which do not lend themselves readily to further oxidation. If the products resulting from chemical oxidation were biodegradable, such process, when sequentially applied along with biological process, is likely to increase the rate of degradation of pollutants like dyes. It has been reported that photocatalysis improve the biodegradability of bio-refractory compounds and the end products of PCO as well as biological oxidation are mainly carbon dioxide and water (Ollis and Al-Ekabi 1993; Tanaka and Ichiwaka 1993). Hence, it is appropriate to study the potential for linking SPC and biological oxidation processes. Most of the cottage silk dyeing industries in Kanchipuram discharge dyeing wastewater, which is low biodegradable in nature, into the municipal drain system. Hence, the feasibility of enhancing the biodegradability of silk dyeing wastewater by SPC treatment prior to such co-disposal with domestic wastewater has to be assessed.
1.6 **SCOPE AND OBJECTIVES OF THE PRESENT STUDY**

The scope of this study is to assess the feasibility of applying SPC process for wastewater reclamation by decolourisation and enhancement of biodegradability of wastewater for cottage silk dyeing industrial applications using indigenous titanium dioxide, the use of which has not been reported, as photocatalyst for such purpose. The scope of this study is depicted in Fig. 1.1.

The objectives of this study are:

1.6.1 To investigate the feasibility of applying solar energy based photocatalytic decolourisation process using indigenous titanium dioxide as photocatalyst for reclamation of silk yarn dyeing rinse wastewater, cotton yarn dyeing rinse wastewater and ground water contaminated with dyeing effluents.

1.6.2 To study the effects of the operating variables of slurry catalyst system (SCS) such as catalyst concentration, colour and concentration of dyes, exposure duration, power input, diurnal and climatic variation in solar insolation, hydrogen ion concentration, chloride ion concentration, liquid depth, material of construction of reactor and temperature on SPC decolourisation of simulated silk dyeing rinse (SDR) wastewater. Further, the feasibility of catalyst reusability and the kinetics of decolourisation are also to be studied.

1.6.3 To investigate the feasibility of developing photocatalytic media system (PCMS) by coating titanium dioxide over sand, hollow glass beads, glass slides and cement concrete slides as alternative to slurry catalyst system; the effects of catalyst loading on retention of coating over the media and decolourisation of simulated SDR wastewater are also to be studied. Further, the relative efficiency
Fig. 1.1 Studies on solar photocatalytic (SPC) process
of the catalyst coated system and the slurry catalyst system (SCS) on decolourisation and the feasibility of photocatalytic medium reusability are to be investigated.

1.6.4 To investigate the feasibility of practical application of SPC decolourisation process for reclamation of rinse wastewater arising from cottage silk yarn dyeing industries and to study the effects of the operating variables of slurry catalyst system (SCS) such as exposure duration, power input and catalyst concentration on decolorisation; the kinetics of decolourisation and the feasibility of catalyst reusability are also to be investigated.

1.6.5 To evaluate the economy of SPC decolourisation process in comparison with conventional decolourisation methods practised in cottage dyeing industries such as chemical coagulation cum precipitation by alum, chemical oxidation by chlorination and adsorption by granular activated carbon.

1.6.6 To study the feasibility of using photocatalytic media system (PCMS) for decolourisation of SDR wastewater including regeneration and reusability of spent photocatalytic media.

1.6.7 To study the feasibility of SPC decolourisation of silk dyeing bath (SDB) wastewater including regeneration and reusability of spent photocatalyst.

1.6.8 To study the feasibility of enhancing the biodegradability of silk dyeing (SD) wastewater (combined wastewater from dye bath and rinse operations) by SPC treatment prior to co-disposal of such wastewater with domestic wastewater. The effects of exposure duration and catalyst concentration of SCS on biodegradability of SD wastewater are also to be investigated. Further, the feasibility of catalyst reusability is also to be studied.