CHAPTER 3

MATERIALS AND METHODS

3.1 GENERAL

In this study, investigations were carried out in order to assess the feasibility of using indigenous TiO\(_2\) as solar photocatalyst for reclamation of silk dyeing wastewater by decolourisation using slurry catalyst system (SCS) and photocatalytic media system (PCMS). Further, the feasibility of enhancement of biodegradability of silk dyeing wastewater by SPC process was also investigated for co-disposal of such wastewater along with domestic wastewater. The various materials used and the methodology adopted for the studies are described in this chapter.

3.2 MATERIALS

3.2.1 Titanium dioxide

Indigenous IS grade titanium dioxide (TiO\(_2\)) manufactured by Travancore Titanium Products Ltd., Thiruvanantapuram (Kerala, India) was used as photocatalyst in the studies without any amendments. The specifications of the TiO\(_2\) is reported to be as per Indian Standards (BIS 1991). It is used as raw material for manufacturing paints. The characteristics of the TiO\(_2\) are furnished in Table 3.1.
Table 3.1 Characteristics of Titanium dioxide

<table>
<thead>
<tr>
<th>Name of Chemical</th>
<th>Titanium dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean particle size</td>
<td>0.4 micron</td>
</tr>
<tr>
<td>Crystalline form</td>
<td>Anatase</td>
</tr>
<tr>
<td>Colour</td>
<td>White powder (Solid)</td>
</tr>
<tr>
<td>Odour</td>
<td>Odourless</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>3.8</td>
</tr>
<tr>
<td>Boiling point</td>
<td>3000°C</td>
</tr>
<tr>
<td>Melting point</td>
<td>1830°C</td>
</tr>
<tr>
<td>Surface area</td>
<td>12-13 m²/g</td>
</tr>
<tr>
<td>Residue on 325 mesh</td>
<td>0.1% max.</td>
</tr>
<tr>
<td>Tinting strength</td>
<td>1200</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.55</td>
</tr>
<tr>
<td>TiO₂ Content</td>
<td>97.5% (minimum)</td>
</tr>
<tr>
<td>Volatiles</td>
<td>0.5% max.</td>
</tr>
<tr>
<td>Water solubles</td>
<td>0.5% max.</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.5% max.</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0140% to 0.0170%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.7% max.</td>
</tr>
<tr>
<td>pH</td>
<td>6 - 8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.1% max.</td>
</tr>
<tr>
<td>Sb₂O₅</td>
<td>0.015% max.</td>
</tr>
<tr>
<td>Cu</td>
<td>0.002% max.</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.0015% max.</td>
</tr>
<tr>
<td>Cr₂O₇</td>
<td>0.001% max.</td>
</tr>
</tbody>
</table>

3.2.2 Dyeing wastewater

The wastewater samples collected from dyeing units located at Kanchipuram, near Chennai, Tamilnadu, which is famous for their silk sarees. The samples were also collected from cotton dyeing industries
located in Tirupur. The coloured ground water was collected from the wells in the vicinity of cotton dyeing industries in Tirupur. The samples were stored at 4°C in light resistant containers and brought to room temperature before using in the experiments.

The wastewater were used in the experiments, without any amendments, unless otherwise stated. However, the samples were filtered through 0.45 micron membranes twice before the measurement of colour in order to eliminate the interference due to catalyst particles. The wastewater samples were scanned for their maximum absorbance wavelength ($\lambda_{\text{max}}$) and calibrated at the $\lambda_{\text{max}}$ within the linear limit.

### 3.2.3 Dyes

The dyes used for preparation of the simulated wastewater were obtained from cottage silk yarn dyeing units located at Kanchipuram. Since, direct dyes are used in these units, the same was taken for the studies. Three primary colours namely red, yellow, and blue and three secondary colours namely, orange, green, and violet were selected for the study. These dyes are reported to be always in great demand from the customers. The maximum absorbance wavelength for the different dyes were scanned and the dyes were calibrated at $\lambda_{\text{max}}$ within their linear limit with respect to their concentration.

### 3.2.4 Materials used for development of photocatalytic media

Two slide media namely glass slides and concrete slides were selected for the study. Similarly, two granular media namely, sand and hollow glass beads were also selected.

Borosilicate glass slides of size 20 mm square and 2.3 mm thickness were obtained from glass manufacturers and used after cleaning the
surfaces. Cement concrete slides of mean size 25 square mm and of mean thickness 9.8 mm were made and used. The cement and sand were used in the ratio of 1:4 for making the concrete slides and the slides were cured for 7 days with distilled water and cleaned with distilled water to remove loosely bound particles.

Clean river sand was collected from river Koratalaiyar near Chennai and washed several times for removal of impurities. The sand passing through 1.0 mm sieve and retained on 0.6 mm sieve was used for coating TiO₂. The specific gravity of sand was 2.62 and the bulk density was 1.659 gm/cc. Hollow glass beads, blown out of borosilicate glass tubes, with mean diameter of 3.47 mm and specific gravity of 0.838 were obtained from glass manufacturers and used after thorough cleaning with distilled water.

3.2.5 Chemicals and reagents

All chemicals and reagents used in the studies are of analytical grade (make : Qualigens / CDH / S.D. Fine Chemicals, India). Alum, bleaching powder and granular activated carbon (wood based) are of commercial grade and used without any amendments.

3.3 EXPERIMENTAL SET UP

The investigations were carried out in borosilicate glass trays/beakers as multiple batch reactors. The reactors were kept inside a waterbath to maintain the temperature around 20°C so that evaporative loss is minimised. The reactors were exposed to sun and operated in parallel in the open terrace of the Centre for Environmental Studies, Anna University, Chennai, India (Latitude : 13°04'N and Longitude : 80°14'15"E).
3.4 ANALYTICAL INSTRUMENTS AND EQUIPMENTS USED

Pyranometer (make: National Instruments, Calcutta, India) was used to measure solar insolation in the range of 300 to 4000 nm. Spectrophotometer (Type: UV-Vis, model: 2000; make: Hitachi, Japan) was used to measure absorbance. Surface area measurement was done using surface area analyser (model: pulse chemisorb - 2700; make: Micrometrics).

