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Fenton-biological treatment processes for the removal of some pharmaceuticals from industrial wastewater

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ABSTRACT

A treatability study of pharmaceutical wastewater from El-Nasr Pharmaceutical and Chemical Company, South-East of Cairo, was carried out. The company discharges both industrial (6000 m^3/d) and municipal wastewater (128 m^3/d) into a nearby evaporation pond without any treatment. The generated raw wastewater is characterized by high values of COD (4100–13,023), TSS (20–330 mg/L), and oil grease (17.4–600 mg/L). In addition, the presence of refractory compounds decreases BOD/COD ratio (0.25–0.30). Analysis of raw wastewater confirmed that pre-treatment is required prior to discharge into public sewers to comply with the Egyptian Environmental laws and regulations. The obtained results indicated that the refractory compounds and their by-products cannot be readily removed by biological treatment and always remain in the treated effluent or adsorbed on the sludge flocs. The application of Fenton oxidation process as a pre-treatment improved the removal of pharmaceuticals from wastewater and appears to be an affective solution to achieve compliance with the law legislation with respect to discharge in a determined receptor medium.

1. Introduction

Pharmaceutical industry produces a wide variety of products. It uses both inorganics and organics as raw materials; the latter is either of synthetic or of plant and animal origin [1]. Generally, most of these wastes are toxic to biological life [2] and are usually characterized by high BOD, chemical oxygen demand (COD) values and a low BOD/COD ratio, which is the main problem causing the failure of biological treatment [1–3]. The existence of such compounds (e.g., pharmaceuticals and hormonally active substances) in the aquatic environment and their possible effects on living organisms are giving rise to growing concern [4]. In fact, more than 50 pharmaceutical compounds have been detected during the last years in different aquatic environmental samples, due to the continuous improvement of the analytical techniques [5–9]. Many of these samples have been collected from wastewater [5,6], and also from surface or ground waters [7]. These compounds originated either from domestic sewage or from hospital or industrial discharges and enter municipal sewage treatment plants.

Previous studies [10,11] show that the common conventional methods of treatment (i.e., biological, physical, and chemical methods) were applied for the treatment of the effluents. Limited success has been achieved because these processes are less effective, or even ineffective against the very stable refractory and toxic compounds [10,11]. Another main draw back of these processes is that they are associated with the generation of large amount of sludge, which requires thermal destruction before final disposal.

Recently, much attention has been paid to separate the source of the refractory or toxic effluent and treat it by advanced oxidation processes (AOPs) using homogeneous or heterogeneous catalysts [11–13]. Fenton system Fe^{n+}/H_2O_2 is one of the most interesting promising oxidative techniques for the abatement of refractory and/or toxic organic pollutants in water and wastewater [14–16]. The high removal efficiencies of this technique can be explained by the formation of strong hydroxyl radical ($HO^{\bullet}$) and oxidation of Fe^{2+} to Fe^{3+}. Both Fe^{2+} and Fe^{3+} ions are coagulants, so the Fenton process can, therefore, have dual function, oxidation and coagulation in the treatment processes. Moreover, iron is a highly abundant, non-toxic element. In addition hydrogen peroxide is easy to handle environmentally. Therefore, the aim of the present study is to investigate the efficiency of the proposed treatment processes for the removal of the refractory organic compounds from pharmaceutical industrial wastewater before being discharged into sewerage system.

2. Materials and methods

2.1. Chemicals and standards

Chloramphenicol, diclofenac, salicylic acid, and paracetamol that obtained from El-Nasr Company in a pure form are widely produced as pharmaceutical agents (Fig. 1). However, nitrobenzene,

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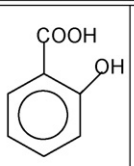
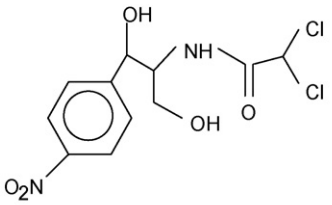
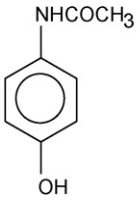
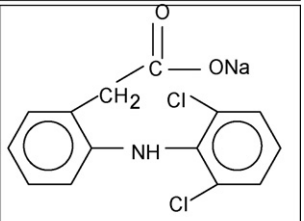
Salicylic acid	Chloramphenicol	Paracetamol	Diclofenac sodium
			
$C_7H_6O_3$	$C_{11}H_{12}O_5N_2Cl_2$	$C_8H_9O_2N$	$C_{14}H_{10}O_2NCl_2Na$

Fig. 1. Chemical formula of some pharmaceutical compounds.

benzoic acid, and phenolic compounds were supplied by Supellco company 99.5% purity. These compounds were represented as by-products of the studied pharmaceuticals. All of these compounds were not subjected to any further purification. C18-Strata cartridge and DPA-6S cartridge (Supelco Co.) were used in solid-phase extraction (SPE) processes. Ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) (from Merck Company) was used as a source of Fe^{2+} catalyst in Fenton process sulfuric acid and sodium hydroxide were purchased from Merck Company. Hydrogen peroxide solution (35%, w/w) in stable form was provided by Flucka Company.

