Photo-Fenton-like and photo-fenton-like oxidation of Procaine Penicillin G formulation effluent

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Abstract

In the present study, the degradation of Procaine Penicillin G (PPG) formulation effluent by Fenton-like (Fe^{3+}/H_2O_2) and UV-A light assisted Fenton-like ($Fe^{3+}/H_2O_2/UV$-A) processes have been investigated at pH = 3. The effects of different process variables such as the initial Fe^{3+} and H_2O_2 concentrations, reaction time and UV-A light on PPG formulation effluent degradation rates have been evaluated. Chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD_5), total organic carbon (TOC) and acute toxicity towards the water flea *Daphnia magna* were selected as the environmental sum parameters to follow the performance of Fenton-like and photo-Fenton-like advanced oxidation processes on the PPG (Procaine Penicillin G) formulation effluent ($COD_o = 600$ mg/l; $BOD_5 = 53$ mg/l; $TOC_o = 450$ mg/l). At optimum reaction conditions (i.e. $[Fe^{3+}] = 1.5$ mM and $[H_2O_2] = 25$ mM, pH = 3), 56% COD and 42% TOC removal where achieved by the photo-Fenton-like process after 30 min treatment time, whereas the removal efficiencies of the dark Fenton-like process were limited to 44% COD and 35% TOC for the same treatment period. The superiority of the UV-A light-assisted Fenton-like process over the dark Fenton-like reaction was more evident in terms of their effect on biodegradability improvement; the BOD_5/COD ratio increased from 0.10 to 0.45 and 0.10 to only 0.24 after application of the photo-Fenton-like and Fenton-like processes, respectively. Based on the results of acute toxicity tests it could be inferred that the photo-Fenton-like process is a suitable method for complete detoxification and partial oxidation of PPG formulation effluent. COD removal efficiency decreased from 56 to 17% for the photo-Fenton-like process and from 44 to 14% for the dark Fenton-like process in the presence of the 1214 mg/l chloride ion (used as a free radical probe compound at acidic pH) after 30 min oxidative treatment, indicating that in both treatment processes the hydroxyl radical ($^{\bullet}OH$) was the major oxidizing agent for PPG.
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Keywords: Photo-Fenton-like oxidation; Antibiotic formulation effluent; Procaine Penicillin G; Biodegradability; Toxicity

1. Introduction

The pharmaceutical industry, which includes four different types of manufacturing processes, i.e. fermentation, chemical synthesis, extraction and formulation [1], often generates moderate-to-high strength wastewater exerting seasonal and operational variations in effluent quality and quantity [2]. Among the effluents originating from different operations in this industry, drug formulation effluent is characterized not only by low wastewater production rates but also extremely poor biodegradability and even toxicity caused by the active ingredients being formulated batch-wise. Particularly those effluents arising from the antibiotic formulation process contain high concentrations of refractory chemicals that lead to the complete inhibition

of activated sludge treatment systems as well as to toxic effects on aquatic organisms in water bodies receiving these effluents [3–5]. Hence, chemical pre-treatment is often required prior to discharge into sewage treatment systems.

Numerous researchers have evaluated the treatment of refractory organic pollutants found in groundwater, surface water and industrial wastewater by so-called advanced oxidation processes (AOPs) [6,7]. AOPs are of great interest for the treatment of contaminated surface and groundwater and for the destruction of toxic and biorefractory organic pollutants found in industrial wastewater and in landfill leachate. AOPs rely on the generation of very reactive oxidizing agents, i.e. free radicals such as the hydroxyl radical ($^{\bullet}OH$). $^{\bullet}OH$ can initiate oxidative degradation reactions of refractory synthetic and natural organic compounds and is capable of mineralizing them ultimately to CO_2 and H_2O owing to their high oxidation potential (+2.80 eV versus NHE) in aqueous solution [8,9].

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There are several oxidative processes involving iron compounds and hydrogen peroxide (H_2O_2) to provide alternative ways of $^{\bullet}OH$ generation. Direct photolysis of H_2O_2 produces $^{\bullet}OH$, however, because of the fact that H_2O_2 only weakly absorbs solar radiation, $^{\bullet}OH$ formation by this process is very slow. H_2O_2, though, can serve as a $^{\bullet}OH$ source via pathways involving iron salts or oxides [10]. The reaction of H_2O_2 with ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron in acidic aqueous solutions which are among the most common homogeneous systems and potential sources of hydroxyl radicals generation. Iron-catalyzed H_2O_2 decomposition known as the Fenton's reaction, provides an alternative way of oxidizing recalcitrant and/or toxic organic compounds present in most industrial wastewaters [11–13].

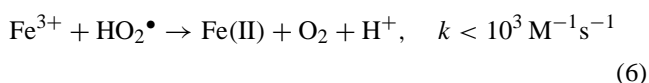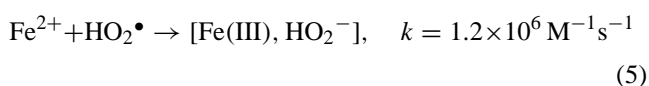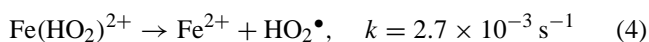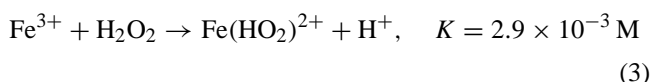The Fenton's reagent has been known for over a century [14].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet}, \quad k = 63\,M^{-1}\,s^{-1} \tag{1}$$
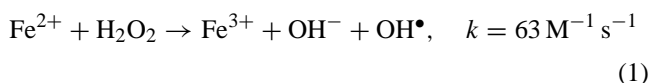
The hydroxyl radical ($^{\bullet}OH$) formed can react with and initiate the oxidation of organic pollutants (shown as R) in acidic, aqueous solutions [15]:

$$^{\bullet}OH + RH \rightarrow R^{\bullet} + H_2O, \quad k = 10^7 \text{ to } 10^{10}\,M^{-1}\,s^{-1} \tag{2}$$
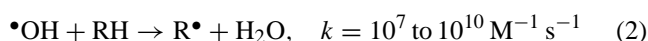
The use of the Fe^{2+}/H_2O_2 couple as an oxidant for wastewater treatment is attractive in many ways; iron is non-toxic, the second most abundant metal and the fourth most abundant element found in the Earth's crust where it is found as Fe^{2+} or Fe^{3+} ions, and H_2O_2 is easy to handle and is environmentally benign. However, for complete mineralization of organic compounds by Fenton's reagent, high doses of H_2O_2 and Fe^{2+} are generally needed because the regeneration of Fe^{2+} ion is relatively slow [13].

