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Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater

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Abstract

The applicability of Fenton's oxidation to improve the biodegradability of a pharmaceutical wastewater to be treated biologically was investigated. The wastewater was originated from a factory producing a variety of pharmaceutical chemicals. Treatability studies were conducted under laboratory conditions with all chemicals (having COD varying from 900 to 7000 mg/L) produced in the factory in order to determine the operational conditions to utilize in the full-scale treatment plant. Optimum pH was determined as 3.5 and 7.0 for the first (oxidation) and second stage (coagulation) of the Fenton process, respectively. For all chemicals, COD removal efficiency was highest when the molar ratio of H_2O_2/Fe^{2+} was 150–250. At H_2O_2/Fe^{2+} ratio of 155, 0.3 M H_2O_2 and 0.002 M Fe^{2+}, provided 45–65% COD removal.

The wastewater treatment plant that employs Fenton oxidation followed by aerobic degradation in sequencing batch reactors (SBR), built after these treatability studies provided an overall COD removal efficiency of 98%, and compliance with the discharge limits. The efficiency of the Fenton's oxidation was around 45–50% and the efficiency in the SBR system which has two reactors each having a volume of 8 m^3 and operated with a total cycle time of 1 day, was around 98%, regarding the COD removal.

Keywords: Biodegradability; Pharmaceutical wastewater; Fenton's reagent; Fenton's oxidation; Pretreatment

1. Introduction

Treatment of pharmaceutical wastewater has always been troublesome to reach the desired effluent standards due to the wide variety of the products produced in a drug manufacturing plant, thus, variable wastewater composition and fluctuations in pollutant concentrations. The substances synthesized in a pharmaceutical industry are structurally complex organic chemical that are resistant to biological degradation. For this reason, conventional treatment methods are usually inappropriate for the treatment of pharmaceutical wastewaters and hence there is a need for advanced oxidation methods [1,2].

Several different alternatives, including steam stripping, activated carbon, advanced oxidation and anaerobic treatment, were considered to be used together with aerobic biological treatment. Among these, Fenton's oxidation, an advanced oxidation method, appeared to be the most promising method, in terms of cost-effectiveness and ease of operation. Recently, in a comprehensive review, Neyens and Baeyens [3] indicated that Fenton's oxidation is very effective method in the removal of many hazardous organic pollutants from wastewaters. Fenton's oxidation can also be an effective pretreatment step by transforming constituents to by-products that are more readily biodegradable and reducing overall toxicity to microorganisms in the downstream biological treatment processes [4]. In the present study, applicability of Fenton's oxidation for the pretreatment of pharmaceutical effluents originating from a medium scale drug manufacturing plant producing various antiseptics and disinfectant solutions was tested under laboratory conditions. Following this pretreatment, aerobic sequencing batch reactor (SBR) technology which is an attractive solution when flexibility and simplicity of operation are concern, was adopted considering the intermittent and fluctuating wastewater discharge from the plant.

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Fenton's oxidation is one of the best known metal catalyzed oxidation reactions of water-miscible organic compounds. The mixture of $FeSO_4$ or any other ferrous complex and H_2O_2 (Fenton's reagent) at low enough pH, results in Fe^{2+} catalytic decomposition of H_2O_2 and proceeds via a free radical chain process that produces hydroxyl radicals [5] which have extremely high oxidizing ability and can oxidize hard to decompose organic compounds in a short time. The Fenton's reagent has not only oxidation function but also coagulation by the formation of ferric-hydroxo complexes [6,7]. The coagulation step acts as a polishing step, and removes the remaining after Fenton's oxidation.

The suggested overall reaction for Fenton's oxidation is given below [8]:

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$$

According to this equation, the pH value has to be in the acidic range to generate the maximum amount of hydroxyl radicals to oxidize organic compounds. However, pH value should not be too low since at very low pH values (<2.0) the reaction is slowed down due to the formation of complex iron species and formation of oxonium ion $[H_3O_2]^+$ [9].

