

Pilot scale advanced photo-oxidation processes for remediation of pharmaceutical wastewater. A case study

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Abstract

The investigation of photochemical degradation of chemical components in pharmaceutical wastewater by use of ultraviolet (UV) irradiation, UV in combination with sodium hypochlorite (UV/NaOCl), and Fenton's reagent (UV/H₂O₂/Fe²⁺) was performed. Objective of this study was to determine the best alternative to the conventional wastewater treatment or pre- / post-treatment in combination with biological treatment to one of the four effluent source outlets. The effect of the advanced oxidation treatments provided varying degree of COD reduction for all four effluents. The results showed UV/H₂O₂/ Fe²⁺ treatments provided maximum chemical oxygen demand (COD) reduction of the anaerobic system outlet effluent. The combination of UV/H₂O₂/ Fe²⁺ (750 mg/L FeSO₄+7500 mg/L H₂O₂) provided reduction in COD up to 75% upon three-hour UV exposure. The initial effluent COD was about 22000 mgO₂/L and the treated effluent BOD₅ /COD ratio was 0.50 showing greater amenability to biological processes. Sodium hypochlorite dosages between 3000 and 10000 mg/L achieved the results with little variation as compared to UV/H₂O₂/ Fe²⁺. Additionally, comparison was made of the UV exposure time required to reach the maximum reduction of COD value and the necessary effective oxidant dose to achieve the desired COD reduction, which could provide predictive model for the treatment of wastewater processes.

Keywords: wastewater treatment, Fenton, photo-Fenton, COD, advanced oxidation processes (AOPs)

INTRODUCTION

Water is our important source of life. Without water, the life on the earth would not be possible [1,2]. The water present on the earth for human usage is quite limited thus, important to look for methods where we can reuse wastewater by undergoing chemical and biological treatments [3÷5]. Additionally, wastewater causes severe harm to our existing water sources and aquatic eco system as well [6,7]. Therefore, industrial wastewater treatment is daunting challenge in front of us. Among industries pharmaceutical industries are major wastewater producing sources causing critical environmental pollution problem [8]. Several wastewater treatments technologies for pharmaceutical wastewater have been developed and reported in the literature [9, 10]. The mismanagement of these treatment methods can lead to inadequate treatment leading to maltreated wastewater discharge into water bodies which produce harmful effect on the human health and environment. Those conventional treatment like activated sludge process, flocculation, clariflocculation, filtration, adsorption, chemical treatment, dumping in large isolated area, precipitation etc. have suffered from being uneconomical and inefficient operation procedures [11, 12]. Due to this, there is an urgent need to develop and operate novel wastewater treatment method which can be efficient at the same time economically feasible too. In order to tackle this problem, Advanced Oxidation Processes (AOPs) involving photochemical and photocatalytic methods can be considered as an alternative or used in combination with existing technologies for efficient wastewater remediation including pharmaceutical wastewater

[13–15]. Due to their ease of application AOPs such as Fenton and Photo-Fenton are studied widely for the degradation of chemical contaminants in the wastewater [16].

AOPs produce active chemical species upon chemical reaction which can be triggered by using light. Chemical species such as hydroxyl radical ($\text{HO}\cdot$) which possess strong oxidizing power and can oxidize almost any organic moiety to CO_2 [17]. As the wastewater contains many organic molecules, their oxidizing power varies as per complex chemical structure of the moiety. In presence of catalyst, the activation of AOPs can be enhanced considerably leading to very rapid generation of powerful oxidizing species [17, 18]. These oxidizing species attack without much selectivity on organic moieties, undergoing several chemical reactions simultaneously. Mostly these kinds of reactions lead to organic radicals resulting in smaller molecule as addition products. Although majority of organic compounds can be remediated by hydroxy radical, some very simple organic molecules such as acetone, oxalic acid, acetic acid, chloroform cannot be degraded by OH radical. Efficiency of an AOP is directly proportional to the generation of hydroxyl radicals and it reacts with organics closer to diffusion-controlled rates.

Already some industries have set up AOPs for their treatment of wastewater [19]. But more research is needed in order to establish treatment criteria as wastewater properties considerably differ from one industry to other due to diverse manufacturing processes. Herein, we report pharmaceutical industry effluent treatment plant (ETP) wastewater collected from four different sources of their existing ETP stages. The chemical and biological properties of four effluents differ significantly from one another. The effects of oxidant sodium hypochlorite (NaOCl), Fe(II) , H_2O_2 concentration, and their ratios, UV radiation were elucidated in case of AOPs. Therefore, this research data generated from pilot scale reactor will guide scientific community for conducting further research, environmental wastewater treatment agencies, and engineers who are setting up ETP for remediation of wastewater. Additionally, this research will show path for where to implement this kind of AOPs in adjunct to existing wastewater treatment facilities of several industries.

MATERIALS AND METHODS

Pilot plant operation

The schematic flow diagram of the constructed pilot plant for the present study is shown in the Figure 1. Initially, the wastewater (effluent I, II, III, or IV) which is to be circulated through different stages of pilot plant was poured in the tank A of the capacity 250 L. Flow rate $0.5\text{m}^3/\text{h}$ was maintained in each stage of operation during circulation. Later on, the oxidant dosing of desired concentration in the form of either NaOCl or H_2O_2 was given as per pilot plant operation condition. The outlet of the bag filter passed through the PCR I (photochemical reactor) where UV light interacts with the dissolved solid in the wastewater. After collection of PCR I outlet in the collection tank B with oxidant dosing, it gets passed through PCR II and outlet solution was collected in the collection tank C. This cycle from PCR I to PCR II was repeated several times to increase the contact time of treatment with UV radiation. Each operational cycle had a contact time of half an hour with that of UV radiation. All experiments were carried out in the same equipment. Pilot plant designs and operation, feed solutions, dosing concentration, analysis, and equipment specifications will be discussed. Each Effluent's testing is separately described.

The PCR is a heart of the pilot plant, as ultraviolet radiation is produced in it which was then used for photochemical oxidation process. The PCR I consists of fourteen long (Figure 2) UV tubes arranged in a parallel fashion as shown in the figure 1 while PCR II consists of ten UV tubes. Both PCRs can produce light of wavelength in the range of $100\div 350\text{ nm}$.

All tanks (A, B, C) were made up of plastics and having capacities of 500 dm^3 (0.5m^3). The air sparging system i.e. diffuser system was attached at the bottom of each tank to provide mixing of reacting solution.

Dosing Chemicals

A) 12% market available sodium hypochlorite (NaOCl) or

B) 50% w/v hydrogen peroxide (H_2O_2) and commercial FeSO_4 as Fe^{2+} was used as an oxidant

Chemical analysis

Chemical analysis was performed by analyzing parameters such as COD (Chemical Oxygen Demand), TSS (Total Suspended Solids), TDS (Total Dissolved Solids) by adjusting pH with HCl for each treatment sample. The chemical oxygen demand (COD), was used as an important indicative parameter during the present study, and was determined by using open reflux method in acidic solution at 150°C for 2h [20]. Other parameters such as TSS, TDS were determined by following standard analysis procedure for water and wastewater as published by American Public Health Association (APHA) [21]. pH was measured using standard pH meter available in the laboratory. Biological oxygen demand (BOD₅) was measured by following method of dissolved oxygen measurement after five days [21]. These tests were conducted on four different effluents (I, II, III, or IV) collected from four different sources of existing ETP of pharmaceutical industry. The physicochemical characteristics of each effluent such as pH, COD BOD₅, BOD₅/COD, TSS, TDS, and colour are summarized in the Table 1.