2.2. Wastewater sampling and preparation

During the study, a continuous monitoring program was carried out for almost 1 year. Six composite samples from end of pipe were collected over the working hours. The company discharges both industrial (6000 m^3/d) and municipal wastewater (128 m^3/d) into a nearby evaporation pond without treatment.

All physicochemical parameters were analysed according to APHA [17]. The total organic carbon (TOC) was determined using PHOENIX TOC. Persulfate ultraviolet method was used for determination the levels of TOC according to APHA [17]. The minimum detectable concentration of this method was 0.01 mg/L.

Solid-phase extraction was used for separation of the pharmaceuticals from the wastewater. The extraction volume was 300 mL. The samples were filtered through a 0.45-μm pore size Whatman filter paper. The filters were pre-washed with n-hexane, acetone, methanol and MilliQ water. The pH of the samples were adjusted to 2.0 with 50% H_2SO_4 and 500 ng of fenoprop was added as a surrogate standard. DPA-6S cartridge (from Supelco Company) was used as the solid phase adsorbent. The adsorbent was pre-conditioned with 2 mL of n-hexane, 2 mL of acetone, 10 mL of methanol and 10 mL of double distilled water (pH adjusted to 2.0). The samples were introduced to the cartridges by means of PTFE tubes at a flow rate of approximately 8 mL/min. After being dried in a stream of nitrogen for 1 h, the pharmaceuticals were eluted from the adsorbent with 4 mL of acetone. The extracts were then evaporated to approximately 100 μL with a gentle nitrogen stream and 1 mL of methanol was added. Evaporation continued until the volume of the extracts was 50 μL. Finally, 450 μL of ammonium hydroxide

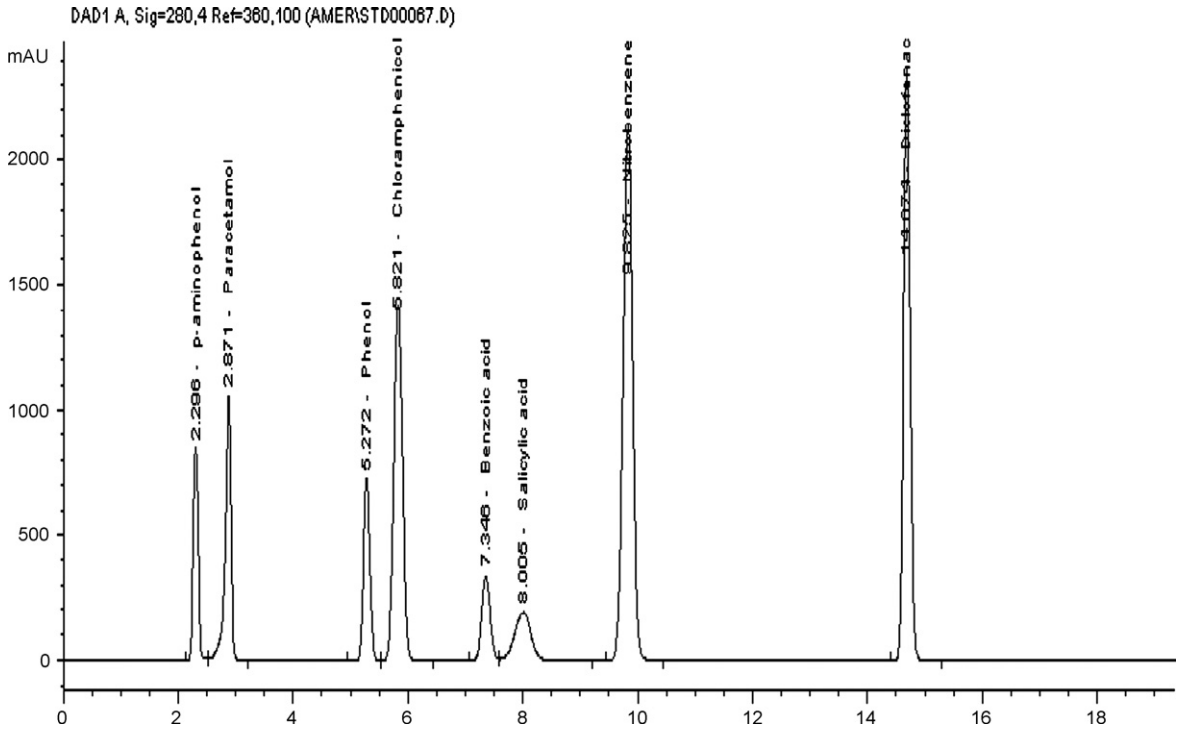


Fig. 2. HPLC Chromatogram for some pharmaceuticals and their by-products.

