CHAPTER 3

MATERIALS AND METHODS

3.1 GENERAL

In this research, the systematic studies were done to develop a coupled treatment system with two step solar photocatalytic and biological treatment processes for the treatment of phenolic wastewaters. The degradation study of phenolic wastewaters by solar photocatalytic process was carried out at the terrace of the Centre for Environmental Studies, Anna University, Chennai. The Unit Operations and Processes Engineering Laboratory and Analytical Laboratory of the Centre were used for carrying out experimental studies and analysis. The various materials used and the methodology adopted for the studies are described in this chapter. Figure 3.1 shows the schematic methodology for this research work.

3.2 MATERIALS

3.2.1 Titanium Dioxide

The photocatalyst employed was commercial titanium dioxide supplied by Degussa P25. According to the manufacturer’s specifications, P25 has an elementary particle size of 30 nm, a BET specific surface area of 50 m$^2$/g and its crystalline mode is 80% anatase and 20% rutile. The catalyst was used as received.
Figure 3.1 Schematic methodology of the research study
3.2.2 Collection of Phenolic Wastewaters

The phenolic wastewater samples were collected from various industries viz. resin manufacturing industry, oil refinery, paper mill, pharmaceutical and chemical industry. The samples were stored at 4°C in light resistant containers and brought to room temperature before using for analysis.

3.2.3 Preparation of Simulated Phenolic Wastewater

The phenol, o-cresol, m-cresol, and p-cresol were used without further purification. Exactly 1g of the compound was dissolved and made up to 1000 mL. The solutions were prepared by dissolving the compounds using double distilled water. The stock solutions were stored in amber bottles in the refrigerator (4°C).

3.2.4 Chemicals and Reagents

All chemicals and reagents used in the studies are of analytical grade (make: Merck, CDH, Qualigens). The double distilled water was used to prepare experimental solution. The pH of the solutions was adjusted using H₂SO₄ or NaOH.

3.2.5 Preparation of Fixed Catalyst System (FCS)

Fiber glass cloth specimens of size 20 × 20 cm were washed with diluted HCl and heat treated in an electric furnace at 500°C for 2 hours before fixation of TiO₂. This treatment ensured complete removal of any organic impurity on the surface of the specimens. An aqueous TiO₂ particle dispersion was used as a source of titanium. The dispersion was loaded onto the fiber
glass cloth using a paint brush, after which the cloth was dried at room temperature.

### 3.3 METHODOLOGY

The detailed methodology consists of the following steps.

#### 3.3.1 Collection and Characterization of Phenolic Wastewaters

The phenolic wastewater samples were collected from the various industries viz. resin manufacturing, oil refinery, paper mill, pharmaceutical and chemical industry and characterized for various physio-chemical parameter viz. pH, phenol concentration, COD, BOD, chlorides and sulphates as per standard methods (APHA 2003). Table 3.1 shows the methods adopted for chemical analysis.

#### 3.3.2 Experimental Setup for Laboratory-Scale Studies on Solar Photocatalytic Oxidation (SPCO)

All photocatalytic experiments were carried out at Anna University campus in Chennai, (13°00.57"N; 80°14.12"E), Tamil Nadu. Open borosilicate glass trays of 1.5 L capacity was used as the reaction vessel. All experiments were conducted using solar light in the month of June and July (UV intensity 22 ±2 W/m²). The suspensions were magnetically stirred in the dark for 30 min to attain adsorption - desorption equilibrium between phenol and TiO₂. Irradiation was carried out in the open air and continuously aerated by a pump to provide oxygen and for the complete mixing of reaction solution. In all cases, 1 L of reaction mixture was irradiated. At specific time intervals, required amount was withdrawn and filtered to separate the catalyst. The samples were analysed for phenol, COD and TOC as per standard methods.
Table 3.1  Methods of chemical analysis

