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Original Research

Combined Methods of Highly Polluted Pharmaceutical Wastewater Treatment – a Case Study of High Recovery

Davor Dolar[1]*, Krešimir Košutić[1], Tatjana Ignjatić Zokić[2], Laszlo Sipos[2], Marinko Markić[2], Mario Župan[2]

[1]Department of Physical Chemistry,
[2]Department of General and Inorganic Chemistry,
Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, HR-10000 Zagreb, Croatia

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Abstract

Our study details the investigation of real pharmaceutical wastewater (PhWW) treatment. A combination of the Fenton process, sand filtration, ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) was tested. The sample of PhWW was highly polluted, containing high chemical oxygen demand (COD, 25,000 $mg \cdot L^{-1}$), total organic carbon (TOC, 4,940 $mg \cdot L^{-1}$), conductivity (κ, 40,000 $mg \cdot L^{-1}$), and total N (4,054 $mg \cdot L^{-1}$) values. The pretreatment (Fenton, sand filter, UF) decreased the above parameters for 62%, 56%, 10%, and 88%, respectively. An additional membrane treatment was required since the values obtained in the pretreatment were above maximum contaminant levels (MCL_S). The next membrane step with the loose NF membrane (HL) COD, TOC, conductivity, and total N additionally decreased for 87%, 71%, 24%, and 32%, respectively. Tight NF (NF90, NF270) and RO (XLE) membranes were used in the final step and, according to the obtained parameters, membrane permeate streams could be discharged into the sewer without any risk to the ecosystem. Finally, and the most importantly, the combined methods of the pharmaceutical wastewater treatment resulted in high recovery of more than 90%.

Keywords: highly polluted pharmaceutical wastewater, Fenton process, membrane processes, recovery

Introduction

The generation of wastewaters in industrial processes is unavoidable, and in most cases a process of reducing the organic load and other contaminants must be employed before water discharge. Domestic sewage is the largest source of water pollution, followed by industrial effluents and agricultural activities [1, 2]. Industrial waste, in particular when it contains harmful chemicals, heavy metals, and other toxic substances, can have far more serious consequences than domestic waste. These hazardous substances pollute surface water, soil, and groundwater and become concentrated in the food chain, and therefore need special treatment before being discharged.

The wastewater generated by industrial activities (chemical, cosmetic, pulp and paper, pharmaceutical industries, etc.) is one of the most complex wastewaters. This complexity, strongly related with the difficulty in establishing simple and, at the same time, effective treatment and disposal method for such a wastewater stream, may be illustrated in terms of many specific characteristics:

(1) a strong organic carbon content often associated with a chemical oxygen demand (COD) level in excess of 10,000 $mg \cdot L^{-1}$ [3-6]

*e-mail: dolar@fkit.hr

Table 1. Wastewater analysis during the first two steps of treatment.

	PhWW	Effluent 1		Effluent 2	
	Conc.	Conc.	*R*(step 1)/%	Conc.	*R*(step 2)/%
COD (mg $O_2 \cdot L^{-1}$)	25,000	9,400	62.4	1,238	86.6
Conductivity ($\mu S \cdot cm^{-1}$)	40,000	35,700	10.7	27,200	23.8
TOC (mg $C \cdot L^{-1}$)	4,940	2.150	56.5	615.2	71.4
pH	6.00	8.24	-	7.60	-
NH_3 (mg $N \cdot L^{-1}$)	170	457	-	370	19.0
Alkalinity (mg$\cdot L^{-1}$ $CaCO_3$)	1,780	1,460	18.0	683.7	53.1
Cl^- (mg$\cdot L^{-1}$)	7,300	8,640	-	6,521	24.5
SO_4^{2-} (mg$\cdot L^{-1}$)	520.0	340.0	34.6	22.24	93.5
Total N (mg$\cdot L^{-1}$)	4,054	498	87.7	340	31.7
Total P (mg$\cdot L^{-1}$)	6.96	0.53		0.32	39.6

(2) an organic carbon content that inherently involves a great variety of complex organic pollutants with a total organic carbon (TOC) level of a few thousands [7, 8].

