

Pre-treatment of penicillin formulation effluent by advanced oxidation processes

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Abstract

A variety of advanced oxidation processes (AOPs; O_3/OH^- , H_2O_2/UV , Fe^{2+}/H_2O_2 , Fe^{3+}/H_2O_2 , $Fe^{2+}/H_2O_2/UV$ and $Fe^{3+}/H_2O_2/UV$) have been applied for the oxidative pre-treatment of real penicillin formulation effluent (average $COD_0 = 1395$ mg/L; $TOC_0 = 920$ mg/L; $BOD_{5,0} \approx 0$ mg/L). For the ozonation process the primary involvement of free radical species such as OH^\bullet in the oxidative reaction could be demonstrated via inspection of ozone absorption rates. Alkaline ozonation and the photo-Fenton's reagents both appeared to be the most promising AOPs in terms of COD (49–66%) and TOC (42–52%) abatement rates, whereas the BOD_5 of the originally non-biodegradable effluent could only be improved to a value of 100 mg/L with $O_3/pH = 3$ treatment (BOD_5/COD , $f = 0.08$). Evaluation on COD and TOC removal rates per applied active oxidant (AOx) and oxidant (Ox) on a molar basis revealed that alkaline ozonation and particularly the UV-light assisted Fenton processes enabling good oxidation yields (1–2 mol COD and TOC removal per AOx and Ox) by far outweighed the other studied AOPs. Separate experimental studies conducted with the penicillin active substance amoxicillin trihydrate indicated that the aqueous antibiotic substance can be completely eliminated after 40 min advanced oxidation applying photo-Fenton's reagent ($pH = 3$; $Fe^{2+}:H_2O_2$ molar ratio = 1:20) and alkaline ozonation (at $pH = 11.5$), respectively.

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1. Introduction

Since the late 1980s a variety of pharmaceuticals have been reported to be present in surface water and effluent of sewage treatment plants (STPs) indicating their poor biodegradability in municipal sewage and STPs [1,2]. Because of their toxicity to various microorganisms, poor microbial elimination efficiencies are particularly expected for antibiotics and various countries regulate the level of antibacterial residues in agricultural, veterinary, dairy, and meat-based food products [2–4].

As a consequence, separation and pre-treatment of antibiotic synthesis and formulation effluent from the total pharmaceutical wastewater should be considered since biological activated sludge processes are practiced at STPs and most pharmaceutical industries [5,6]. For example, during the formulation stage of antibiotics, highly diluted but still toxic

and/or recalcitrant liquid effluent is generated for which alternative chemical treatment methods (i.e. granular activated carbon adsorption, ozonation, Fenton's oxidation and co-precipitation) have to be employed for pre-treatment and biodegradability improvement. Until now, only few studies dealing with the advanced oxidation of antibiotic substances found in water or wastewater have been reported in the scientific literature [7–12].

Advanced oxidation processes (AOPs) have been defined as aqueous phase oxidation processes which are based primarily on the intermediacy of the hydroxyl radical (OH^\bullet) attacking aggressively and almost non-selectively inorganic as well as organic compounds, including a variety of xenobiotics and micropollutants [13–15]. An immense body of literature has been already devoted to the applications of AOPs to industrial effluents of diverse nature. The most widely known and effective AOPs include ozonation combined with UV-light and/or H_2O_2 , Fenton, photo-Fenton reagents (homogenous AOPs) and heterogeneous, mainly TiO_2 -mediated photocatalysis, all of which have specific advantages and drawbacks [14–16]. Either generation of ozone or production

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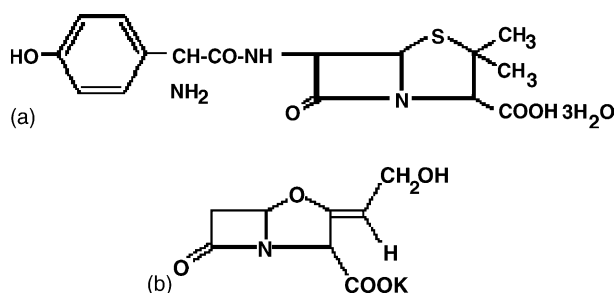


Fig. 1. Chemical structure of amoxicillin trihydrate (a), i.e. the penicillin formulation active agent, and potassium clavulanate (b).

of OH^\bullet via artificial UV-light as in the case of the $\text{H}_2\text{O}_2/\text{UV-C}$ and photo-Fenton processes require a significant energy and chemicals input [16]. Besides the conversion of chemical oxidizing agents (Ox) to active oxidants (AOx), i.e. free radicals for effective contaminant degradation is a process of extremely low efficiency. The high electrical energy demand and consumption of chemical reagents make AOPs energy intense and application limited techniques that need to be carefully optimized and applied only for pre-treatment or polishing of refractory, toxic pollutants [17].