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Parameter</th>
<th>Analytical Methods</th>
<th>Instrument</th>
<th>APHA 2003 Reference</th>
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<tr>
<td>1.</td>
<td>pH</td>
<td>Potentiometry</td>
<td>pH 197, WTW Germany</td>
<td>4500 B</td>
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<td>2.</td>
<td>DO</td>
<td>Membrane electrode method</td>
<td>WTW OXI – 197</td>
<td>4500 O - G</td>
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<tr>
<td>3.</td>
<td>BOD</td>
<td>Winkler’s method</td>
<td>Titration</td>
<td>5210 B</td>
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<tr>
<td>4.</td>
<td>COD</td>
<td>Dichromate digestion</td>
<td>Titration</td>
<td>5220 C</td>
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<tr>
<td>5.</td>
<td>TOC</td>
<td>High temperature combustion</td>
<td>Micro C, Analytic Jena</td>
<td>5310 B</td>
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<td>6.</td>
<td>TDS</td>
<td>Gravimetric method</td>
<td>Oven, Balance</td>
<td>2540 C</td>
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<tr>
<td>7.</td>
<td>TSS</td>
<td>Gravimetric method</td>
<td>Oven, Balance</td>
<td>2540 D</td>
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<tr>
<td>8.</td>
<td>TKN</td>
<td>Distillation</td>
<td>B 324, Buchi distillation unit</td>
<td>4500 N&lt;sub&gt;org&lt;/sub&gt; B</td>
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<tr>
<td>9.</td>
<td>Phosphate</td>
<td>Spectrophotometry-Stannous chloride method</td>
<td>Specord 40, Analytica Jena</td>
<td>4500-P D</td>
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<tr>
<td>10.</td>
<td>Chlorides</td>
<td>Argentometric method</td>
<td>Titration</td>
<td>4500 Cl'B</td>
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<td>11.</td>
<td>Phenol, &lt;i&gt;o&lt;/i&gt;-cresol, &lt;i&gt;m&lt;/i&gt;-cresol</td>
<td>Spectrophotometry-4 amino antipyrine method</td>
<td>Specord 40, Analytica Jena</td>
<td>5530 D</td>
</tr>
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<td>12.</td>
<td>&lt;i&gt;p&lt;/i&gt;-cresol</td>
<td>Spectrophotometry-λ&lt;sub&gt;max&lt;/sub&gt;-279 nm</td>
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<td>-</td>
</tr>
<tr>
<td>13.</td>
<td>MLSS and MLVSS</td>
<td>Gravimetric method</td>
<td>Oven, Balance</td>
<td>2540 G</td>
</tr>
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<td>14.</td>
<td>SVI</td>
<td>Gravimetric method</td>
<td>1000 mL cylinder</td>
<td>2710 D</td>
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</tbody>
</table>
3.3.3 Lab-Scale Feasibility Studies on Solar Photocatalytic Degradation of Phenolic Wastewaters by Suspended Catalyst System (SCS)

In order to study the effects of operating parameters in SCS, the experiments were conducted under the operating conditions at pH (3-9), catalyst dosage (0.15 -1 g/L), catalyst reuse (15 trails), initial pollutant concentration (10-100 mg/L), aeration (pre-aeration, with and without aeration), chlorides (50-200 mg/L), sulphates (50-200 mg/L), liquid volume (0.25-1.5 L), solar light intensity (throughout the year) and contact time (5 hours) for degradation of phenolic wastewaters. The schematic methodology for the studies is depicted in Figure 3.2.

3.3.3.1 Effect of control conditions

In order to study the effect of solar irradiation and catalyst (TiO₂), three sets of experiments were conducted viz. phenolic wastewater with the solar in the absence of TiO₂, phenolic wastewater with TiO₂ in dark, and phenolic wastewater under solar irradiation with TiO₂. The pH, phenol concentration and catalyst amount were kept as 6, 50 mg/L and 0.25 g/L respectively.

