Jr. of Industrial Pollution Control 23 (1)(2007) pp 157-164

TREATABILITY STUDY OF PHARMACEUTICAL WASTE WATER BY COMBINED SOLAR PHOTO FENTON AND ACTIVATED SLUDGE PROCESS

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Key words : Solar photo fenton oxidation, Hydroxyl radicals, Biodegradability.

ABSTRACT

In the present study, the treatability of wastewater from a pharmaceutical industry by combined solar photoFenton oxidation and activated sludge process was investigated. The wastewater was considered non-biodegradable as it contained significant amount of organic compounds whose degradation was not possible by conventional biological treatment system. The characteristics of the wastewater have shown to contain high COD (25600 mg/L) and BOD_3 (4890 mg/L) and the biodegradability of wastewater measured, as BOD_3/COD ratio was 0.19. In order to enhance the biodegradability of the pharmaceutical wastewater, photoassisted oxidation process, H_2O_2/ Fe^{2+}/ Solar was applied to the wastewater as a pretreatment step to biological degradation. The influence of the reaction parameters such as pH, dosage of HaC^ and Fe(II) and BOD_3/ COD as a function of the time of photochemical pretreatment were studied. A COD removal of 88% was observed in one-hour photochemical treatment time at pH 3 and at the dosage of H_2O_2 (65 mL) and Fe^{2+} (1.34 g). The biodegradability of wastewater has enhanced from 0.19 to 0.4 (measured as BOD_3/ COD ratio) after 40 min photochemical treatment time. The combined solar photoFenton oxidation and biodegradation of wastewater has resulted in BOD removal of 93 % and COD removal of 95 %.

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INTRODUCTION

Contamination of soil, ground water, surface water and air with hazardous and toxic chemicals is one of the major problems faced by the industrialised world today. The need to remediate contaminated areas has led to the development of new technologies that emphasise the destruction of pollutants rather than the conventional approach to disposal. Biological processes do not always give satisfactory results, especially when applied to the treatment of industrial wastewater because many organic substances produced by the chemical and other related industries are inhibitory, toxic or resistant to biological treatment. Therefore, integration of chemical and biological processes can provide best alternative wastewater treatment options in purifying wastewaters that are not readily biodegradable. An efficient integrated chemical/biological process should consist of a brief chemical pretreatment step to convert initially bioresistant compounds to more readily biodegradable compounds followed by a subsequent biological process.

Advanced oxidation processes increasingly gain importance in wastewater reclamation. They offer a useful alternative for the treatment of effluents with a high organic matter. The system photoFenton (H_2O_2/Fe^{2+}/Solar) has attracted much attention due to its high efficiency in the oxidation of a variety of organic compounds (Carneiro *et al.* 2006). PhotoFenton oxidation is a process, which is based on the generation of hydroxyl radicals, which are highly reactive oxidants. The hydroxyl radicals have been extremely effective in the destruction of organic chemicals and they are non-selective. An important drawback of this process is that their operational costs compared to those of biological treatment, which are, at present, the cheapest one (Mamma *et al*. 2004). Therefore, the combination of photoassisted Fenton process as pretreatment followed by an inexpensive biotreatment, would seem to be an economically attractive option (Lapertot *et al.* 2006). Various coupled systems have been proposed to treat different kinds of industrial wastewaters such as effluents from pesticide industry, textile industry, etc. The scope of the present study was to investigate the treatability of pharmaceutical wastewater by combined solar photoFenton oxidation and activated sludge process and to study the effect of operating variables viz. pH, concentration ofH_2O_2 and Fe^{2+}, contact time on the degradation of the wastewater.

In India, more than 16000 industries are involved in the manufacturing and formulation of various drugs and in Tamil Nadu there are about 16 large and medium scale industries in operation (TNPCB 2005). In general, the pharmaceutical industries adopt conventional biological treatment for treating their wastewaters, the results of which are far from satisfactory level. Pharmaceutical wastewater distinguishes itself from other wastewaters because of its high content of organic matter. The characteristics of the wastewater analyzed were pH 4, TSS 440 mg/L, TDS 4196 mg/L, BOD 4890 mg/L and COD 25600 mg/L.