We have therefore investigated the feasibility of different AOP combinations (O_3 at elevated pH, $\text{H}_2\text{O}_2/\text{UV-C}$, Fenton and photo-Fenton processes) for the degradation and biodegradability improvement of a penicillin formulation wastewater. It was particularly aimed at lowering the refractory (non-biodegradable) organic content of the wastewater thereby achieving high partial oxidation (COD removal) and low ultimate oxidation (TOC removal) efficiencies at acceptable treatment times and reaction conditions (i.e. oxidant dose and electrical power requirements). Hereby the Ox and AOx dose per COD or TOC removal rate was also taken into account as to establish a scientific basis for selecting the most promising AOP techniques for antibiotic formulation effluent. The efficiency of AOPs in completely destroying the refractory, active ingredient has also been confirmed in separate studies.

2. Experimental

2.1. Penicillin formulation effluent and chemical agents

All reagents used in the study (oxidant H_2O_2 , catalysts $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were provided at analytical grade.

The penicillin effluent used in this study was penicillin formulation washwater of BIOMENT BID[®] (active ingredient: penicillin amoxicillin trihydrate; $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_5\text{S} \cdot 3\text{H}_2\text{O}$, molecular weight = 419.4 g/mol, Fig. 1a, assisted by the β -lactamase inhibitor clavulanate potassium; $\text{C}_8\text{H}_8\text{KNO}_5$, molecular weight = 237.3 g/mol, Fig. 1b), which was supplied by a pharmaceutical company located in Istanbul,

Table 1

Chemical composition of the penicillin formulation (the exact amount of active agent and inactive ingredients, i.e. formulation additives was strictly confidential)

Formulation component	Function
Amoxicillin trihydrate	Active substance
Potassium clavulanate/syloid	Active ingredient
Xanthan gum	Additive
Sunett	Additive
Aerosil 200	Additive
Silicon dioxide	Additive
Dry lemon	Flavor
Tutti frutti	Flavor
Citric acid anhydrous	Buffer

Turkey. The selected washwater corresponded to approximately 24% of the total daily effluent ($=150 \text{ m}^3/\text{day}$), of which 47% was process water. The collected effluent was stored at $2\text{--}4^\circ\text{C}$ before use for up to 4 weeks. Prior to all experiments, effluent suspensions were filtered through glass fiber filters with a pore size of $1.2 \mu\text{m}$ to obtain a clear reaction solution. The formulation composition and corresponding effluent characterization (i.e. the mixture of all washwaters) are summarized in Tables 1 and 2, respectively. In separate treatability experiments advanced oxidation of aqueous amoxicillin was investigated in order to demonstrate the degradability of the active substance. The concentration of amoxicillin active ingredient for these experiments was selected considering its maximum concentration being expected in formulation washwater (i.e. $<400 \text{ mg/L}$). This practical information has been obtained from the staff responsible of the penicillin processing stage of the pharmaceutical manufacturing plant.

2.2. The ozone reactor

One liter penicillin wastewater samples were ozonated for 1 h in a borosilicate glass bubble column in semi-batch mode

Table 2

Environmental characterization parameters for the penicillin formulation effluent

Parameter	Value
Total COD (mg/L)	1555
Filtered COD (mg/L) ^a	1395
Soluble COD (mg/L) ^b	1250
TOC (mg/L)	920
BOD ₅ (mg/L)	0.00
pH	6.95
Alkalinity (mg CaCO_3/L)	85
TSS (mg/L)	145
VSS (mg/L)	105
TKN (mg/L)	100
TP (mg/L)	8.00
Cl^- (mg/L)	105
Absorbance at $\lambda = 436 \text{ nm}$ (1 cm)	0.024

^a Filtered through glass fiber filter ($1.20 \mu\text{m}$ cutoff).