3.3.3.2 Effect of adsorption

In the dark adsorption studies, 250 mL volume of wastewater at pH in the range of 4-11, phenol concentration varied in the range of 10-60 mg/L, and catalyst amount in the range of 0.5 -2 g/L were mixed and shaken for 5 h to allow the equilibrium to reach. The conical flasks were covered by aluminum foil during shaking.
Figure 3.2 Schematic methodology of Slurry Catalyst System (SCS)
3.3.3.3 Effect of catalyst dosage

In Slurry Catalyst System (SCS), catalyst dosage is an important parameter that had been extensively studied. The optimal catalyst dosage reported in literature was in a wide range. Even for the same catalyst (Degussa P25), a big difference in optimal catalyst dosage from 0.5 to 2 g/L was reported. Till now no general conclusion has been made. Hence in order to study the effect of catalyst dosage on degradation of phenol, o-cresol, m-cresol and p-cresol wastewaters by SCS, a series of experiments was conducted with reactions slurries containing phenol, o-cresol, m-cresol and p-cresol concentration of 50 mg/L, and at pH 6. The catalyst amount was varied in the range of 0.15 - 1 g/L.

3.3.3.4 Effect of pH

In order to study the effect of pH on degradation of phenol, o-cresol, m-cresol and p-cresol wastewaters by SCS, a series of experiments was conducted with reaction slurries containing phenol, o-cresol, m-cresol and p-cresol concentration of 50 mg/L and catalyst amount of 0.25 g/L. The initial pH of the wastewater was varied in the range of 3-9.

3.3.3.5 Effect of initial pollutant concentration

In order to study the effect of initial pollutant concentration on degradation of phenol, o-cresol, m-cresol and p-cresol wastewaters by SCS, a series of experiments was conducted with reaction slurries at pH 6, Catalyst amount 0.25 g/L and initial concentration was varied in the range of 10-100 mg/L.
3.3.3.6 Effect of chloride

Industrial wastewaters contain, apart from the pollutants, different salts at different concentrations. The real phenolic wastewaters collected from industries contain chloride up to 200 mg/L. Based on that, the effect of chloride concentration on degradation of phenolic wastewaters was studied. A series of experiments were conducted with reaction slurries at pH 6, catalyst amount 0.25 g/L and phenol concentration 50 mg/L. The concentration of chlorides by adding sodium chloride was varied in the range of 50 - 200 mg/L. Blank controls were also run without addition of sodium chloride.

3.3.3.7 Effect of sulphate

The presence of sulphate is common in industrial wastewaters. They may have a positive or negative effect on the photocatalytic degradation. Various researchers have reported conflicting results. Therefore, a systematic study is required to delineate the effects of sulphate in the wastewaters. The real phenolic wastewaters collected from industries contain sulphates up to 200 mg/L. Based on that, the effect of sulphate concentration on degradation of phenol wastewaters was studied. A series of experiments were conducted with reaction slurries at pH 6, catalyst amount 0.25 g/L and phenol concentration 50 mg/L. The concentration of sulphate by adding sodium sulphate was varied in the range of 50 - 200 mg/L. Blank controls were also run without addition of sodium sulphate.

3.3.3.8 Effect of aeration

Presence of electron acceptors is recommended so as to prevent the recombination reaction between the generated positive holes and electrons.
Generally aeration is used for this purpose as it also provides uniform mixing and suspension of the catalyst in the case of slurry catalyst system and also it is economical source of oxygen. Hence, the effect of aeration on degradation of phenolic wastewaters was studied. A series of experiments were conducted with reaction slurries at three conditions viz. aeration before reaction, aeration during reaction and without aeration at pH 6, catalyst amount 0.25 g/L and phenol concentration 50 mg/L.

3.3.3.9 Effect of liquid volume

In order to study the effect of liquid volume on degradation of phenolic wastewaters by SCS, a series of experiments were conducted with reaction slurries at pH 6, catalyst amount 0.25 g/L, phenol concentration 50 mg/L and the volume of the wastewaters were varied in the range of 0.25 -1.5 L.

3.3.3.10 Effect of contact time

In order to study, the complete degradation of phenol, o-cresol, m-cresol and p-cresol wastewaters by SCS, the effect of contact time was studied by conducting a series of experiments with reaction slurries pH 6, catalyst amount 0.25 g/L and phenol, o-cresol, m-cresol and p-cresol concentration 50 mg/L. The contact time was extended up to 5 hours.