MATERIALS AND METHODS

Composite samples of the wastewater were collected from a pharmaceutical

industry located at Kancheepuram District, Tamil Nadu, India and stored under refrigeration (4° C) until use. The wastewater was analysed for various physiochemical parameters as per the standard methods of analysis. The wastewater had characteristics of pale brown color with disagreeable odor, pH 4, TSS 440 mg/L, TDS 4196 mg/L, BOD 4890 mg/L and COD 25600 mg/L. Fenton reagent was prepared using ferrous sulphate and hydrogen peroxide that were purchased from Merck Company. The molar ratio of Fenton reagent was arrived as per the stoichiometric requirements with respect to COD (i.e. 1 g COD = 1 g O_2 = 0.03125 mol of O_2 = 0.0625 mol of H_2O_2 = 2.125 g of H_2O_2). The percent purity was estimated by iodometric titration method.

The solar photoFenton oxidation process was carried out in a plexiglass reactor of size 0.17 x 0.17 x 0.18m with an operating volume of 4 L. The volume of the sample used throughout the study was 500 mL. The experimental setup was placed under the sunlight. The contents of the reactor were continuously mixed using a magnetic stirrer. The effects of operating variables were studied by varying the variable under study and keeping the other variables constant. Samples were taken at regular intervals of time and analysed for COD removal after quenching with sodium hydroxide solution (Kavitha *et al.* 2004). For assessment of biodegradability, samples were analysed for BOD^ reduction and biodegradability was measured as BOD3/COD ratio. H_2O_2 and Fe (II) were used at a concentration of 65 mL and 1.34 g respectively.

The biodegradation of pharmaceutical wastewater was carried out in a lab scale fully aerobic sequencing batch reactor (SBR). The SBR was adopted for the work, since all the operations like fill, react, settle and draw can be carried out in a single tank. The SBR was made of acrylic material with an operating volume of 4 L. The pH of the phototreated pharmaceutical wastewater was adjusted to 7 using 0. 1 N sodium hydroxide solution. The sequencing batch reactor (SBR) system was initially fed with sludge taken from the activated sludge process treatment plant of the same pharmaceutical industry. The reactor was then slowly fed with phototreated pharmaceutical wastewater (adjusted pH to 7) that was given 40 min contact time of photochemical treatment to make the microorganisms adapt to the new environment. The acclimatized sludge was used for further study. The retention time in each fill and draw run was 8 hours. The DO concentration during the experiment was maintained above 2 mg/L. Samples were collected and analysed for BOD_3 and COD reduction. The experiments were repeated by varying the MLSS concentration.

RESULT AND DISCUSSION

Pretreatment by Solar PhotoFenton Oxidation Process

The enhancement of biodegradability of raw pharmaceutical wastewater using solar photoFenton [Fe $^+$/H_2O2/Solar] process was evaluated. The optimal concentrations of H^O? and Fe^{2+}, pH is to be determined at which maximum efficiency could be obtained. Therefore, H^Oo and Fe~$^+$ concentrations and pH were optimized and the study on the assessment of biodegradability was

carried out.

Effect of H_2O_2 concentration

The effect of dosage of FLO? was studied for various molar ratios of 10:1,15:1,18:1 and 20:1. The pH of wastewater was 4 and dosage of Fe^{2+} was taken as 1.34 g. The maximum efficiency of COD reduction of 86% in 60 min was observed in 18:1 molar ratio (65 mL). The efficiency increased with the increased quantity of H_2O_2 due to the effect of additional OH° radicals produced and above these concentration the efficiency got decreased. Excessive H_2O_2 reacts with OH° competing with organic pollutants and consequently reducing treatment efficiency (Rodriquez *et al*. 2005).