On the other hand, at high pH (pH > 4), the generation of hydroxyl radicals gets slower because of the formation of the ferric-hydroxo complexes [6]. Therefore, the initial pH value has to be between 2 and 4 to generate the maximum amount of hydroxyl radicals to oxidize organic compounds [5–7,10,11–16].

The present paper is basically about the treatability studies carried out adopting the Fenton oxidation process to the pharmaceutical wastewater of concern. Also presented in the paper is the performance of the treatment plant realized thereafter which mainly includes Fenton oxidation and SBR type aerobic biological treatment units.

2. Materials and methods

2.1. Wastewater

The wastewater used is from a medium scale drug manufacturing plant in Turkey producing various disinfectants, tincture of iodine, hydrogen peroxide and antiseptic solutions. The total number of products amount to 10, including an antiseptic gargle and an antiseptic liquid soap formulated with the same active ingredient, several other antiseptic solutions with different active ingredients and disinfectant solutions for medical use. The intermittent cleaning of the tanks used in the production processes and domestic utilization of the tap water make up the wastewater coming out of the plant.

The plant has intermittent and fluctuating wastewater flow with variable wastewater composition depending on the production regime. The plant has two separate manufacturing lines, both of which are operated as batch reactors. Neither of the manufacturing lines is dedicated to a specific product and the production regime greatly differs with respect to demand. Thus, the same equipment, though in different configurations, are used in manufacturing the company's whole range of products. Naturally, this requires through cleaning and validation prior to the reuse of the equipment. However, the regimen of equipment cleaning also varies greatly with the different processes used for each product. Besides, when successive batches of the same product are manufactured, the equipment may not be washed and cleaned between the batches, depending on the potential for carryover of contaminants or degraded materials into the final product.

Typically; pharmaceutical wastewaters that originate from the washing of the equipments amount to about to 2–3 m^3/day and that from washing of bottles increases this volumetric flow rate to approximately 6–7 m^3/day. Domestic wastewater from the plant is around 5 m^3/day.

The company decided to construct a wastewater treatment plant that will satisfy the discharge limits stated by the Turkish Water Pollution Control Regulation (WPCR), for the pharmaceutical and domestic wastewaters. The Regulation requires that BOD_5 of the wastewaters should be reduced down to 50 mg/L in order to discharge to a receiving water body.

2.2. Methodology

The general approach in the treatability studies was to optimize the operational conditions in the Fenton's oxidation unit to achieve maximum treatment efficiency while minimizing the use of chemicals (acid and base for pH adjustment, and hydrogen peroxide and ferric sulphate as the Fenton's reagents) and hence minimizing operation costs of the treatment plant. The main idea was to maximize the overall treatment efficiency considering units, Fenton's oxidation and biological treatment. Therefore, improved biodegradability after Fenton's oxidation was as important as reduction in waste load in Fenton's oxidation.

As part of the treatability studies, analyses of chemical oxygen demand (COD) and 5-day biochemical oxygen demand (BOD_5) were carried out to investigate biodegradability of the pharmaceutical effluents from the plant. Because the plant produced its pharmaceutical wastewaters intermittently, it was not practical to sample from the actual washing process. Furthermore, all of the products were not being produced during the treatability studies. Therefore, treatability studies were conducted with synthetic wash waters prepared by diluting each product, except hydrogen peroxide. The "product" H_2O_2 was excluded from treatability studies for Fenton's oxidation because the wash waters from H_2O_2 production would contain only dilute H_2O_2. Hydrogen peroxide is unstable in basic solution, and above pH 7 it would decompose to yield oxygen and water. The synthetic wash waters were then mixed with domestic wastewater, in proportion to their daily average volumes (domestic/pharmaceutical = 3.5/1.5), for COD and BOD_5 analyses. The average COD and BOD_5 concentrations in the mixed wastewaters for each product and the active ingredients of each are presented in Table 1. As shown, some of the products are almost non-biodegradable with BOD_5/COD ratio below 0.59.