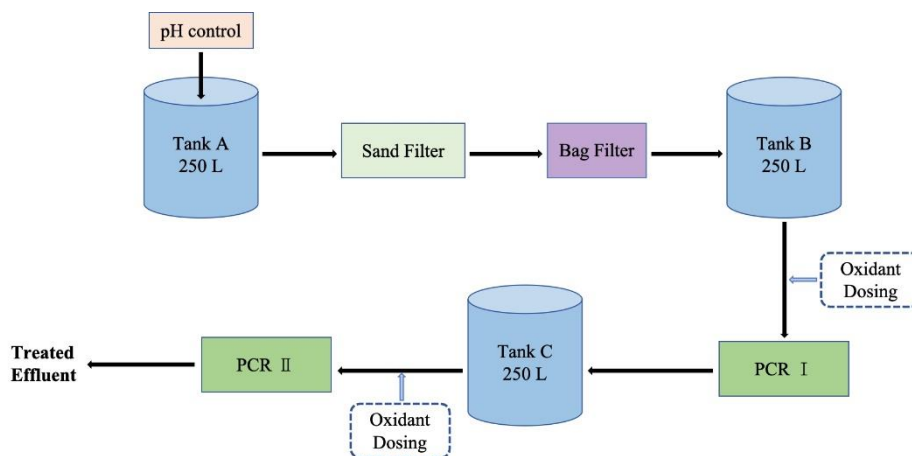


Fig. 1. Schematic representation of Pilot Plant used for experiment

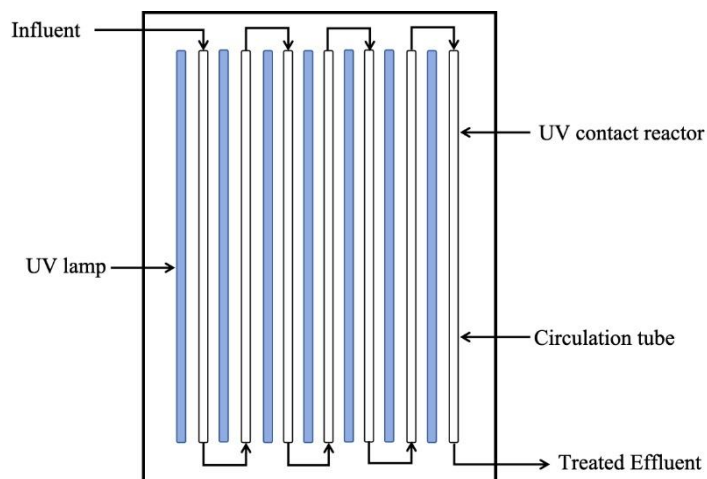


Fig. 2. Schematic representation of photochemical reactor (PCR)

Characteristics of each effluent used for the present study

In table 1 are presented the characteristics of the studied effluents.

Table 1. Physical-chemical properties of the effluents under study

Effluent	pH	COD (mgO ₂ /L)	BOD ₅ (mgO ₂ /L)	BOD ₅ /COD	TSS (ppm)	TDS (ppm)	Colour
I: Outlet of chemical treatment 2	6.0÷7.0	1800÷2700	300÷400	0.12÷0.16	90÷250	12000÷15000	Pale Yellow
II: Outlet of chemical treatment 1	6.0÷7.0	2500÷4500	400÷600	0.13÷0.16	250÷500	15000÷18000	Dark Yellow

III: Outlet of the biological treatment plant	7.0÷8.0	12000÷16000	4000÷6000	0.30÷0.45	2500÷4500	17000÷20000	Dark Brown
IV: Outlet of the anaerobic treatment plant	7.0÷8.0	22000÷26000	8000÷15000	0.32÷0.51	2500÷4000	27000÷32000	Greenish

RESULTS AND DISCUSSION

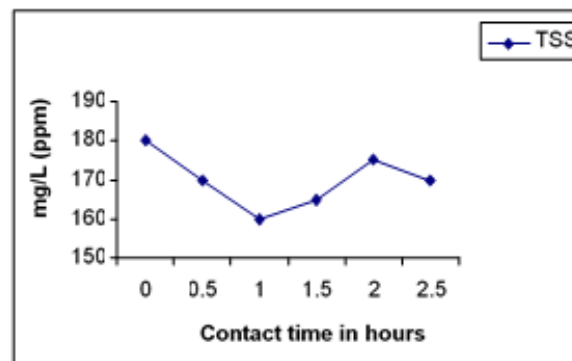
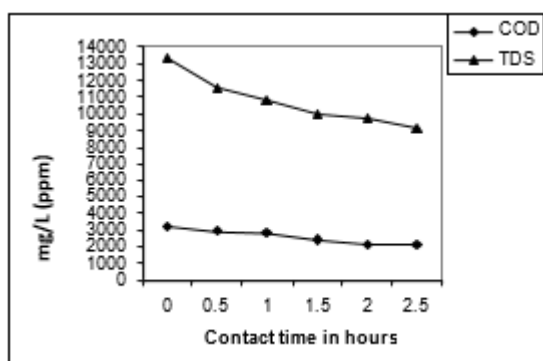
In this research work, we have checked the applicability of advanced photo-oxidation processes involving UV radiation such as NaOCl, Fenton's reagent to treat the pharmaceutical wastewater collected from four different outlets of existing ETP. There might be similar trend in the analysis can be observed due to presence of similar active chemical constituents but in different concentrations. The example of this kind is the effluent I and II, as the effluent I is from chemical treatment 2 outlet and effluent I from chemical treatment 1 outlet. Both can have nearly same chemical constituent but, effluent II is having higher concentration of chemical constituents than that of effluent I. The effluent III is from aerobic treatment outlet and effluent IV is from anaerobic treatment outlet. Before the UV/H₂O₂, UV/NaOCl treatment studies began, the COD reduction upon individual treatment by H₂O₂, NaOCl and UV radiation is investigated. As shown in the Table 2, individual treatment by UV, H₂O₂ and NaOCl did not substantially reduce the COD of the wastewater (Effluent II and Effluent IV).