Ferric ion also catalyses hydrogen peroxide decomposition. In the absence of light and of complexion ligands other than water, the mechanism of H_2O_2 decomposition in acidic solution involves the formation of hydroperoxyl radicals ($HO_2^{\bullet}$) and $^{\bullet}OH$ by the following reaction steps [16–18];

$$Fe^{3+} + H_2O_2 \rightarrow Fe(HO_2)^{2+} + H^+, \quad K = 2.9 \times 10^{-3}\,M \tag{3}$$

$$Fe(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet}, \quad k = 2.7 \times 10^{-3}\,s^{-1} \tag{4}$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow [Fe(III), HO_2^-], \quad k = 1.2 \times 10^6\,M^{-1}s^{-1} \tag{5}$$

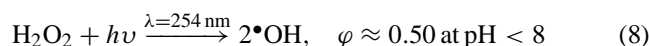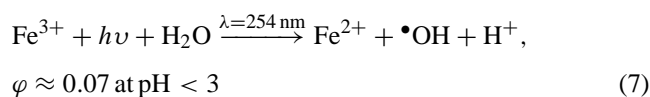$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe(II) + O_2 + H^+, \quad k < 10^3\,M^{-1}s^{-1} \tag{6}$$

In aqueous solution, the proportion of different iron species varies with the acidity of the solution. At pH of about 0, ferric ion exist as $[Fe(H_2O)_6]^{3+}$. $[Fe^{III}]^{3+}$ is the predominant Fe^{III} species at pH < 2. At pH > 2, Fe^{III}–hydroxy complexes ($[Fe^{III}(OH)]^{2+}$, $[Fe^{III}(OH)_2]^+$, $[Fe_2^{III}(OH)_2]^{4+}$) may also catalyze the decomposition of H_2O_2 [16]. According to results obtained by Pignatello [12], approximately half of the Fe(III) exists as Fe^{3+} ion and half as $Fe(OH)^{2+}$ at pH = 2.8 which is the optimum for the photo-Fenton process.

The $Fe^{2+}/Fe^{3+}/H_2O_2$ system has its maximum catalytic activity at pH = 2.8–3.0. As such, an increase or decrease in the pH sharply reduces the catalytic activity of iron. At elevated pH, the ferric ion precipitates as ferric hydroxide and at lower pH, the complexation of Fe^{3+} with H_2O_2 is inhibited [19].

Former investigations have already shown that upon irradiation by UV, near-UV, or visible light, Fe^{3+} can promote the photooxidation of organic compounds [18]. The reasons for the positive effect of UV irradiation on the degradation rate include the photolysis of Fe^{3+} that leading to the production of $^{\bullet}OH$ and Fe^{2+}. Moreover, $^{\bullet}OH$ are also produced via direct H_2O_2/UV photolysis (slow reaction) and the reaction of H_2O_2 with Fe^{2+} produced by photoreduction of Fe^{3+} [15]:

$$Fe^{3+} + h\upsilon + H_2O \xrightarrow{\lambda=254\,nm} Fe^{2+} + {}^{\bullet}OH + H^+,$$
$$\varphi \approx 0.07 \text{ at pH} < 3 \tag{7}$$

$$H_2O_2 + h\upsilon \xrightarrow{\lambda=254\,nm} 2{}^{\bullet}OH, \quad \varphi \approx 0.50 \text{ at pH} < 8 \tag{8}$$

The molar extinction coefficient of Fe^{3+} ($\varepsilon \approx 1500$–$3500\,M^{-1}\,cm^{-1}$) is much higher than that of H_2O_2 ($\varepsilon = 18.6\,M^{-1}\,cm^{-1}$).

Considering the above mentioned facts, the aim of the this work was to present experimental results concerning the degradation of a penicillin formulation effluent containing the antibiotic PPG comparatively by the Fenton-like and photo-Fenton-like AOPs. PPG was selected as the organic index pollutant because of its high consumption rate and its poor biodegradability. The specific objective of this study was to establish the characteristics of Fenton-like and photo-Fenton-like oxidation processes for the effective degradation of PPG formulation effluent. For that purpose, a series of experiments have been conducted to determine the most important process variables of the Fenton-like reagent such as initial H_2O_2 and Fe^{3+} concentration, treatment time, effect of UV-A light at acidic pH (=3). After establishment of optimum process conditions, Fenton-like and photo-Fenton-like process efficiencies were comparatively evaluated in terms of biodegradability improvement (i.e. the BOD_5/COD ratio), detoxification (measured as the changes in PPG effluent acute toxicity towards *Daphnia magna*) and mineralization (TOC abatement). In order to identify the dominant reaction pathway of the selected oxidation processes, the effect of chloride ion added as a $^{\bullet}OH$ probe compound on COD abatement rates was also examined.
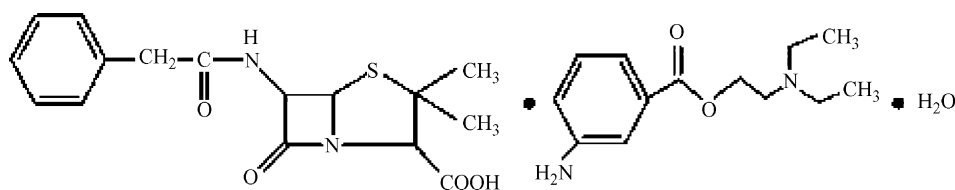
Fig. 1. Structure of Procaine Penicillin G (antibiotic formulation active ingredient).

2. Experimental

2.1. Materials

The antibiotic formulation PPG (Solubility in water: 100 g/l; available as an injectable suspension of 300,000 U/ml; molecular weight of Penicillin G potassium salt, $C_{16}H_{17}KN_2O_4S = 372.5$ g/mol; molecular weight of Procaine, $C_{13}H_{20}N_2O_2 = 263.3$ g/mol) was purchased from a pharmaceutical company located in Istanbul, Turkey. All other chemicals used in the experiments and analyses were of at least analytical grade. The basic structure of PPG is depicted in Fig. 1.