Communication with the plant and an analysis of the flow records, though scarce, indicated that the wash waters contained the product with an average of 1/100 dilution. In the preparation

Table 1
Products: their active ingredients and organic load

Name	Active ingredients	COD (mg/L)	BOD_5 (mg/L)	BOD_5/COD
Hydrogen peroxide	Hydrogen peroxide	900	85	0.09
Drogryl	Difenhydramine chloride, zinc oxide	900	175	0.19
Polyod	Povidon iodine	1390	110	0.08
Mucosis	*S*-Carboxymethylcysteine	1810	1070	0.59
Klorhex gargle	Chlorhexidine gluconate	2050	700	0.34
Zefan	Benzalkonyum chloride	2150	100	0.05
Tincture of iodine	Iodine, sodium iodide	2600	1425	0.55
Klorhex liquid soap	Chlorhexidine gluconate	3850	250	0.06
Savlex	Cetrimide, chlorhexidine gluconate	4050	675	0.17
Bugumentol	Menthol	6920	3600	0.52

of the synthetic wash waters, three different dilution factors, 1/50, 1/100 and 1/500, were used to account for the variations in pharmaceutical wastewater flows due to changes in washing requirements for different production regimes and also due to the extra dilution by the addition of bottle washing wastewaters to equipment wash waters.

2.3. Experiments

The major operational conditions that would affect the treatment of the pharmaceutical effluents from the plant using Fenton's reagent are temperature, initial pH, H_2O_2 and Fe^{2+} dosages, second stage (coagulation stage) pH and waste load. The effects of these parameters on treatment efficiency were investigated. First, the effects of temperature, initial pH and second stage pH were studied using a 1:1 mixture of synthetic wash waters prepared with 1/100 dilution of each product. After the determination of optimum values for temperature and pH, the effect of initial COD on COD removal efficiency was tested using synthetic wash waters prepared with 1/50, 1/100 and 1/500 dilution of each product. Further experiments to optimize H_2O_2 and Fe^{2+} dosages were conducted at the selected optimum pH values and temperature, using synthetic wash waters prepared with the selected dilution. The effect of H_2O_2 and Fe^{2+} dosages on COD removal efficiency was investigated for a H_2O_2 concentration range between 0.8 and 5 M and Fe^{2+} doses between 0.002 and 0.033 M. The Fe^{2+} doses were kept constant at 0.033 M while studying the effect of H_2O_2 dosage, and H_2O_2 concentration was kept constant at 2.5 M in the tests for Fe^{2+} dosage.

2.4. Experimental procedure

The experiments were conducted in batch reactors and 100–200 mL wastewater samples were used in the experiments. The sample was heated up to the determined temperature (50 °C). The pH of the heated sample was adjusted to the required value with sulphuric acid (1 M) and sodium hydroxide (10 M). Required amounts of $FeSO_4{\cdot}7H_2O$ and H_2O_2 were added to the sample. The solution was stirred. Thirty minutes were allowed for the completion of the reaction (the equilibration time is reported to be in the range 10–30 min by Kuo [6], Solozhenko et al. [10], Zhang et al [17], and Kang et al. [18]). Then, another 30 min were allocated for precipitation. The supernatant was then decanted. The pH of the decanted supernatant was then adjusted to the desired value to initiate coagulation. Two hours were allowed for precipitation. After precipitation, the supernatant was decanted for COD measurement and for BOD_5 test for the selected samples (those treated with optimal dosage).

All the experiments conducted were carried out in duplicate sets. All measurements were performed in parallels in each set. The removals reported are the average of the parallel measurements of the duplicate sets and the parallel measurements.

2.5. Materials

$FeSO_4{\cdot}7H_2O$, NaOH and H_2SO_4, which were used during experiments, were purchased from Merck KGaA (Germany). H_2O_2 solution of 50% was provided by the Plant, where H_2O_2 solution of 30% is used for producing their "product" H_2O_2. Ferric sulphate was added to the system in solid form.