The treatment of various industrial wastewaters has always been considered as a challenging issue for scientists [4, 9]. In the recent past, different treatment schemes such as coagulation [2, 8], ozone and activated carbon [4, 10], ion exchange [11], Fenton [10-12], membrane bioreactors [6, 13], nanofiltration (NF), and reverse osmosis (RO) [14-16] have been tested and suggested. However, results also identified significant drawbacks and indicated that no single technology could be applied to the industrial wastewater as a stand-alone treatment option.

Industrial production can also be considered a source of significant amounts of reusable effluents. Thus, industry should be encouraged to invest in improved water management, more recycling, and more efficient treatments. It is also important to raise awareness in government and various industries in the world to invest in wastewater treatment and recycling in order to preserve the natural water resources.

This experimental study was performed to evaluate the efficacy of the combination technique for the treatment of pharmaceutical wastewater (PhWW) effluent obtained from a local site. Since the majority of the reported literature deals with simulated effluents, the current investigation emphasizes the treatment of real industrial wastewater. Due to the complexity of the highly polluted pharmaceutical wastewater, various techniques in this work were used for its treatment. The pretreatment was done by the advanced oxidation process (Fenton), sand filtration, and ultrafiltration (UF). After that, effluent was treated by NF and RO.

Materials and Methods

Characterization of Highly Polluted Raw Pharmaceutical Wastewater

A fresh sample of wastewater was obtained from pharmaceutical industry and no pretreatment (decantation, filtration, etc.) was done. The major physico-chemical properties are given in Table 1, column 2, including COD, conductivity (κ), TOC, pH, etc., where COD indicates the concentration of all organic compounds that can be fully oxidized using strong oxidizing agents, whereas TOC usually indicates the amount of all the organics present in the system. The PhWW (200 L) was stored in a plastic carboy and used within 1 h in the treatment experiments.

The wastewater treatment process consisted of several steps (Fig. 1), the first involving Fenton's oxidation treatment with sand filtration and UF of the PhWW to reduce COD and TOC, among others. The second stage consisted of a loose NF membrane and the third stage involved tight NF and RO membranes to eliminate the salts contained in the loose nanofiltration permeate.

Fenton's Oxidation Experiments

The first step of the treatment was Fenton's advanced oxidation experiment (Fig. 1, part A). The advanced oxidation processes (AOP) proved to be highly effective for the removal of most of the pollutants in wastewaters [17]. Also, Photo-Fenton reaction is well-known in the literature as an efficient method for wastewater and soil treatment [18]. Furthermore, the Fenton system Fe^{n+}/H_2O_2 is one of the most promising oxidative techniques for the abatement of refractory and/or toxic organic pollutants in water and wastewater [12, 19]. 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. Therefore, the Fenton process can have dual function in the treatment processes, namely oxidation and coagulation. Moreover, iron is an abundant, non-toxic element and can be easily removed, while hydrogen peroxide is easy to handle environmentally.

The parameters affecting the Fenton process include dosages of $FeSO_4$ and H_2O_2 and operating pH. The optimum pH has been found to be around 3 in the majority of

cases [11, 20] and hence is recommended as the operating pH. On the other hand, adjusting the original pH of the used PhWW (6.0, Table 1) to the optimal range (around 3) would consume a considerable amount of acid, increasing the treatment cost. Therefore, the parameter choice should be a tradeoff between reaction efficiency and treatment cost. Due to economic reasons, a reduction of COD by 50% was chosen as the optimal condition. The optimal concentration of H_2O_2 and Fe^{2+} was determined by the JAR test. The PhWW (1 L) was treated with different concentrations of H_2O_2 (10-150 g·L^{-1}) and Fe^{2+} (0.1-110 g·L^{-1}) and various combinations of these concentrations. The optimal dosage of H_2O_2 and Fe^{2+} was found to be 32 and 0.6 g·L^{-1}, respectively.

