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**SCIENTIFIC PAPER**

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# TREATMENT OF REAL PARACETAMOL WASTEWATER BY FENTON PROCESS

**Article Highlights**

- Real paracetamol (PCT) wastewater was pre-treated by Fenton process
- Best experimental conditions of Fenton process were determined
- Mass balance calculations were studied to show the mass distributions
- Fenton process was found as a promising method for the treatment of PCT wastewater

**Abstract**

*The study investigated the pretreatment of real paracetamol (PCT) wastewater of a pharmaceutical industry by Fenton process. At the best experimental conditions ($COD/H_2O_2$ = 1/1, $Fe^{+2}/H_2O_2$ = 1/70, settling method:centrifuging, pH 6 at settling step), 92.7, 92.7, 95.5, 99.1, 99.9 and 99.4% of chemical oxygen demand (COD), total organic carbon (TOC), 5-day biological oxygen demand ($BOD_5$), PCT, para-amino phenol (PAP) and aniline were removed, respectively. Changes in the concentrations of these parameters were also investigated for both oxidation and settling steps of Fenton process. It was found that COD and TOC were removed at the settling step (precipitation) whereas PCT, PAP and aniline were removed at the oxidation step. Mass balance calculations were also studied to show the mass distributions of COD in different phases (gas + foam, effluent and sludge). Fenton process was found as an effective method for the pretreatment of real PCT wastewater for discharging in a determined collective treatment plant.*

*Keywords: chemical oxygen demand, Fenton process, mass balance, real paracetamol wastewater, total organic carbon.*

Over the last two decades, a large variety of pharmaceutical drugs including analgesics, anti-inflammatory, beta-blockers, antimicrobials, blood lipid regulators and so on, has been detected at low contents of micrograms per liter in soils, surface waters, ground waters and even in drinking waters [1-9]. Pharmaceutical drugs can reach aquatic environment from domestic waste or industrial wastewater, hospitals and health centers [10].

Unused drugs, manufacturing waste and sewage sludge can also be introduced into the environment by way of landfill leachates [11]. Pharmaceuticals can reach sewage treatment plants by way of domestic and hospital wastewater without being completely metabolized and changed. Although they are treated in these plants, they can be present in the aquatic environment [11] or they are discharged directly without any treatment [12]. Classical biological treatment plants do not have enough efficieny to remove this kind of compounds [12,13] as they are designed to treat only urban and industrial wastewater. Removal efficienies of this kind of plants are usually evaluated by parameters as particulate matter, phosphate, metal ions, pathogens and nitrogen, but not pharmaceuticals [12]. Thus, low cost and easily applied methods must be developed beyond the conventional ones for removing these substances.

Paracetamol (PCT), a common analgesic and antipyretic drug [14], has a widespread usage as the raw material of many drugs. Pharmaceutically ineffective main metabolites of PCT are glucuronide

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(55%) and sulphate (35%) [15]. About 1-3% of PCT is excreted without being changed by the uretic system. Besides being a good pain reliever, a certain amount of PCT can also be used for controlling brown tree snakes and cause hepetotoxicity in humans. As there are lots of organisms in the environment and each organism has different sensitivities, pharmaceuticals can be qualified as risk factors for the environment [14].

Recent studies show that in addition to advanced oxidation processes (AOPs) [16-26], adsorption [10], pure bacterial cultures [27], active sludge [28], subsurface flow constructed wetlands [29] and anaerobic treatment [20] can be used for PCT removal from wastewater. In the traditional environmental engineering technologies, wastewater treatments are usually realized by the parameters: chemical oxygen demand (*COD*), 5-day biological oxygen demand ($BOD_5$), and total organic carbon (*TOC*).

Over the past few years, AOPs have been used to reduce the contamination based on the presence of stable pharmaceuticals [30,31]. Complex organic chemicals are formed during the production of pharmaceuticals and it is not easy to remove these compounds biologically. As a result, AOPs are more appropriate than conventional methods for treatment of pharmaceutical wastewater [32]. AOPs comprises Fenton, photo-Fenton, ozonation combined with UV-light and/or $H_2O_2$, mainly $TiO_2$-mediated photocatalysis [30], electrolysis, wet air oxidation, ultrasound and ionizing radiation, microwaves, pulsed plasma and the ferrate reagent [31].