Dissolved oxygen was measured using D.O. meter (model: 50B; make: Yellow Spring Instruments, U.S.A.). Membrane filter holder (make: Tarson, Calcutta, India) with cellulose nitrate membrane filters of pore size of 0.45 micron (make: Sartorius, Germany) were used for separation of catalyst particles before colour measurement. Peristaltic pumps (Make: Miclins, Chennai, India) and aquarium air pumps (make: Super, Chennai, India) were used for aerating the contents. pH meter (model: DI767, make: Digisun, India) and conductivity meter (model: 304, make: Systronics, Chennai, India) were used. The analysis were done according to the standard methods for the examination of water and wastewater (Greenberg et al. 1992).

3.5 EXPERIMENTAL METHODOLOGY

In order to achieve the various objectives listed in section 1.6, the following experimental methodology was adopted. Substrate samples of volume of one litre of appropriate strength were taken in multiple batch reactors with waterbath. Catalyst solution of appropriate volume and concentration was added to the substrate as required. Air supply was maintained through perforated tubing as and when required. The solar insolation was measured at every minute and averaged for 10 minutes interval, unless otherwise stated.
Decolourisation by SPC process on simulated silk dyeing wastewater and silk dyeing industrial wastewater using slurry catalyst system (SCS) and photocatalytic media system (PCMS) were studied. The feasibility of enhancement of biodegradability of silk dyeing (SD) wastewater (which consist of both dyeing bath wastewater and rinse wastewater) by SPC process was also investigated.

All samples were taken in triplicate after mixing the contents with glass rod, at specified time intervals, and filtered through membrane filters twice operated under vacuum. The first portion of the filtrate was discarded. Dark control and aerated control experiments were carried out without sunlight and with aeration, respectively, in order to assess the effect of dark adsorption and aeration on decolourisation, respectively. Experimental blank control was also run without addition of catalyst in order to study the effect of direct photolysis on decolourisation. The experimental set up was covered with black polyethene film paper till the experiment started, and, also as and when required. Since, multiple reactors were employed, the loss of substrate and catalyst due to sampling were not compensated.

Simulated wastewater (prepared using dye solutions) and the wastewater samples were filtered twice through 0.45 micron membrane filter before absorbance measurement. The true absorbance (TA) value of samples were measured at relevant \( \lambda_{\text{max}} \) against distilled water as blank. The pH of all samples were adjusted to standard pH of 7.6 before spectrophotometric measurement, with the original sample as control. The wastewater samples were calibrated for various concentrations within the linear limit. Filtered stock dye solutions of concentration 1 g/L were prepared and used with suitable dilution by double distilled water to prepare simulated wastewater. Wastewater from dyeing operations was suitably diluted by double distilled water, if required, before spectrophotometric measurement.
3.6 FEASIBILITY STUDIES ON DECOLOURISATION BY SOLAR PHOTOCATALYTIC PROCESS

The investigations on the feasibility of SPC decolourisation of silk dyeing rinse (SDR) wastewater by slurry catalyst system (SCS) were carried out on 6 batches of wastewater collected from silk dyeing units. The catalyst concentration adopted was 1000 mg/L based on values reported in the literature. The contents were exposed to solar insolation for 2 hours between 11:30 and 13:30 hours under aerated condition. At the end of exposure to irradiation, the extent of decolourisation was measured. Similarly, the feasibility of decolourisation of cotton dyeing rinse wastewater and coloured groundwater were also investigated under similar operating conditions.

3.7 DECOLOURISATION OF SIMULATED SILK DYEING RINSE WASTEWATER BY SLURRY CATALYST SYSTEM

Detailed studies were limited to decolourisation of SDR wastewater, since decolourisation of cotton dyeing rinse wastewater and ground water contaminated by dyeing effluents was found not feasible. The studies on decolourisation of simulated silk dyeing rinse (SDR) wastewater were conducted with slurry catalyst system (SCS). The schematic work plan for the studies is depicted in Fig. 3.1.

3.7.1 Simulation of SDR wastewater

In order to investigate the effects of the various operating variables on SPC decolourisation by SCS, simulated SDR wastewater was prepared using dyes of popular colours. Three primary colours namely red, yellow and blue, and, three secondary colours namely orange, green and violet were selected for the investigations. Three batches of wastewater for each of the six colours were collected from rinse operations of silk dyeing process. The dyes used in the dyeing process, from where the 18 batches of wastewater...
Fig. 3.1 Decolourisation of simulated SDR wastewater by slurry catalyst system
collected, were also obtained in order to prepare the simulated SDR wastewater.

Dye solutions of concentration in the range of 5 to 25 mg/L were prepared. The dye solutions and the wastewater samples were filtered through Whatman filter paper No.42 in order to remove the suspended impurities. The true absorbance (TA) values for the industrial wastewater and the corresponding dye solutions (simulated SDR wastewater) were measured.

It was found that the true absorbance values for most of the SDR wastewater samples were less than that of the dye solutions of initial concentration of 10 mg/L, prepared out of the same dyes used in the dyeing process. Based on the above simulation studies, the concentration of dye in the simulated SDR wastewater was arrived at as 10 mg/L. Simulated SDR wastewater were prepared using the direct dyes obtained from the dyeing units and calibrated based on their true absorbance values after filtering through 0.45 micron membranes as discussed in section 3.5.