2.6. Analytical methods

COD of the samples were measured according to an EPA approved reactor digestion method (for a COD range 0–1500 mg/L with a HACH DR2000 instrument). If a water or wastewater sample includes hydrogen peroxide, the standard COD test will be interfered since the dichromate ions react with H_2O_2 in an acidified solution [6,19,20]. Because of this reason, COD measurements were performed only after the Fenton's coagulation stage. Since H_2O_2 is unstable in basic solution, after raising the pH above 7 for the initiation of Fenton's coagulation, it decomposes to give oxygen and water and lose its oxidation ability [6] so that no interference is of importance.

pH measurements were performed using a pH meter (Model 2906, Jenway Ltd., UK) and a pH probe (G-05992-55, Cole Parmer Inst. Co., USA)

In addition to COD, BOD_5 tests were conducted for the selected samples, those treated with optimal dosage, to investigate the effect of Fenton's treatment on biodegradability. The BOD_5 tests were conducted using the mixture of Fenton-treated synthetic wash waters with domestic wastewaters, in proportion to their daily average volumes (domestic/pharmaceutical = 3.5/1.5), to simulate the operating conditions foreseen for the wastewater treatment plant. The BOD_5

of the samples were measured following Standard Methods [21].

3. Results and discussion

3.1. Treatability studies with Fenton's oxidation

3.1.1. Effect of temperature and pH

The effect of temperature on COD removal efficiency was tested at room temperature and at 50 °C, and no significant differences were observed in the treatment efficiency for the tested temperatures (data not shown). Thus, all further experiments were carried out at room temperature, for practical and economic reasons. Research findings indicate that the temperature of the wastewater almost does not affect the efficiency of COD removal in Fenton's oxidation [22], although the redox reaction can be accelerated by raising the temperature [6,10,17], as expected. The time required for the oxidation to be completed at room temperature was about 10–20 times longer than at 50 °C which required several minutes (data not shown).

When tested with the initial pH range 3.0–4.5, no significant differences in treatment efficiency were observed though pH 3.5 produced slightly better results (Fig. 1). This finding is in line with recent research findings that suggest that the optimum pH for Fenton's oxidation is independent from the nature of wastewater and at around 3–5. Kuo [6] studied five different types of artificial dyeing wastewater and found that the best pH for Fenton's oxidation is below 3.5. Similarly, Tang and Huang [11–13] studied the removal of chlorinated aliphatic organics and they suggest that the optimal pH is 3.5. It was reported by Kang and Chang [7] that for dyeing wastewaters the removal efficiency of COD decrease with the increasing pH values and the pH range for the maximum removal of both COD and color is 3–5. The tests performed by Kochany and Lugowski [15] revealed that optimum conditions for Fenton's treatment require pH around 4. In a recent study, Zhang et al. [17] reported the optimum pH as 2.5 for the treatment of landfill leachate by Fenton's oxidation.

Thereafter, the effect of the second stage (i.e. coagulation) pH on treatment efficiency was searched. The pH of the solution, after oxidation at pH 3.5, was varied from 7 to 9 and the effect on the residual COD was searched. This pH did not seem to affect the treatment efficiency as long as it was equal to or greater than 7. Therefore, the pH was adjusted to 7 before Fenton's coagulation.

3.1.2. Effect of initial COD

The success of Fenton's treatment depends on the formation of hydroxyl radicals. Less scavenging of hydroxyl radicals occurs as initial organic substrate concentration increases. In order to investigate the effect of initial COD on COD removal efficiency, three different dilution factors of 1/50 (0.02), 1/100 (0.001) and 1/500 (0.002) were tested. The ratio of 1/100 was tested as it is the typical dilution of the products resulting from equipment washing. The dilution of the products by a factor of 1/500 was studied to simulate the dilution resulting from the addition of bottle washing wastewaters to the wash waters from production. Bottle washing increases the wastewater from the plant to about 6–7 m^3/day instead of its average 2–3 m^3/day at other times. The dilution factor of 1/50 was investigated to account for the variations due to changes in washing requirements for different production regimes. As presented in Fig. 2, initial COD had considerable effect on efficiency. The COD removal efficiency was relatively higher for lower initial COD values, or at higher dilutions of the products. However, in lower dilution ratios (1/50 to 1/100), average COD removals did not differ considerably. Furthermore, at the lowest dilution studied (1/50), there was a very high variability in COD removal for different products which indicates more pronounced effect of species type on oxidizability at high initial COD levels. These findings are in line with previous studies. According to Tang and Huang [14], the amount of H_2O_2 required for a specific percent removal of the organic compounds depends on the initial organic concentration to be oxidized. Similarly, Tang and Tassos [5] reported that Fenton oxidation of bromoform shows weak dependence on initial concentration as they observed only 30% increase in removal, with a six-fold increase in initial bromoform concentration (from about 50 to 300 μg/L).