Fenton's oxidation of PhWW was carried out in a reactor as follows: firstly, Fe^{2+} catalyst was added to PhWW from a freshly prepared $FeSO_4 \cdot 7H_2O$ stock solution under a continuous bubbling of air. Thereafter, wastewater was heated at approximately 60ºC. Then, H_2O_2 was gradually added directly to the reaction solution during 40 min. The reaction was completed by spiking the sample with concentrated NaOH solution to increase the pH to 7-8. After cooling the reaction solution to the ambient temperature, and prior to treatment with NF and RO membranes, the samples were filtered by the sand filter with a granulation of 0.8-1.2 mm and UF in order to remove the formed $Fe(OH)_3$ flocs. The sand filtration and UF were used after the Fenton process, since the sand filter has good potential for removing ferric precipitates that would otherwise cause a significant flux decline and membrane fouling [21].

Ultrafiltration is very often used as a pretreatment to NF and RO processes [22, 23]. It is a powerful tool for the reduction of fouling potential of NF/RO membranes, which increases the overall efficiency and is also very suitable, since the turbidity of the influent can be up to 100 NTU. The working pressure was 3 bar, while the active surface of the membrane was 0.20 m^2.

The ferrous sulfate ($FeSO_4 \cdot 7H_2O$, p.a.) was purchased from Sigma-Aldrich (Steinheim, Germany), while the hydrogen peroxide solution (30%, w/w) and NaOH were all purchased from Gram-Mol (Zagreb, Croatia).

The subsequent steps in the experiment were the membrane treatment processes (Fig. 1 parts B and C).

Nanofiltration

The following procedure of NF was performed in a pilot plant. No pH adjustment was made prior to the experimental studies, since the pH values of the investigated wastewater samples (6.0-8.45) fell within the ranges recommended by the manufacturers. The pilot plant [24] was designed for a maximum operating pressure of 20 bar.

Effluent 1 from the pretreatment was used as feed in the NF experiments on a pilot plant unit (Fig. 1 part B), where a commercially available loose nanofiltration membrane, an HL module with molecular weight cut-off (MWCO) value of 150-300 Da, was employed. The membrane module was spiral wound 2540: *L*-1000 mm and *D*-64 mm provided by Desal, Osmonics, GE Infrastructure Water & Process Tech., Vista, CA. The active surface of the membranes was 2.5 m^2. The operation conditions during the experiments were: the pressure feed P_{feed}-9.2 bar; the pressure on membrane element P_m-8 bar, and recirculation of retentate Q-600 L·h^{-1}. The membrane module was stored in a 1.5% sodium disulfite and before treatment of effluent 1 it was rinsed with pipe water. After the treatment, a membrane module was cleaned with alkali (1.5%-RoClean