2.2. Photoreactor and light source

Photo-Fenton-like experiments were carried out in a 80 ml capacity borosilicate glass beaker where the reaction solution was directly irradiated with a 125 W black light bulb (BLB) lamp emitting UV-A light in the 300–370 nm wavelength range with a broad maximum light emission at 365 nm. The incident light flux of the BLB lamp was found as $I_o = 1.7 \times 10^{-3}$ Einstein per minute by actinometry [20]. During all experiments, the reaction solution was vigorously mixed from the reactor bottom by means of a magnetic stirrer at 400 rpm to provide effective mixing and aeration of the reactions solution. The (dark) Fenton-like experiments were conducted in the same beaker except that the UV-A light source was not turned on for these experiments.

2.3. Analytical procedure

BOD_5 and COD measurements were conducted in accordance with standard methods [21]. For the BOD_5 measurements real sewage sludge that was previously acclimated to an aqueous glucose + peptone (including all necessary buffers and nutrients) solution was used as the seed source. The following chemicals were used in the form of stock solutions: The reagents $Fe(NO_3)_3 \cdot 9H_2O$ (0.25 M) and H_2O_2 (11.42 M) as well as H_2SO_4 and NaOH (6 N) for pH adjustment. TOC (total organic carbon) measurements were performed on a calibrated organic carbon analyzer (Shimadzu TC-1000).

2.4. Experimental procedure

For experimental analyses samples of the reaction medium were withdrawn at regular time intervals ($t =$ 0–30 min). Residual iron and H_2O_2 were removed prior to COD measurements in order to prevent their positive interference with the analytical procedure and in particular with the COD measurements. Ferric iron was precipitated out by increasing the pH of the reaction solution to pH $\geq$ 9.5. The remaining, unreacted H_2O_2 was destroyed with diluted enzyme catalyst solution made from *Micrococcus lysodeikticus* (Fluka Chemie; 174380 AU/ml; one activity unit destroys 1 μmol H_2O_2 at $T = 20\,^{\circ}C$ and pH = 7 in 1 min).

Residual (unreacted) hydrogen peroxide was determined in separate experiments via molibdate-catalyzed iodometric spectrophotometry [22].

2.5. Acute toxicity assessment

Acute toxicity of the raw and pre-treated samples was tested using 24 h-born water flea *Daphnia* as described in Standard Methods [21]. Test animals were grown by a 16 h light (with 1000 lx), 8 h dark cycle. They were regularly fed with the algae *Selenastrum capricornutum* (300,000 cells/ml) and *Schizosaccharomyces cerevisiae* (200,000 cells/ml) as well as baker's yeast. Acute toxicity tests were repeated four times using 20 daphnids in 50 ml-test beakers at a pH of 8.0, providing a minimum dissolved oxygen concentration of 6 mg/l at $T = 20\,^{\circ}C$ constant temperature. A blank was also run in parallel series. Results were expressed as percent death or immobilization out of 20 young test daphnids after 24 h. The ED_{50} (in percent volumetric basis) value for the raw effluent that is defined as the percent effective dilution of the effluent sample causing 50% death or immobilization of young test organisms (in the present study the water flea *Daphnia magna*) at different dilution rates of PPG, has been calculated from interpolation of percent dilution versus percent death semi-logarithmic plots that have been established for different sample dilutions.

3. Results and discussion

3.1. Effect of initial Fe^{3+} concentration

All preliminary optimization experiments have been performed under UV-A light irradiation. To elucidate the role of initial Fe^{3+} concentration on the photo-Fenton-like oxidation of PPG formulation effluent, a series of experiments varying the concentration of iron between 0.1 and 5 mM thereby keeping the initial hydrogen peroxide concentration
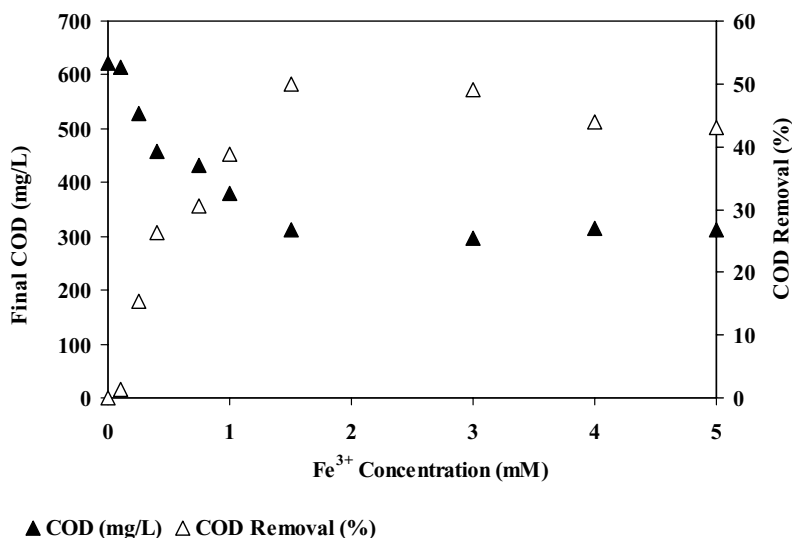
Fig. 2. Effects of Fe^{3+} ion dose on COD removal rates obtained for PPG formulation effluent oxidation with $Fe^{3+}/H_2O_2/UV$-A. Experimental conditions: $[H_2O_2]_o = 20$ mM, pH $= 3$, $COD_o = 623$ mg/l, treatment time $= 30$ min.

fixed at $[H_2O_2] = 20$ mM, were carried out. Fig. 2 presents the effects of Fe^{3+} ion concentration on the COD removal from PPG formulation effluent. From the figure it can be seen that an increase of the applied Fe^{3+} concentration up to 1.5 mM has a positive effect upon COD removal efficiency. At concentrations exceeding 1.5 mM Fe^{3+}, COD removal rates decreased slightly, revealing that an optimum ferric iron concentration exists for effective COD abatement. This may be attributable to the formation of an orange-brown iron precipitate (ferric hydroxide flocs) in the reaction solution during photochemical treatment, hindering effective light absorption and hence ferric iron photo-reduction. Photochemically-induced ferrous iron formation as shown in Eq. (7) is thought to be the slow, rate determining step of the photo-Fenton-like reaction [7]. For an initial Fe^{3+} concentration of 1.5 mM, 50% COD removal was obtained after 30 min treatment. Considering the above mentioned results, the optimum Fe^{3+} concentration was selected as 1.5 mM for the proceeding experiments.