Table 1
Physicochemical characteristics of the raw and treated wastewater using the activated sludge treatment process at optimum operating conditions of mg/L.

Parameter	Raw wastewater			Treated wastewater biologically		
	Max[a]	Min[b]	[c]Mean ± S.D.[d]	Max	Min	Mean ± S.D.
pH	12	3.3	8.4 ± 4.5	8.6	7.9	8.2 ± 0.4
TRS	37,604	1749	17,385 ± 18,361	33,544	4.6	13,966 ± 17,460
TSS	330	20	133.3 ± 171	236	0.26	92.09 ± 126.2
TDS	37,554	1729	17,251 ± 18,384	33,504	4.3	13,874 ± 17,477
COD	13,023	4100	9,703 ± 4,880	4625	1390	3,046.8 ± 1,619
BOD	3900	1050	2,650 ± 1,457	1526	460	989 ± 533
BOD:COD	0.3	0.25	0.27 ± 0.03	0.33	0.31	0.32 ± 0.01
TOC	4679.4	1868.2	3,321.5 ± 1,408.0	2025	808.4	1217.8 ± 699.1
Oil and grease	600	17.4	214.9 ± 333.5	180	9.2	69.2 ± 96.1
Phenols	69	21.2	43.4 ± 24.1	49	4.8	33.9 ± 25.2
TKN	1156.4	546	763.5 ± 340.9	570	220	344.5 ± 195.6
Nitrate	1.41	0.7	0.94 ± 0.41	0.85	0.32	0.61 ± 0.27
Nitrite	3.93	<0.2	1.58 ± 2.07	0.32	<0.2	0.13 ± 0.17
Ammonia	585	<0.02	295.8 ± 292.6	180.7	12.9	90.7 ± 84.6
Total alkalinity	640	415	518.3 ± 113.6	550	320	435 ± 162
Total phosphorus	14.2	4.4	8.3 ± 5.2	38.4	5	18.6 ± 17.6
Sulphide	120	8.69	53. ± 59	51	8.5	29.5 ± 21.2
Sulfate	788	94	376.8 ± 364.4	350	78	203.1 ± 137.3

TRS, total residual solids; TSS, total suspended solids; TDS, total dissolved solids.
[a] Maximum.
[b] Minimum.
[c] Mean of 6 samples.
[d] Standard deviation.

(0.1 mol/L) was added and the extracts were stored at −18 °C until analysis [18].

2.3. Sludge samples preparation

The sludge samples were air dried and sieved to <0.4 mm. Approximately 5 g sludge samples were accurately weighed (500 ng of fenoprop was added as a surrogate standard), and then placed into 50-mL polypropylene centrifuge tubes. About 10 mL of extraction buffer was added. The extraction buffer consisted of a 2:1:1 mixture of methanol, 0.1 M citric acid buffer with pH adjusted to 4.0 by NaOH and 10 mM Na_2EDTA buffer with pH adjusted to 4.0 using 50%H_2SO_4. The tubes were vortex mixed for 1 min and then placed into an ultrasonic bath for 15 min (water temperature 40 °C), and then the tubes were centrifuged for 10 min at 3000 rpm. The supernatant was decanted into a 500 mL glass bottle, and the sediment residue was extracted once more. The supernatant was combined, diluted to approximately 500 mL with ultra-pure water, and then the pH adjusted to approximately 3.0 using 50% H_2SO_4.

DPA-6S cartridges were used for separation and clean up of the pharmaceuticals from the supernatant. Each cartridge was pre-conditioned sequentially with 6.0 mL of methanol, 6.0 mL of ultra-pure water and 6.0 mL of 10 mM Na_2EDTA buffer at pH 3.0. The samples were passed through the SPE columns at a flow rate of approximately 10 mL/min. The cartridges were washed with ultra-pure water (10 mL, pH 3.0) before being dried with a flow of nitrogen gas for 1 h. After that, each cartridge was eluted with three 2-mL of methanol. The analytes were concentrated under a flow of N_2 gas to about 20 μL and then dissolved in 40% aqueous methanol to a final volume of 1.0 mL.

2.4. Fenton-coagulation process

Fenton process was carried out at room temperature by adding various doses of $FeSO_4{\cdot}7H_2O$. The pH was adjusted at 3.0 ± 0.2 using 1N H_2SO_4 and kept at the same value during the reaction. The required amount of H_2O_2 was fed by a dosing pump during a period of 15 min, and then the coagulation experiments were conducted with the jar test method. This method was preceded with rapid mixing of the Fenton treated effluent at 100 rpm for 5 min, slow mixing at 40 rpm for 30 min, and then standstill for 30 min. After 30 min settling time, the supernatant was withdrawn, filtered through 0.45 μm, treated with enzyme Catalase to remove residual H_2O_2. Hydrogen peroxide residue was determined by the colorimetric method by adding 3.0 mL of 0.25 mol/L hydroquinone, 2.0 mL of 0.125 mol/L anilinium sulphate, 0.1 mL of 0.5% ammonium molybdate to 25 mL of sample. The solution was mixed and allowed to stand for 10 min. The solution was measured at 550 nm against

Table 2
HPLC analysis of the raw and treated wastewater using the activated sludge treatment process at optimum operating conditions of mg/L.