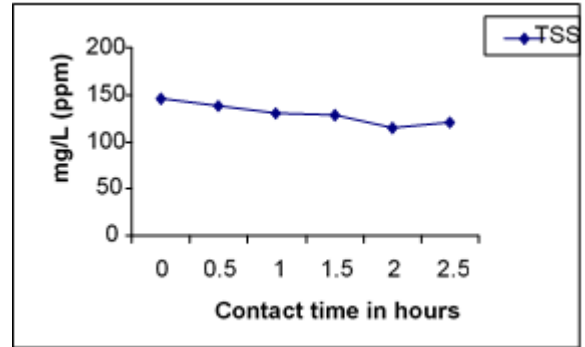
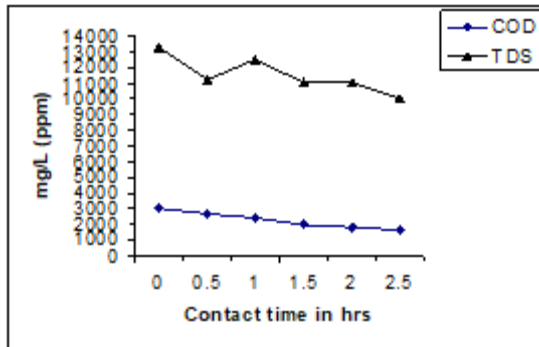
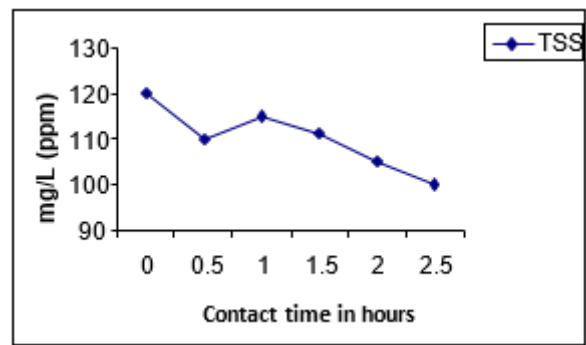
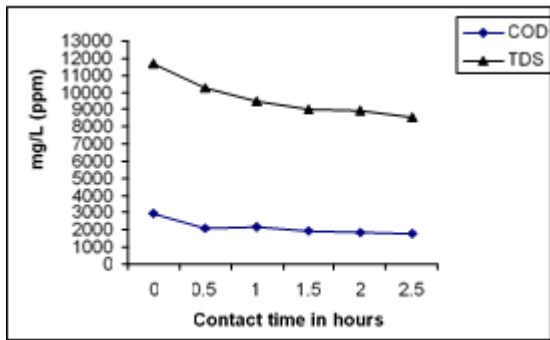
Table 2. Effect of UV, Fe²⁺/H₂O₂, NaOCl on COD

Reagent/ Method	Effluent	COD (mgO ₂ /L)		Contact time in hours	Concentration ppm	% Reduction
		Initial	Final			
UV	Effluent II	3216	3014	3.0	-	6.28
	Effluent IV	24763	22363	3.0	-	9.69
Fe ²⁺ /H ₂ O ₂	Effluent II	3216	2818	-	250/2500	12.37
	Effluent IV	24763	20140	-	500/5000	18.66
NaOCl	Effluent II	3216	3094	-	3000	6.22
	Effluent IV	24763	21339	-	5000	13.82

Experimental data for effluent I

Test #1 and #2 were carried out by using 2000 and 3000 ppm NaOCl solution, respectively. Both treatments showed somewhat similar results (Figure 3a, and b). The steep decrease in COD as well as TDS was obtained after ½ hour contact time with UV radiation. This is because of immediate action of hydroxyl radical (HO[•]) on dissolved organics contaminants present in wastewater within ½ hour of treatment and later on change in COD as well as TDS nearly remains constant. This clearly indicated that the decrease in COD is directly proportional to TDS. Upon ½ hour treatment COD did not show any significant change, which may be attributed to the presence of TSS in the form of carbonates, bicarbonates, as these ions can interfere in the oxidation process. There was not much variation in the TSS observed which indicated that there was not much effect of treatment on the TSS.

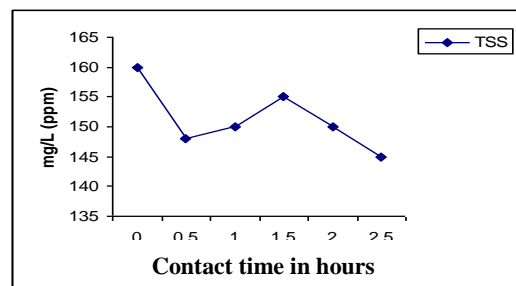
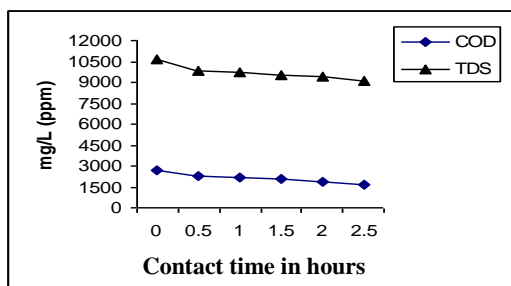




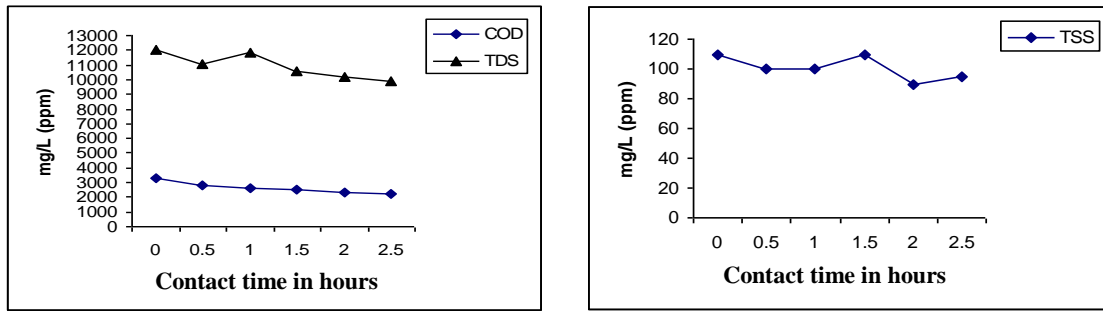
c)

Fig. 3. Results showing changes in COD, TDS, and TSS after treatment of NaOCl on Effluent I a) TEST#1, effect of 2000 ppm NaOCl /UV by adjusting pH 6.0 with HCl b) TEST#2, effect of 3000 ppm NaOCl /UV by adjusting pH 6.0 with HCl c) TEST#3, effect of 4000 ppm NaOCl /UV by adjusting pH 6.0 with HCl

Test#3 results showed (Figure 3c) that even if the concentration of NaOCl was increased, the reduction in COD was not observed up to remarkable level. The level of TSS did not affect much even at higher concentration of an oxidant. In the Test# 4 and #5, the effect of Fe^{2+} doses in the Photo-Fenton oxidation process on the treatment of wastewater were investigated. In the Test# 4 and #5, Fe^{2+} doses 250 ppm and 500 ppm were administered, respectively under controlled oxidation (2500 ppm H_2O_2 , pH 2). The sharp removal of COD and TDS was observed during first ½ hour (Figure 4a and b). This is due to the attack of hydroxyl radical (HO^{\bullet}) on dissolved organics and as time passes the rate of hydroxyl radical (HO^{\bullet}) generation decreases and therefore, COD and TDS nearly remained constants. From controlled oxidation result, it is cleared that $Fe^{2+}:H_2O_2$ ratio is very important deciding factor in the reduction of COD values. The ratio of $Fe^{2+}:H_2O_2$ should be maintained at 1:10. The Table 3 has summarized results of all tests for effluent I.



a)



b)

Fig. 4. Results showing changes in COD, TDS, and TSS after treatment of Fenton's reagent on Effluent I: a) Test#4, effect of 250 ppm Fe^{2+} /2500ppm H_2O_2 by adjusting pH 2.0 with HCl b) Test#5, effect of 500 ppm Fe^{2+} /2500ppm H_2O_2 by adjusting pH 2.0 with HCl