3.3.3.11 Effect of light intensity

Considering the abundance of solar irradiation in tropical countries like India, the use of the photocatalysis with solar irradiation would be an advantage when compared to artificial light. The sunlight intensity is highly variable during the day or year, and therefore this was considered during
evaluation of solar driven processes. UV light provides the photons required for the electron transfer from valence band to conduction band of the photocatalyst. The energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent upon the light intensity. Therefore, the effect of solar light intensity is important. In order to study the effect of solar light intensity on degradation of phenolic wastewaters the experiments were repeated at every day of the year during 9.00 to 17.00 hours with reaction slurries at pH 6, catalyst amount 0.25 g/L and phenol concentration 50 mg/L.

3.3.3.12 Separation of catalyst from treated water

Even though the TiO$_2$ is non-toxic, it can be reused for several trials for degradation of phenol and also it reduced operating cost of the treatment. Hence it is necessary to separate the TiO$_2$ from the aqueous solution before transferring to further treatment (post treatment) or its disposal to watercourse. The batch sedimentation experiments were carried out in a standard graduated cylinder with a volume of 1 L. The pH of the suspensions was adjusted to 7 by using 0.1 N of sodium hydroxide solution and the suspensions were allowed to settle. The height of the solid – liquid interface was then measured using the graduations on the cylinder at timed intervals. And also measurement of absorbance was carried out with UV-Vis spectrophotometer at 400 nm.

3.3.3.13 Effect of catalyst reuse

In order to study the effect of reusability of catalyst on degradation of phenolic wastewaters, a series of experiments was conducted at optimum condition with fresh catalyst as control. The used TiO$_2$ was wasted, heated to
dryness and used in new experiments with fresh phenolic wastewater. The reusability experiments were continued until the catalyst lost its activity.

3.3.4 Feasibility Studies on Solar Photocatalytic Degradation of Phenolic Wastewaters by Fixed Catalyst System (FCS)

Even though, solar photocatalytic degradation by slurry catalyst system was performed efficiently in the degradation of phenolic wastewaters, there are some problems, such as exponential decrease of the available light with distance from a light source due to the absorbance of UV light by particles themselves. Also separation of catalyst, recycle of TiO$_2$ particles from treated wastewaters was difficult. Hence, the feasibility of degradation of phenolic wastewaters by Fixed Catalyst System (FCS) was studied. The effect of catalyst loading in the range of 0.15-3 g/L and reusability of FCS up to 4 trails was studied for the degradation of phenolic wastewaters. The schematic methodology for the studies is depicted in Figure 3.3.

3.3.4.1 Effect of catalyst loading

In order to study the effect of catalyst loading on the degradation of phenolic wastewaters by Fixed Catalyst System (FCS), a series of experiments were conducted at pH 6, phenol concentration 50 mg/L and the TiO$_2$ amount was varied in the range of 1-5 g/L with 1-5 times coated on Fiber glass cloth respectively.

3.3.4.2 Effect of reuse

In order to verify the activity of used catalyst and check out its life time, on degradation of phenolic wastewater, a series of experiments were conducted at pH 6, phenol concentration 50 mg/L and TiO$_2$ amount 3 g/L.
with fresh catalyst as control. The used TiO$_2$ system was washed, dried at room temperature and used in new experiments with fresh phenol wastewater.

Figure 3.3  Schematic methodology of Fixed Catalyst System (FCS)
3.3.5 Feasibility Studies on Degradation of Phenolic Wastewaters by Solar/TiO₂/H₂O₂ System

The Solar/TiO₂ system was not effectively removed the phenol concentration more than 50 mg/L. And, also the chloride and sulfate ions gave negative effects on the phenol removal efficiency even at low concentration of 50 mg/L. But the real industrial wastewaters contain phenol concentration in the range of 100 – 500 mg/L and chloride and sulfate concentration in the range of 50 – 200 mg/L. Hence, in order to accelerate the rate of reaction, the Hydrogen peroxide is used as electron acceptor. The effect of H₂O₂ dosage in the range of 0.15-1.5 g/L, pollutant concentration in the range of 100 – 500 mg/L and combined effects of inorganic salts in the range of 50 – 200 mg/L was studied for the degradation of phenolic wastewaters. Hydrogen peroxide was removed from treated solution by adding an excess of sodium sulphite. Aeration was then used to convert the remaining sulphite into sulphate (Maria et al 2006). The concentration of H₂O₂ as indicated by the hydrogen peroxide test strips was monitored over time. The schematic methodology for the studies is depicted in Figure 3.4.