Compound	Raw wastewater			Treated wastewater biologically		
	Max[a]	Min[b]	[c]Mean ± S.D.[d]	Max	Min	Mean ± S.D.
p-Aminophenol	142.94	0.14	62.94 ± 72.94	56	2.61	25.10 ± 27.67
Paracetamol	154.11	5.61	69.68 ± 76.32	41.94	2.17	19.45 ± 20.39
Phenol	295.49	0.51	130.18 ± 150.69	45.27	2.09	19.66 ± 22.69
Chloramphenicol	87.96	0.41	38.84 ± 44.74	32.37	10.11	21.24 ± 15.74
Diclofenac	12.37	0.48	5.60 ± 6.11	8.98	0.05	3.71 ± 4.68
Benzoic acid	152.44	2.51	67.91 ± 76.78	105.22	0.77	46.09 ± 53.58
Salicylic acid	714.41	1.03	314.68 ± 364.39	181.64	0.89	76.15 ± 94.09
Nitrobenzene	74.64	0.05	32.84 ± 38.12	46.65	0.09	20.25 ± 23.9

[a] Maximum.
[b] Minimum.
[c] Mean of 6 samples.
[d] Standard deviation.

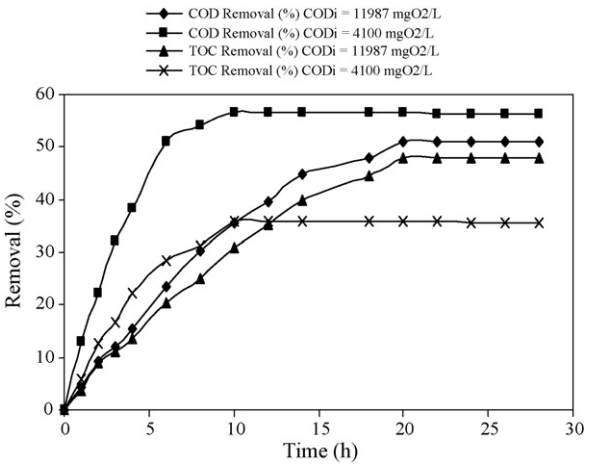


Fig. 3. Effect of detention time on the biological treatment for raw wastewater using activated sludge process.

a reagent blank in a 10 mm cell [19]. Physicochemical characteristics of the treated wastewater were analysed according to APHA [17]. The pH values for oxidation and coagulation experiments were controlled at 3.0 ± 0.2 and 8.5 ± 0.2, respectively, with 0.1N sulfuric acid or sodium hydroxide.

2.5. Biological process

Raw and pretreated wastewaters with Fenton were subjected to the biological treatment. Two-liter plexiglass laboratory columns were used. Air was fed continuously at a rate of 120 mL/min to ensure an excess of dissolved oxygen. Biomass was taken from an activated sludge process of a municipal wastewater treatment plant. Collected activated sludge was acclimated for both raw wastewater conditions and Fenton treated effluent. Sludge acclimatization was carried out for 4 weeks. Air supply was adjusted to maintain a minimum concentration of 2.0 mg O_2/L using an O_2 probe located at the top of the reactor. The pH was maintained in the range of 7.0–8.0 ± 0.2. Nutrient levels were maintained in the ratio of COD:N:P at 100:5:1, respectively. Air supply to the columns was turned off once a day and the sludge was allowed to settle for 60 min, then the supernatant was drained. The columns were refilled with various ratios of wastewater. Nutrients was added to the raw wastewater and Fenton treated effluent to keep the ratio (100:5:1) for COD:N:P, respectively. After 4 weeks acclimation period, a considerable amount of sludge was produced. COD, TOC, pH, mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were measured daily to understand the activity of the reactor.

In order to study the effect of aeration time and the sludge loads on the treatment process, an appropriate volume of mixed liquor suspended solids was transferred to different columns followed by the addition of wastewater. Air supply was adjusted to maintain a minimum dissolved oxygen concentration of 2.0 mg/L. The system was allowed to operate 24 h and the experiment was carried out using MLSS of 3–4 g/L. Samples were withdrawn at regular intervals to follow COD and TOC. Sludge volume and sludge index, MLSS and MLVSS were also determined.

Table 3
Effect of BOD/COD ratio on the efficiency of the activated sludge treatment process at optimum operating conditions.