The Fenton system is one of the most promising methods among all AOPs for removal of organic pollutants [33], while also cost-effective and easily operated [32], although it has some disadvantages, such as the necessity to be operated in a limited pH range [31] and the formation of sluge that has to be separated by an additional operation [34]. Advanced oxidation with Fenton's reagent is based on ferrous ions, hydrogen peroxide ($H_2O_2$) and hydroxyl radicals ($HO^{\bullet}$) produced by the catalytic decomposition of $H_2O_2$ in acidic solution [35]. The main chemicals of the Fenton reaction are hydrogen peroxide and iron, which are environmentally friendly, inexpensive and safe [36]. Formation of $HO^{\bullet}$ and oxidation of $Fe^{2+}$ to $Fe^{3+}$ explains the efficiency of this system [33]. The $HO^{\bullet}$, which is known as the second strongest oxidant after fluorine [37] and has the ability of oxidizing organic compounds in a short time [32], is the main oxidizing species of the Fenton system.

The main reactions of the Fenton system are shown below [38]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^- \quad (1)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (2)$$

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (3)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2 \quad (4)$$

$$Fe^{3+} + O_2^{-\bullet} \rightarrow Fe^{2+} + O_2 \quad (5)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^- \quad (6)$$

The Fenton process consists of pH adjustment, oxidation reaction, neutralization-coagulation and precipitation. The $H_2O_2/Fe^{2+}$ ratio is the major factor affecting the coagulation and oxidation stages [39].

Efficiency of wastewater treatment is usually evaluated by the parameters of *COD*, $BOD_5$ and *TOC*. It has been known that pollutants such as PCT, para-amino phenol (PAP) and aniline have negative effects on both human health and the environment. A comprehensive study involving multi-parameters like *COD*, $BOD_5$, *TOC*, PCT, PAP and aniline has not been reported yet for the pretreatment of a high strength pharmaceutical wastewater. It is apparent from the literature that although much attention has been given to the treatment of synthetic wastewater [21-26], there are almost no systematic papers available in the literature specifically devoted to a study of real PCT wastewater. It is seen that synthetic PCT wastewaters have been used in most of the recent studies. Studying with synthetic wastewater is much easier than studying with real wastewater as the pollutant concentrations can be defined and the interferences of the involuntary substances can be prevented in synthetic wastewaters. In addition to these, synthetic wastewaters may not completely reflect the real case situation. For this reason, the present study aims at fulfilling the gap in this field by focusing upon some investigations on Fenton process as an effective method for the pretreatment of real PCT wastewater.

Considering the above-mentioned facts, the specific objectives of this study were: 1) to investigate the removal of organic matter, PCT, PAP, aniline in treatability of real PCT wastewater using Fenton process and 2) the mass balance using the removal mechanism of COD in different phases.

## EXPERIMENTAL

### Wastewater source and characteristics

Wastewater was obtained from a pharmaceutical factory which is in the first rank for PCT production in Marmara Region of Turkey. According to

the process, main part, 80% of the produced PCT is exported to USA and Europe, 10% is sold to the other pharmaceutical factories in Turkey and the remaining 10% is used as the raw material of other drugs produced by the factory. Process flow diagram of the factory is shown in Figure 1a. As shown in Figure 1a, para-aminophenol (PAP) is synthesized as by-product for PCT production. Nitrobenzene, aniline, $H_2SO_4$, $H_2$ and $H_2O$ are used in PCT synthesis. PCT molecule is formed after the reaction of PAP and acetic anhydride and the stage of crystallization. Figure 1b shows the molecules of nitrobenzene, aniline and PAP.

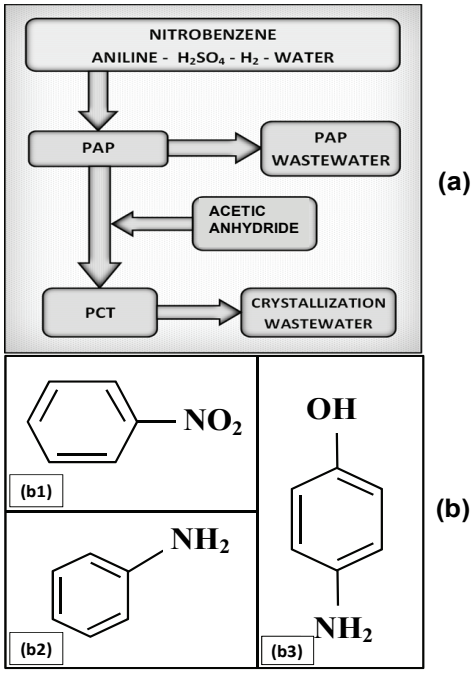



*Figure 1. a) Steps of PCT and PAP synthesis; b) chemical structure of the compounds in PCT synthesis: b1) nitrobenzene, b2) aniline and b3) PAP.*

The main characteristics of real PCT wastewater are shown in Table 1. High *COD* value of the wastewater is related to the high concentrations of PCT, PAP and aniline. Wastewater flow is nearly 200 $m^3$/day in the process. Pollutant concentrations of the wastewater can change day by day according to the process operations.