The presence of an optimum ferric iron concentration is in complete agreement with a recent study of Rodríguez et al. [18]. In their work, the photo-Fenton process was applied to improve the ultimate biodegradability of otherwise refractory textile industry wastewater. An optimum Fe^{3+} concentration of 1.4 mM has been found for effective mineralization.

In another study, Wu et al. [23] investigated the photodegradation of Malachite Green (MG) under visible light irradiation ($\lambda > 470$ nm) in the presence of Fe^{3+}/H_2O_2 or Fe^{2+}/H_2O_2 in comparison with their corresponding dark reactions. They found that visible light irradiation significantly accelerated MG degradation and the optimum Fe^{3+} concentration was found determined as 0.4 mM.

3.2. Effect of initial H_2O_2 concentration

The selection of an optimum H_2O_2 concentration for PPG formulation effluent degradation is very important in order to achieve maximum treatment performance and particularly due to the cost of H_2O_2. The effect of initial H_2O_2 concentration on final COD and percent COD removal efficiency was investigated by the addition of various concentrations of the H_2O_2 to the PPG formulation effluent. Photo-Fenton-like oxidation of PPG formulation effluent was investigated at varying initial H_2O_2 concentrations between 5 and 40 and 1.5 mM Fe^{3+} at pH $= 3$. It was found that percent COD removal increased with increasing H_2O_2 dose up to a maximum value of 56% obtained at a H_2O_2 concentration of 25 mM. Upon further increase of H_2O_2, COD removal leveled off due to the fact that H_2O_2 itself may act as a $^\bullet$OH scavenger at excessive levels in accordance with the bimolecular reaction given below [18];

$$^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O,$$
$$k_{\bullet OH, H_2O_2} = 2.7 \times 10^7 M^{-1} s^{-1} \qquad (9)$$
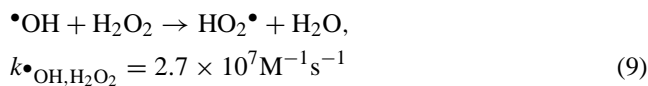
Considering the above indicated results, the appropriate initial H_2O_2 concentration was selected as 25 mM for the succeeding experiments. Fig. 3 elucidates the consequences of increasing H_2O_2 concentration on the COD removal of PPG formulation effluent with photo-Fenton-like process.

Conclusively, the optimum $Fe^{3+}:H_2O_2$ molar ratio that was required for the highest COD removal efficiency in the present work was established as 1:17 for the Photo-Fenton process.
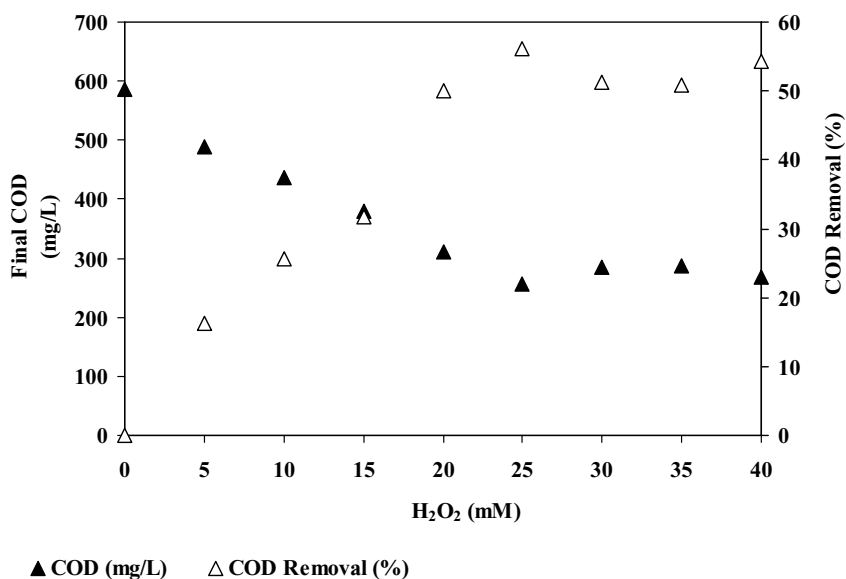
Fig. 3. Effects of H_2O_2 dose on COD removal rates obtained for PPG formulation effluent oxidation with $Fe^{3+}/H_2O_2/UV$-A. Experimental conditions: $[Fe^{3+}]_o = 1.5$ mM, pH = 3, $COD_o = 586$ mg/l, treatment time = 30 min.

3.3. Baseline experiments for the photo-Fenton-like process

The comparison of the different baseline experiments in terms of final effluent COD and COD removal efficiencies is presented in Fig. 4.

Photo-Fenton-like, Fenton-like, UV-A irradiation alone, Fe^{3+}/UV-A and H_2O_2/UV-A experiments were conducted in order to investigate their individual and composite effects on the degradation of PPG formulation effluent. By the photo-Fenton-like and Fenton-like processes run at optimum reaction conditions for PPG formulation effluent COD_o adjusted to 600 mg/l, 56 and 44% COD removals were achieved after 30 min treatment, respectively. On the

other hand, only 4% of COD removal was observed for the Fe^{3+}/UV-A process conducted in the absence of H_2O_2, and no COD removal was obtained for H_2O_2/UV-A and UV-A only control experiments, speaking for $^{\bullet}OH$ involvement for effective PPG oxidation. However, the contribution of ferric iron photo-reduction to $^{\bullet}OH$ production is only minor as compared with that of in situ formed Fe^{2+} iron-catalyzed H_2O_2 decomposition, known as the Fenton's reaction and shown in reaction (1). Fig. 4 also indicates that the Fenton-like process is slightly enhanced upon UV-A light irradiation.