3.7.2 Effect of control conditions on decolourisation of simulated SDR wastewater

The control experiments were carried out on simulated SDR wastewater for the 6 dyes selected. Besides the standard SPC system, dark control (without light), blank control (without catalyst) and aerated control were also run in order to ascertain the effect of dark adsorption, direct photolysis and aeration, respectively, on decolourisation. The relative decolourisation of the dyes selected was observed. The catalyst concentration adopted was 1000 mg/L. The concentration of dye was 10 mg/L. The reactors (in duplicate) were exposed to solar irradiance for one hour between 12:00 and 13:00 hours, the period during which the insolation was fairly constant, though variations are bound to occur.
3.7.3 Effect of pH on $\lambda_{\text{max}}$ and decolourisation of simulated SDR wastewater

The pH of the SDR wastewater was found to be in the range of 5.96 to 8.12 (based on the 18 samples collected for the feasibility studies). Hence, the effect of hydrogen ion concentration on $\lambda_{\text{max}}$ of the 6 simulated SDR wastewater was studied in the pH range of 3 to 10. Further, the effect of hydrogen ion concentration, on decolourisation of dyes were also studied at pH 4.7 and 9. The pH correction was made by addition of $\text{H}_2\text{SO}_4$ or $\text{NaHCO}_3$ solutions. In order to ensure uniformity, the pH of all the samples were brought to a standard pH of 7.6, before spectrophotometric measurement. The effect of this pH correction on $\lambda_{\text{max}}$ of the untreated simulated SDR wastewater samples was found insignificant.

3.7.4 Effect of catalyst concentration on decolourisation of simulated SDR wastewater

The effect of catalyst concentration on decolourisation of six simulated SDR wastewater was studied with catalyst concentration ranging from 250 to 1500 mg/L. The experiments were conducted with duplicate reactors exposed to solar irradiance between 12.00 and 13.00 hrs.

3.7.5 Effect of exposure time and power input on decolourisation

Time taken for visual decolourisation for the six simulated SDR wastewater solutions of concentration 10 mg/L was investigated between 11:00 and 14:00 hours. The extent of decolourisation was inspected at 30 minutes interval so that the time taken for visual decolourisation can be estimated. The effect of exposure time to solar irradiance on decolourisation was investigated for 60 minutes between 12:00 and 13:00 hours at 10 minutes interval using multiple reactors. The half life period ($t_{0.5}$), power input required for 50% decolourisation ($p_{0.5}$), dye removal rate ($\mu_t$) and power
input for removal of unit weight of dye ($\mu_2$) were arrived at using graphical plots. The experiments were repeated 3 times for all the 6 simulated SDR wastewater.

### 3.7.5.1 Kinetics of photocatalytic decolourisation

In photocatalytic mineralisation of organic pollutants, the initial rate of disappearance of the pollutants ($r$) has been widely reported to fit into the following Langmuir-Hinshelwood model (Davis 1994).

\[
\begin{align*}
    r &= \left( \frac{-dC_0}{dt} \right) \\
    &= \left[ \frac{k_1k_2[C_o]}{1 + k_1[C_o]} \right]
\end{align*}
\]  

(3.1)

where

- $r$ - initial rate of disappearance
- $C_0$ - initial concentration of pollutant
- $t$ - reaction time (duration of exposure)
- $k_1$ - adsorption coefficient providing a measure of the adsorption of organics on the surface of catalyst
- $k_2$ - constant providing a measure of the intrinsic reactivity of the photoactivated catalyst surface with the pollutant.

On integration and simplification, the equation (3.1) results in equation (3.2) as follows.

\[
\begin{align*}
    t &= \frac{1}{k_1k_2} \ln \left( \frac{C_0}{C} \right) + \frac{1}{k_2} (C_0 - C)
\end{align*}
\]  

(3.2)

Rearranging the terms of equation (3.2), the equation (3.3) is obtained which is the sum of zero order and first order rate equation.
When 'C₀' is very small, the equation (3.3) reduces to the equation (3.4) by neglecting the second part of the equation which becomes negligible and substituting the product $k_1k_2$ by $K_1$, and rearranging the terms,

$$\ln \left( \frac{C}{C_0} \right) = -K_1 t$$  \hspace{1cm} (3.4)

Thus a plot of $\ln \left( \frac{C}{C_0} \right)$ versus irradiation time should yield a straight line whose slope equals to the apparent rate constant 'K,'. In this study, the reported kinetics of decolourisation of low concentration dyeing wastewater, was verified using linear regression modelling as follows.

$$\ln \left( \frac{C}{C_0} \right) = A e^{-K_1 t}$$  \hspace{1cm} (3.5)

Where

- $C$ : Concentration of residual colour, mg/L.
- $C_0$ : Initial concentration of colour, mg/L.
- $K_1$ : Kinetic rate constant, min⁻¹
- $t$ : Exposure duration, minutes, and
- $A$ : Pre-exponential factor

Similarly the kinetics of decolourisation with respect to power input $(P)$, was studied using equation (3.6).

$$\left( \frac{C}{C_0} \right) = A e^{-K_2 P}$$  \hspace{1cm} (3.6)

where

- $K_2$ : Kinetic rate constant based on power input, Wh⁻¹
- $P$ : Cumulative power input, Wh
- $A_1$ : Pre-exponential factor
The kinetics of decolourisation for all the 6 simulated SDR wastewater was studied and repeated thrice.

3.7.6 Effect of diurnal variation on decolourisation

The effect of diurnal variation on decolourisation of simulated SDR wastewater (direct red 28) was studied in the time interval of 09.00 and 17.00 hours at one hour interval. The ratio, $\theta_1$, between the percent colour removal for 1 hour beginning at 12.00 hours ($R_{12\,hrs}$) and other timings ($R_t$) was arrived at. The experiments were repeated 6 times.

3.7.7 Effect of climatic conditions on decolourisation

The effect of climatic conditions on decolourisation of simulated SDR wastewater (direct red 28) was studied for clear blue sky, partly cloudy and sky overcast conditions during 12:00 and 13:00 hours. The ratio, $\theta_p$, between the percent colour removal for other climatic conditions ($R_{oc}$) and the clear blue sky conditions ($R_{cs}$) was arrived at. Further, the dye removal rate ($\mu_t$), was also arrived at. The experiments were repeated 6 times.