Effect of Fe^{2+} concentration

The effect of Fe^{2+} concentration on the degradation of wastewater was studied by varying the concentration of iron in the range of 10:1, 15:1, 18:1 and 20:1. while the pH of the wastewater taken was 4 and the concentration of H_2O_2 was 65 mL. The volume of wastewater taken was 500 mL. The maximum efficiency of COD reduction of 82% in one hour was observed in 15:1 molar ratio (1.34 g). An increase in the concentration of Fe^{2+} did not improve the COD reduction and Fe^{2+} acts only as catalyst. (Malato *et al.* 1999). The rate of Fenton process decreases, when the ferrous ion dosage is more than optimum level and H_2O_2 decomposition increases throughout the reaction period (Kang *et al*. 1999).

Effect of pH

The pH has a significant role in determining the efficiency of photoFenton process. The pH value influences the generation of hydroxyl radicals and thus the oxidation efficiency. The effect of pH was studied by taking optimum dosage of Hi>O_2 and Fe^{2+}. A maximum efficiency of 85% COD removal was observed at pH 3.

It has been established that at higher pH values the degradation rate decreases due to the formation of ferric oxyhydroxide (Shemer *et al*. 2006). Furthermore, the oxidation potential of hydroxyl radical is known to decrease with an increase in the pH and at a pH below 2, hydrogen peroxide can stay stable forming an axonium ion (H_2O_2) which makes hydrogen peroxide more stable and presumably reduce the reactivity with ferrous ion (Modirshahla *et al*. 2006).

Effect of liquid depth

The effect of liquid depth was studied by varying the liquid depths as 5 cm, 10 cm and 15 cm by varying the volume of wastewater while keeping the other operational parameters at optimal conditions. There is not much deviation in COD removal efficiency for depths 5 cm and 10 cm. This was in conformity of the earlier reports (Josephine, 2002 and Thangarani, 2005).

Effect of contact time on degradation/biodegradability

The experimental work aimed at how the solar photoFenton oxidation process enhances the biodegradability of pharmaceutical wastewater, which contained non-biodegradable different organic compounds. BOD/COD constitutes a good measure of the biodegradability of a wastewater. From the analysis,

it was observed that the BOD^/COD ratio in the wastewater was quite low (0.19). The effect of contact timedied at pH 3 and at optimum dosage of biodegradability was studied at pH3 and at optimum dosages of H_2O_2/Fe^{2+}. Samples were collected at regular intervals of time and analysed for BOD3 and COD reduction. COD removal efficiency of 88% was observed in one-hour irradiation and biodegradability of the wastewater measured as BOD3?COD ratio has gradualy increased from 0.19 to 0.4 after 40 min. photochemical treatment time. This was in conformity of the report (Sarria *et al.* 2000(. He showed that the BOD/COD ratio of phototreated effluent (AMBI) increased from 0.16 to 0.7 after photochemical oxidation. Isil and Ferhan (1999) concluded that the photocatalytic oxidation led to an increase in the BOD_5/COD of pulp bleaching wastewater. Pulgarin et al (1999) concluded that photoassisted Fenton system used as pretreatment for an aromatic and non- biodegradable compound generates in a very short period of time (30 min) intermediates with very oxidized functional groups being not toxic and as biodegradable as urban wastewater. The experimental results of solar photo Fenton treatment are presented in Fig 1 to 6.

Biodegradation of Photo-Oxidized Pharmaceutical wastewater

The biodegradation of photo-oxidized wastewater was carried out in a sequencing batch reactor (SBR). The results are presented in Table 1. The highest overall performance of combined treatment system was obtained at MLSS concentration of 3490 mg/L. The combined solar photoFenton oxidation and biodegradation of the pharmaceutical wastewater has resulted in 93% of BOD removal and 95% COD removal. Mileno Lapertot *et al.* (2006) reported thai biodegradability of wastewater containing pesticides was enhanced by the photoFenton process after 12-35 min and concluded that the photo Fenton treatment consistently enhances the biodegradability of wastewater containing pesticides.