As seen in Table 1, pollutant concentrations are extremely high and the *BOD*/*COD* ratio is very low in PCT wastewater. Badawy *et al.* [33] indicated that wastewater having *BOD*/*COD* ratio between 0.25-0.30 cannot be treated biologically. Likewise, Tekin *et al.* [32] point out the resistance of pharmaceutical wastewater to biological treatment and treatability of this wastewater by AOPs instead of classical methods. It can be clearly seen that the PCT wastewater must be pretreated chemically, as conventional biological treatment methods are not appropriate for this kind of wastewater.

*Table 1. Main characteristics of PCT wastewater*

| Parameter | Value |
|---|---|
| pH | 9.0-9.5 |
| Chemical oxygen demand, *COD* / mg $L^{-1}$ | 36,000-76,800 |
| 5-day biological oxygen demand, $BOD_5$ / mg $L^{-1}$ | 15,120-21,500 |
| Total organic carbon, *TOC* / mg $L^{-1}$ | 12,000-24,312 |
| Paracetamol, PCT, ppm | 37-294 |
| Para-amino phenol, PAP, ppm | 1273-4604 |
| Aniline, ppm | 1699-2915 |
| Total suspended solids, *TSS* / mg $L^{-1}$ | 350-380 |

The industries producing chemical raw materials (such as PCT) are generally located in the large-scale organized industrial zones. The wastewaters of the different industries are collected and treated in a common wastewater treatment plant. As the wastewaters of these industries have different characteristics, the *BOD*/*COD* ratio of the other wastewaters are not same as the ratio of PCT wastewater. The aim of the study is developing a system for the pretreatment of mere PCT wastewater.

### Fenton process

Wastewater samples were kept in a refrigerator at 4 °C and *COD* measurements were made prior to calculate chemical dosages for each sample in Fenton experiments. Fenton experiments were performed at room temperature in a glass beaker by mixing at 300 rpm. $FeSO_4 \cdot 7H_2O$ solution (source of $Fe^{+2}$) was prepared in 3 M $H_2SO_4$ and added to the sample at the beginning of the experiment. pH was adjusted at 3.0±0.2 by using 3 M $H_2SO_4$, and kept at the same value by using 6 M NaOH during the reaction [33]. For that reason, $H_2O_2$ was dosed continuously at each minute by an automatic pipette (Brand 704782) during the reaction time. Durán *et al.* [21] indicated the enhancement in mineralization process with continuous addition of $H_2O_2$. After Fenton's oxidation, the pH was adjusted at 6.0 for the settling step.

### Analytical procedure

Experimental analyses were performed by the procedures described in standard methods [40], *COD* (closed reflux – titrimetric method, 5220 C), *BOD* (5--day test, 5210 B), *TSS* (dried at 103-105 °C, 2540 D). *TOC* analyses were performed by TOC-TN analyzer (HACH-LANGE IL550 TOC-TN), based on combustion catalytic oxidation method, using a highly sensitive multi-channel non-dispersive infrared detector

[41]. PCT, PAP and aniline were quantified using the official chromatographic method based on high-performance liquid chromatography (HPLC) according to the procedures described in the European Pharmacopoeia 8.0 [42]. The HPLC system comprised of a Shimadzu liquid chromatograph, model 20A, coupled to an UV-visible detector (SPD-20A), auto-injector (SIL-20A) and a degasser DGU-20A5, controlled by a personal computer. Shimadzu EZstart 7.4 chromatography software was used for processing of data and peaks integration. A Shim-pack CLC-ODS C18 column (size: $l$ = 0.25 m, Ø = 4.6 mm, stationary phase: octylsilyl silica gel for chromatography R (5 μm)) was used inside a CTO-10AS oven (Shimadzu, Kyoto, Japan) maintained at 35 °C. Mobile phase was a mixture of 375 volumes of a 17.9 g/L solution of disodium hydrogen phosphate R, 375 volumes of a 7.8 g/L solution of sodium dihydrogen phosphate R and 250 volumes of methanol R containing 4.6 g/L of a 400 g/l solution of tetrabutylammonium hydroxide R. The flow rate was 1.5 mL/min, the sample injection volume 20 mL, and the detector absorption wavelength 245 nm [42]. All analytical measurements were done in triplicate to observe the reproducibility of each test. A magnetic stirrer (RCT, 0-1500 rpm) was used during the experiments. The pH and temperature was measured with a Hanna - HI 2211 pH/ORP meter. Beckman Coulter Allegra X-12 was used for centrifuge. All analyses were performed at room temperature (24±2 °C).