COD (mg/L)	BOD (mg/L)	BOD:COD ratio	%COD removal
11,987	3000	0.25	61
4,100	1050	0.26	66
1,292	381	0.29	63
13,023	3900	0.30	76
3,987	1560	0.39	76
525	268	0.50	92

Table 4
HPLC analysis of the sludge (mg/kg) produced from the biological treatment processes.

Compound	Synthetic mixture	Real wastewater	Pre-treated with Fenton
p-Aminophenol	2225	12,360	25
Paracetamol	2875	14,580	16
Phenol	2475	8,500	22
Chloramphenicol	5075	9,620	<0.02
Benzoic acid	1825	12,450	36
Salicylic acid	3475	18,320	43
Nitrobenzene	1300	23,600	13
Diclofenac	2600	1,560	2

2.6. Analytical measurements

HPLC was used (Model Agilent 1100 Series), equipped with microvacuum degasser, quaternary pump, diode array detector (DAD), and Zorbax SB-C18 analytical column (4.6 mm × 250 mm, 5 μm). A mixture of methanol, water, and 25% acetic acid was used as a mobile phase at a flow rate 1 mL/min. The column temperature was kept at 30 °C. The column was eluted with the following gradient elution for 7 min with 50% methanol and 50% H_2O + 25% acetic acid and then with 80% methanol to 20% H_2O + 25% acetic acid over the course of 20 min. Then the percentage of methanol was raised to 100% in, held at this percentage for 15 min. Before the next injection, the column was allowed to equilibrate for 8 min [20]. Fig. 2 shows HPLC chromatograms of studied compounds.

3. Results and discussion

3.1. Wastewater characterization

Physico-chemical characteristics showed that the wastewaters generated from pharmaceutical company contain high loads of organic pollutants represented by COD, BOD_5 values, suspended solids, oil and grease, phenol, sulfate, sulphide, total Kjeldahl nitrogen (TKN), ammonia (NH_3), total phosphorus (TP). The BOD_5/COD ratio ranged from 0.25 to 0.30 with an average of 0.27 (Table 1). This confirms that these types of wastewaters are hardly biodegradable. In addition, HPLC analyses confirmed that the raw wastewater samples contained some refractory organic compounds. Diclofenac, chloramphenicol, paracetamol drugs and their by-products p-aminophenol, phenol, benzoic acid, nitrobenzene and salicylic acid were detected in all wastewater samples and their mean concentrations are 5.60, 38.84, 69.68, 62.94, 130.18, 2.51, 32.84 and 1.03 mg/L, respectively (Table 2). Phenylacetic acid, by-products of diclofenac, was not detected in any wastewater samples. It is worth mentioning that the majority of current wastewater treatment plants (WWTPs) were not designed to deal with this type of compounds, consequently they can enter into sewage effluent and this become a potential risk in production of drinking water [21–23]. Previous studies revealed that wastewaters produced from pharmaceutical industries pose several problems for successful biological treatment. These wastewaters contain relatively high levels of suspended solids and soluble organics, while there are many of which are recalcitrant [21–23].

Table 5
Physicochemical characteristics of pre-treated wastewater of initial COD 11,987 mg O_2/L by Fenton process followed by biological treatment.

Parameter	Units	Fenton treatment			Biological treatment		Total % removal
		Raw	Treated	% Removal	Treated	% Removal	
pH	–	12	8	–	7.9	1.25	–
TRS	mg/L	37,604	36,003	4.26	33,200	7.79	11.71
TSS	mg/L	50	35	30.00	11	68.57	78.00
TDS	mg/L	37,554	36,038	4.04	33,189	7.91	11.62
COD	mg O_2/L	11,987	3987.5	66.73	950	76.18	92.07
BOD	mg/L	3000	1560	48.00	550.8	64.69	81.64
BOD:COD	–	0.25	0.39	–	0.57	–	–
TOC	mg/L	4679.4	2007.9	57.09	423.6	78.90	90.95
Oil and grease	mg/L	27.3	12	56.04	2.3	80.83	91.58
Phenols	mg/L	69	12.5	81.88	0.035	99.72	99.95
TKN	mg/L	1156.4	466	59.70	75.8	83.73	93.45
Nitrate	mg/L	1.41	0.82	41.84	<0.1	99.39	99.65
Nitrite	mg/L	0.787	<0.2	98.73	<0.2	100.00	100.00
Ammonia	mg/L	585	106.4	81.81	4.2	96.05	99.28
Total alkalinity	mg/L	640	531	17.03	215	59.51	66.41
Total phosphorus	mg/L	4.4	<0.5	100.00	7.8[a]	NA	–
Sulphide	mg/L	120	33.6	72.00	8.5	74.70	92.92
Sulfate	mg/L	788	341.2	56.70	70.3	79.40	91.08

Reaction time = 1.5 h; COD/H_2O_2 = 1:2.2; pH 3; Fe^{2+}/H_2O_2 = 1:50; detention time = 12 h in biological treatment. NA = not analysed.
[a] Due to addition of phosphorus salt as a nutrient to the Fenton treated effluent.