Table 3. Summary of the results for treatment effluent I

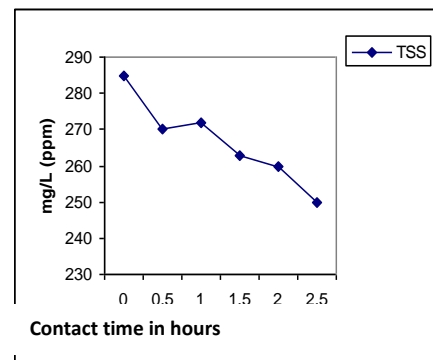
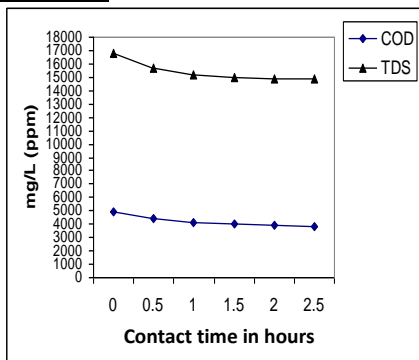
Tests	Oxidants		UV Contact time in hours	% COD reduction
	NaOCl (ppm)	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ (ppm)		
1	2000	-	2.5	34.43
2	3000	-	2.5	40.40
3	4000	-	2.5	46.53
4	-	250 / 2500	2.5	31.25
5	-	500 / 2500	2.5	37.04

Experimental data for effluent II

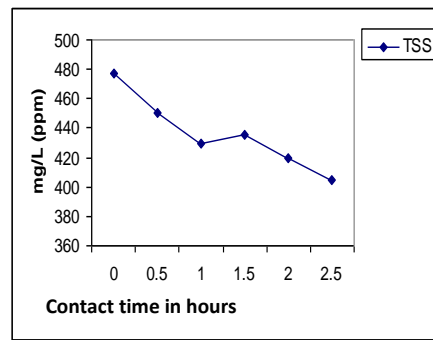
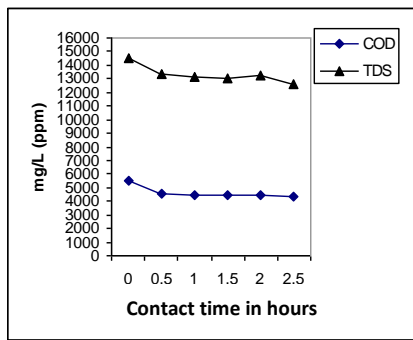
As mentioned earlier, effluent I was the wastewater from the chemical treatment 1 outlet which contains higher concentration of the chemical contaminants compared to the effluent I. It showed nearly similar trend in the COD, TDS and TSS as that of effluent I indicating that the concentration of chemical contaminants presents in the wastewater determine the removal rate of COD and TDS. The graphs with individual tests#1 to #5 shown in Figure 5 and Figure 6. Test #2 was conducted by using 5000 ppm of NaOCl and it showed that there was not much decrease in COD and TDS observed as compared with Test#1 (Figure 5a and b). This indicated that the increase in oxidant concentration have not much effect on the results (Figure 5c). In addition, for Fenton treatment effluent II did not show significant changes (Figure 6 a and b). The Table 4 has summarized results of all tests for effluent II.

Table 4. Summary of the results for treatment effluent II

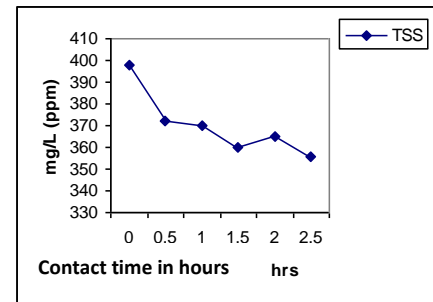
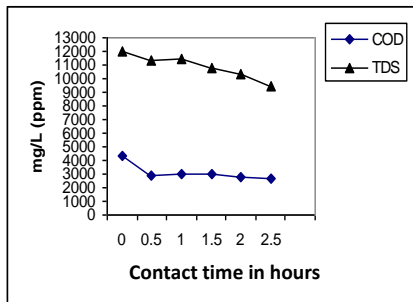
Tests	Oxidants		UV Contact time in hours	% COD reduction
	NaOCl, ppm	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$, ppm		
1	2000	-	2.5	22.23
2	5000	-	2.5	22.86
3	10000	-	2.5	37.95
4	-	250 / 2500	2.5	44.09
5	-	500 / 5000	2.5	46.16



a)

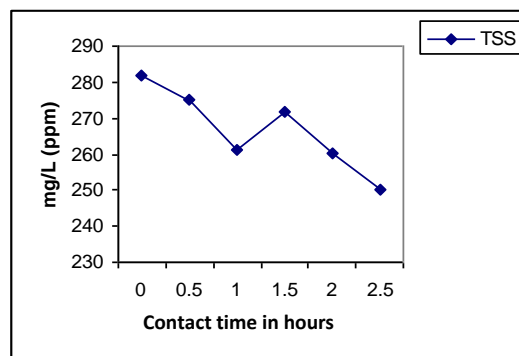
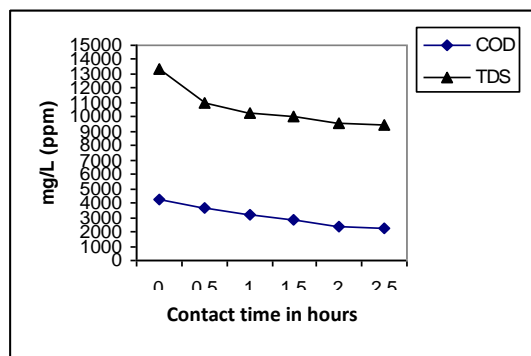


b

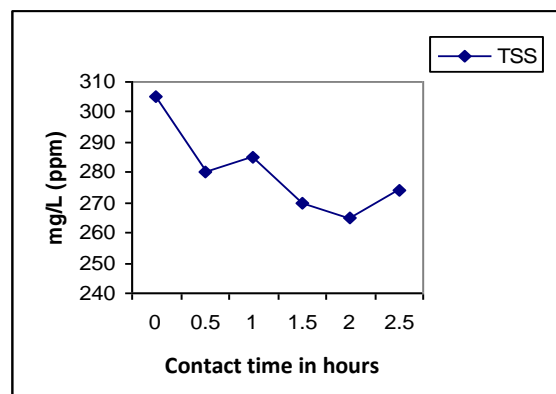
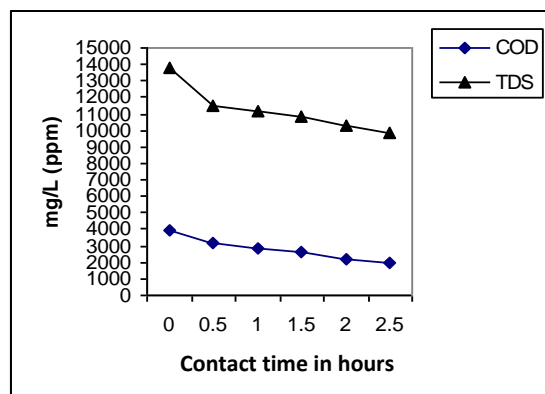


c)