3.7.8 Effect of dye concentration on decolourisation

The effect of dye concentration on decolourisation of simulated SDR wastewater (direct red 28) was studied in the range of 5 to 15 mg/L during 12:00 and 13:00 hours. The range of dye concentration was selected to cover the range of 50 to 150% of the concentration of dye (viz. 10 mg/L) normally expected in the SDR wastewater. The relative decolourisation efficiency for 5, 10 and 15 mg/L concentrations was studied in terms of half life period ($t_{0.5}$), $K_t$ and $\mu_t$. The experimental studies were repeated thrice. The ratio, $\theta_d$, between the rate constants, ($K_t$) for 5 mg/L and other initial dye concentrations were arrived at.
3.7.9 Effect of liquid depth on decolourisation

The effect of liquid depth in the range of 25, 50 and 75 mm on decolourisation of simulated SDR wastewater (direct red 28) was investigated. The experiments were repeated thrice. The ratio, \( \theta_4 \), between the rate constants \( K_1 \) for 25 mm liquid depth and the other liquid depths was arrived at.

3.7.10 Effect of temperature on decolourisation

The effect of temperature on decolourisation of simulated SDR wastewater was investigated over a range of 20\(^\circ\), 30\(^\circ\) and 40\(^\circ\)C with direct red 28 dye of concentration 10 mg/L. The temperature was maintained at the desired level by keeping the reactor inside the water bath and addition of appropriate quantity of ice cubes / cold water / hot water as and when required. Addition of hot water was found necessary in the initial stage of the experiment for 30\(^\circ\) and 40\(^\circ\)C controls. The ratio, \( \theta_5 \), between the \( K_1 \) for 20\(^\circ\)C and other temperatures was arrived at, taking \( (K_1)^{20\circ C} \) as unity. Further, the activation energy for the SPC decolourisation was also arrived at using the following expression.

In terms of the rate constant, \( K_1 \), the relationship between temperature and activation energy is given by equation (3.7).

\[
\frac{(K_1)^{T_2}}{(K_1)^{T_1}} = \frac{E_a(T_2-T_1)}{R' \, T_1 \, T_2}
\]  

(3.7)

where

\( (K_1)^{T_1}, (K_1)^{T_2} = \) rate constants at temperature \( T_1 \) (293\(^\circ\) Kelvin) and \( T_2 \) (313\(^\circ\) Kelvin), respectively

\( R' = \) gas constant (8.134 J/mol \(^\circ\)Kelvin)

\( E_a = \) activation energy, (kJ/mol)
3.7.11 Effect of material of construction on decolourisation

The effect of material of construction on decolourisation of simulated SDR wastewater (direct red 28) was investigated using borosilicate glass, stainless steel, PVC and plain cement concrete surface reactors. The experiments were run with dark control in order to estimate the effect of dark adsorption. The liquid depth in the reactor was 2.5 cm and the reactors are provided with waterbath. The PCC reactor was made out of cement:sand mortar (1:4) and encased by a glass container to minimise seepage of wastewater and was soaked with distilled water before treatment in order to minimise dark adsorption by the reactor material. The ratio, $\theta_o$, between the percent decolourisation for PCC reactor ($R_{pcc}$) and other reactors were arrived at taking $R_{pcc}$ as unity. The experiments were repeated thrice.

3.7.12 Effect of chloride concentration on decolourisation

The effect of chloride concentration on decolourisation of 6 batches of simulated SDR wastewater was investigated by adding sodium chloride in the range of 100 to 1000 mg/L. Blank controls were also run without addition of sodium chloride.

3.7.13 Catalyst reusability for decolourisation

The catalyst reusability was investigated on decolourisation of six simulated SDR wastewater with fresh catalyst as control. The spent catalyst was separated by filtration through 0.45 micron filter, after visual decolourisation was noticed in the control reactors and the same was reused, after drying. The spent catalyst separated from a system was used again for decolourisation of the same untreated wastewater. Multiple reactors with appropriate volume of wastewater and catalyst concentrations were adopted for the various systems taking into account of the catalyst lost during each stage of filtration for separation of catalyst. The reusability experiments
were continued till the catalyst recovered was sufficient enough to conduct further decolourisation experiments.

The ratio, $\theta$, between percent decolourisation for the fresh catalyst and the spent catalyst was taken as the indicator of the catalyst reusability. The systems were operated with several multiple batch reactors in order to separate catalyst required for subsequent runs. The systems were provided with aeration in order to speed up the process to minimise the time taken for the experimental run. The reactors were operated till no colour was visible in the control reactors.

3.7.14 Loss of catalyst under suspension

In order to arrive at the catalyst escape under suspension in SCS, the suspended catalyst concentration (SCC), after 3 hours of quiescent settling after the treatment, was estimated based on 20 batches of experiments on decolourisation of simulated SDR wastewater.

3.8 DECOLOURISATION OF SIMULATED SILK DYEING RINSE WASTEWATER BY PHOTOCATALYTIC MEDIA SYSTEM

Though, SPC process by slurry catalyst system was efficient in decolourisation of simulated SDR wastewater, a technical limitation of this method, is the need for the separation of the catalyst particles after treatment. The huge cost and the necessity for skilled operation and maintenance, rules out the possibility adoption of catalyst separation in cottage industries. Hence, the feasibility of decolourisation of simulated SDR wastewater by photocatalytic media system (PCMS) was investigated as an alternative to slurry catalyst system (SCS). The schematic work plan for the studies is depicted in Fig.3.2
Decolourisation of simulated SDR wastewater by photocatalytic media system (PCMS)

Feasibility of photocatalytic media development (PCM)

Glass Slides (4 mg/cm²)
Concrete Slides (4 mg/cm²)
Hollow Glass Beads 10% (w/w)
Sand 5% (w/w)

Photocatalytic Glass Slides (PCGS) (5 mg/cm²)
Photocatalytic Concrete Slides (PCCS) (5 mg/cm²)
Photocatalytic Sand (PCS) (5% w/w)

Simulated SDR wastewater - decolourisation studies
Control experiments - Dark, Blank, PCM system

PCGS
Catalyst loading 1-10 mg/cm²
PCGS Vs SCS
PCGS Reusability
Kinetics

PCS
Catalyst loading 1-10% (w/w)
PCS Vs SCS

Fig. 3.2 Decolourisation of simulated SDR wastewater by photocatalytic media system (PCMS)
3.8.1 Feasibility of photocatalytic media development