## RESULTS AND DISCUSSION

### Investigation of the best experimental set

Each different Fenton experiment was named as "set" and in each set *COD*/$H_2O_2$-$Fe^{+2}$/$H_2O_2$ ratios and reaction time were used as variables of the present study. The aim of this investigation is obtaining the highest *COD* removal efficiency using the chemical dosages during the shortest reaction time. High *COD* removal efficiencies were obtained between 1/2 and 1/0.8 for *COD*/$H_2O_2$ ratios. Similar ratios (*COD*/$H_2O_2$ in range 1/4.4-1/1.1) were used in the study of Badawy *et al.* [33] and high efficiencies were obtained. The selected sets having high *COD* removal efficiencies are summarized in Table 2. As seen in Table 2, set 25 (*COD*/$H_2O_2$ = 1/1, $Fe^{+2}$/$H_2O_2$ = 1/70 and

*Table 2. COD removal efficiencies (%) of different sets*

| Set | *COD*/$H_2O_2$ | $Fe^{+2}$/$H_2O_2$ | Reaction time, min | *COD* removal efficiency, % |
|---|---|---|---|---|
| 1 | 1/2 | 1/10 | 60 | 80.9 |
| 2 | 1/2 | 1/10 | 45 | 78.7 |
| 3 | 1/2 | 1/15 | 75 | 79.7 |
| 4 | 1/2 | 1/15 | 60 | 83.3 |
| 5 | 1/2 | 1/15 | 45 | 80.2 |
| 6 | 1/2 | 1/15 | 30 | 76.9 |
| 7 | 1/2 | 1/20 | 75 | 79.6 |
| 8 | 1/2 | 1/20 | 60 | 79.6 |
| 9 | 1/2 | 1/20 | 45 | 82.9 |
| 10 | 1/2 | 1/20 | 30 | 82.2 |
| 11 | 1/2 | 1/20 | 15 | 82.2 |
| 12 | 1/2 | 1/25 | 75 | 79.8 |
| 13 | 1/2 | 1/25 | 60 | 79.8 |
| 14 | 1/2 | 1/25 | 45 | 78.7 |
| 15 | 1/2 | 1/25 | 30 | 78.7 |
| 16 | 1/2 | 1/40 | 45 | 81.1 |
| 17 | 1/2 | 1/40 | 30 | 80.7 |
| 18 | 1/1.4 | 1/15 | 30 | 78.0 |
| 19 | 1/1.4 | 1/15 | 15 | 76.0 |
| 20 | 1/1 | 1/15 | 30 | 73.3 |
| 21 | 1/1 | 1/15 | 15 | 75.0 |
| 22 | 1/1 | 1/25 | 30 | 80.5 |
| 23 | 1/1 | 1/25 | 15 | 78.9 |
| 24 | 1/1 | 1/50 | 15 | 84.2 |
| **25** | **1/1** | **1/70** | **15** | **88.1** |
| 26 | 1/1 | 1/90 | 15 | 83.5 |
| 27 | 1/0.8 | 1/70 | 15 | 82.0 |

reaction time of 15 min) was determined as the best experimental set.

### Improvement studies for the best experimental set

Settling alternatives, different pH for the settling step and different reaction times were studied for obtaining higher removal efficiencies in the best experimental set.

### Determination of settling method

In the present experiments, wastewater was kept for 1 day in a measuring cylinder for settling and thereafter, *COD* measurements were conducted with the sample taken from the supernatant of the wastewater. Su *et al.* [26] indicated that leaving the samples overnight prevented the remaining $H_2O_2$ from affecting *COD* measurements. The seperating point of effluent and sludge could not be determined even waiting for 1 day. So, it was determined to study different settling alternatives to separate the effluent from the sludge. Adding anionic and cationic polyelectrolytes (p.e.) and centrifuging were tested for the best experimental set (Figure 2a).

As seen in Figure 2a, 91.9 and 88.1% *COD* removal efficiencies were obtained from the effluents after 1 day and 92.7 and 89.1% after 2 days for anionic and cationic polyelectrolytes (p.e.), respectively. It could be seen that settling time had a positive effect on COD removal efficiency for both p.e. On the other hand, *COD* removal efficiency of centrifuged sample was 92.3%.