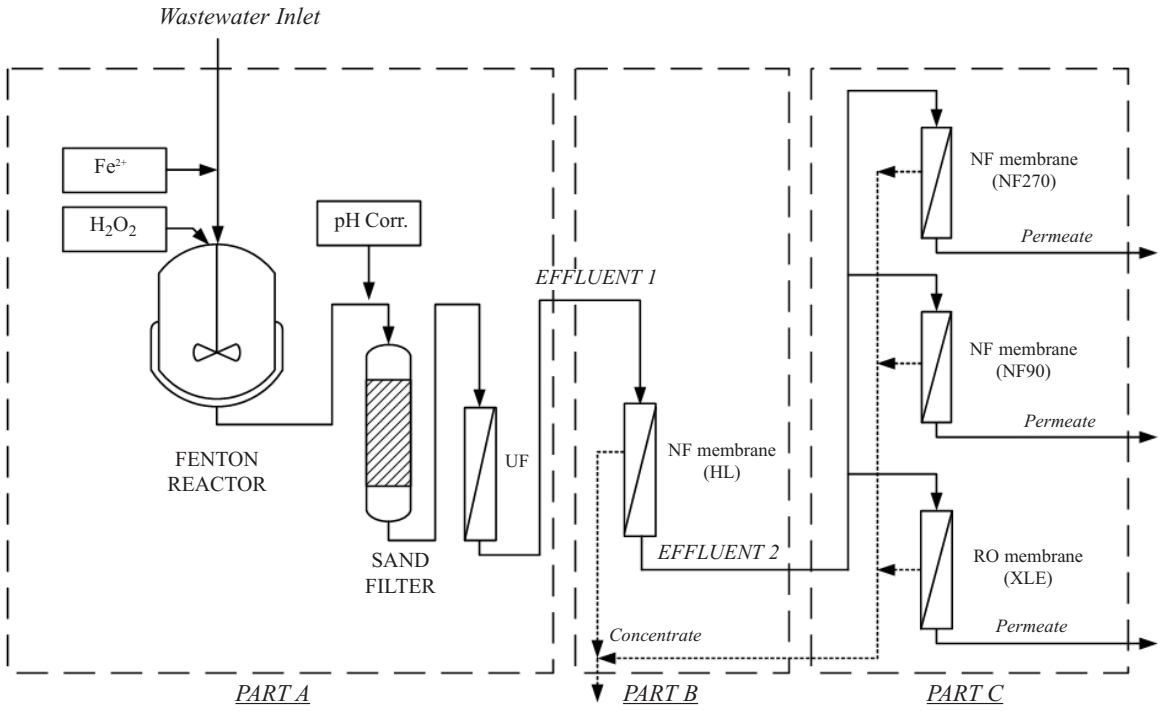

Fig. 1. Scheme of pharmaceutical wastewater treatment.

P211, Avista Technologies (UK) Ltd) and acidic (1.5%-RoClean P303, Avista Technologies (UK) Ltd) agents for cleaning, washed with the pipe water and then with the demineralized water.

The initial volume of the pretreated PhWW was 200 L and during the operation the retentate stream was recirculated to the feed tank. Therefore, the feed solution was continuously concentrated (volume reduction factor, *VRP*).

VRP was defined as:

$$VRP = \frac{V_0}{V_R} = \frac{V_0}{V_0 - V_p} \quad (1)$$

...where V_0 represents the processed feed volume, while V_R and V_P represent the retentate and permeate volumes (L), respectively.

The permeate recovery was calculated according to the following formula:

$$\text{Recovery}\,(\%) = \frac{V_P}{V_0} \times 100 \quad (2)$$

The Final Membrane Treatment

The final step was a treatment of effluent 2 with dense nanofiltration membranes (NF90 and NF270) and reverse osmosis membranes (XLE). All the membranes were from Dow/FilmTec, Midland MI, and were used in laboratory set-up as described in the previous research [25].

The aliquots collected after each step were subsequently subjected to analytical measurements.

Analytical (Environmental) Parameters

The conductivity, COD, TOC, total N, total P, free ammonia (NH_3), phosphate (PO_4^{3-}), nitrate (NO_3^-), nitrite (NO_2^-), sulfate (SO_4^{2-}), chloride (Cl^-), and pH were monitored. All parameters were measured three times and the average values are given in all tables. Standard deviations were under 11%.

Conductivity was determined by conductometer (SCHOTT Instruments Lab 960, Germany), while concentrations of TOC were determined by a Shimadzu TOC-VWS carbon analyzer (Japan). All other chemical characteristics of the PhWW (mentioned in this section) before and after treatment were analyzed according to standard methods for the examination of water and wastewater [26]. All chemicals used throughout the experiment were at least of analytical grade.

Results and Discussion

Characterization of the Raw Pharmaceutical Wastewater

The analysis of the PhWW in terms of conventional environmental parameters is given in Table 1, column 3. As shown in this table, the organic content of the PhWW was characterized by a high COD and TOC levels of around 25,000 and 5,000 mg·L^{-1}, respectively. These results indicate that the PhWW contained a very high load of organic matter. The high concentrations of total N (4,054 mg·L^{-1}) and total P (6.96 mg·L^{-1}) can have great impact on the environment. The most common problem with the effluents discharged in the environment from the municipal or industrial plants is eutrophication. This phenomenon is responsible for the dramatic growth of algae occurring in the internal and the coastal waters. Also, a significant fraction of total N and total P may:

(1) accumulate in soils
(2) move from the land into surface waters
(3) migrate into groundwaters
(4) enter the atmosphere via ammonia volatilization and nitrous oxide production

Also, the PhWW was characterized by very high conductivity, ammonium, and chloride concentrations of 40,000 μS·cm^{-1}, 170 mg·L^{-1}, and 7,300 mg·L^{-1}, respectively.