Two slide media, namely, glass slides and concrete slides and two granular media, namely, sand and hollow glass beads were taken for the studies on the feasibility of developing photocatalytic media (PCM). The virgin media were cleaned with distilled water, dried for one hour and calcined at 500 ± 50°C for 30 minutes. The feasibility of coating TiO₂ over support media by thermal treatment was investigated. TiO₂ coating of 4 mg/cm² was initially applied over glass slides of size 2.0 cm x 2.0 cm and cement concrete slides of size 2.5 cm x 2.5 cm. The slides were air dried for one hour and calcined at 500 ± 50°C for 30 minutes. Similarly, TiO₂ coating was applied over clean river sand and hollow glass beads at 5% (w/w) and 10% (w/w), respectively. The media after coating were gently rinsed with distilled water to remove loosely bound particles present, if any. The residual catalyst coating retained over the media was estimated in order to select the media for further studies.

3.8.2 Feasibility of decolourisation of simulated SDR wastewater by photocatalytic media

The feasibility of decolourisation of simulated SDR wastewater (direct red 28 dye of concentration 10 mg/L) by photocatalytic media (PCM) was investigated. Photocatalytic glass slides (PCGS) having a total area of 200 sq.cm. with initial applied coating of 5 mg/cm², photocatalytic concrete slides (PCCS) having a total area of 200 sq.cm. with initial applied coating of 5 mg/cm² and 20 gms of photocatalytic sand (PCS), with initial applied coating of 5% by mass of media, were used in the studies.

The photocatalytic slides and sand were placed in reactors of size: 15 cm x 15 cm x 4.5 cm (Volume of wastewater - 500 ml) and 10 cm (dia) x 4.5 cm (volume of wastewater - 200 ml), respectively. The reactor contents
were exposed to sunlight between 11:30 and 13:30 hrs. Dark control and blank control (without media) were run, simultaneously, inorder to ascertain the extent of decolourisation due to dark adsorption and direct photolysis, respectively. The decolourisation experiments were run in duplicate and repeated for 6 times.

3.8.3 Effect of catalyst loading over media on decolourisation

The catalyst loading over glass slides was varied from 1 mg/cm² to 10 mg/cm² in order to study the effect of loading on catalyst retention over media. Similarly, the catalyst loading over sand was also varied from 1 to 10% by weight of media. The effect of catalyst loading over media on decolourisation of 500 ml of simulated SDR wastewater (direct red 28 dye of concentration 10 mg/L) for the various loading was also studied for both PCGS and PCS. 200 sq.cm of PCGS and 60 gm of PCS were used in the experiments.

3.8.4 Comparison of photocatalytic media system and slurry catalyst system

The decolourisation efficiency of photocatalytic sand and glass slides was compared with that of the slurry catalyst system (SCS) loaded with similar mass of catalyst used for coating, i.e. 600 mg in 500 ml (1200 mg/L). PCGS (200 sq.cm) with 3 mg/cm² of TiO₂ coating and PCS of 60 gm with 5% TiO₂ loading (by weight) were used in the experiments. 500 ml of simulated SDR wastewater (direct red 28 solution) of concentration 10 mg/L was used and exposed to solar irradiance for 2 hours between 11:30 and 13:30 hrs. The reactors were operated in duplicate. The reactors were of size 15 x 15 x 4.5 cm. The ratio, θ₀, between the percent decolourisation for PCGS and SCS, and, the ratio, θ₀, between the percent decolourisation for PCS and SCS were arrived at. The experiments were repeated 6 times.
3.8.5 Kinetics of decolourisation of simulated SDR wastewater by PCGS and SCS

The relative kinetics of decolourisation by PCGS and SCS was also studied. PCGS (200 sq.cm with 3 mg/cm² applied catalyst loading) were used for decolourisation of 500 ml of simulated SDR wastewater (direct red 28 of concentration 10 mg/L). Similarly, 600 mg of TiO₂ was used in the SCS systems. The ratio, \( \theta_{10} \), between kinetic rate constants (\( K_r \)) for PCGS and SCS was arrived at. The experiments were repeated thrice.

3.8.6 Reusability of PCGS for decolourisation of simulated SDR wastewater

The reusability of spent photocatalytic glass slides (PCGS) was investigated with fresh PCGS as control. 500 ml of simulated SDR wastewater (direct red 28 of 10 mg/L concentration) was used as substrate. The ratio, \( \theta_{11} \), between the percent decolourisation for the fresh and spent catalytic media in one hour (12.00 to 13.00 hrs) was taken as the indicator to assess the catalyst reusability. The media was repeatedly reused until the catalyst dislodged exceeded 50% of the catalyst retained on PCGS, initially. The experiments were conducted in duplicate reactors and repeated thrice.

3.9 DECOLOURISATION OF SILK DYEING RINSE WASTEWATER BY SLURRY CATALYST SYSTEM

On successful completion of the studies on the feasibility of SPC decolourisation of simulated SDR wastewater, the studies were extended to decolourisation of dyeing wastewater from silk dyeing industries, which comprised of silk dyeing bath (SDB) wastewater and silk dyeing rinse (SDR) wastewater. The studies on decolourisation of SDR wastewater was conducted as follows. The schematic work plan for the studies is depicted in Fig. 3.3
Fig. 3.3 Decolourisation of silk dyeing (SD) wastewater
3.9.1 Effect of control conditions on decolourisation

The experimental investigations on the feasibility of SPC decolourisation of silk dyeing rinse (SDR) wastewater by slurry catalyst system (SCS) were conducted on wastewater samples collected from silk dyeing process. The effect of dark control, blank control and aerated control on decolourisation of SDR wastewater were studied in addition to the standard SPC system with a litre of SDR wastewater. The catalyst concentration adopted was 1000 mg/L and the reactor contents were exposed to solar irradiance for one hour between 12:00 and 13:00 hour. The experiments were conducted in duplicate reactors. The experiments were repeated for six batches of SDR wastewater. The pH of the wastewater samples were adjusted to pH 7.6 before spectrophotometric measurement. It was also found that there was no significant effect due to this pH adjustment on $\lambda_{\text{max}}$ of the absorbance value of wastewater samples.