In conclusion, in terms of COD removal rates obtained after 30 min treatment PPG formulation effluent
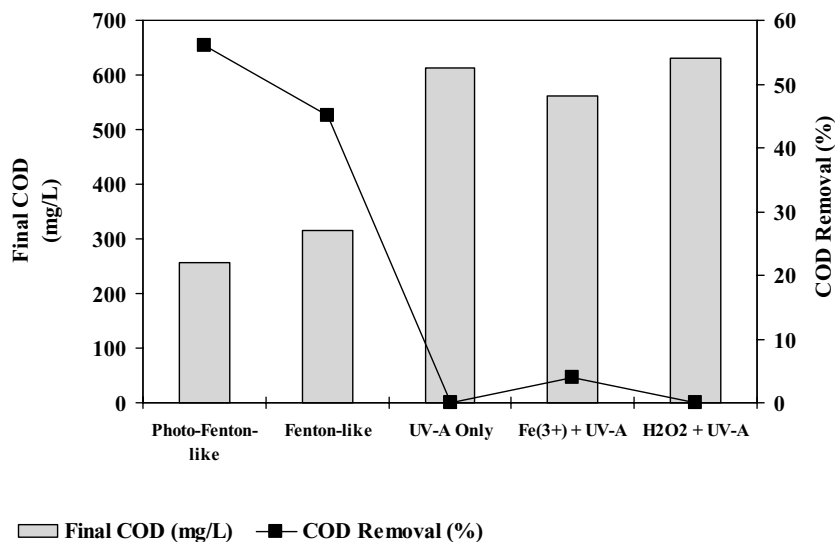

Fig. 4. Baseline experiments for photochemical treatment of PPG formulation effluent. Experimental conditions: $[Fe^{3+}]_o = 1.5$ mM, $[H_2O_2]_o = 25$ mM, pH = 3, $COD_o = 585$ mg/l, treatment time = 30 min.

degradation proceeded in the following decreasing order: $Fe(III)/H_2O_2/UV-A > Fe(III)/H_2O_2 > Fe(III)/UV-A > H_2O_2/UV-A = UV-A$.

3.4. Kinetic comparison of photo-Fenton-like and Fenton-like processes

Upon irradiation with UV, near-UV (UV-A) and visible light, iron salts can promote the photocatalytic oxidation of organic compounds at faster rates and lower concentrations than is typically the case for dark Fenton or Fenton-like processes. The principal reaction being responsible for accelerated $^\bullet OH$ formation is the pH-dependent photo-dissociation of Fe(III)–hydroxy complexes, mainly in the form of $Fe(OH)^{2+}$, as has already been given as the initiation reduction in the reaction (7) [24].

Fig. 5(a) presents changes in COD values of PPG formulation effluent during $Fe^{3+}/H_2O_2/UV-A$ and Fe^{3+}/H_2O_2 oxidation as a function of treatment time. From the figure it is obvious that unlike the Fenton process (Fe^{2+}/H_2O_2) where the immediate reaction of ferrous iron with hydrogen peroxide causes a fast, practically instantaneous oxidation of the parent pollutant or environmental sum parameter,

an initial lag-phase was observed for treatment with dark and the UV-A light-assisted Fenton-like reagents, wherein no COD removal was observed. The reasons for this delay in COD abatement could be attributed to the preliminary formation of oxidation intermediates that are resistant to oxidation. These first PPG intermediates (shown as $R^\bullet$ in the following reaction) may complex Fe^{3+}, forming more photo-active, transient species that further degrade to reactive oxidation products [25];

$$PPG + {}^\bullet OH \rightarrow R^\bullet + Fe(III)$$
$$\rightarrow R–Fe(III)^* \rightarrow Fe(II) + R^+ \qquad (10)$$
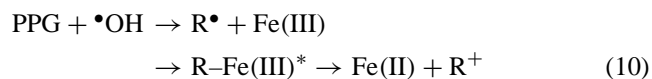
It could be demonstrated that after 10 min treatment COD started to decrease progressively leading to significant COD removals even after 30 min reaction. However, further extension of the treatment time to 60, 90, 120 and 180 min did not significantly improve COD removal efficiencies and the fast COD abatement that started after 10 min treatment appreciably slowed down after 30–40 min. The ultimate COD removal rates were found as 61 and 55% after 3 h for photo-Fenton-like and Fenton-like processes, respectively (not shown data). Hence, the effective reaction time for
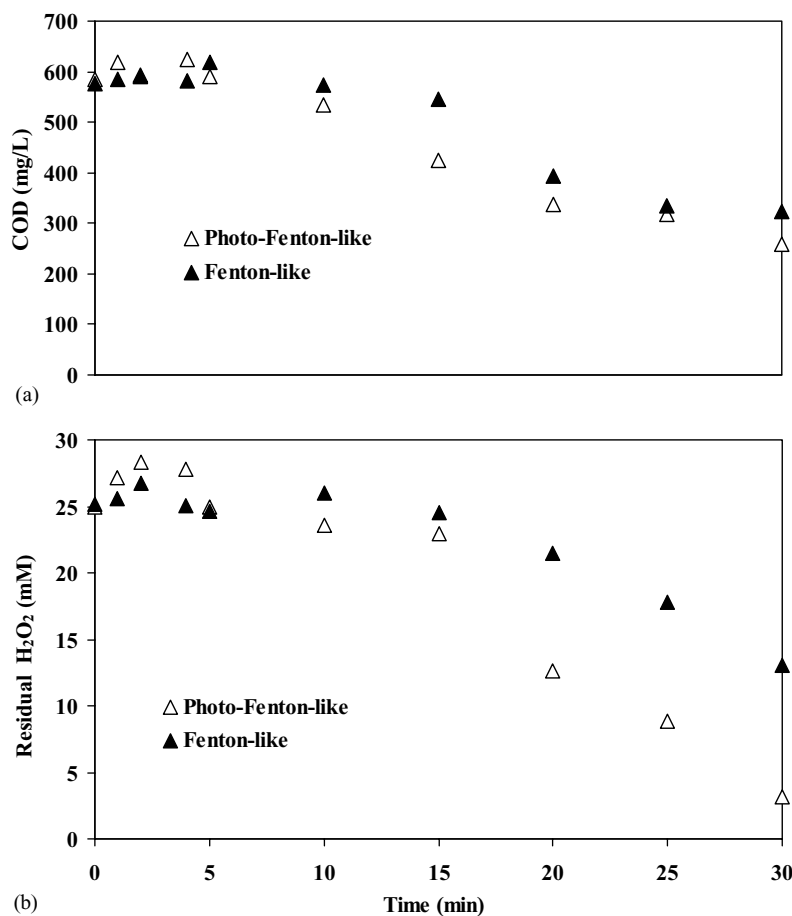