When all the results were compared, it was seen that the highest *COD* removal efficiency was obtained from the sample containing anionic p.e. after settling for 2 days. On the other hand, the second highest removal efficiency was obtained from the sample centrifuged 2 h later after oxidation. Centrifuging was

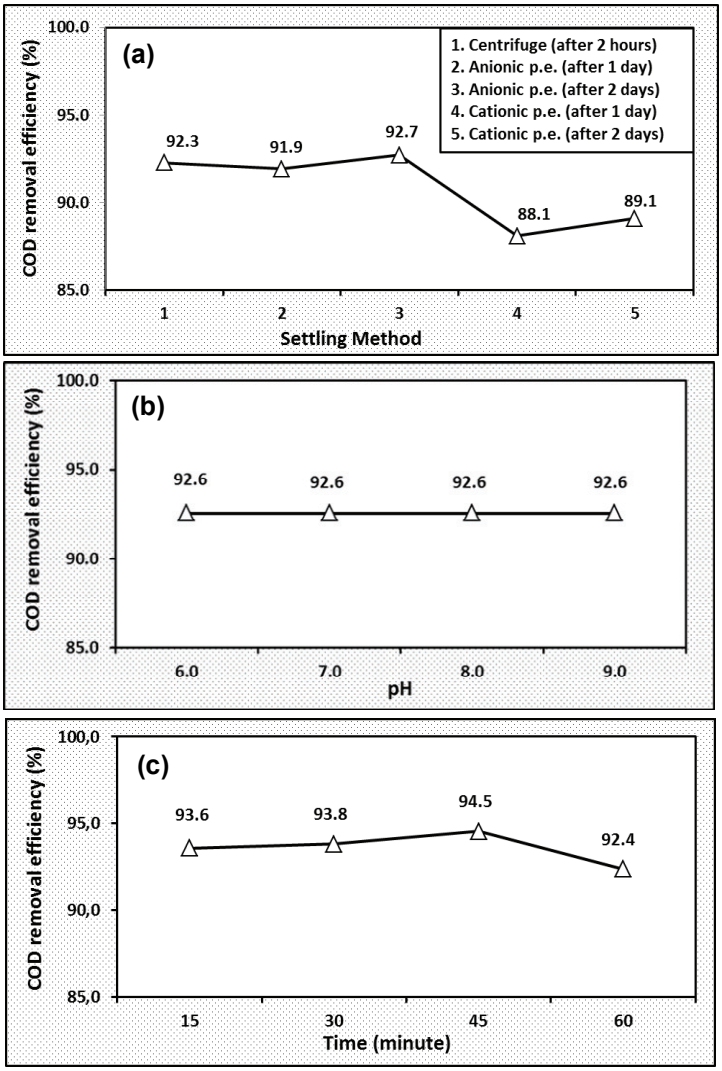



*Figure 2. a) COD removal efficiencies of different settling methods; b) effect of pH on COD removal efficiency at settling step; c) effect of reaction time on COD removal efficiency.*

determined as the best settling method considering the facts like settling time, sludge formation and little difference between the removal efficiencies of the methods. After various trial runs, it was decided that the mixture after oxidation was better to be centrifuged for minimum 20 min at 3750 rpm (also used in the experiments depicted in Figure 2a).

### Effect of pH at settling step

According to Turkish Water Pollution Control Regulation [43], pH value of the wastewater has to be between 6-9 for discharge standards. In the experiments, pH was adjusted with centrifugation at 6.0 after oxidation step. In order to determine the effect of pH at the settling step, pH was adjusted at 6.0, 7.0, 8.0 and 9.0 after the oxidation experiments. The obtained results are depicted in Figure 2b.

As seen in Figure 2b, increase in pH for the settling step had no effect on *COD* removal efficiencies. Increasing the pH to 6.0 would be enough for the settling step after oxidation. Therefore, the pH was set to 6.0 in the other experiments.