Fig. 5. Results showing changes in COD, TDS, and TSS after treatment of NaOCl on Effluent II a) Test#1 Treatment of 2000 ppm NaOCl/UV by adjusting pH 6.0 with HCl b) Test#2 Effect of 5000 ppm NaOCl/UV by adjusting pH 6.0 with HCl c) Test#3 Effect of 10000 ppm NaOCl/UV by adjusting pH 6.0 with HCl



a)



b)

Fig. 6. Results showing changes in COD, TDS, and TSS after treatment of Fenton's reagent on Effluent II: a) Test#4 Effects of 250 ppm Fe²⁺/2500ppm H₂O₂ by adjusting pH 2.0 with HCl b) Test#5 Effects of 500 ppm Fe²⁺/5000ppm H₂O₂ by adjusting pH 2.0 with HCl

Experimental data for effluent III

As this effluent was collected from an aerobic system outlet therefore, it contains TSS which was generated by metabolism of microorganisms. Test#1 was conducted with 5000 ppm of NaOCl. As the effluent III contains mainly biodegradable compounds therefore, it did not show much reduction in COD values (Figure 7a). Here one thing should be noted, the reduction in COD was continued up to 1 ½ hr UV contact time even with smaller extent. This may be due to the absence of carbonate interference which was occurred during treatment of effluent I and effluent II caused by addition of lime as a precipitant. Test# 2 was carried out by using twice concentration of NaOCl as compared to test#1 it showed result as shown in Figure 7b. Also, for Fenton treatment effluent II did not show significant changes (Figure 8). The Table 5 has summarized results of all tests for effluent III.

Table 5. Summary of the results for treatment effluent III

Tests	Oxidants		UV Contact time in hours	% COD reduction
	NaOCl (ppm)	Fe ²⁺ /H ₂ O ₂ (ppm)		
1	5000		3.0	37.80
2	10000		3.5	32.24
3		500 / 5000	5.0	36.93

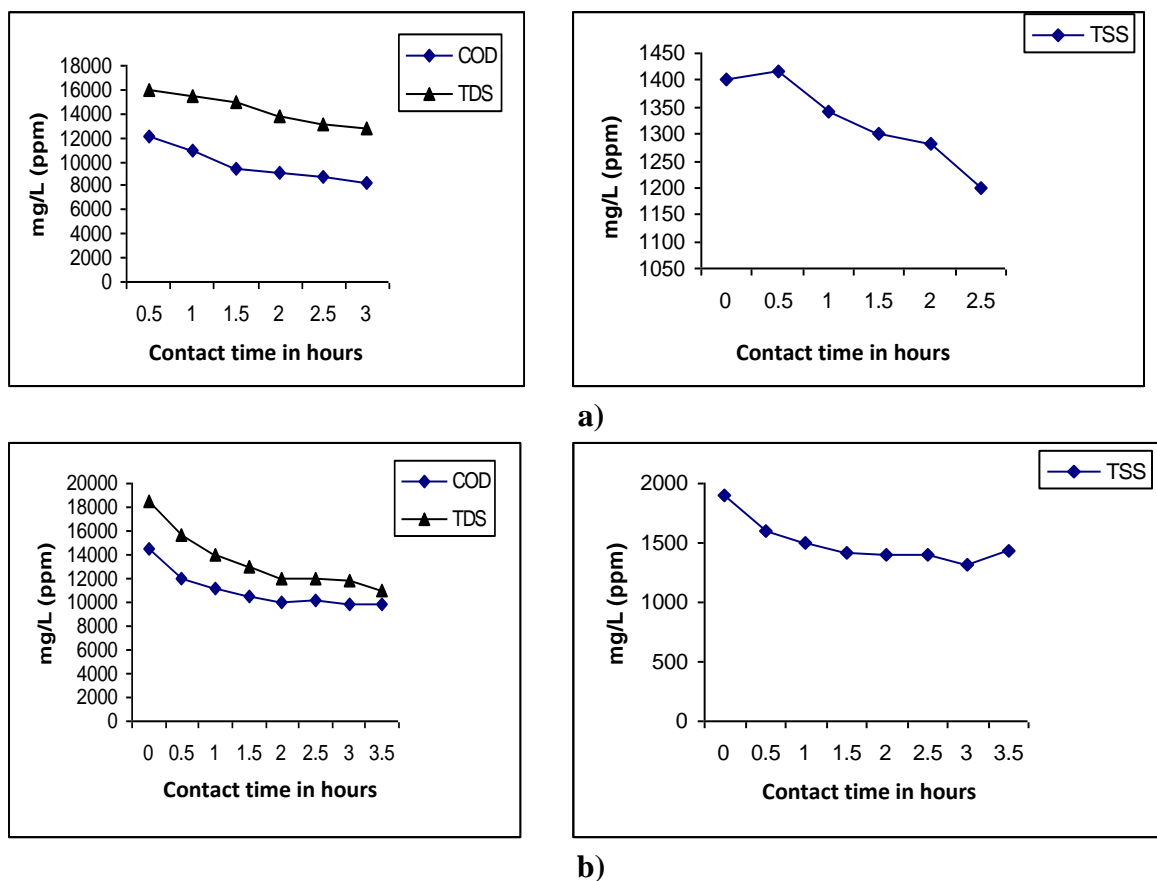


Fig. 7. Results showing changes in COD, TDS, and TSS after treatment of NaOCl on Effluent III a) Test#1 Effect of 5000 ppm Sodium Hypochlorite/UV by adjusting pH 6.0 with HCl b) Test#2 Effect of 10000 ppm Sodium Hypochlorite/UV by adjusting pH 6.0 with HCl

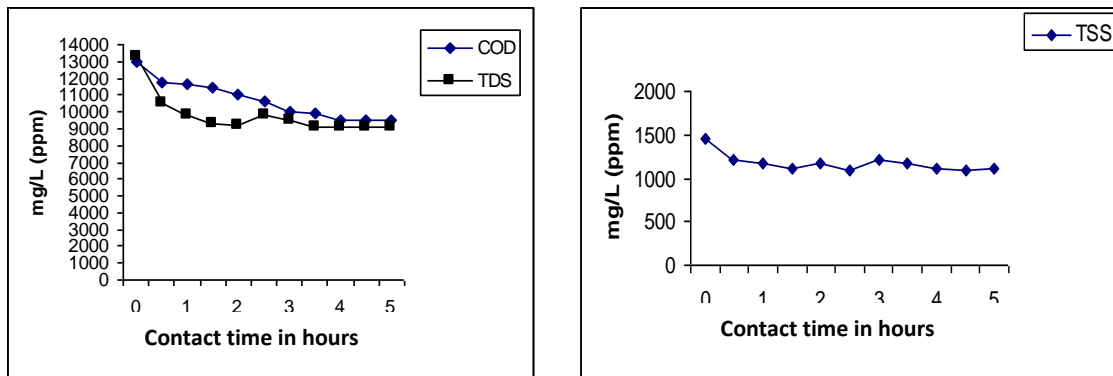
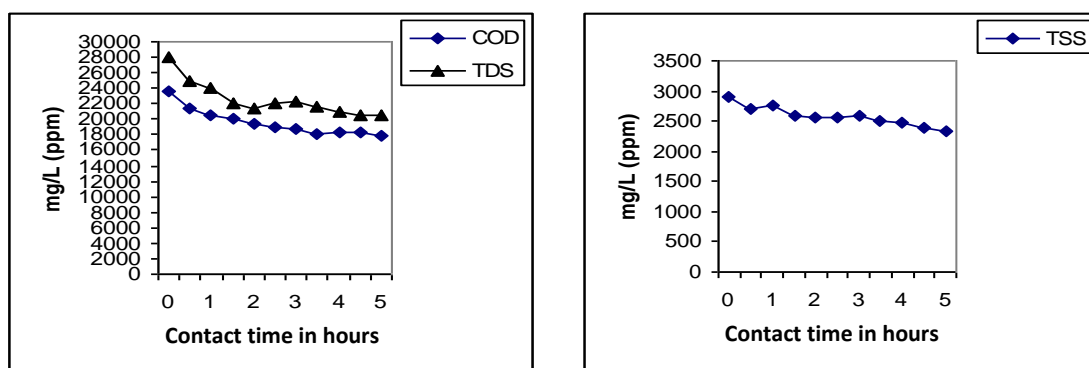