3.9.2 Effect of catalyst concentration on SDR wastewater decolourisation

The effect of catalyst concentration on decolourisation of SDR wastewater was studied on 10 batches of wastewater. The reactors were run in duplicate with a litre of wastewater with liquid depth of 2.7 cm. The catalyst concentration added was ranging from 250 to 2000 mg/L. The optimum catalyst concentration arrived at from the experiments was adopted as catalyst concentration for further studies, on decolourisation of SDR wastewater.

3.9.3 Time taken for visual decolourisation of SDR wastewater

The time taken for visual decolourisation was investigated on 10 batches of SDR wastewater with appropriate optimum catalyst concentration. One litre of wastewater was kept in reactors of size
21x21x5cm and exposed to solar irradiance between 09.00 and 17.00 hours at various time intervals. The feasibility of decolourisation on 26 batches of SDR wastewater samples was also conducted based on the optimum catalyst concentration arrived at for the 10 batches of wastewater.

3.9.4 Effect of exposure time and power input on decolorisation of SDR wastewater and kinetics of decolourisation

The effects of exposure time and power input on decolourisation and the kinetics of decolourisation of SDR wastewater were investigated on 6 batches of SDR wastewater and also on simulated SDR wastewater having equal dye concentration. The simulated SDR wastewater was prepared out of the dyes used in the dyeing process from where the SDR wastewater samples were collected. Six batches of SDR wastewater, at a rate of two samples for each of the 3 primary colours, namely, red, blue and yellow, were collected and subjected to decolourisation.

The rate constants, $K_1$ and $K_2$, for both the simulated SDR wastewater and SDR wastewater were arrived at using equations 3.5 and 3.6, respectively, by measuring the residual colour at 10 minutes interval using multiple batch reactors with a litre of wastewater. The catalyst concentration adopted was 1300 mg/L. The experiments were conducted between 12:00 and 13:00 hours. The ratios, $\theta_{12}$, and, $\theta_{13}$, between the rate constants $K_1$ and $K_2$ for simulated SDR wastewater and SDR wastewater, respectively, were arrived at for 6 batches of wastewater. The dye removal rate ($\mu_1$) and the power input per unit weight of dye removed ($\mu_2$) were arrived at. Similarly, the ratios, $\theta_{14}$ between $\mu_1$ for simulated SDR wastewater and SDR wastewater and, $\theta_{15}$, between $\mu_2$ for SDR wastewater and simulated SDR wastewater, respectively, were also arrived at.
3.9.5 Reusability of spent catalyst for decolourisation of SDR wastewater

The feasibility of reusing the spent catalyst for decolourisation of six batches of SDR wastewater was investigated. The reactors loaded with fresh catalyst were treated as controls. Multiple reactors with appropriate volume of wastewater and catalyst concentration were adopted taking into account of the catalyst lost during filtration. The spent catalyst was separated after 4 hours of decolourisation of SDR wastewater. It was again used for decolourisation of the same batch of untreated wastewater. The relative decolourisation efficiency of the fresh and the spent catalyst was taken as the indicator for reusability of catalyst. The reusability experiments were repeated until the mass of catalyst recovered was sufficient enough to conduct further decolourisation experiments. The system was operated under aeration in order to speed up the process to minimise the time taken for the experimental run, which will not affect the catalyst reusability.

3.9.6 Economics of SPC decolourisation of SDR wastewater

The economics of the SPC decolourisation process was compared with that of the conventional decolourisation methods practised in cottage industries such as chemical coagulation cum precipitation (CCP), adsorption by activated carbon (AAC) and chemical oxidation by chlorination (COC). The units are designed to reclaim 1000 litres of SDR wastewater expected from a typical small scale silk dyeing unit in a day, processing silk yarn dyeing with direct dyes like Kanchipuram silk dyers. The relative economy of the various alternative methods were compared by taking the unit operating cost (based on chemical consumption alone. The costing does not envisage any other chemical addition or regeneration which are not appropriate for the cottage industrial applications.
3.9.6.1 Decolourisation by chemical coagulation cum precipitation

The economics of the CCP process was worked out on the basis of chemical requirement based on 6 batches of SDR wastewater. The jar test method was followed for chemical precipitation. Since pH of the wastewater was alkaline in nature, the studies were conducted without any pH amendments to the SDR wastewater. Alum was added in the range of 25 to 150 mg/L of SDR wastewater. The contents were rapidly mixed for 3 minutes followed by slow mixing for 15 minutes and settling for 30 minutes. The samples were filtered through 0.45 micron filter and the residual colour was determined. The dosage, beyond which there was no appreciable reduction in colour was taken as the optimum dosage.

Reinforced cement concrete (R.C.C. M20 and Fe 415 grade steel) tanks (in duplicate) of size: 0.6m x 0.6m x 0.45m (L.D.) with a free board of 0.15m are recommended for batch treatment wherein coagulation, flocculation and precipitation can take place. The reactors shall be provided with mixing arrangements and electrical accessories. The reactors are capable of handling 1000 litres of wastewater in 3 batches in a day.