Fig. 5. (a) COD and (b) H_2O_2 abatement rates for photo-Fenton-like and Fenton-like experiments. Experimental conditions: $[Fe^{3+}]_o = 1.5$ mM, $[H_2O_2]_o = 25$ mM, pH = 3, treatment time = 30 min.

acceptable COD abatement was fixed as 30 min and this time period was used in all subsequent PPG formulation effluent treatment experiments.

The fate of H_2O_2 during Fenton-like and photo-Fenton-like processes was also investigated in separate experiments. Fig. 5(b) depicts H_2O_2 consumption kinetics observed during dark and UV-A light assisted Fenton-like experiments at optimized reaction conditions. From the figure it is evident that H_2O_2 abatement via reactions (1) and (3) was proportional to COD removal kinetics. For instance, only approximately 3 mM H_2O_2 remained in the reaction medium for the photo-Fenton-like process, whereas a residual H_2O_2 of 13 mM was finally measured for the dark Fenton-like reaction, corresponding to 88 and 48% H_2O_2 consumption, respectively.

The high residual H_2O_2 observed for the less efficient Fenton-like process is attributable to the relatively slow and poor COD abatement kinetics obtained for the dark reaction. In order to demonstrate the superiority of the UV-A light assisted Fenton-like process under different reaction conditions, photo-Fenton-like and Fenton-like treatment of PPG formulation effluent were also kinetically compared. COD abatement rates could be expressed as a first-order reaction according to the following equation:

$$\frac{dCOD}{dt} = -k_{COD} \times COD \qquad (11)$$

where k_{COD} is the first-order COD abatement rate constant (expressed in min^{-1}) for PPG formulation effluent degradation by Fenton-like and photo-Fenton-like oxidation processes. Time dependent changes in COD values of PPG formulation effluent could be fitted to first-order reaction kinetics for specified time intervals depending upon the duration of the lag period for the Fenton-like and photo-Fenton-like experiments. Table 1 summarizes k_{COD} values obtained for dark and UV-A light assisted Fenton-like reactions at two different initial Fe^{3+} (0.5 and 1.5 mM) and H_2O_2 (20 and 25 mM) concentrations together with the treatment process-specific time interval wherein first-order COD removal kinetics were observed.

From Table 1 it is obvious that the positive effect of UV-A light assistance is more pronounced at low oxidant and catalyst concentrations. While COD removal rate decreased dramatically from 44 to only 3% as is also reflected by the k_{COD} being close to zero for 0.5 mM Fe^{3+}/20 mM H_2O_2, COD removal kinetics obtained for the photo-Fenton-like process

were not significantly inhibited at low concentrations of hydrogen peroxide and ferric iron. The obtained results reveal that the photo-Fenton-like process should be preferred to minimize chemical requirements if only partial COD removal is aimed. At optimized concentrations (1.5 mM Fe^{3+} and 25 mM H_2O_2) the photo-Fenton-like is still a bit faster than the dark Fenton-like reaction.

3.5. Effect of initial COD

Wastewaters from the formulation subcategory of the pharmaceutical industry are usually classified as mid-strength COD wastewaters (COD = 300–2100 mg/l, BOD_5 = 70–1000 mg/l) [26]. In the present study, an initial COD value of 600 mg/l has been selected to represent typical COD values for PPG formulation effluent. Photo-Fenton-like experiments were carried out to define effectiveness of the optimized experimental conditions for different initial COD values (200, 400, 800 and 100 mg/l) besides 600 mg/l. Fig. 6 shows the effect of varying the initial COD of PPG formulation effluent on COD removal efficiency. For the optimum initial concentrations of Fe^{3+} and H_2O_2 and under UV-A light irradiation, 56, 52, 59, 39 and 27% COD removals were obtained for the initial respective COD values 200, 400, 600, 800 and 1000 mg/l. The results presented in Fig. 6 demonstrate that COD removal efficiency decreased dramatically with increasing penicillin formulation effluent strength and that the optimum reaction conditions selected for an initial COD of 600 mg/l have to be re-established for higher initial COD values.

3.6. Biodegradability improvement

The BOD/COD ratio constitutes an appropriate measure of the biodegradability of a wastewater. Accordingly, effluents with BOD_5/COD ratios exceeding 0.4 may be considered as readily biodegradable [27,28]. Fig. 7 depicts BOD_5/COD values of the PPG formulation effluent before and after pre-treatment with the photo-Fenton-like and Fenton-like processes at optimized reaction conditions. As is evident in Fig. 7, the BOD_5/COD ratio increased from 0.10 to 0.45 after application of the photo-Fenton-like process, but only to 0.24 after dark Fenton-like oxidation, indicating that photo-Fenton-like pre-treatment of PPG formulation effluent is by far more effective in biodegradability

Table 1
First-order COD abatement rate constants (k_{COD} values), obtained correlation coefficients (R^2) and time intervals (t) selected for kinetic evaluation of PPG formulation effluent advanced oxidation at varying initial concentrations of Fe^{3+} and H_2O_2