3.3.5.1 Effect of H₂O₂ dosage

In order to keep the efficiency of the added H₂O₂, it is necessary to choose the optimum concentration of H₂O₂ according to the type and concentration of the pollutants. Hence the effect of addition of H₂O₂ was studied by conducting, a series of experiments with reaction slurries at pH 6, Catalyst amount 0.25 g/L, phenol concentration 50 mg/L and H₂O₂ dosage was varied in the range of 0.15 – 1.5 g/L.
3.3.5.2 Effect of method of H₂O₂ addition

In order to study the effect of step wise addition of H₂O₂ at regular intervals during the reaction instead of adding the entire amount in the beginning of the reaction, the study was conducted at pH 6, Catalyst amount 0.25 g/L, and H₂O₂ dosage 0.3 g/L. The addition of H₂O₂ by increments of 25 % of their total amount added to the reaction was made every 30 min. up to 2 hours. And, also second addition of H₂O₂ after one hour instead of single addition was studied.
3.3.5.3 **Effect of initial phenol concentration**

In order to study the effect of initial concentration on degradation of phenolic wastewaters, a series of experiments was conducted with reaction slurries at pH 6, Catalyst amount 0.25 g/L, H₂O₂ dosage 0.3 g/L and initial concentration was varied in the range of 100 -500 mg/L. The control experiments without H₂O₂ and without TiO₂ were also conducted.

3.3.5.4 **Effect of inorganic salts**

In order to study the combined effect of inorganic salts (chlorides and sulphates) on degradation of phenolic wastewater by solar/TiO₂/H₂O₂ process, studies were conducted at pH 6, catalyst amount 0.25 g/L, phenol concentration 50 mg/L and H₂O₂ dosage 0.3 g/L, the salts concentration was varied in the range of 50 mg/L - 200 mg/L, (ie. 50 mg/L chloride + 50 mg/L sulphates - 200 mg/L chloride + 200 mg/L sulphates) based on the real industrial wastewaters. The control experiments without inorganic salts were also conducted.

3.3.6 **Optimization of Solar Photocatalytic Degradation of Phenolic Wastewater by Response Surface Methodology**

The effects of the three critical factors viz., pH, TiO₂ and Phenol concentration on the photocatalytic degradation of phenolic wastewaters were simulated and evaluated using Response Surface Methodology (RSM). This methodology has shown to be a valuable tool to model complex process such as the light - enhanced photocatalytic reaction and to achieve at minimal cost, optimal experimental parameters. RSM is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes performing a minimal number of well-chosen experiments. It uses
an empirical mathematical model (polynomial) to represent the response (Y) in the experimental field, which depends on the controllable inputs that are natural variables.

Table 3.2 Experimental range and levels of the independent test variables

<table>
<thead>
<tr>
<th>Variables</th>
<th>Ranges and levels</th>
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<td></td>
<td>-1</td>
</tr>
<tr>
<td>Initial pH (A)</td>
<td>5</td>
</tr>
<tr>
<td>Catalyst amount (B) (g/L)</td>
<td>0.2</td>
</tr>
<tr>
<td>Phenol concentration (C) (mg/L)</td>
<td>45</td>
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A class of three level of complete Box-Behnken design for the estimation of parameters in a second order mode was developed by Box-Behnken. Basically, the optimization process involves 3 major steps, which include performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the response and checking the adequacy of the model. The effect of several factors influencing the phenol degradation, such as pH concentration of the phenol and catalyst amount were chosen as the critical variables and designated as A, B and C respectively. The low, middle and high level of the variables will be designed as -1, 0 and +1 respectively. The actual design of experiments is listed in Table 3.2. The three significant independent variables A, B, C and the mathematical relationship of the response Y on these variables can be approximated by a second-degree polynomial equation (Douglas 2004).