### Effect of reaction time

In the experiments investigating the best conditions, the sets with different *COD*/$H_2O_2$-$Fe^{+2}$/$H_2O_2$ ratios were studied for various reaction times. The best experimental set was studied for 15, 30, 45 and 60 min, and *COD* removal efficiencies were found for each reaction time (Figure 2c). As seen in Figure 2c, 93.6, 93.8, 94.5 and 92.4% *COD* removal efficiencies were obtained for 15, 30, 45 and 60 min reaction times, respectively. Increase in reaction time had a positive effect on the *COD* removal efficiency until 45 min. It could be easily recognized that the removal efficiencies were close to each other. Although the removal efficiency is a bit more in 45 min compared to 15 min, it is obvious that the costs are much more in 45 min by taking into consideration the factors as consumptions of chemicals for pH adjustment and electric power. Furthermore, the unpaired *t*-test concluded that there was insufficient evidence for a significant difference between *COD* removal efficiencies since the two-tailed *p*-values (0.9934-0.9987) are higher than the chosen $\alpha$ level of 0.05. By conventional criteria, this difference is considered to be not statistically significant. Therefore, the small difference in the removal efficiencies can be ignored. Consequently, 15 min was accepted as the best reaction time in the present Fenton process.

### Removal efficiencies in terms of other parameters

All the recent experiments were based on *COD* removal efficiencies. Besides *COD*, $BOD_5$, *TOC*, PCT, PAP and aniline measurements were performed for the best experimental set and removal efficiencies for each parameter were shown in Figure 3a.

As mentioned before, the best experimental set was repeated for several times and *COD* removal efficiency was found as 92.7±0.6%. Removal efficiencies for the parameters $BOD_5$, *TOC*, PCT, PAP and aniline were found as 95.5±0.1, 92.7±0.1, 99.1±0.1, 99.9±0.2 and 99.4±0.2%, respectively.

### Change in all the parameters during Fenton process

In all the experiments, pollutant measurements were only conducted in the effluent after the Fenton process. In order to determine the change in all the parameters during the Fenton process, samples were taken at each 5 min during the oxidation and after settling.

### Change *COD* and *TOC*

*COD* and *TOC* during the oxidation and settling steps are illustrated in Figure 3b. As seen in Figure 3b, Fenton process was divided in two steps as oxidation and settling. As mentioned before, $H_2O_2$ was dosed every minute in the oxidation step. Samples were taken at each 5 min after dosing the required amount of $H_2O_2$. *COD* and *TOC* concentrations had decreased during the oxidation and settling steps. However, a sharp decrease in the concentrations of both parameters after the oxidation step could be easily seen. As a result of these, it can be commented that the parameters *COD* and *TOC* were removed in the settling step by the mechanism of precipitation [39].

### Change in the concentrations of PCT, PAP and aniline

Concentrations of PCT, PAP and aniline during the oxidation and settling steps are shown in Figure 3c. As seen in Figure 3c, PCT, PAP and aniline showed a gradually decreasing trend as *COD* and *TOC* within the first 5 min of the oxidation reaction. This study focused on removing essential parameters defined in the local regulations. Therefore, the decreases in *COD* and *TOC* concentrations had more significances than the other parameters as PCT, PAP and aniline. But even so, the analysis of these parameters (PCT, PAP and aniline) were carried out besides *COD* and *TOC* by taking samples at intervals of 5 min for the aim of determining the time-dependent changes in the concentrations. When the decreases in concentrations of these three parameters (PAP, *COD* and *TOC*) were examined within the subsequent time period, it could be seen that their removal was realized by the mechanism of oxidation.