Depending upon the results from this part of the study, it was decided that all further experiments will be conducted using synthetic wash waters prepared by 1/50 dilution of the products. This selection was based on the fact that, the expected dilution from the plant is typically in the range 1/100 to 1/50 and there is

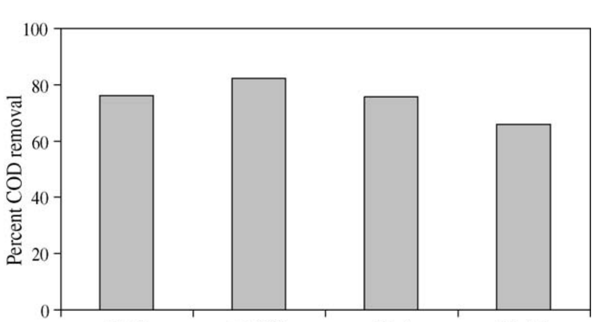


Fig. 1. Effect of first stage pH on removal efficiency ($H_2O_2/Fe^{2+} = 150$).

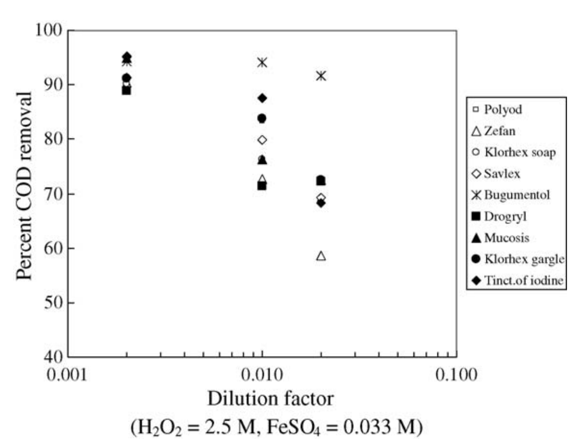


Fig. 2. Effect of initial COD on removal efficiency.

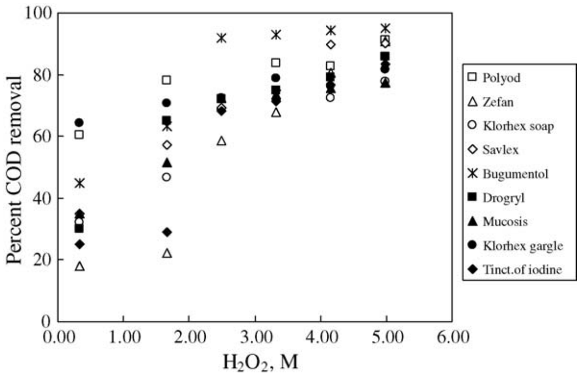


Fig. 3. Removal efficiency with varying H_2O_2 dosage (Fe^{2+} = 0.033 M).

not much variability in the COD removal for this dilution range. Moreover, it would be safe to work with this dilution as the worst case would be simulated.

3.1.3. *Effect of H_2O_2 and Fe^{2+} dosages and H_2O_2/Fe^{2+} ratio*

It is clear in Fig. 3 that higher H_2O_2 doses generated more hydroxyl radicals, which, in turn, improved the COD removal efficiency. With an increase of H_2O_2 doses from 0.8 to 5 M, at constant Fe^{2+} dosage of 0.033 M, average COD removal efficiency increased from about 40% to 85%. As seen in this figure, the H_2O_2 dosage that yielded COD removals higher than 50% was 2.5 M. Keeping the H_2O_2 dosage constant at this concentration, an increase in Fe^{2+} doses from 0.003 to 0.01 M almost doubled the average COD removal efficiency (Fig. 4). Further increasing the Fe^{2+} dosage, on the other hand, resulted in lower COD removal efficiencies. This could be possibly due to the scavenging action of superfluous Fe^{2+} for the hydroxyl radical [23].

