Phenols is a common pollutant discharged by polymeric resin production, chemical industries, textile industries, oil refineries, coking plant, etc. It is considered as a bio-refractory pollutant in wastewaters due to their high toxicity, high oxygen demand and low biodegradability. The efficiency of the biological treatment is often hampered by the presence of bio-refractory pollutants, though they are most economical and conventionally used treatment strategies. On the other hand, photocatalysis oxidizes almost all pollutants, but considering the economical aspects, the use of photocatalysis alone as treatment may not look lucrative. Thus, a hybrid method consisting of using photocatalysis to increase the biodegradability of the wastewaters up to a desired level followed by biological treatment is perhaps needed for the future to achieve an overall performance to meet the limits of the environmental legislation. In this research, the solar photocatalytic treatment was used as a pretreatment method to increase biodegradability prior to the biological treatment process.

The wastewater samples were collected from the phenolic wastewaters generating industries (viz. Resin manufacturing, oil refinery, paper mill, pharmaceutical and chemical industry) and characterized for various physio-chemical parameters viz. pH, phenol concentration, COD, BOD, chlorides and sulphates. Studies were conducted with simulated wastewaters based on the concentration of the pollutants in the real wastewaters. The Laboratory scale feasibility studies on solar photocatalytic oxidation (SPCO) had been carried out in order to study the effects of
operating parameters. In suspended catalyst system, maximum phenol removal of 95% was observed in 0.25 g/L catalyst dosage. The effect of pH on degradation of phenol, o-cresol, m-cresol and p-cresol were varied in the range of 3 - 9. The maximum removal efficiency was observed at pH 6, 7.5, 8 and 6 for phenol, o-cresol, m-cresol and p-cresol respectively. It was observed that the phenol removal and rate of degradation increased with increase in pollutant concentration up to 50 mg/L and then decreased. In order to study the effects of aeration, experiments were carried out with aeration and without aeration. When the wastewater was not aerated, the phenol decreased much faster than aerated at the initial stage at t ≤ 2, hours but the rate becomes extremely slower after that at t ≥ 2. It was observed that the phenol removal efficiency reached its maximum of 95% at maximum UV light intensity of 32 W/m² and the minimum phenol removal efficiency of 59% at minimum UV light intensity of 20 W/m². The effect of chlorides and sulphates were studied by varying the chlorides and sulphates concentration in the range of 50 – 200 mg/L. It was observed that the presence of these ions decreased the degradation rate of phenol due to a decrease in the adsorption of the pollutant and it act as hydroxyl ion scavengers.

The effect of addition of H₂O₂ in the range of 0.15 – 1.5 g/L was studied on the photocatalytic degradation of phenol. The addition of H₂O₂ from 0.15 – 0.3 g/L increased the degradation from 75 to 99% and then decreased. In solar/TiO₂ process, for pollutant concentration of 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L and 500 mg/L, the phenol removal was 54%, 35%, 22%, 22% and 20% respectively, whereas in solar/TiO₂/ H₂O₂ process the phenol removal was 97%, 70%, 54%, 47% and 45% for each corresponding pollutant concentration. Compared with solar/TiO₂ system, it
was found that solar/TiO$_2$/H$_2$O$_2$ system could accelerate the phenol removal rate. In solar/TiO$_2$ process, for salt concentration of 50 mg/L, 100 mg/L, 150 mg/L and 200 mg/L the phenol removal was 19%, 15%, 12% and 12% respectively, whereas in solar/TiO$_2$/ H$_2$O$_2$ process, the phenol removal was 94%, 92%, 90% and 90% for each corresponding salt concentration. It was observed that degradation rate sequences for solar / TiO$_2$ process is o-cresol > m-cresol > phenol > p-cresol, and for solar / TiO$_2$/ H$_2$O$_2$ process, the sequences is slightly modified to m-cresol > o-cresol > phenol > p-cresol. When compared to rate of degradation, the solar / TiO$_2$/ H$_2$O$_2$ is two to three times faster than the solar / TiO$_2$ process.

Batch type solar photocatalytic reactors viz. single baffle reactor, multiple baffle reactor, cascade reactor and solar pond reactor were constructed for conducting bench-scale experiments. Evaluation of the 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. The single baffle reactor showed the maximum phenol removal of 80% with recycle flow rate of 500 mL/min. The biodegradability of the phenol, o-cresol, m-cresol, and p-cresol was evaluated through the evolution of the BOD/ COD ratio. For untreated samples of 100 - 500 mg/L pollutant concentration, the BOD/COD ratio is zero, while solar photocatalytic treatment of 2, 2, 3, 4 and 5 hours enhanced the biodegradability values to 0.53, 0.41, 0.40, 0.44, and 0.40 for phenol concentration of 100, 200, 300, 400 and 500 mg/L respectively.

Performance of the sequencing batch reactor treating phenol wastewater at influent concentrations from 100 -500 mg/L was evaluated. The phenol removal efficiency was found to be 100%, 99%, 95%, 79% and 68% for phenol concentration of 100, 200, 300, 400, and 500 mg/L respectively.
The inhibitory effect seemed to be more pronounced with the increase in the phenol concentration by a decreasing rate constant (k) from 1.135 h$^{-1}$ to 0.248 h$^{-1}$ when the influent phenol concentration was increased from 100 to 500 mg/L. The maximum phenol removal of 85% and the best sludge settling properties at SRT 10 days and SBR cycle time of 8 hours was obtained.

The coupled reactor was operated in semi-continuous mode. The photocatalytic reactor treated the phenol wastewater in batch cycles providing phototreated wastewater to the biological sequential batch reactor. When 500 mg/L concentration of phenol wastewater was subjected to coupled processes, it was observed that the solar photocatalytic treatment was able to remove 44% of initial phenol concentration in 5 hours and the pretreated wastewater was transferred to the biological treatment, where 93% removal of phenol in 2 hours was achieved. In general, the overall phenol removal efficiency in the coupled processes was found to be 96%. The improvement in the first-order rate constant (k) value from 0.2 h$^{-1}$ to 1.2 h$^{-1}$ in biological treatment was also observed. Results obtained from this research indicated that the solar photocatalytic treatment could be a suitable pretreatment method for enhancing biodegradability of phenolic wastewaters treated in the coupled solar photocatalytic and biological treatment system. Also, it was observed that the coupled treatment processes could be able to improve the phenol removal efficiency and reduce the treatment time when compared to the individual process, which would imply a lower total volume of biological reactor and lower energy consumption (requirements for mixing and aeration) to achieve an overall performance to meet the limits of the environmental legislation.