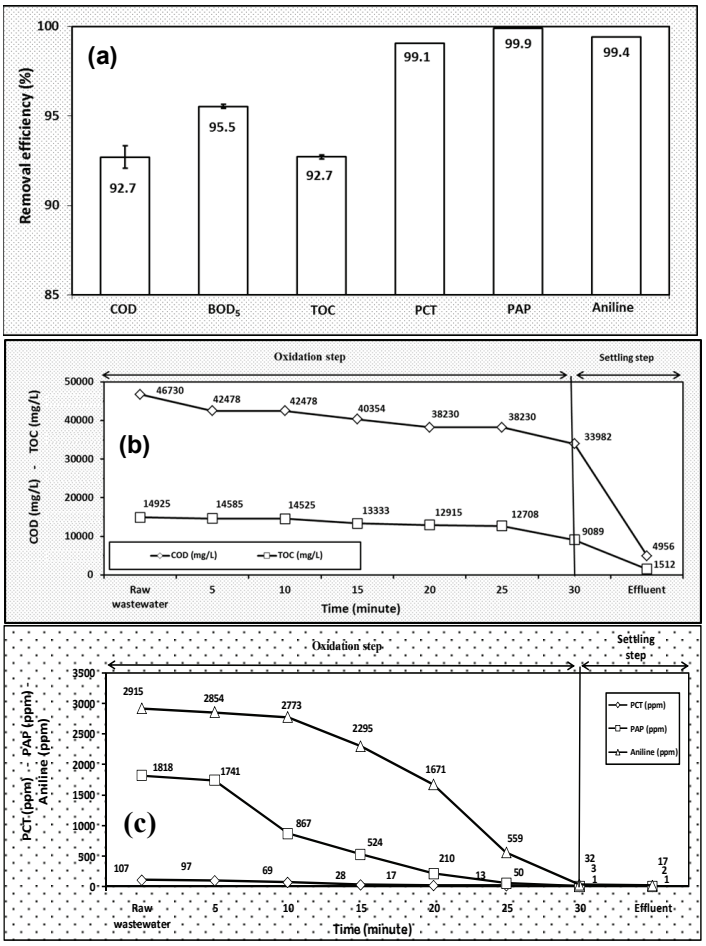



*Figure 3. a) Removal efficiencies of all the parameters for the best experimental set; b) change in the concentrations of COD and TOC during Fenton process; c) change in the concentrations of PCT, PAP and aniline during Fenton process.*

Consequently, *COD* and *TOC* were removed in settling step while PCT, PAP and aniline were removed in the oxidation step.

It could also be seen that the molecules PCT, PAP and aniline were almost completely degraded in the oxidation step of Fenton process. Nevertheless, *COD* and *TOC* concentrations of the mixture were still considerably high. Andreozzi *et al.* [16] also indicated the by-products synthesized in PCT degradation.

### *COD* of different phases after Fenton process

In this study, mass balance calculations were also conducted to explain the removal mechanisms of *COD* in different phases. *COD* concentrations of the phases (gas + foam, effluent, sludge) after Fenton process are depicted in Figure 4. As seen in Figure 4, mass distribution of *COD* in gas + foam, effluent and sludge phases were calculated as 11132, 2678 and 18901 mg, respectively. In each set of Fenton experiments, gas discharge and foam formation was observed. The decrease of *COD* concentration was derived from the *COD* content of gas and foam. Sludge and

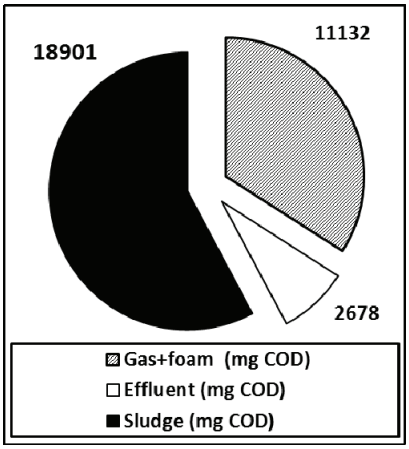



*Figure 4. Mass distribution of COD in different phases in Fenton process.*

effluent were formed from the mixture and it could be seen that a large quantity of *COD* passed to the sludge in the settling step. This case also verified the hypothesis that the removal of *COD* was realized by the precipitation mechanism. Studies about collection

of the gas and disposal of the sludge will be done in the future research.

### Comparisons with literature data

Different treatment methods used for PCT removal in the literature are given in Table 3. As seen in Table 3, in addition to advanced oxidation technics, the other methods like adsorption, pure bacterial cultures, active sludge and anaerobic treatment has also been used in PCT removal. Removal efficiencies have usually been determined over the parameters PCT and *TOC*. PCT and *TOC* removal efficiencies have changed within wide ranges as 30-99.9% and 10-99%, respectively. However, these removal efficiencies were obtained by using synthetic wastewater. It can been seen that removal efficiencies in the preesent study are considerably high when compared with the literature.

## CONCLUSIONS

PCT sythesis wastewater, which had high concentrations of *COD* and *TOC*, was pretreated by Fenton process used as an effective advanced oxidation process. Significant removal efficiencies were obtained at the best experimental conditions as follows: *COD*/$H_2O_2$ ratio 1/1, $Fe^{+2}/H_2O_2$ ratio 1/70, reaction time 15 min, settling by centrifuging at pH 6. Removal efficiencies as 92.7±0.628% *COD*, 95.5±0.123% $BOD_5$, 92.7±0.107% *TOC*, 99.1% PCT, 99.9% PAP and 99.4% aniline were obtained at these conditions. Removal mechanisms of *COD* and *TOC* were identified as precipitation, and as oxidation for PCT, PAP and aniline. The findings of this study clearly indicated that under the optimal conditions, real PCT wastewater could be effectively pretreated with the contribution of the Fenton process used as a feasible and promising method. Finally, it should be noted that this work has only focused on a local problem of a specific industry that produces paracet-