According to the presented results, the selected PhWW was highly polluted pharmaceutical wastewater and has to be treated combining several treatments. The choice in this work was Fenton process, sand filtration, UF, NF, and RO in order to meet maximum contaminant levels (MCL_S) for the discharged effluent in natural aquifers or sewer systems.

Fenton Process, Sand Filtration, and Ultrafiltration

Analysis of effluent 1 (PhWW after Fenton process, sand filtration and UF) is given in Table 1, column 3. The results show that the above-mentioned processes reduced COD and TOC for 62% and 56%, respectively. A little lower decrease of TOC value compared to COD implies that some of the organic compounds were degraded into organic byproducts instead of being mineralized to CO_2 and H_2O. The conductivity was still high (reduced for 10%), due to the addition of $FeSO_4$ during the Fenton process. The total N and total P were satisfactorily removed, 88% and 95%, respectively. The concentration of total P decreased below MCL_S, but the concentrations of total N and other parameters were above MCL_S values and required additional treatment.

Nanofiltration Using the Looser Membranes

Effluent 1 was further treated by nanofiltration on the pilot plant using an HL membrane spiral wound module. Column 4 of Table 1 presents results from the beginning (first hour) of the nanofiltration procedure. The COD and TOC contents during step 2 were additionally reduced for 86.6 and 71.4%, respectively. According to these results, it can be concluded that the effluent after NF contains a high concentration of ions and organic components of low molecular mass. This could have been expected due to the HL membrane pore size bigger than 0.71 nm [25] and MWCO between 150-300 Da. The conductivity was reduced only for 24%, due to the very high initial conductivity value

Table 2. The permeate analysis after NF/RO treatment with flux for each membrane and the corresponding MCL_S values.

	Feed	NF90	NF270	XLE	MCL_S Surface water	MCL_S Sewer system
COD (mg $O_2 \cdot L^{-1}$)	4,725	288.1	952.0	136.4	125	700
Conductivity ($\mu S \cdot cm^{-1}$)	31,800	1,835	2,100	1,200	-	-
TOC (mg $C \cdot L^{-1}$)	1,579	155.2	580.0	123.1	30	-
pH	7.75	8.60	8.06	n.s.	6.50-9.00	6.50-9.50
NH_3 ($mg \cdot L^{-1}$)	471	83.0	336	90	10	-
Cl^- ($mg \cdot L^{-1}$)	6,966	290	5,886	147	-	d.s.
SO_4^{2-} ($mg \cdot L^{-1}$)	14.60	0	1.27	0	250	d.s.
Total N ($mg \cdot L^{-1}$)	523	93.0	281	105	10	d.s.
Total P ($mg \cdot L^{-1}$)	0.18	n.s.	0.08	n.s.	2	d.s.
J ($L \cdot m^{-2} \cdot h^{-1}$)	-	40.31	98.50	26.41	-	-

n.s. – no sample
d.s. – determined separately for discharge into public sewer system if the collection system has wastewater treatment plant

(35,000 $\mu S \cdot cm^{-1}$). Dolar et al. [25] reduced conductivity with the same membrane for 66%, but with much lower conductivity in the feed (2,000 $\mu S \cdot cm^{-1}$). At this stage of treatment two parameters were below MCL_S (sulfate and total P).

The initial volume of the PhWW was 200 L, and after the treatment there was 15 L of retentate, so *VRP* and recovery were 13.3 and 92.5%, respectively. A recovery higher than 90% shows that the volume of the retentate can be small compared to the large amount of the PhWW influent.

Final Step – Nanofiltration and Reverse Osmosis

The feed sample for the last step of the treatment (NF/RO treatment) was fractions (10 L) of the whole amount of permeate after the nanofiltration treatment with HL membrane. The results of step 3 are presented in Table 2. The differences between the initial content of the step 2 permeate (effluent 2) and the feed concentration values in Table 2 (2nd column) were caused by the changing separation effect during batch circulation mode of step 2. Namely, the feed during step 2 became more and more concentrated and therefore the membrane rejection gradually decreased, which is a well-known effect in batch membrane processes [27, 28].