\[
y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2
\] (3.1)
The regression equation obtained after analysis of variance gives the level of degradation as a function of different concentration of phenol, pH and catalyst amount. Regression mode containing 3 linear (A, B and C), 3 quadratic (A², B² and C²) and 3 interaction terms plus 1 block term was employed by using the design expert. The design was performed because relatively few experimental combinations of the variables were needed to estimate potentially complex response functions. A total of 17 experiments were necessary to estimate the 10 coefficients of the model using multiple linear regression analysis. The above equation was solved by using the design expert (Stat - Ease Inc. version 7) to estimate the response of the independent variables. The maximum predictable response for photocatalytic degradation of phenol was also obtained.

3.3.7 Experimental Setup for Bench-Scale Solar Photocatalytic Reactor Studies

Four bench-scale solar photocatalytic reactors were fabricated viz. single baffle reactor, multiple baffles reactor, cascade reactor and solar pond reactors of 5 L capacity with Non-concentrating suspended catalyst system without any UV transparent walls and solar tracking system. The reactors were constructed for conducting bench-scale experiments. The irradiated surface area and volume of reactor was 0.08 m² and 5 L respectively. The set up consisted of a flow-through reactor placed on a platform under solar irradiation. The wastewater was continuously recycled with the help of circulating pump.

Single baffle reactor (Reactor 1) was made from an extruded double skinned acrylic panel with built in flow channels of cross – section of 0.4 m × 0.1 m. The size of reactor was 0.4 m × 0.2 m × 0.1 m. Figure 3.5 depicts the photographic view of single baffle reactor. Multiple baffles reactor
(Reactor 2) was built of acrylic in the form of pond divided with baffle plates of about 0.1 m height at specific intervals. The size of reactor was 0.4 m × 0.2 m × 0.1 m. Figure 3.6 depicts the photographic view of multiple baffles reactor. Cascade reactor (Reactor 3) was composed of 6 nos. of acrylic stairs with stair size of 0.16 m × 0.08 m × 0.1 m (L × W × H). The wastewater flowed over the steps before being collected in a tank, from which it was elevated with a pump to top of the steps for recirculation. Figure 3.7 depicts the photographic view of cascade reactor. Solar pond (Reactor 4) consisted of shallow pond reactor of size 0.4 m × 0.2 m × 0.1m open to atmosphere was fabricated. The pond was equipped with a mixing facility. Figure 3.8 depicts the photographic view of solar pond reactor.

Figure 3.5 Photographic view of single baffle reactor
Figure 3.6  Photographic view of multiple baffle reactor

Figure 3.7  Photographic view of cascade reactor
3.3.8 Studies on Bench-Scale Reactors for Degradation of Phenolic Wastewaters by Solar/TiO$_2$ System

Evaluation of the solar photocatalytic reactors performance was carried out by varying the volume of wastewaters in the range of 1-5 L and the recycle flow rates in the range of 250 – 750 mL/min. for the degradation of phenolic wastewaters. All experiments were conducted using solar light on clear sunny days in the month of April and May (UV intensity 32 ±2 W/m$^2$). The tests were started at 10 a.m and stopped at 4 p.m. At specific time intervals, required amount was withdrawn and filtered to separate the catalyst. The samples were analysed for phenol, and TOC as per standard methods. The schematic methodology for the studies is depicted in Figure 3.9.
Figure 3.9  Schematic methodology of studies on solar photocatalytic reactors

Degradation of phenolic wastewaters

Bench - Scale Solar Photocatalytic Reactors

1. Single baffle reactor
2. Multiple baffle reactor
3. Cascade reactor (STEP)
4. Solar pond reactor

Volume of wastewater
(1 – 5 L)

Recycle flow rate
(250, 500, 750 mL/min)

Compare the efficiency of the solar photocatalytic reactors
3.3.8.1 **Effect of volume of wastewaters**

In order to study the effect of volume of wastewaters on degradation of phenolic wastewaters, a series of experiments were conducted in four reactors with reaction slurries at pH 6, catalyst amount 0.25 g/L and phenol concentration 50 mg/L and the volume of wastewaters was varied in the range of 1 - 5 L with a recycle flow rates of 250, 500 and 750 mL/min.