Figs. 3 and 4 indicate that the efficiency of treatment is dependent upon the amounts of H_2O_2 and Fe^{2+} available in the system. The plot of H_2O_2/Fe^{2+} ratio versus removal efficiency in Fig. 5 reached a plateau for ratios between 150 and 250, where COD removals are the highest for each product. This is because, when either of them is overdosed, H_2O_2 and Fe^{2+} can both react with the hydroxyl radicals and therefore inhibit the oxidation reac-

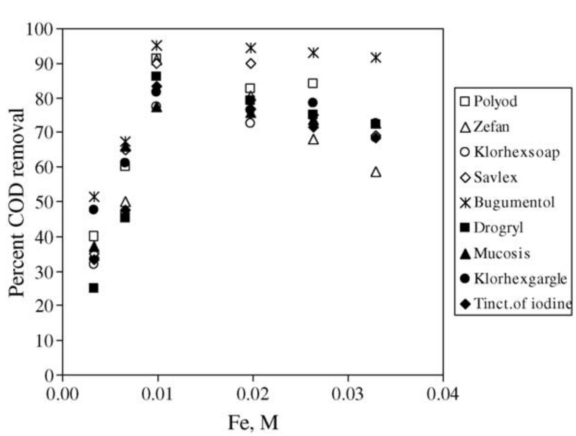


Fig. 4. Removal efficiency with varying $FeSO_4$ dosage (H_2O_2 = 2.5 M).

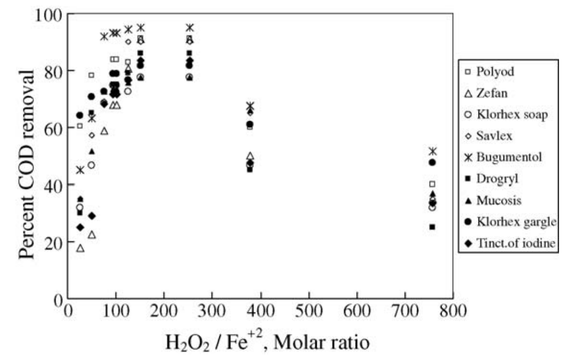


Fig. 5. Removal efficiency with varying H_2O_2/Fe^{2+} ratio.

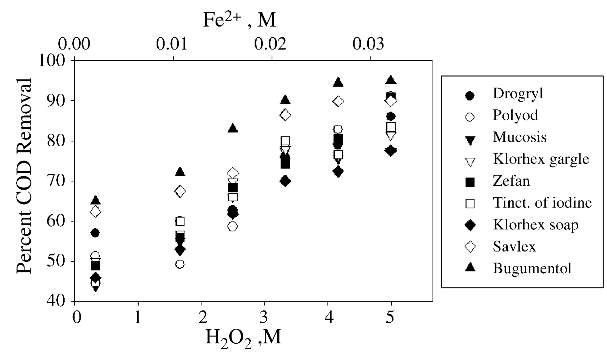


Fig. 6. Removal efficiency at H_2O_2/Fe^{2+} ratio of 155.

