CHAPTER 5

SUMMARY AND CONCLUSION

Treatability studies were conducted on chemical oxidation of phenolic compounds in simulated water and in industrial wastewater using ferrous ion as a catalyst and peroxide as oxidant under normal, solar and UV light. The experimental results and observations of the present study have been discussed in the light of the available literature. The major findings and conclusions drawn there from are outlined below:

1) Preliminary studies on screening of transition metals revealed that both ferrous and ferric ions could effectively catalyse the oxidation reaction of phenol. Since ferric ion exhibited an initial lag phase during the reaction, ferrous ion is considered as a suitable catalyst for the removal of phenol effectively in a relatively short interval of time.

2) Experiments were conducted to study the operating variables like pH, hydrogen peroxide, ferrous ion and initial phenolic compound concentration governing the Fenton process by varying one variable at a time. The removal of phenolic compound was measured by the decrease in COD value, which was evaluated as their degradation efficiency. Maximum degradation efficiency for each variable represents the optimum condition of the corresponding phenolic compound.

3) Detailed investigations were carried out for the degradation of phenol, 2-CP, DCP, TCP, 2-NP, 4-NP, DNP, TNP, MP, DMP and TMP in the presence of
ferrous ion and peroxide. Fenton system is sensitive to pH change and maximum degradation occurred in the pH range of 2.5-3.5. The optimum pH observed during the degradation of all the phenolic compounds (irrespective of the nature of the substituents) remained same.

4) Increase in peroxide concentration with respect to phenolic compounds increased the degradation efficiency for all the phenolics studied. The optimum molar ratio was found to be 1:14 for phenol and chlorophenols; 1:12 for nitrophenols; 1:17 for mono methylphenols; 1:20 for DMP and 1:27 for TMP.

5) Maximum degradation efficiency was obtained at Fe$^{2+}$ ion of 0.81 mM for phenol; 0.45 mM for 2-CP and 0.36 mM for DCP, TCP, DNP and TNP. In mono nitrophenols maximum efficiency was observed at 0.45 mM. 2-, 4-MP, DMP and TMP showed maximum efficiency at 0.90 mM, 1.1 mM and 1.3 mM of Fe$^{2+}$ ion respectively.

6) Molar ratio with respect to H$_2$O$_2$: Ph: Fe$^{2+}$ in the range of 14:1:2.6 for phenol; 14:1:3.6 for CP; 14:1:3.4 for DCP; 14:1:2.9 for TCP resulted in same degradation efficiency inspite in increase in initial phenolic concentration. In case of methylphenols and nitrophenols the following molar ratio in the range of 17:1:2.1 for 2, 4-MP; 17:1:2.6 for 3-MP; 20:1:1.5 for DMP; 27:1:1.1 for TMP; 12:1:3.2 for 2, 4-NP; 12:1:3.0 for DNP and 12:1:2.4 for TNP was maintained. A similar trend as observed for phenol and chlorophenols was experienced for methylphenols and nitrophenols.

7) At optimum conditions, the maximum degradation efficiency obtained for 200 mg/L of phenolic compound was 80 - 82% for phenol, 2-CP, 2-NP, 4-NP and mono MP; 70-75% for DMP, DCP, DNP, TCP and TNP while 69% was obtained for TMP.
8) Fenton process follows pseudo-first order kinetics with respect to the decomposition of phenol.

9) Fenton oxidation reaction was completely suppressed with 0.1 M of t-BA for phenol, 2-CP, 2-MP and 2-NP while lowering the concentration of t-BA to 0.01 M, the degradation efficiency remained same for the compounds mentioned.

10) The effect of air and nitrogen on the degradation efficiency was studied for phenol, 2-CP, 2-MP and 2-NP as a model compound and compared with normal conditions. It was observed that the degradation efficiency for all these compounds remained same at normal, air and nitrogen saturated solutions.

11) The presence of nitrate, perchlorate, carbonate, bicarbonate and sulphates didn’t affect the kinetics of phenol degradation whereas the presence of chloride above 1000 mg/L decreased the rate of the reaction. The oxidation reaction was completely suppressed with phosphate, hydrogen phosphate and fluoride above 50 mg/L, due to non-availability of ferrous ion for the reaction by forming stable complexes with the above mentioned anions.

12) Maximum degradation efficiency for all the phenolic compounds was achieved at 303 K (30 °C) irrespective of the nature of the substituents. The activation energy, enthalpy and entropy for the phenolic compounds were in the range of 1.5-4.5 kcal/mol; 0.94-3.9 kcal/mol and −52.52 to −60.76 cal K⁻¹mol⁻¹. The result suggests that the Fenton oxidation process for all phenolic compounds proceed through a common degradation mechanism.

13) During the degradation of phenolic compounds by Fenton process several intermediates were formed. Benzoquinone and hydroquinone were detected as intermediates during the oxidation of phenol and 2-MP. The absence of these
compounds during the degradation reactions of chlorophenols, nitrophenols, DMP and TMP suggests the possibility that the oxidation reactions proceed through the formation of chloro, nitro and methyl substituted benzoquinones. In chloro and nitro substituted phenols, release of near stoichiometric amount of inorganic chloride and nitrate was observed.

14) Data on mineralisation efficiency for all phenolic compounds by Fenton process was in the range of 21-44%. Low mineralisation efficiency was encountered for tri-substituted phenols followed by di-substituted compounds. High efficiency was observed for mono-substituted phenols and phenol.

15) The peroxide concentration decreased during the oxidation of all the phenolic compounds as it was consumed during the reaction and their concentration reached below a detectable level. The concentration of ferrous ion decreases as the reaction proceeds due to the conversion of ferrous to ferric ion during the \(\cdot\)OH radical production.