3.3.8.2 **Effect of recycle flow rate**

In order to study the effect of recycle flow rate on degradation of phenolic wastewaters, a series of experiments were conducted in three reactors with reaction slurries at pH 6, catalyst amount 0.25 g/L and phenol concentration 50 mg/L and recycle flow rate was varied in the range of 250 – 750 mL/min with 1- 5 L volume of wastewater.

3.3.9 **Enhancement of Biodegradability of Phenol, o-cresol, m-cresol and p-cresol Wastewaters by Solar/TiO$_2$/H$_2$O$_2$ System**

As the phenol, o-cresol, m-cresol and p-cresol are non-biodegradable in nature, the feasibility of enhancement of biodegradability of wastewater was carried out by solar/TiO$_2$/H$_2$O$_2$ system, in a single baffle reactor with volume of wastewater 5 L and recycle flow rate at 500 mL/min. The simulated phenolic wastewater was prepared based on the concentrations of phenol and inorganic ions of real industrial wastewaters. The wastewaters was prepared by adding phenol concentration in the range of 100-500 mg/L, chloride concentration of 200 mg/L, and sulphate concentration of 200 mg/L. Likewise simulated o-cresol, m-cresol and p-cresol wastewater were also prepared and studied. The biodegradability was evaluated through the evolution of the BOD / COD ratio. As a reference, this
parameter for biodegradable municipal wastewater is of around 0.4. It should be noticed that BOD/COD ratio higher than 0.4 indicate a readily and rapidly degradable solution while ratio below 0.4 involve the presence of slowly biodegradable compounds.

### 3.3.10 Experimental Setup for Bench-Scale Biological Treatment Process-Sequencing Batch Reactor (SBR)

Two identical plexiglass reactors of dimensions $20 \times 15 \times 25$ cm ($L \times W \times H$) with a total working volume of 7 L were operated in parallel with FILL, REACT, SETTLE and DRAW periods in the ratio of 1:5:1:1 to constitute a cycle time of 8 h. Aeration was provided using air stones and temperature was maintained under room conditions, between 25 and 30°C, while keeping the concentration of Dissolved Oxygen (DO) not lower than 3 mg/L. All operating conditions of the SBR process are summarized in Table 3.3.

#### Table 3.3 Operating conditions of the SBR process

<table>
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<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fill period (h)</td>
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</tr>
<tr>
<td>React period (h)</td>
<td>5, 9, and 21</td>
</tr>
<tr>
<td>Settle period (h)</td>
<td>1</td>
</tr>
<tr>
<td>Draw period (h)</td>
<td>1</td>
</tr>
<tr>
<td>Idle period (h)</td>
<td>4 and 16</td>
</tr>
<tr>
<td>SRT (d)</td>
<td>10, 20, and 30</td>
</tr>
</tbody>
</table>

The bioreactor was seeded with activated sludge coming from the recirculation stage of municipal wastewater treatment plant in Nessapakkam,
Chennai and acclimatized to the base mix of the following, glucose, sodium bicarbonate, magnesium sulphate, potassium dihydrogen phosphate, ferrous sulphate, manganese sulphate, starch, urea and calcium chloride. The glucose and starch were gradually replaced by phenol as the sole substrate. During each cycle, 5 L of the feed solution was introduced continuously during the FILL period and same volume of treated wastewater was removed during the DRAW period. After the attainment of stable operating conditions in terms of the COD and the Mixed Liquor Suspended Solids (MLSS) concentration for each influent phenol concentration, the effluent COD and phenol concentrations, the Sludge Volume Index (SVI) and MLSS concentration was determined. At each influent phenol concentration, the concentration of D.O, COD and phenol in the mixed liquor during the REACT period was determined. The Figure 3.10 depicts the photographic view of sequencing batch reactor.