3.9.6.2 Decolourisation by chemical oxidation by chlorination

The economics of decolourisation by chlorination was worked out for the same 6 batches of wastewater studied for chemical precipitation using jar test method. Bleaching powder dosage in the range of 10 to 60 mg/L was adopted. The contents were stirred rapidly for 10 minutes. The samples were analysed for residual colour after filtering through 0.45 micron membrane filters. RCC tanks (in duplicate) of size: 0.6m x 0.6m x 0.45m (L.D) with free board of 0.15m are recommended to handle 1000 litres of wastewater in 3 batches in a day. The reactors shall be provided with mixing arrangements and electrical accessories.
### 3.9.6.3 Decolourisation by adsorption by activated carbon

The decolourisation of the same 6 batches of SDR wastewater by adsorption was also investigated. Freundlich isotherm constants were estimated by batch adsorption studies using the locally available wood based granular activated carbon (GAC). The carbon was ground until it passes through 325 mesh sieve. Grinding of carbon will not significantly affect its adsorptive capacity but will increase the rate of adsorption. Six flasks were set up and carbon was added to five flasks in the order of 0.5g, 0.75g, 1.0g, 1.25g and 1.5g, respectively, and the sixth flask was kept as blank control. 100ml of wastewater was added to each one of the flask and the flasks were placed on gyrator shaker for a period of 2 hours. The samples were filtered through 0.45 micron membrane filters to remove the carbon particles and filtrate was analysed for residual colour. The wastewater in the blank control was also filtered through membranes before colour measurement. Freundlich isotherm constants were estimated in order to arrive at the carbon dosage required to result in a residual dye concentration equivalent to 1.0 mg/L after treatment using the Freundlich model (equation 3.8) as follows.

\[
\frac{X}{M} = K_a C_e^{\frac{1}{n}}
\]

where

- \(X\) : weight of dye adsorbed
- \(M\) : weight of carbon added
- \(C_e\) : Equilibrium concentration of dye
- \(K_a, n\) : Empirical constants of isotherm

RCC tanks (in duplicate) of size 0.6m x 0.6m x 0.45m with 0.15m free board are recommended. The reactors shall be provided with mixing arrangement and electrical accessories.
3.9.6.4 Decolourisation by SPC process

The extent of decolourisation by SPC process was studied with the same 6 batches of SDR wastewater, which were subjected to decolourisation by the conventional methods discussed above. The catalyst concentration adopted was 1300 mg/L based on the earlier findings (Table 4.48). The experiments were conducted in duplicate reactors with a litre of wastewater exposed to solar irradiance for 4 hours between 10:30 and 14:30 hours. The liquid depth adopted was 2.7 cm. The operating cost per m³ for reclamation of SDR wastewater was worked out based on reusing of spent catalyst (without regeneration) for seven times. Though, it was found that the catalytic activity was not exhausted even after 10 uses, the reusability was limited to 7 times taking into account of the loss during treatment and separation (Table 4.53). No special structures or mechanical gadgets are proposed, in view of the shallow depth. However, periodical manual mixing is recommended in order to mix the catalyst and to minimise the mass transfer limitation.

Shallow masonry tanks (in duplicate, each to handle 50% of the average daily flow of 1000 litres) are proposed. The tanks shall be lined with PVC thin sheets inside in order to avoid fouling of catalyst by the impurities present in the ingredients of the material of construction of the reactor. The size of each reactor shall be: 4.3m x 4.3m with 2.7cm liquid depth with a free board of 0.15m. The floor of the tank shall be of PCC (1:3:6) and the side walls shall be of brick masonry (1:6).

3.9.6.5 Costing

As the installation cost of the reactor and accessories for all the four methods were found similar (Rs. 40,000/- approximately), the economics of decolourisation alternatives was evaluated in terms of the operating cost alone. The operating cost per cubic metre of the SDR wastewater was...
worked out based on the prevailing market prices at Rs.80 per kg for titanium dioxide, Rs.3 per kg for alum, Rs.25 per kg for bleaching powder and Rs.30 per kg for GAC. The cost of regeneration for carbon and catalyst and the cost of sludge management facilities has not been taken into account, as the same were not appropriate for cottage industrial applications.

3.10 DECOLOURISATION OF SILK DYEING RINSE WASTEWATER BY PHOTOCATALYTIC MEDIA SYSTEM

The feasibility of decolourisation of SDR wastewater by photocatalytic glass slides (PCGS) was investigated, since other PCM developed, were found less efficient than PCGS. The schematic work plan for the studies is depicted in Fig. 3.3. 500 ml of SDR wastewater was used as substrate and exposed to solar irradiance for 2 hours between 11:30 and 13:30 hours. The reactors of size 15 x 15 x 4.5 cm were operated in duplicate with 200 sq.cm. of PCGS with catalyst loading of 3 mg/cm². The liquid depth adopted was 2.7cm. The studies were repeated for 6 batches of SDR wastewater.

3.10.1 Reusability of PCGS for SDR wastewater decolourisation

The reusability of spent photocatalytic glass slides with catalyst coating of 3mg/cm² was investigated. 500ml of SDR wastewater was used as substrate. The glass slides were removed after two hours of exposure. The studies were repeated for 6 batches of SDR wastewater for 2 cycles.

3.10.2 Regeneration of PCGS

Since, it was found that the PCGS got exhausted after first use, the regeneration of the same was attempted. In the absence of standard regenerants for such purpose, distilled water, sodium-bi-carbonate (0.1M)
and nitric acid (0.1N) were used for regeneration of the exhausted PCGS. The catalytic media with catalyst coating of 3 mg/cm² was kept immersed with 1.5 cm liquid depth in 500 ml of distilled water, NaHCO₃ (0.1M) and HNO₃ (0.1N), respectively, for 30 minutes after rinsing the PCGS with respective regenerants. In all the three methods, the efficiency of the regenerated PCGS media was evaluated with the fresh PCGS media (with similar catalyst loading) as control for decolourisation of silk dyeing rinse wastewater. The studies were repeated for 3 batches of SDR wastewater.

3.11 DECOLOURISATION OF SILK DYEING BATH WASTEWATER

The feasibility of SPC decolourisation of silk dyeing bath (SDB) wastewater component of silk dyeing wastewater was also investigated. The schematic work plan for the studies is depicted in Fig. 3.3

The true absorbance value for raw and treated wastewater was estimated with 10% dilution. The feasibility of decolourisation of silk dyeing bath (SDB) wastewater was investigated by slurry catalyst system (SCS) on 6 batches of SDB wastewater with 1500 mg/L of catalyst concentration. The reactors were run in duplicate and exposed to solar irradiance under aerated condition between 10:30 and 14:30 hours. The system was operated with aeration to keep the catalyst under suspension, since most of the catalyst was found settled.