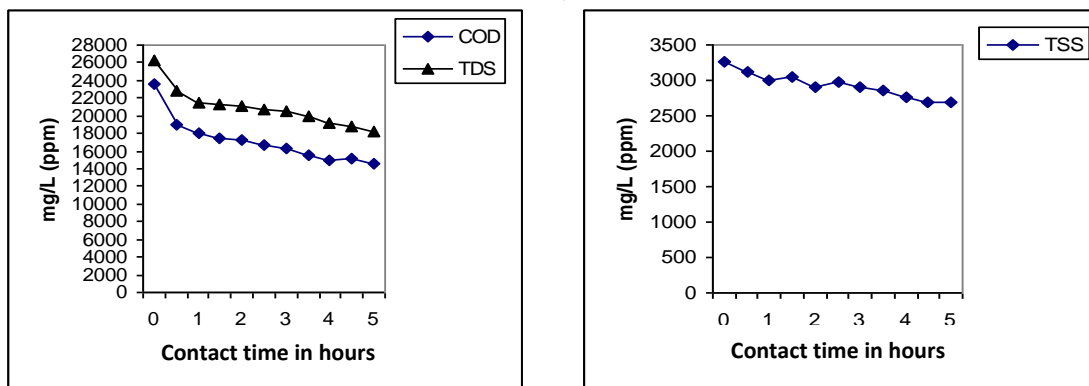
Fig. 8. Results showing changes in COD, TDS, and TSS after treatment of Fenton’s reagent on Effluent III: Test#3 Effects of 500 ppm Fe²⁺/5000ppm H₂O₂ by adjusting pH 2.0 with HCl

Experimental data for effluent IV

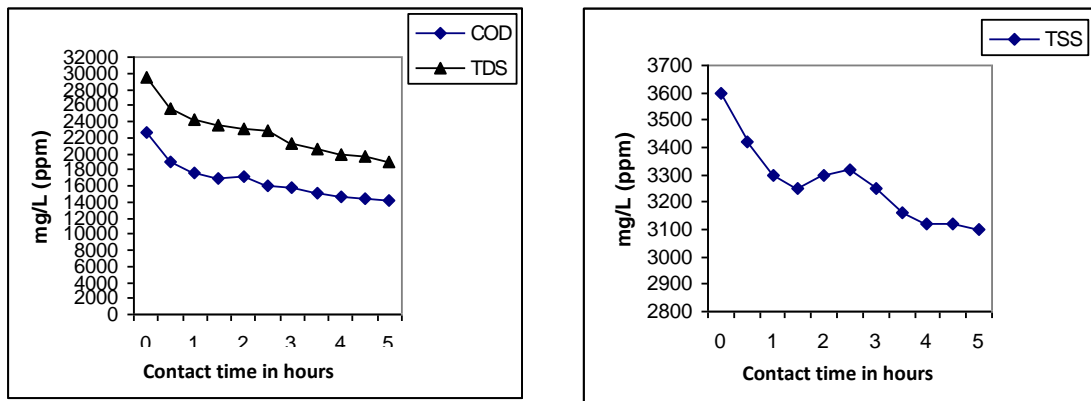
Effluent IV was collected from the anaerobic treatment outlet on the reacted aromatics and volatile fatty acids. Test# 1 was conducted by using 5000 ppm NaOCl while test #2 was conducted by using 10000 ppm NaOCl. Test# 1 result showed (Figure 9a) that after four hours of contact time with UV radiation, the values of COD and TDS changed with little variation. This may be because of lower oxidant dose and when test# 2 was carried out in presence of 10000 ppm NaOCl, the decrease in COD continue to found up to 3 ½ hours contact time in UV reactor (Figure 9b). Test# 3 was conducted at still higher concentration of oxidant dose up to 15000 ppm of NaOCl and the obtained result is shown in Figure 9c. It showed decrease in COD and TDS up to 3 hours of contact time. The effluent IV showed amenability for photo-oxidation treatment.



a)



b)



c)

Fig. 9. Results showing changes in COD, TDS, and TSS after treatment of NaOCl on Effluent IV: a) TEST#1 Effect of 5000 ppm NaOCl /UV by adjusting pH 6.0 with HCl b) TEST#2 Treatment of 10000 ppm NaOCl/UV by adjusting pH 6.0 with HCl c) TEST#3 Treatment of 15000 ppm NaOCl/UV by adjusting pH 6.0 with HCl

From test# 1, 2 and 3, it is clear that oxidant concentration can be considered as an important parameter along with contact time of UV radiation. Another point is also clear that UV/NaOCl treatment worked better in presence of non-biodegradable and volatile organic compounds. Test# 4 was conducted by using 250 ppm Fenton reagent. It showed continuous decrease in COD and TDS values even though after 5 hours contact time (Figure 10), this may be attributed to lower concentration of oxidant.

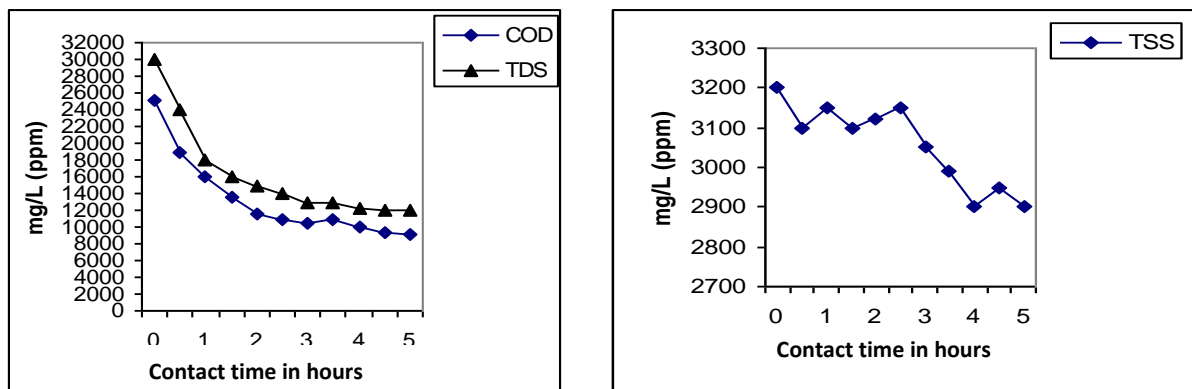


Fig. 10. Results showing changes in COD, TDS, and TSS after treatment of Fenton's reagent on Effluent IV: Test#4 Effect of 250 ppm Fe^{2+} /2500ppm H_2O_2 on COD & TDS by adjusting pH 2.0 with HCl

Test# 5 was conducted by increasing concentration of oxidant, 500 ppm $FeSO_4$ + 5000 ppm H_2O_2 . It showed that after 5 hours of contact time COD and TDS followed decreasing trend (Figure 11a). This can be attributed to lower concentration of Fenton reagent as in the test# 4. Test# 6 was conducted by using 750 ppm $FeSO_4$ +7500 ppm H_2O_2 . After 3 hours contact time COD and TDS remains constant as shown in Figure 11b. Test# 7 was conducted by using 1000 ppm $FeSO_4$ +10000 ppm of H_2O_2 . It also showed that after 3 hours contact time COD and TDS remains constant (Figure 11c).