CONCLUSION

In the present work, treatability of wastewater from a pharmaceutical industry was evaluated by combining solar photoFenton oxidation and activated sludge process. Raw Pharmaceutical wastewater had low biodegradability (0.19) as determined from BOD_3/COD ratio. In order to enhance the biodegradability of pharmaceutical wastewater, solar photoFenton oxidation process was applied

Table 1

Performance of combined treatment solar photoFenton oxidation and activated sludge process (MLSS 3490 mg/L)

Parameter	Raw waste water	Influent concentration (Phototreawaste water)		Effluent concentedration (Biologically treated waste water)		Overall Removal Efficiency
	(mg/L)	(mg/L)	%Reduction	(mg/L)	%Reduction	%
BOD	4500	1740	61	300	83	93
COD	22800	4200	82	1200	71	95

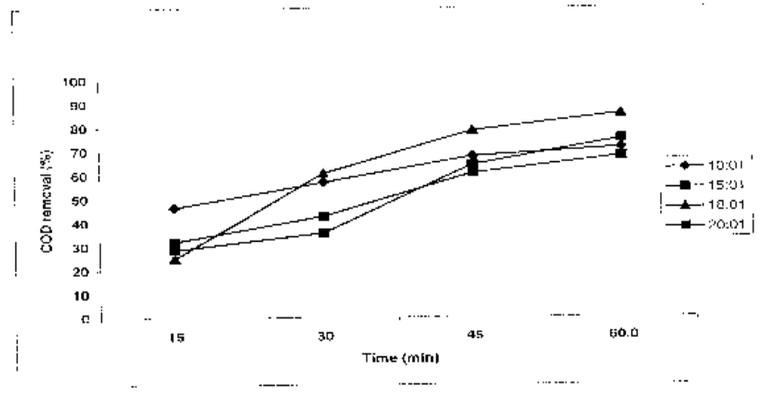

Fig. 1 Effect of H_2O_2 concentration

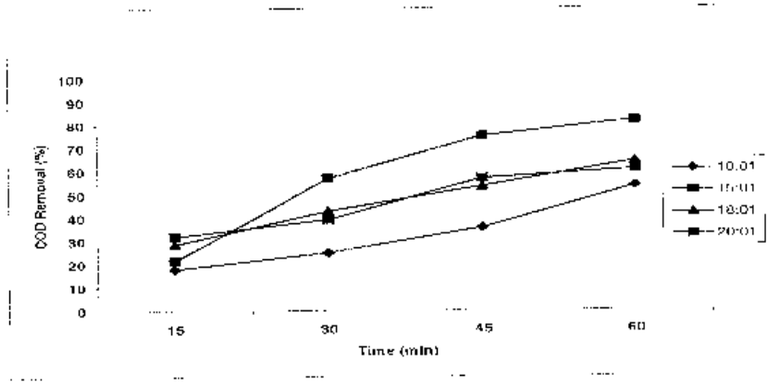

Fig. 2 Effect of Ferrous Ion (Fe^{2+}) concentration

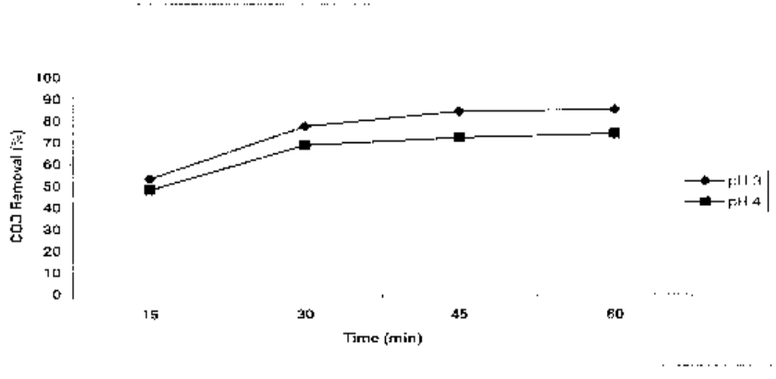

Fig. 3 Effect of pH

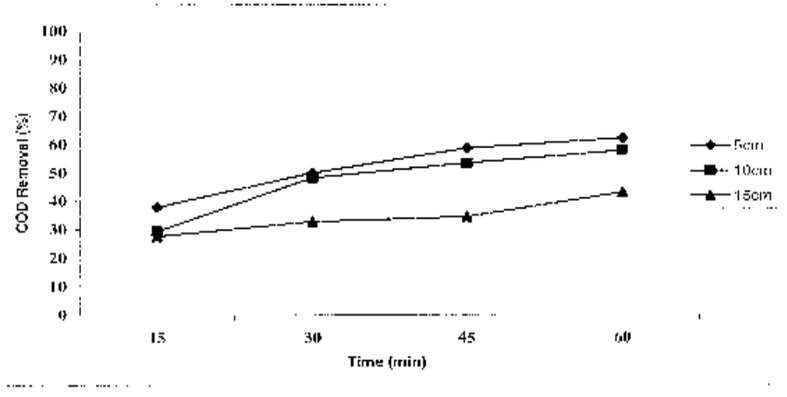