Figure 3.10 Photographic view of sequencing batch reactor
3.3.11 Bench-Scale Optimization Studies on Biological Sequencing Batch Reactor (SBR)

Performance of the sequencing batch reactor was studied in phenol wastewater at influent concentrations in the range of 100-500 mg/L, aeration time in the range of 6-21 hours and SRT in the range of 10-20 days. The schematic methodology for the studies is depicted in Figure 3.11.

3.3.11.1 Effect of air stripping

In order to verify that biological degradation was the major route for phenol removal, it is necessary to measure the removal of phenol by air stripping. The removal of phenol due to aeration was studied at phenol concentration 200 mg/L in the absence of biomass.

3.3.11.2 Effect influent phenol concentration

In order to study the effect of influent concentration on degradation of phenolic wastewaters, experiments were conducted at cycle time 8 h, SRT 10 days and phenol concentration was varied in the range of 100 – 500 mg/L.

3.3.11.3 Effect of aeration time

In order to study the effect of aeration time on degradation of phenolic wastewater, experiments were conducted at phenol concentration 500 mg/L, SRT 10 days and the aeration time was varied in the range of 5-21 h.
Biodegradation of phenolic wastewaters

pH = 6.5 – 7.5
Temp = 25° – 30° C
COD: N: P = 100: 5: 1
MLSS = 4000 ± 100 mg/L

Initial Phenol Concentration
(100 – 500 mg/L)

Aeration time
(5, 9, 21 h)

SRT
(10, 20, 30 days)

SBR cycle time
(8, 12, 24 h)

Cycle per day
(1, 2, 3)

Pre-treated wastewater

Kinetic Analysis

Figure 3.11 Schematic methodology of biological treatment process
3.3.11.4 Effect of MLSS concentration

In order to study the effect of MLSS on degradation of phenolic wastewater, experiments were conducted at phenol concentration 500 mg/L, SRT of 10 days and the cycle time of 8 h. The effect of biomass concentration on the treatment performance was studied under the concentration of MLSS in the range of 3000 - 5000 mg/L.

3.3.11.5 Effect of operation cycle per day

In order to study the effect of operation cycle per day on degradation of phenolic wastewater, experiments were conducted at phenol concentration 500 mg/L, SRT of 10 days and the cycle time of 8 h. The effect of operation cycle per day on the phenol removal was studied under 1, 2 and 3 cycles per day.

3.3.11.6 Effect of SRT

In order to study the effect of SRT on degradation of phenolic wastewater, experiments were conducted at phenol concentration 500 mg/L, and the cycle time of 8 h. The effect of SRT on the phenol removal was studied under three different periods of SRT 10, 20 and 30 d.

3.3.12 Treatability Studies on Coupled Treatment Process

Treatability studies on coupled solar photocatalytic and biological treatment was studied in semi-continuous flow mode at optimum conditions at pH 6, Catalyst amount 0.25 g/L, H₂O₂ dosage 0.3 g/L for degradation of phenolic wastewaters. The simulated phenolic wastewater was prepared based on the concentrations of phenol and inorganic ions of real industrial
The wastewaters was prepared by adding phenol concentration in the range of 100-500 mg/L, chloride concentration of 200 mg/L, and sulphate concentration of 200 mg/L. The wastewaters were transferred to biological system after solar photocatalytic pretreatment based on evolution of the BOD / COD ratio. The schematic methodology for the studies is depicted in Figure 3.12.

Figure 3.12  Schematic methodology of coupled treatment process
3.3.13 Design of Pilot-Plant System and Treatment Cost Estimation

The design of coupled pilot-plant solar photocatalytic and biological treatment system was done for treating 1 m³ containing phenol concentration of 500 mg/L. Design was done based on the reactor configuration, Rate constant, i.e., kinetics of the process, Desired destruction level or destruction and removal efficiency (DRE). Total cost of the treatment plant was calculated by including capital cost and operating cost. The capital cost includes cost of reactor, storage and settling tanks, piping, fittings, pumps, blowers, controls, installation, auxiliary and capital contingency. The Operational and Maintenance (O & M) cost includes catalyst, oxidant, pre and post-treatment, filters, energy, and maintenance.