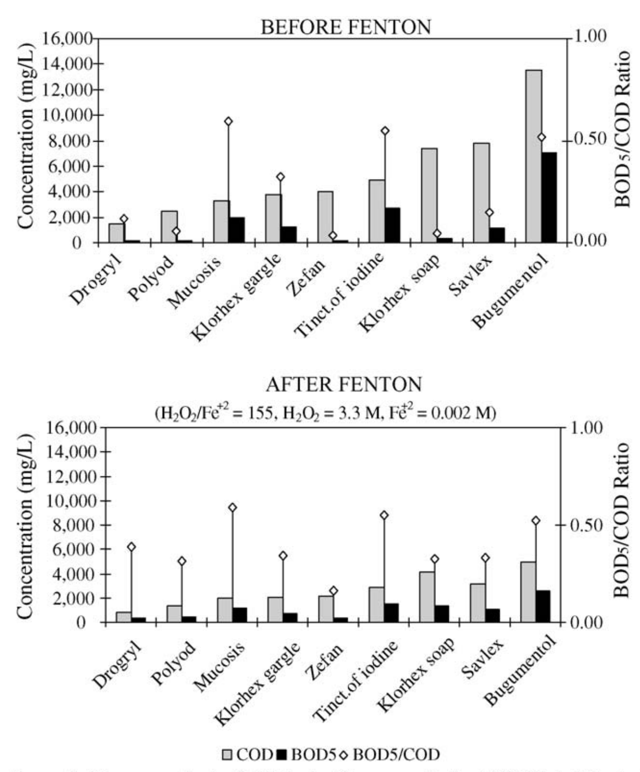


Fig. 7. Composition of Fenton-pretreated synthetic wash waters mixed with domestic wastewater.

Table 2
COD removal efficiencies in pharmaceutical wastewater and in combined wastewater

% COD removal	Pharmaceutical wastewater (Fenton-treated synthetic wash water)[a]	Combined wastewater (mixture of wash water and domestic wastewater)[b]
Minimum	45	40
Average	52	48
Maximum	65	63

[a] For samples treated with minimum H_2O_2 and $FeSO_4$ dosages at H_2O_2/Fe^{2+} ratio of 155.
[b] The mixing ratio is domestic/pharmaceutical: 3.5/1.5 (v/v).

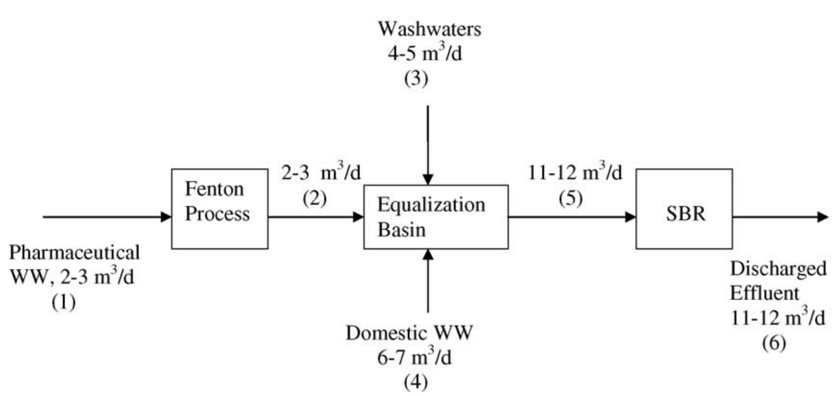
tions [11–14]. Morais and Zamora [24] also pointed out that optimal molar H_2O_2 to Fe^{2+} ratio of 329 has to be maintained to improve the biodegradability of mature landfill leachates. On the other hand, Tang and Tassos [5] reported a much smaller optimal molar ratio of 3.7–1.9 to achieve the maximal degradation efficiency. Kochany and Lugowski [15] and Zang et al. [17] reported similar optimal ratio values for the treatment of nitrification inhibitors (4.0) and for landfill leachate (1.5) with Fenton's reagent. In another study where amine oxidation by Fenton's reagent was investigated, Casero et al. [22] reported a higher optimum molar H_2O_2/Fe^{2+} ratio of 5–40. All these findings indicate that the optimal H_2O_2/Fe^{2+} ratio varies highly with type of waste to be oxidized.

As seen in Fig. 6, at the molar H_2O_2/Fe^{2+} ratio of 155, COD removal increased with increasing doses of H_2O_2. This finding indicates that, in order to achieve maximum COD removal, as well as an optimum H_2O_2/Fe^{2+} ratio, sufficient concentration of Fenton's reagent is also needed to produce adequate amount of hydroxyl radicals. In addition, on the condition that the H_2O_2/Fe^{2+} ratio is optimum, required H_2O_2 and $FeSO_4$ doses can be reduced or tuned up significantly.