3.11.1 Reusability of spent catalyst

The reusability of spent catalyst was investigated for 6 batches of SDB wastewater by separating the catalyst after 4 hours of decolourisation experiment. The other experimental conditions were as discussed in section 3.7.13. Reactors with fresh catalyst were treated as control.
3.11.2 Regeneration of exhausted catalyst

The catalyst used for decolourisation of SDB wastewater was found exhausted immediately after first use for all the 6 batches of wastewater studied. Hence, the spent catalyst after exhaustion was separated and the attempts were made to regenerate the same. The regeneration was done with distilled water, sodium bi-carbonate (0.1M) and nitric acid (0.1N). The spent catalyst after exhaustion was separated by filtration through 0.45 micron membrane. Then, it was made a slurry of 0.1% concentration with distilled water, NaHCO₃ (0.1M) and HNO₃ (0.1N), separately, and stirred for 30 minutes by magnetic stirrer, dried, and reused for decolourisation of SDB wastewater. The catalyst concentration adopted, was 1500 mg/L.

In all the cases, the decolourisation efficiency of regenerated catalyst was compared with that of the fresh catalyst as control.

3.12 STUDIES ON ENHANCEMENT OF BIODEGRADABILITY OF SILK DYEING WASTEWATER BY SPC PROCESS

Cottage silk dyeing units in Kanchipuram discharge the silk dyeing (SD) wastewater, which consist of both dyeing bath wastewater and rinse wastewater, into the municipal drain system and the municipal wastewater is subjected to biological treatment. As the SD wastewater was low bio-degradable in nature, the feasibility of enhancement of biodegradability of such wastewater by SPC process prior to co-disposal with domestic wastewater was studied. The schematic work plan for the studies is depicted in Fig. 3.4. The SD wastewater were irradiated after adding 1500 mg/L of catalyst for 2 hours between 12.00 and 14:00 hrs under aerated conditions. Since, most of the catalyst in the unaerated SPC system was found in settled conditions, the SPC system was operated with aeration, to keep the catalyst under suspension.
Fig. 3.4 Biodegradability enhancement studies on Silk Dyeing (SD) Wastewater
The change in recalcitrant chemical oxygen demand, COD$_R$, (COD - BOD$_5$), biodegradability index, BDI, (BOD$_g$/COD) and bio-refractory index, BRI, (COD$_r$/COD) were taken as the indicators of enhancement of biodegradability of SD wastewater. The experiments were also conducted with dark control and blank control in addition to the standard aerated SPC system. The experiments were repeated for 3 batches of SD wastewater. The untreated wastewater samples were filtered through Whatman filter No.42. for removal of suspended and floating impurities. However, the treated wastewater samples were not filtered for separation of the catalyst particles.

3.12.1 Inoculum development

The inoculum (seed) was first developed in the laboratory based on the untreated SD wastewater. The stock biomass was developed using MLSS collected from a sewage treatment plant at Chennai and raw domestic wastewater collected from the sewage treatment system at Kanchipuram. The inoculum reactor (4.5 litres capacity) was operated with 22 hours of aeration, followed by settling for 1.5 hours and decantation for 0.5 hour. The decanted portion of the reactor contents was replaced by raw SD wastewater at a incremental rate of 10% of the reactor contents every day. After 2 weeks, the inoculum reactor was operated fully with SD wastewater continuously with a mean cell residence time of 6 days. The same procedure was adopted for developing inoculum based on SPC treated SD wastewater. The inoculum thus developed was used for determination of BOD.

3.12.2 Effect of seed on BOD determination

The effect of biological seed on BOD estimation was assessed based on two types of seed organisms developed. The seeds based on untreated SD wastewater ($S_a$) and SPC treated SD wastewater ($S_b$) were used for estimation of BOD$_5$ of same batch of SPC treated SD wastewater. Though,
no significant variation was observed between the BOD values based on the two seed, further BOD estimation was done by the seed developed from the respective treated /untreated SD wastewater, acclimatised for a week. The wastewater (treated/untreated) were stored at 4°C and brought to the room temperature before testing. The samples were analysed without separation of catalyst, since TiO₂ is reported to be non bio toxic (Mills et al 1993). Hence, it is not likely to interfere with the BOD determination. Thus, the possibility of removal of biodegradable intermediates formed, due to adsorption by filter membranes during separation of the catalyst particles is avoided.

3.12.3 Effect of exposure duration on biodegradability

The effect of exposure duration on the biodegradability of SD wastewater was studied on four batches of wastewater. The duration of exposure was varied from 1 to 4 hours. The timings of the exposure were 1 hour (12:00 to 13:00 hrs), 2 hours (11:30 to 13:30 hrs), 3 hours (11:00 to 14:00 hrs); and 4 hours (10:30 to 14:30 hrs), respectively. The timings were so selected that the fluctuation in solar radiation was minimum. Reactors (in duplicate) containing a litre of SD wastewater with liquid depth of 2.7cm and 1500 mg/L of catalyst concentration were exposed to solar irradiance under aerated conditions. The duration beyond which there was no appreciable change in the biodegradability of SD wastewater was taken as the appropriate time of exposure for such studies.

3.12.4 Effect of catalyst concentration on biodegradability

The effect of catalyst concentration on the biodegradability of four batches of SD wastewater was investigated with catalyst concentration ranging from 1000 mg/L to 4000 mg/L. The reactors were operated in duplicate under aerated conditions. The catalyst concentration beyond which
there was no appreciable change in the biodegradability of SD wastewater was taken as the appropriate catalyst concentration for such studies.

3.12.5 Reusability of spent catalyst for enhancement of biodegradability

The feasibility of reusing the spent catalyst was investigated by separating the catalyst after conducting the experiments for 2 hours with catalyst concentration of 1500 mg/L. The experiments were repeated for 4 batches of SD wastewater. The multiple reactors were operated under aerated conditions. The change in BDI and BRI of the SD wastewater was taken as the indicator for reusability of catalyst.