The last two columns of Table 2 present the MCL_S values for discharging the treated water to a sewer system or natural aquifers (surface water), according to Croatian Environmental law NN 94/2008. The data in Table 2 obviously show that the reverse osmosis XLE membrane provided the highest COD (97.1%), TOC (92.2%) and the conductivity (96.2%) reduction in the NF/RO process, while the nanofiltration NF270 membrane showed the lowest efficiency (79.8%, 63.3%, and 93.4%). This also is in agreement with the MWCO values and pore sizes of the investigated membranes. According to Košutić et al. [29], pore sizes were 0.67 nm for XLE, 0.81 nm for NF90, and 0.90 + 1.56 nm for NF270, while the membranes' thin layer porosity (pore size and pore size distribution) were determined indirectly by the solute transport method using the fine-pore model. At the operating pressure of 25 bar, the COD, TOC, and κ values of the permeate (effluent) from NF90 membrane were 288.1 $mg \cdot L^{-1}$ (93.9%), 155.2 $mg \cdot L^{-1}$ (90.2%), and 1,835 $\mu S \cdot cm^{-1}$ (94.2%), respectively. The separation efficiency of the NF90 membrane was very close to that of the reverse osmosis XLE membrane, because the active layer structure of the tight NF membrane (NF90) was at the narrow pore end of the NF separation range. The results of the other measured parameters show high efficiencies with all the examined membranes.

The obtained fluxes were in agreement with the theory, because according to the MWCO of the membranes used, the flux sequence should be J(NF270) > J(NF90) > J(XLE).

The effectiveness of the whole treatment (Fenton, sand filtration, UF, NF, and RO) is presented in the last column of Table 3. These results indicate that the combination of the selected treatments was appropriate for this kind of highly polluted wastewater, because the reduction of measured parameters was higher than 90%.

A comparison of the results of the current study with those obtained in previous research on the use of these membranes for the distinct type of wastewaters shows good agreement. The COD reduction in this research is consistent with previous works [30, 31]. There are deviations for a few percentages, but this was to be expected due to dependency on the wastewater characteristics and operating conditions.

The results obtained in this study show that the PhWW treated in this manner could be discharged to the sewer system, but for discharge to surface waters the approach needs to be further investigated. The next step of this work will be to find a treatment to meet MCL_S for the discharge to the surface water or natural aquifers.

Table 3. Overall effectiveness of the treatment.

	Raw water	Permeate
	Conc.	R/%
COD (mg $O_2 \cdot L^{-1}$)	25,000	96.2-99.5
Conductivity ($\mu S \cdot cm^{-1}$)	40,000	94.7-97.0
TOC (mg $C \cdot L^{-1}$)	4,940	88.3-97.5
NH_3 (mg $N \cdot L^{-1}$)	170	-
Cl^- (mg $\cdot L^{-1}$)	7,300	19.4-98.0
SO_4^{2-} (mg $\cdot L^{-1}$)	520.0	99.7-100
Total N (mg $\cdot L^{-1}$)	4,054	93.1-97.7
Total P (mg $\cdot L^{-1}$)	6.96	98.8

Conclusions

From the results presented above, the following major conclusions were drawn:

- The combined treatment, including Fenton process, the sand filter, UF, NF, and RO, used in the treatment of this pharmaceutical wastewater proved to be effective.
- The optimum concentrations of Fe^{2+} and H_2O_2 for Fenton process were 0.6 g $\cdot L^{-1}$ and 32 g $\cdot L^{-1}$, respectively, and the pretreatment was found to be effective in the reduction of COD, TOC, total N, and total P. It can be considered as an effective pretreatment of this type of wastewater.
- The additional decline of measured parameters was achieved by membrane processes. With NF and RO membranes, COD, TOC, conductivity, SO_4^{2-}, total N, and total P were lowered for 90-99%, 73-94%, 94-97%, 99-100%, 44-81%, and 75%, respectively. Other parameters declined more than 30%.
- The recovery, which was greater than 90%, significantly reduced the volume of retentate (effluent) for further treatment or disposal.

The treated effluent could be discharged to the sewer system under the condition that the appropriate wastewater monitoring and sampling facilities are installed. The wastewater flow and composition should be measured by the wastewater producers and checked by the authorities on a regular basis.

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