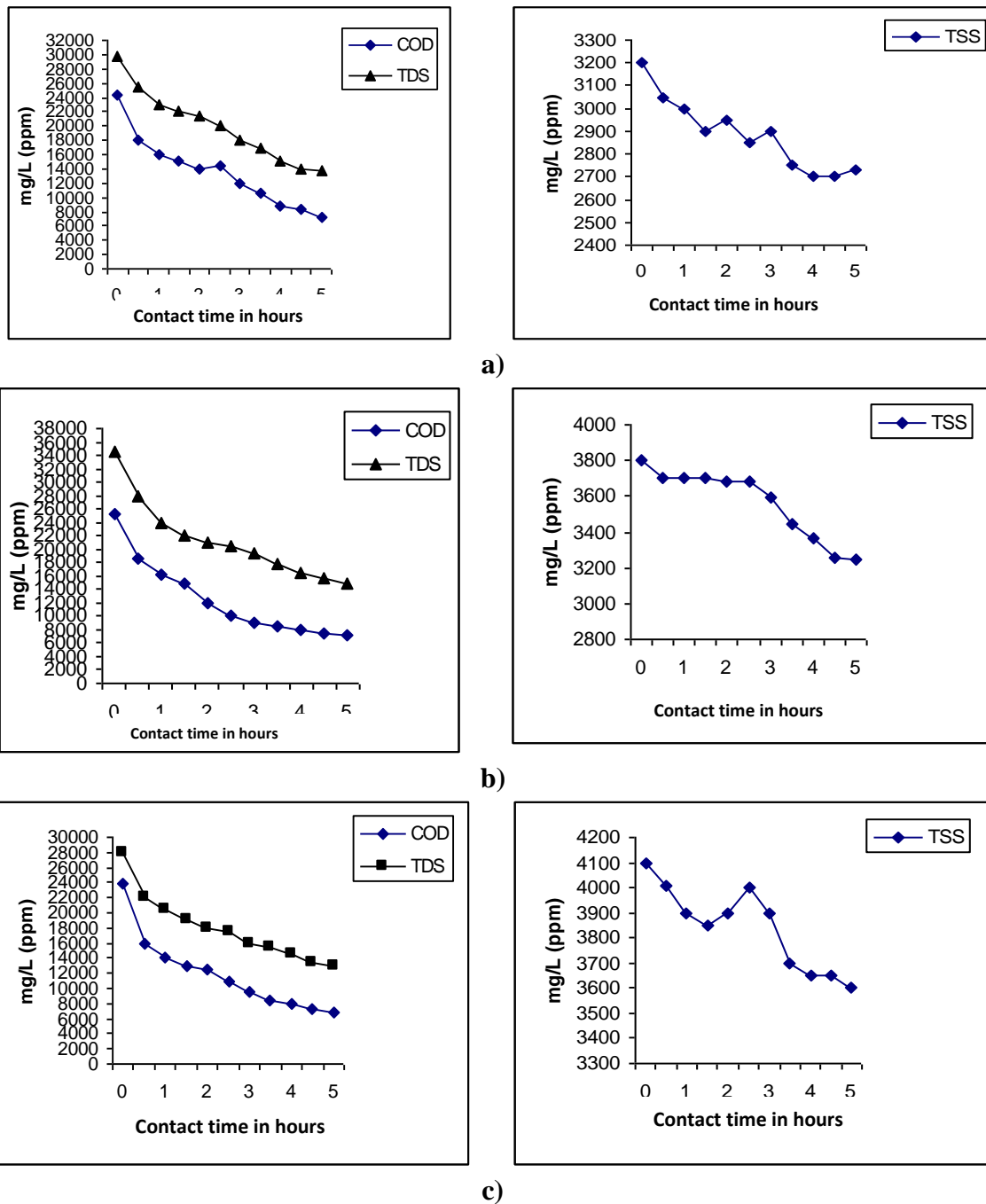


Fig. 11. Results showing changes in COD, TDS, and TSS after treatment of Fenton's reagent on Effluent IV: a) Test#5 Treatment of 500 ppm Fe^{2+} /5000ppm H_2O_2 by adjusting pH 2.0 with HCl b) Test#6 Treatment of 750 ppm Fe^{2+} /7500ppm H_2O_2 by adjusting pH 2.0 with HCl c) Test#7 Treatment of 1000 ppm Fe^{2+} /10000ppm H_2O_2 by adjusting pH 2.0 with HCl

From test# 5 and 6 it is clear that even if concentration of oxidant is increased, the decrease in COD and TDS can be occurred up to certain limit. Beyond that limit, oxidant concentration doesn't affect further the wastewater characteristics. The Table 6 has summarized results of all tests for effluent IV.

Table 6. Summary of the results for treatment effluent IV

Tests	Oxidants		UV Contact time in hours	% COD reduction
	NaOCl, ppm	Fe^{2+}/H_2O_2 , ppm		
1	5000	-	5.0	24.14
2	10000	-	5.0	36.93
3	15000	-	5.0	38.30

4	-	250 / 2500	5.0	64.24
5	-	500 / 5000	5.0	67.88
6	-	750 / 7500	5.0	72.42
7	-	1000 / 10000	5.0	71.06

Photo-Fenton as a pre-treatment step

From above obtained results, it is necessary to decide where to apply the advanced photo-oxidation process in the effluent treatment plant. Therefore, the choice was made to apply photo-Fenton process as a pre-treatment step in coupling with biological treatment process for the effluent IV because of two main reasons:

- 1) It showed greater amenability for Photo Fenton reaction while other effluents had not shown significant reduction in COD values.
- 2) Second important reason is that the BOD₅ of the treated effluent showed higher values and therefore, corresponding BOD₅/COD ratio is also higher as shown in Table 7 and Figure 12. This is the main indication for showing greater amenability for biodegradation.