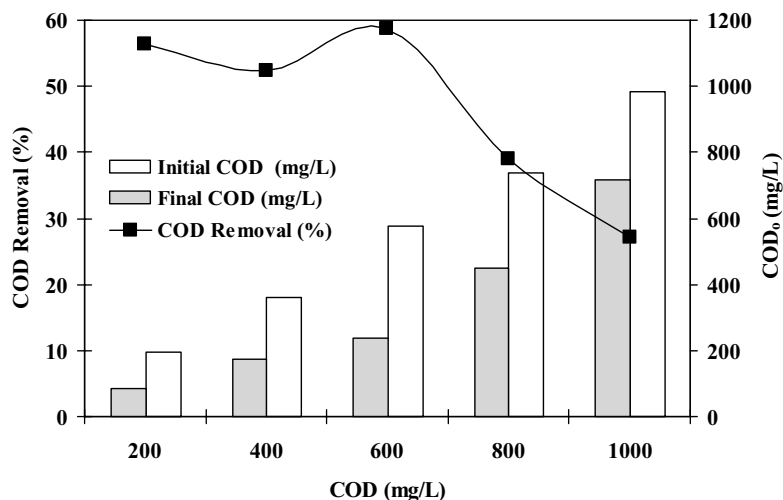| Type of process	$[Fe^{3+}]_o$ (mM)	$[H_2O_2]_o$ (mM)	$k_{COD} \times 10^2$ (min^{-1})	R^2	t (min)
Photo-Fenton-like	1.5	25	3.4	0.98	5–30
	0.5	20	3.0	0.96	20–30
Fenton-like	1.5	25	3.0	0.93	5–30
	0.5	20	1.2	0.99	20–30

Fig. 6. COD removal rates obtained for the photo-Fenton process at different initial COD values. Experimental conditions: $[Fe^{3+}]_o = 1.5\,mM$, $[H_2O_2]_o = 25\,mM$, pH = 3, treatment time = 30 min.

improvement than the Fenton-like reaction. It can also be concluded that a significant change in biodegradability is only attained when the parent compound (being the ultimate source of recalcitrance in the PPG formulation effluent) is thoroughly oxidized. Although the Fenton-like process was almost as effective as the UV-A light assisted Fenton-like oxidation in terms of COD removal at optimized reaction conditions, from the above indicated results it can be inferred that photocatalytic reaction products seemed to be more biodegradable than those of the dark Fenton-like process.

Similar results have recently been reported by Chamarro et al. [28] who applied the Fenton's reagent for the oxidation of formic acid, phenol, 2,4-dichlorophenol and nitrobenzene. They have found that treatment with Fenton's reagent increased the biodegradability ratio (=BOD_5/COD) from practically 0 to 0.4 for 4-chloropenol. Also, an acceptable biodegradability could only be achieved when the initial, recalcitrant pollutant (original, parent compound) was completely eliminated. In a related study, Sarria et al. [27] investigated the oxidation of 5-amino-6-methyl-2-benzimidazolone (AMBI), an important precursor in the industrial production of dyes, by photo-assisted Fenton's reaction. It could be established that pre-treatment of AMBI produces completely biocompatible products that could be completely mineralized by a succeeding biotreatment step.

3.7. Chloride ion as a free radical scavenger

In order to provide evidence that the major oxidizing agent of the Fenton-like and photo-Fenton-like processes applied for PPG formulation effluent degradation is the $^\bullet$OH radical, chloride ion (Cl$^-$) was selected as the $^\bullet$OH probe compound. Cl$^-$ ion has been selected for its well-known strong free radical scavenging effect at acidic pH [6,8,29]. It has
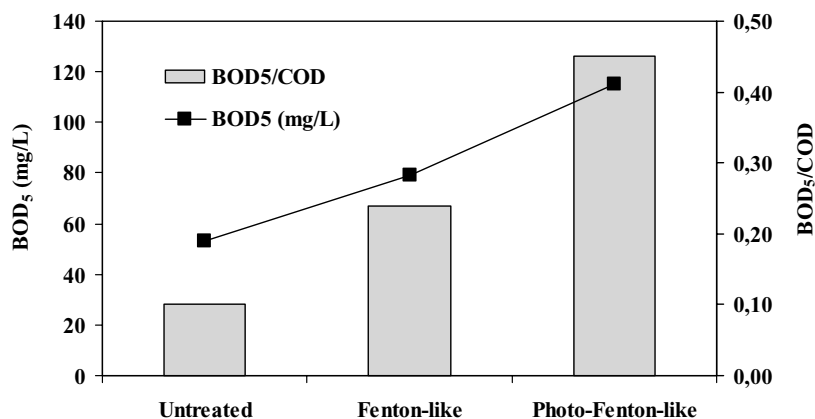

Fig. 7. Biodegradability results for PPG formulation effluent before and after chemical pre-treatment. Experimental conditions: $[Fe^{3+}]_o = 1.5\,mM$, $[H_2O_2]_o = 25\,mM$, pH = 3; treatment time = 30 min.
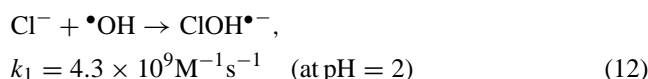
Table 2
The effect of varying Cl^- concentrations on percent COD removal efficiencies and final COD values obtained for PPG formulation effluent after chemical oxidation

Cl^- (mg/l)	Fenton-like		Photo-Fenton-like	
	COD (%)	Final COD (mg/l)	COD (%)	Final COD (mg/l)
0	44	324	56	257
152	30	400	42	344
303	25	447	37	376
455	20	453	30	417
607	17	486	23	466
910	16	546	21	480
1214	14	567	17	491

Experimental conditions: $[Fe^{3+}]_o = 1.5$ mM, $[H_2O_2]_o = 25$ mM, pH = 3, treatment time = 30 min.

been postulated that Cl^- vigorously reacts with $^\bullet OH$ to form $ClOH^{\bullet -}$ as is given below [30]:

$$Cl^- + {}^\bullet OH \rightarrow ClOH^{\bullet -},$$
$$k_1 = 4.3 \times 10^9 M^{-1} s^{-1} \quad \text{(at pH = 2)} \qquad (12)$$

Considering the above indicated kinetic equation, Cl^- ion was added to PPG formulation effluent at varying concentrations ranging between 152 and 1214 mg/l before initiating the Fenton-like and photo-Fenton-like reactions at optimized conditions. The chloride concentration was not elevated further because at chloride concentrations exceeding 1500 mg/l, chloride started to interfere with COD measurements. The effect of increasing Cl^- ion concentration on COD removal efficiency is shown in Table 2.

From the above table it is evident that an increase in Cl^- ion concentration led to a significant decrease in COD removal efficiencies for both oxidation processes. At the highest studied chloride concentration, COD removal efficiencies gradually dropped to almost complete inhibition of PPG oxidation. These results are indirect evidence that mainly $^\bullet OH$ radicals are involved in both oxidation processes.