Fig. 4 Effect of liquid depth

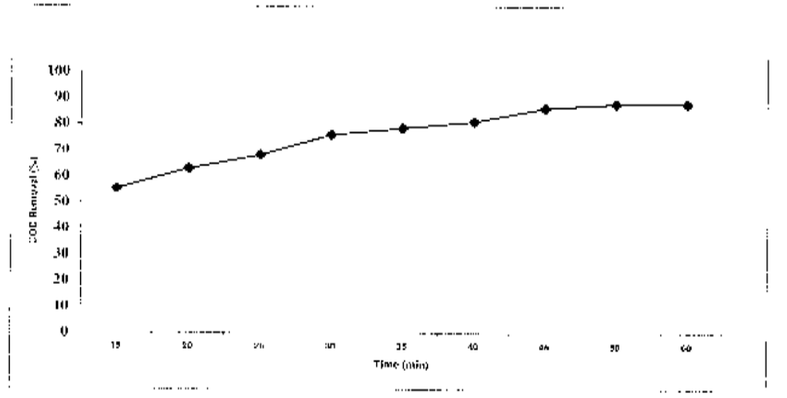

Fig. 5 Effect of contact time

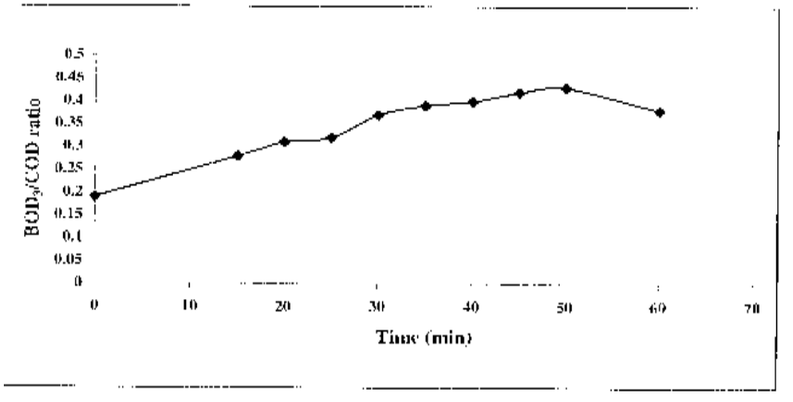

Fig. 6 Assessment of Biodegradability

to the wastewater as a pretreatment step to biological degradation. The pretreatment of photoFenton oxidation process led to an increase in biodegradability of the wastewater from 0.19 to 0.4 in 40 min photochemical treatment time. The combined solar photoFenton oxidation and biodegradation of the wastewater has resulted in 93% BOD removal and 95% COD removal. In conclusion, the combined solar photo Fenton oxidation and activated sludge process could be used as an alternative technique for the degradation of wastewater from pharmaceutical industries located in tropical areas. For the treatment of large quantities of pharmaceutical wastewater, a pilot plant study for scaling up of the solar photoFenton process need to be conducted to evaluate its applicability in the field.

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