Table 7. BOD₅: COD in raw and treated effluent of Effluent IV

Raw effluent			Treated Effluent		
COD mgO ₂ /L	BOD ₅ mgO ₂ /L	BOD ₅ :COD	COD mgO ₂ /L	BOD ₅ mgO ₂ /L	BOD ₅ :COD
24480	8124	0.33	6300	3220	0.51

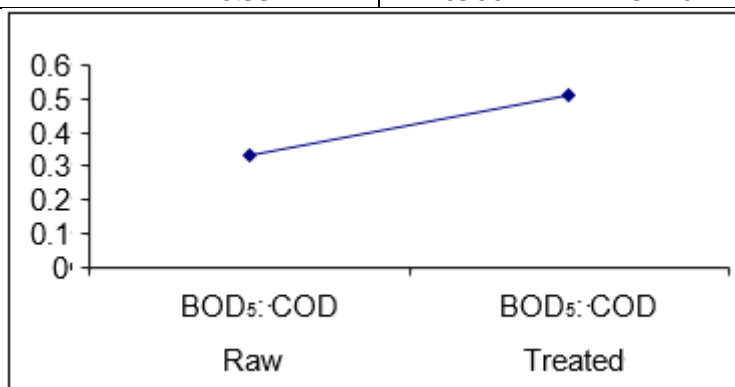


Fig. 12. BOD₅: COD in raw and treated effluent of Effluent IV

Biodegradability evolution of photo-treated solution

From the summary of obtained results for Photo Fenton treatment process is presented in Table 8. Following concentration conditions were fixed for the pre-treatment of effluent IV: [Fe²⁺] = 750 ppm, [H₂O₂] = 7500 ppm.

In order to evaluate the biocompatibility of generated effluent after photo-Fenton pre-treatment step, the small aeration tank was set up as shown in Figure 13. After maintaining pH 7.50 with alkali (NaOH) seed culture was added to maintain the MLSS (Mixed Liquor Suspended Solids) up to 4000 mg/L collected from running activated sludge process and results in the form of COD, TSS, TDS was noted after 24 hours (1 day) as noted in Table 9.

Table 8. COD reduction against Fenton reagent dosages

Fenton reagent dosages	% COD reduction
FeSO ₄ (250) + H ₂ O ₂ (2500)	64.24
FeSO ₄ (500) + H ₂ O ₂ (5000)	67.88
FeSO ₄ (750) + H ₂ O ₂ (7500)	72.42
FeSO ₄ (1000) + H ₂ O ₂ (10000)	71.06

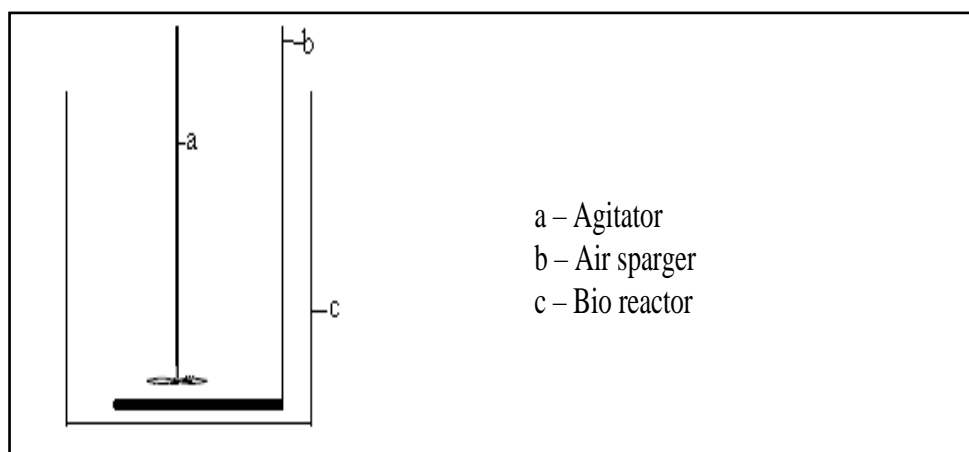


Fig. 13. Schematic Diagram of the Pilot Scale Bioreactor Experimental Apparatus

Table 9. Results of Pilot Scale Bioreactor

Day	COD (mgO ₂ /L)	TDS (mg/L)	Day	COD (mgO ₂ /L)	TDS (mg/L)
1	6800	13340	5	3452	11349
2	5660	12463	6	3238	10545
3	4597	12170	7	3120	10538
4	4130	11789	8	3215	9830

From observations of pilot scale bioreactor, it is cleared that anaerobic outlet wastewater after Fe²⁺/UV /H₂O₂ was biodegradable and showed excellent reduction in COD could be used for commercial application in the ETP of pharmaceutical industry therefore, following scheme of treatment process can be established to achieve desired COD reduction (Figure 14).

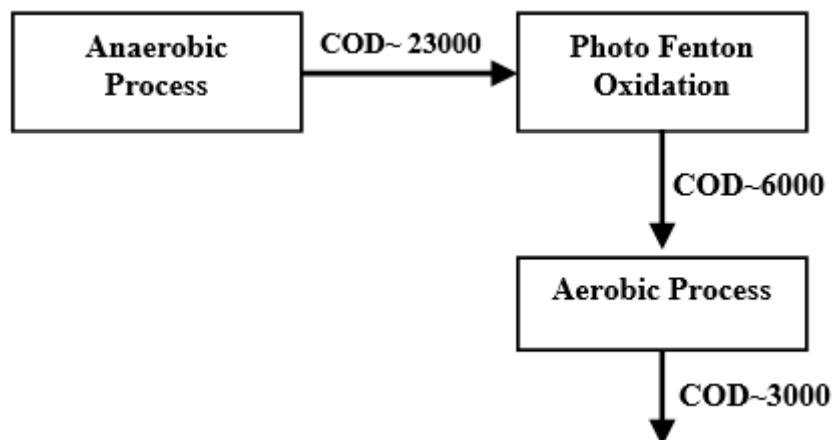


Fig. 14. Schematic Representation of proposed wastewater treatment

CONCLUSIONS

In the present study, the efficiency of the advanced oxidation processes for the remediation of pharmaceutical wastewater was analyzed in the pilot scale plant. Anaerobic treatment outlet provides the greatest reduction in the COD, while aerobic treatment outlet effluent does not show remarkable effect. Which indicates that the efficiency of Photo Fenton process as well as UV/ NaOCl gets altered by biodegradable or non-biodegradable chemical contaminants present in wastewater. Effluent from anaerobic outlet generated by H₂O₂/UV/Fe²⁺ method found to be higher biodegradable than itself. Present study illustrated the significance of the H₂O₂/UV as a pretreatment method for pharmaceutical wastewater. Here we demonstrated the strategy of coupling of chemical-biological treatment system to four different sourced ETP effluents. This type of application strategy is useful to visualize broader

problem in one perspective. The effluents (I and II) were non-biodegradable and effluent IV was biodegradable therefore, photo-Fenton process was used as post-treatment and pre-treatment, respectively. In case of effluent I and II, there may be absence of enzymes required for degradation, and considered to be maintaining biorecalcitrance properties even though photo-Fenton used as post-treatment. This indicated that effluent properties determine whether to apply for hybrid system of chemical-biological processes for wastewater treatment. While effluent IV showed higher efficiency of degradation when pre-treatment with photo-Fenton system was performed. Anaerobic /Photo Fenton sequential step-treatment is the most efficient method to treat pharmaceutical wastewater. This is quite convenient process as there is no sludge generation therefore, sludge disposal related problems can be totally avoided. The reduction in the COD obtained is very high as compared to other single conventional wastewater treatment process. Present research will pave ways to conduct further research in this direction.

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