3.8. Effects on acute toxicity

Antibiotic formulation effluents contain high concentrations of refractory compounds may potentially inhibit activated sludge processes and cause toxic effects on aquatic organisms in receiving water bodies where they are discharged after biological treatment [5]. Hence, on-site chemical pre-treatment is a general requirement for antibiotic formulation effluent prior to discharge into biological treatment plants publicly owned sewage treatment works, the latter being the most often case in Turkey.

Acute and long-term toxicity effects of antibiotics are well known. For instance, Kümmerer et al. [4] studied the biodegradability and genotoxicity of some clinically important antibiotic drugs. None of the tested chemicals were biodegradable and they imparted serious genotoxicity.

Table 3
Percent death rates for *Daphnia magna* obtained before and after Fenton-like and photo-Fenton-like pre-treatment of PPG formulation effluent

Type of process	Death in 25% PPG dilution (%)	Death in 50% PPG dilution (%)
No treatment	25	60
Photo-Fenton-like	0	35
Fenton-like	10	n.d.[a]

Experimental conditions: $[Fe^{3+}]_o = 1.5$ mM, $[H_2O_2]_o = 25$ mM, pre-treatment pH = 3, pre-treatment time $t = 30$ min, percent ED_{50} value of raw PPG formulation effluent = 43% (on volumetric basis).

[a] n.d.: Not determined.

Similarly, Wollenberg et al. [3] carried out the acute and the chronic toxicity tests on nine antibiotics used both therapeutically and as growth promoters in intensive farming on the fresh water crustacean *Daphnia magna*. From their observations they have concluded that oxalic acid may potentially cause adverse effects on the aquatic environment. In another study, Goi and Trapido [31] demonstrated that the Fenton's reagent appeared to be the most efficient and cheapest way for the detoxification of nitrophenols.

In the present part of the study, acute toxicity of raw and pre-treated PPG formulation effluent was investigated using *Dapnia magna* as the test organism. Table 3 presents acute toxicity test results for raw (untreated) as well as photo-Fenton-like and Fenton-like treated PPG formulation effluent.

Based on the acute toxicity test results presented in Table 3 it can be concluded that photo-Fenton-like pre-treatment is a suitable method for complete detoxification of PPG formulation effluent.

3.9. Effects on TOC abatement

It has been established that although both the $Fe(II)/H_2O_2$ and $Fe(III)/H_2O_2$ reagents are capable of completely degrading refractory organic chemicals, neither one is able to mineralize these pollutants completely. The extent of TOC removal (mineralization) was reported to be independent of the oxidation state of the iron source employed and to reach ultimately about 40–60%, depending on the amount of added Fe^{2+}/Fe^{3+}, H_2O_2 as well as reaction temperature, all of which have to be optimized for every case study [13]. In Table 4 final TOC values and percent TOC removal efficiencies obtained after employing Fenton-like and

Table 4
Percent TOC removal and final TOC values obtained for pre-reatment of PPG formulation effluent with Fenton-like and photo-Fenton-like oxidation processes

Type of process	TOC removal (%)	Final TOC (mg/l)
Photo-Fenton-like	42	259
Fenton-like	35	294

Experimental conditions: $[Fe^{3+}]_o = 1.5$ mM, $[H_2O_2]_o = 25$ mM, pre-treatment pH = 3, pre-treatment time $t = 30$ min.

photo-Fenton-like oxidation processes for PPG formulation effluent mineralization are summarized.

From the above table it is clear that in complete accordance with obtained COD removal rates, biodegradability ratios and acute toxicity test results, UV-A light has also an accelerating effect on TOC removal from PPG formulation effluent. Considerable enhancement in TOC abatement rates for photo-assisted Fenton-like oxidation has already been evidenced in former experimental work [32].

4. Summary and conclusions

The present study reports the treatability of synthetic penicillin formulation effluent bearing Procaine Penicillin G (PPG) with the photo-Fenton-like and Fenton-like advanced oxidation processes. The following conclusions could be drawn from the experimental results.

Optimum Fe^{3+} and H_2O_2 concentrations to achieve the highest COD removal efficiency have been established as 1.5 mM and 25 mM, respectively, for photo-Fenton-like oxidation of PPG formulation effluent ($COD_o = 600$ mg/l).

At optimized reaction conditions, 56 and 44% COD removal were obtained after 30 min treatment with photo-Fenton-like and Fenton-like processes, respectively. Further extension of reaction time did not appreciably improve COD removal for both processes.

Photo-Fenton-like and Fenton-like processes followed first-order kinetics with respect to COD removal rates. UV-A light irradiation had a profound effect on COD abatement kinetics of PPG formulation effluent. The accelerating influence of UV-A light irradiation was more evident at low Fe^{3+} and H_2O_2 concentrations, where the dark reaction failed to remove COD effectively.

H_2O_2 consumption almost paralleled the COD abatement rates. Nearly 90% of the initially present H_2O_2 was depleted at the end of the photo-Fenton-like process, indicating the correlation between oxidant consumption and oxidation efficiency.

Varying the initial COD of the PPG formulation effluent beyond a critical value without changing the oxidant and catalyst concentration inhibited COD removal performance dramatically. COD removal efficiency decreased at COD values higher than 600 mg/l speaking for the necessity of organic loading oriented process optimization for antibiotic formulation effluent.

Biodegradability of the PPG formulation effluent expressed as the BOD_5/COD ratio increased from 0.10 to 0.45 after application of the photo-Fenton-like process, but only to 0.24 for the Fenton-like process, indicating that the photo-assisted Fenton-like process was more effective in biodegradability improvement than the dark oxidation reaction.

Increase of Cl^- ion concentration which was selected as the $^{\bullet}OH$ probe compound for the present study, led to a significant decrease in COD removal rates for both

Photo-Fenton-like and Fenton-like reactions revealing that in both processes the major oxidizing specie is the $^{\bullet}OH$ radical.

Based on the results obtained for biodegradability, acute toxicity and TOC abatement experiments, it can be inferred that the photo-Fenton-like treatment is the more suitable method for biodegradability improvement, complete detoxification, and effective mineralization of PPG formulation effluent.

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