16) During the degradation of phenolic compounds by Fenton process, highly oxidized species namely oxalate and acetate were formed as a result of rupturing of the aromatic phenolic ring. The concentration of oxalate formed was approximately twice the concentration of acetate in case of chlorophenols and nitrophenols while their concentrations were same in mono methylphenols. The concentration of acetate was twice and thrice the concentration of oxalate formed during the oxidation of DMP and TMP respectively.

17) The oxalate and acetate ions were subjected to Fenton and photo-Fenton processes. These acids were not degraded by Fenton process while more than 60% mineralisation occurred in photo-Fenton process. Mineralisation reaction in both these acids were attributed to photolysis of ferric carboxylates.
18) In both solar and UV Fenton processes more than 90% of phenol, chlorophenols, nitrophenols and mono methylphenols were mineralized. DMP and TMP exhibited 91% and 87% mineralisation in solar-Fenton while more than 90% efficiency was observed in UV-Fenton process. In both solar and UV-Fenton processes, increase in mineralisation efficiency compared to Fenton process was encountered together with concomitant decrease in acetate and oxalate ions.

19) In photo-Fenton processes, the peroxide concentration decreased and was not detectable at the end of the reaction. The ferrous ion concentration decreased during initial stages of the reaction and then increased as a result of photo-reactions of ferric compounds. Indeed, photo-decarboxylation of ferric complexes plays a major role in re-generation of ferrous ion.

20) Cyclic generation of Fe$^{2+}$/Fe$^{3+}$ ions during photo-Fenton processes suggests the possibility of photo-oxidation occurring at lower iron concentrations. It was observed that complete degradation of phenol, mono methylphenols, DMP and TMP occurred with 50% of initial ferrous ion concentration used for Fenton process while with 25% of optimum Fe$^{2+}$ ion (Fenton process), more than 90% degradation efficiency was exhibited by chlorophenols and nitrophenols in both solar and UV-Fenton processes.

21) The viability of utilizing the iron hydroxide formed after treatment was investigated for both Fenton and solar-Fenton processes using phenol as a model compound. The recycled iron can be used for 3 times without any loss in degradation efficiency by both these processes.

22) Feasibility study was conducted with granular ferric hydroxide (GFH) in a packed bed reactor as a source of iron instead of soluble ferrous salts by using phenol as a model compound in the presence of solar light. The effect of pH,
The recirculating rate and bed height for the GFH columns were determined for mineralising phenol. Maximum mineralisation of 97% occurred at optimum pH of 3.0 ± 0.2 for phenol. The recirculating rate and bed height were observed as critical operating conditions and found to be 210 mL/h and 5 cm respectively.

The efficacy of GFH columns was investigated with tri-substituted phenols. At optimum conditions, the mineralisation efficiency of TCP, TMP and TNP were 72%, 89% and 98% respectively. The presence of acetate and oxalate were detected for the phenolic compounds studied. Chloride and nitrate formed during TCP and TNP oxidation were detected but their concentrations were found to be in low quantities.

Application of Fenton and solar-Fenton process to simulated coal conversion wastewater showed that parent phenolic compounds were removed within 30 min of the reaction time by both these processes. Solar-Fenton process was carried out with 50% reduction from optimum Fe$^{2+}$ ion concentration as in Fenton process. The mineralisation efficiency for simulated wastewater by Fenton and solar-Fenton processes were 49% and 91% respectively.

Experiments were conducted with simulated chlorophenolic and nitrophenolic wastewater. The mineralisation efficiency for simulated chlorophenolic and nitrophenolic wastewater were 41% and 25% by Fenton process while more than 90% mineralisation occurred with 25% of optimum Fe$^{2+}$ ion concentration (obtained in Fenton process) by solar-Fenton process. The result suggests that both Fenton and solar-Fenton processes can be applied to chlorophenolic and nitrophenolic wastewater for converting the compounds to harmless products and inorganic chloride and nitrate respectively.
Feasibility of Fenton and solar-Fenton was investigated by applying it to industrial wastewater containing phenol. The mineralisation efficiency in both resin manufacturing and refinery wastewater was more than 90% in solar-Fenton process at 50% reduced iron concentration than in Fenton process.

Based on the present investigations, it may be concluded that Fenton and photo-Fenton processes can be used to remove phenolic compounds from wastewater. High mineralisation efficiency was obtained by the use of solar and UV-light in Fenton system for all the phenolic compounds studied and were also highly comparable. In solar-Fenton process, relatively small area would be sufficient to treat wastewater with high efficiency since the results presented here were obtained by exposition the beakers. Further, the simplicity in operation and low cost intrinsic to solar energy can compensate the small differences in photo-mineralisation rates as compared to UV-Fenton process, especially in tropical regions like India, where solar incidence is high and abundant almost throughout the year. Hence, solar-Fenton process will be a viable alternative technology to the existing methods for treating phenolic compounds in water and wastewater.

In this arena of study, considerable scope still exists for investigating the following aspects:

* Develop support materials in which Fe-ions cluster remained fixed and doesn’t allow leaching off iron from the catalyst.

* Extending the treatment process at neutral pH by developing homogeneous iron-complexes.

* Scaling up the solar-Fenton process by constructing parabolic collectors, which can capture both diffuse and direct sunlight to treat industrial wastewater containing phenol.
* More specific studies like aeration, fluidisation of catalyst bed and oxidant concentration are to be focused for GFH column studies for better application to phenolic wastewater treatment.

* Fenton treatment can be used as a pretreatment process for removing refractory and recalcitrant compounds and combining with biological processes with a view to reduce the cost further.