At the H_2O_2/Fe^{2+} ratio of about 155, the minimum dosage studied, 0.3 M H_2O_2 and 0.002 M Fe^{2+}, yielded COD removal efficiencies ranging from 45% to 65% for the synthetic wash waters prepared by 1/50 dilution of the products (Fig. 6). Keeping the ratio constant at 155, increasing H_2O_2 to 5 M and Fe^{2+} to 0.032 M resulted in COD removal efficiencies ranging from 77% to 95%. The COD and BOD_5 values of the Fenton-treated samples of this dosage, measured after mixing with domestic wastewater at the ratio of domestic/pharmaceutical = 3.5/1.5, are presented in Fig. 7, together with the COD and BOD_5 values measured in mixed samples prepared with untreated synthetic wash waters, for comparison. It is evident in this figure that, although only the "pharmaceutical" portions of the "mixed" samples were treated with Fenton's oxidation while the domestic wastewater did not receive any kind of treatment, the overall reduction in COD concentrations in the mixed samples were comparable to those in the synthetic wash waters, owing to the dilution provided by mixing. The average, minimum and maximum COD removal efficiencies observed in mixed samples and in the synthetic wash waters are presented in Table 2.

3.2. Full-scale treatment plant

On the basis of the treatability study findings, a wastewater treatment plant which mainly consists of Fenton oxidation



Line	COD, mg/l	BOD_5, mg/l
1	35000-40000	2100-2500
2	17500-22000	4000-4300
3	-	-
4	300-350	150-180
5	4000-4500	750-1000
6	60-80	15-20

Fig. 8. Treatment plant.

and SBR type aerobic biological treatment unit was designed, constructed and put into operation. In the treatment plant (Fig. 8), other than these two basic units, there is an equilization tank ($6\,m^3$) which collects other wastewaters coming from the process tank washing operations and discharge into the Fenton oxidation reaction tank ($2\,m^3$) where the wastewaters are pre-treated with Fenton's reagent. The pre-treated wastewaters are then conveyed to another equalization basin ($4\,m^3$) before being introduced into the SBR where mixed with the domestic wastewater. There are two SBR units each having a volume of $8\,m^3$ and operated with a total cycle time of 1 day (12 h filling, 8 h reaction and 2 h settling period).

Based on the results from the above summarized treatability studies, The Fenton's unit of the treatment plant was operated under the following conditions: initial pH 3.5; second stage pH 7; 0.3 M H_2O_2 and 0.002 M Fe^{2+} doses at a H_2O_2/Fe^{2+} molar ratio of about 150.

The treatment plant established was monitored for a period of 2 months and the following general performance was observed. In general, treatment with Fenton's oxidation was found to improve the biodegradability of the wash waters. The COD removal efficiency attained in this unit was between 45% and 50%. After Fenton's oxidation, the BOD_5/COD ratio of the wastewater was increased by about 3–5 times and concurrently an average COD removal efficiency of 98% was achieved in the SBRs. The BOD_5 values measured at the outlet of the treatment plant by the competent authority, during this 2-month period were in the order of 15–20 mg/L which corresponded to 98% overall BOD removal efficiency. This was well below the discharge limit of 50 mg/L set in the discharge standards. This was also reflected in the toxicity dilution factor (TDF) measurements by the Provincial Authority, which indicated that toxicity was greatly reduced. The TDF is defined as the minimum dilution factor required for the survival of all 10 specimens of *Lebistes reticulatus* after 48 h. The TDF values measured by the Provincial Authority consistently dropped to 2, after the new system was put to operation from its earlier value of 5–10.

4. Conclusions

The following conclusions can be drawn from this study:

- The results in the use of Fenton's reagent indicated that the overall treatment efficiency was best at an initial pH of 3.5 and second stage (coagulation) pH of 7.0.
- For all pharmaceutical products (with a COD range 900–7000 mg/L), average COD removal efficiency was highest when the ratio of H_2O_2/Fe^{2+} was around 150–250. At a constant H_2O_2/Fe^{2+} molar ratio of about 155, 0.3 M H_2O_2 and 0.002 M Fe^{2+}, provided 45–65% COD removal.
- Treatment with Fenton's oxidation improved the biodegradability and reduced the toxicity of the pharmaceutical wastewaters. Fenton oxidation was an effective pretreatment method for the non-biodegradable portions of the pharmaceutical wastewater, which renders them more biodegradable for following biological processes.

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