3.2. Biological treatment (activated sludge)

Aeration period during 24 h was examined. The sludge weight was ranged from 3 to 4 g/L. Sludge analysis and percentage of COD degradation were carried out on all effluents after half-an-hour of settling. Fig. 3 shows the effect of aeration period on the biological treatment of raw pharmaceutical wastewater of high initial COD 11,987 mg O_2/L the optimum detention time was 20 h, while it decreases to 10 h in case of raw wastewater of initial COD 4100 mg O_2/L. The percentage of the removal of COD and TOC by the biological treatment depends mainly on the characterization of the wastewater, especially on the presence of non-biodegradable substances and COD/BOD ratio. The percentage of COD removal was 51% and 56% while the percentage of TOC removal was 48% and 36% of wastewater of initial COD 11,987 and 4100 mg O_2/L, respectively (Fig. 3). These poor results of removal of COD and TOC are attributed to the presence of refractory organic compounds which are hardly biodegradable. These refractory compounds cannot be readily removed and always remain in the effluent of biological treatment process (Table 2). A high removal efficiency of 76% was obtained for initial COD of 13,023 mg/L O_2. The high efficiency of the removal related to the increase of BOD/COD ratio (Table 3).

Recent data confirmed that the conventional aerobic operations of sewage treatment plants resulted in the incomplete removal of pharmaceuticals, hence as much as 80% of the total load of pharmaceuticals entering sewage treatment plant discharged into surface water [18]. On the other hand, biodegradation, at best, loads only to a partial removal of some pharmaceutical residues.

The analysis of sludge produced during the activated sludge process showed that portion of the pharmaceutical compounds and their by-products adsorbed on the sludge flocs and caused secondary pollution problems for sludge disposal and reuse (Table 4). Therefore, the biologically treated pharmaceutical wastewaters do not comply with the Egyptian environmental law 93/1962 and its Decree No. 44/2000. The law effectively requires pre-treatment of industrial wastewater prior to its discharge into public sewers. Therefore, an effective waste minimization program includes pollution prevention control and pre-treatment has to be conducted to reduce the amount of hazardous wastewater generated from the company.

Table 6
Physicochemical characteristics of pre-treated wastewater of initial COD 4100 mg O_2/L by Fenton process followed by biological treatment.

Parameter	Units	Fenton treatment			Biological treatment		Total % removal
		Raw	Treated	% Removal	Treated	% Removal	
pH	–	9.8	8.0	–	8	–	–
TRS	mg/L	12,802	2430	81.0	1161	52	91.0
TSS	mg/L	330	85	74.0	11	87	96.6
TDS	mg/L	12,472	2445	80.0	1150	53	90.7
COD	mg O_2/L	4100	525	87.0	38	93	99
BOD	mg/L	1050	268	74.0	16	94	98
BOD:COD	–	0.26	0.5	–	0.85	–	–
TOC	mg/L	1868.2	122.0	93.0	7.0	94	99
Oil and grease	mg/L	17.4	3.8	78.0	0.5	87	97
Phenols	mg/L	21.2	1.2	94.0	<0.01	0.0	100
TKN	mg/L	546	129	76.0	13	90	97
Nitrate	mg/L	0.7	0.15	78.6	<0.1	-	100
Nitrite	mg/L	3.93	<0.2	100.0	<0.2	-	100
Ammonia	mg/L	302.4	44	85.4	9.6	78	97
Total alkalinity	mg/L	415	190	54.2	99	48	76
Total phosphorus	mg/L	14.2	2.2	84.5	0.6	73	95
Sulphide	mg/L	30.4	9.5	68.7	1.2	87	96
Sulfate	mg/L	248.4	98.6	60.3	20	80	92

Reaction time = 1.5 h; COD/H_2O_2 = 1:2.2; pH 3; Fe^{2+}/H_2O_2 = 1:50; detention time = 10 h in biological treatment.

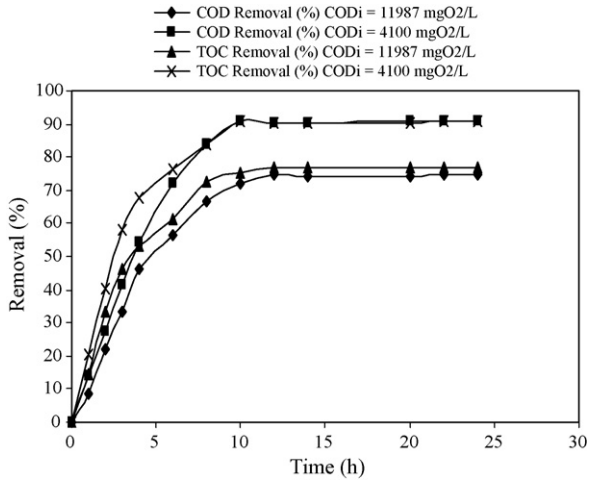


Fig. 4. Effect of detention time on the biological treatment for raw wastewater pre-treated by Fenton process at optimum conditions using activated sludge process.