*Table 3. Different treatment methods used for PCT removal in the literature*

| Type of wastewater | Treatment method | Removal efficiency | Reference |
|---|---|---|---|
| Synthetic PCT wastewater | Ozonation | 30% *TOD* | [16] |
| Synthetic PCT wastewater | $H_2O_2$ photolysis | 40% *TOD* | [16] |
| Synthetic PCT wastewater | Advanced electrochemical oxidation | 100% *TOD* | [19] |
| Real PCT wastewater | Fenton | 75% *COD* | [20] |
| Real PCT wastewater | Fenton +anaerobic treatment | 98% *COD* | [20] |
| Synthetic PCT wastewater | Ultrasonic irradiation | 100% PCT, 39% *TOD* | [17] |
| Synthetic PCT wastewater | Subsurface flow constructed wetlands | 99.9% PCT | [29] |
| Synthetic PCT wastewater | Adsorption (vegetable sponge) | 40% PCT | [10] |
| Synthetic PCT wastewater | Adsorption (active carbon) | 45% PCT | [10] |
| Synthetic PCT wastewater | Adsorption (sugar cane bagasse) | 60% PCT | [10] |
| Synthetic municipal wastewater effluent containing PCT | Photo-Fenton | 83% *COD*, 71%, *TOD*, 94% $BOD_5$ | [21] |
| Synthetic PCT wastewater | Photo-Fenton | 60% DOC | [22] |
| Synthetic PCT wastewater | A combination of three microbial strains | 100% PCT, 87.1% *TOD* | [27] |
| Synthetic PCT wastewater | Advanced oxidation processes | 80-99% *TOD* | [23] |
| Synthetic PCT wastewater | Activated sludge | 90% PCT | [28] |
| Synthetic PCT wastewater | Fenton | 99.6% PCT | [24] |
| Synthetic PCT wastewater | Sonolysis | 13% *TOD* | [25] |
| Synthetic PCT wastewater | $TiO_2$ pho*TOD*atalysis | 71% *TOD* | [25] |
| Synthetic PCT wastewater | Sonolysis + pho*TOD*atalysis | 67% *TOD* | [25] |
| Synthetic PCT wastewater | Ultrasound + $Fe^{+3}$ | 10% *TOD* | [25] |
| Synthetic PCT wastewater | UV+ $Fe^{+3}$ | 66% *TOD* | [25] |
| Synthetic PCT wastewater | Fenton | 99% PCT, 34%, *COD*, 14% *TOD* | [26] |
| **Real PCT wastewater from pharmaceutical industry** | **Fenton** | **92.7% *COD*, 95,5% $BOD_5$, 92.7% *TOD*, 99.1% PCT, 99.9% PAP, 99.4% aniline** | **Present study** |

amol, and suggests the Fenton process for the aquatic wastes of the industry, but there are complex systems for the industry of other pharmaceuticals. Based on the advantages of the method described in this study, it can be concluded that additional studies are worthy of investigation by future work to explore the treatability of different types of pharmaceuticals and intermediates during the treatment.

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NAUČNI RAD

# OBRADA OTPADNE VODE SA PARACETAMOLOM FENTONOVIM PROCESOM

*U ovom radu izvršen je pretretman otpadne vode zagađene paracetamolom (PCT) iz farmaceutske industrije Fentonovim procesom. Pri najboljim eksperimentalnim uslovima pretretmana (odnos HPK/$H_2O_2$ = 1,1, $Fe^{2+}$/$H_2O_2$ = 1,70, metoda taloženja: centrifugisanje i pH 6 u fazi taloženja) procenat uklanjanja hemijske potrošnje kiseonika (HPK), ukupnog organkog ugljenika (TOC), PCT, para-aminofenola (PAP) i anilina iznose 92,7, 92,7, 95,5, 99,1, 99,9 i 99,4%, redom. Promena ovih parametara je analizirana za taložni i oksidacionu fazu Fentonovog procesa. Nađeno je da se HPK i TOC uklanjaju u taložnoj fazi, a da se PCT, PAP i anilin uklanjaju u oksidacionoj fazi. Bilansi mase su pokazali distribuciju HPK u različitim fazama (gas + pena, otpadna voda i mulj). Utvrđeno je da je Fentonov proces efikasna metoda za pretretman otpadne vode sa PCT u postrojenju za tretman otpadne vode.*

*Ključne reči: hemijska potrošnja kiseonika, Fenton proces, bilans mase, otpadna voda sa paracetamolom, ukupni organski ugljenik.*