Due to the inability of activated sludge treatment method to remove the refractory organic compounds from pharmaceutical wastewaters, a number of researches attempted to explore the combination of two or more technologies to achieve the required degree of treatment. One of these methods is advanced oxidation processes followed by biological processes, which, have been proposed as an attractive alternative for the treatment of the wastewater contains toxic or non-degradable pollutants [10,24,25].

3.3. Integrated removal of refractory pharmaceuticals (Fenton's methods followed by activated sludge)

The Fenton reaction (Fe^{2+}/H_2O_2), and Fenton-like reactions (Fe^{3+}/H_2O_2), have been widely applied in the treatment of non-biodegradable wastewater in the field of advanced oxidation processes. The formation of $OH^{\bullet}$ radical depends on several factors such as pH value, dose of Fe^{2+}, initial concentration of H_2O_2 and the ratio between organic loads and H_2O_2 [14,15].

The efficiency of Fenton process as a pre-treatment step of wastewater was investigated. The effects of pH and dose of hydrogen peroxide were studied. The maximum TOC degradation of 61.8% and COD degradation of 63.8 for real wastewater were obtained within1.5 h at a pH 3. Previous study carried out by Kuo and Lo [26] revealed that more $Fe(OH)^{+}$ is formed at pH in the range from 2 to 4. The activity of $Fe(OH)^{+}$ in Fenton and photo Fenton reaction and the decomposition of H_2O_2 in acidic medium was very fast in producing HO radicals.

The amount of H_2O_2 is considered one of the most important factors which should be considered in the Fenton oxidation. The effect of hydrogen peroxide dose on the efficiency of the oxidation process was investigated under the operating conditions (reaction time = 1.5 h, pH 3, Fe^{2+}/H_2O_2 = 1:100 and the concentration ratio of COD/H_2O_2 varied from 1:1.1 to 1:4.4). It was found that TOC and COD removal efficiency increases with increasing peroxide dose. Maximum removal efficiency was attained at COD/H_2O_2 ratio of 1:2.2.

To obtain the optimal (Fe^{2+}) dose, investigations were carried out by using different Fe^{2+}/H_2O_2 molar ratios equivalent to 1:10, 1:25, 1:50 and 1:100. The results showed that the maximum degradation of TOC and COD was found at Fe^{2+}/H_2O_2 molar ratio of 1:50. Further increase of Fe^{2+}/H_2O_2 molar ratio actually decreases the extent of degradation of wastewater. The higher addition of iron salt by using Fenton treatment caused the recombination of OH radicals with Fe^{2+}.

The Fenton treatment of wastewater collected from the end of pipe of the company was carried out at the treatment operating conditions (reaction time 1.5 h, COD/H_2O_2 1:2.2, pH 3 and Fe^{2+}/H_2O_2 1:50). Under these conditions, the degradation of COD ranged from 67% to 87%. The results presented in Tables 5 and 6 showed that the quality of treated effluent is quite satisfactory and the treated effluent complied with the Egyptian law for discharge of industrial wastewater into public sewerage system.

A significant reduction in post-treatment detention time was achieved. Moreover, the COD and TOC removal was observed when it compared with that for raw wastewater (Fig. 4). Moreover, the activated sludge was of good quality as indicated by the sludge volume index (SVI) which ranged from 66 to 99 and from 65 to 105 for initial COD of 11,987 and 4100 mg O_2/L, respectively [27]. Microscopical examination of the sludge revealed the presence of a great variety of number of bacteria either aggregated in the sludge flocs or freely dispersed in the liquor. Moreover, the sludge contains many colonies of protozoa, especially stalked ciliates such as *opercularia*, *paramecium*, and *rotifers* such as *trachelophyllum*.

The results stated in (Tables 5 and 6) confirmed that the Fenton oxidation is one of the most effective in treatment this type of wastewater. It can also be considered as a viable pre-treatment solution for the destruction of hardly biodegradable compounds which inhibit the post-treatment biological process.

Fenton as a pre-treatment process would increase the biodegradability and/or remove the toxicity of the wastewater by the converting the persistence compounds in the wastewater into easily biodegradable matters. This allows the subsequent biological degradation to be achieved in a short detention time. Complete removal of chloramphenicol, diclofenac, p-aminophenol, benzoic acid, nitrobenzene and salicylic acid in the final effluent results from the coupling of Fenton and biological activated sludge processes (Tables 7 and 8). Martinez et al. [16] who studied the pre-oxidation of an extremely polluted pharmaceutical wastewater (chemical oxygen demand value of 36,200 mg/L) using Fenton's reagent. The parameters influencing the COD removal of the wastewater, namely temperature, ferrous ion, and hydrogen peroxide concentrations, were optimized to achieve a COD global reduction of 56.4%. Fenton's reaction proved to be a feasible technique for the pre-oxidation

Table 7
HPLC analysis for pre-treated wastewater of initial COD 11,987 mg O_2/L by Fenton process followed by biological treatment.

Compound	Fenton treatment			Biological Treatment		Total % removal
	Raw (mg/L)	Treated (mg/L)	% Removal	Treated (mg/L)	% Removal	
p-Aminophenol	142.94	9.38	93.4	<0.02	100.0	100.0
Paracetamol	154.11	3.85	97.5	0.23	93.9	99.8
Phenol	295.49	5.33	98.2	0.80	84.9	99.7
Chloramphenicol	87.96	<0.02	100.0	<0.02	-	100.0
Benzoic acid	152.44	3.01	98.0	<0.01	100.0	100.0
Salicylic acid	714.41	2.94	99.6	0.09	97.1	100.0
Nitrobenzene	74.64	0.20	99.7	<0.01	100.0	100.0
Diclofenac	12.37	0.05	99.6	<0.05	100.0	100.0

Reaction time = 1.5 h; COD/H_2O_2 = 1:2.2; pH 3; Fe^{2+}/H_2O_2 = 1:50; detention time = 12 h in biological treatment.

Table 8
HPLC analysis for pre-treated wastewater of initial COD 4100 mg O_2/L by Fenton process followed by biological treatment.

Compound	Fenton treatment			Biological treatment		Total % removal
	Influent	Effluent	% Removal	Effluent	% Removal	
p-Aminophenol	45.74	2.84	93.8	<0.02	100.00	100.00
Paracetamol	49.32	1.02	97.9	0.08	92.46	99.84
Phenol	94.56	1.73	98.2	0.10	94.06	99.89
Chloramphenicol	28.15	<0.01	100.0	<0.01	<0.01	100.00
Benzoic acid	48.78	1.02	97.9	<0.01	100.00	100.00
Salicylic acid	228.61	1.01	99.6	0.02	98.02	99.99
Nitrobenzene	23.89	0.02	99.9	<0.01	100.00	100.00
Diclofenac	3.96	<0.01	100.0	<0.01	<0.01	100.00

Reaction time = 1.5 h; COD/H_2O_2 = 1:2.2; pH 3; Fe^{2+}/H_2O_2 = 1:50; detention time = 10 h in biological treatment.

of the wastewater under study, and can be considered a suitable pre-treatment for this type of wastewaters.

Duran et al. [28] mentioned that Fenton's reagent has two important advantages compared to the coagulation–flocculation processes namely a disinfecting action, since the fecal coliforms and *Salmonella* sp. Contents were completely eliminated in treated wastewater, and the sludge production was 10% lower than the one found for coagulation–flocculation process. Ramirez-Zamora et al. [29] studied the characteristics of the coagulation and Fenton's reagent sludge yielded by the treatment of a municipal wastewater. They found that the Fenton sludge presented preferable characteristics such as the specific resistance to filtration (SRF), metals and pathogen content.

To describe the organic removal performance in an activated sludge process, the effect of biological adsorption (biosorption) of organic pollutants in the wastewater by the activated sludge must be taken into account [30]. Sludge analysis using HPLC is summarized in Table 3. The obtained results showed that portion of the model compounds and their by-products transferred from liquid phase to solid phase and thus cause secondary pollution problems. The amount of adsorbed compounds on the sludge decreased in case of pretreated wastewater by Fenton process.

4. Conclusion

Information gathered from the present study indicates that wastewaters generated from pharmaceutical company contain high loads of organic pollutants represented by COD, BOD_5 values, suspended solids, oil and grease, phenol, sulfate, sulphide, total Kjeldahl nitrogen, ammonia (NH_3), total phosphorus and high concentration of refractory and priority compounds such as diclofenac, chloramphenicol, paracetamol drugs and their by-products p-aminophenol, phenol, benzoic acid, nitrobenzene and salicylic acid were detected in all wastewater samples and their mean concentrations are 5.60, 38.84, 69.68, 62.94, 130.18, 2.51, 32.84 and 1.029 mg/L, respectively. Generally, the final wastewater from the company is not complying with the National Environmental Laws and its regulations. The biologically treated wastewaters do not comply with the Egyptian environmental law 93/1962 and Decree No. 44/2000. Fenton as a pre-treatment process would increase the biodegradability and/or remove the toxicity of the wastewater, which represent physicochemical characteristics of the raw wastewater and their treated effluents by means of Fenton process followed by biological activated sludge.

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