^b Filtered through membrane filter ($0.45 \mu\text{m}$ cutoff).

wherein the ozone + oxygen gas mixture was continuously sparged at a rate of 1.3 L/min through a fritted dispersion disc with a diameter of 5 cm. Ozone was produced by a corona discharge PCI GL-1 model pilot scale ozone generator with a maximum capacity of 20 g/h ozone. Teflon tubing was used for all connections from the ozone generator to the reaction vessel. All excess (unreacted) gaseous ozone leaving the column was collected in two gas washing bottles connected in series and filled with 10% KI solution, whereas two other gas washing bottles with 2% KI solution were directly placed after the gas introduction line to determine and calibrate exact O_3 input rates. Beforehand, an ozone feeding rate of 2760 mg/(L h) was selected for all ozonation experiments. Ozone transfer efficiency (i.e. absorbed ozone O_{3A} , %) was determined by measuring the input and off-gas concentrations of each pre-ozonation experiment iodometrically [18]. The mass transfer coefficient of ozone in the semi-batch reactor was determined for ozonation in acidic pure water by employing the indigo spectrophotometric method [19] as 0.22 min^{-1} .

2.3. The photoreactor for H_2O_2/UV and Fenton experiments

A 2000 mL capacity annular Plexiglas reactor equipped with a 21 W low pressure mercury arc lamp emitting UV-C light at 253.7 nm and being placed into a quartz sleeve housing was used throughout the experiments. Photochemical reactions were run for 60 min and 10–15 mL samples were taken from the reactor at regular time intervals for COD analysis. The light intensity and effective pathlength of the UV-C lamp were determined as 3.65 W/L ($=1.73 \times 10^{-4}$ Einstein/L/s) and 1.72 cm, respectively, using H_2O_2 actinometry [20]. The reaction solutions were vigorously mixed from the reactor bottom by means of a magnetic stirrer to provide a continuously mixed reaction solution throughout the experiment.

2.4. Analytical measurements

Catalase made from bovine liver (Sigma, 13 000 AU/mL at pH = 7 and 25 °C) was added for residual, unreacted H_2O_2 destruction to prevent positive interference with COD measurements. During the oxidation processes involving H_2O_2 , residual H_2O_2 was first determined via molybdate-catalyzed iodometric titration [21]. Sulfur, BOD₅ and other conventional parameters of the raw and/or treated penicillin formulation samples were measured in accordance with Standard Methods [22]. COD was determined using a procedure described in ISO 6060-1986 [23]. TOC values were measured only at optimized process conditions in accordance with the highest percentage of degraded COD.

In order to confirm that the penicillin active substance could be completely eliminated during advanced oxidation, aqueous amoxicillin trihydrate ($C_0 = 400 \text{ mg/L}$) subjected to alkaline ozonation at pH = 11.5 and to photo-Fenton's

treatment at pH = 3 (in the presence of 1 mM Fe^{2+} and 20 mM H_2O_2) has been analyzed by HPLC at the Research and Development Division of the pharmaceutical manufacturing plant from which actual penicillin formulation effluent containing at least 80% active substance (i.e. the penicillin amoxicillin trihydrate) has been obtained. The following procedure has been adopted for amoxicillin analysis by HPLC: Reprosil-Pur ODS-3 column (dimension: 250 mm × 4 mm), UVDAD detection at $\lambda = 274 \text{ nm}$; eluent = acetonitrile/ H_2O (9:1) + 0.5% v/v H_3PO_4 with a detection limit of 0.32 mg/L.

3. Results and discussion

3.1. Ozonation experiments

For the ozonation experiments the initial pH was selected as the main process variable. Fig. 2 displays COD abatement rates obtained for penicillin formulation effluent at varying initial pH values as a function of ozonation time. From Fig. 2 it is evident that COD removal rates increase with increasing pH as is expected as a consequence of enhanced ozone decomposition rates at elevated pH values. Ozone decomposition to free radicals could also be confirmed by simple comparison of the absorbed ozone rates; only 38% of the applied ozone dose was absorbed at pH = 3, whereas this rate increases to 67 and 72% at pH = 7 and pH = 11.5, respectively. This observation was strong evidence of accelerated ozone decomposition rates that is expected to improve ozone mass transfer rates as well as COD removal efficiencies [24]. However, during ozonation the effluent pH decreased gradually and not less than four units at pH = 7.0 and pH = 11.5 as a direct result of carboxylic acid accumulation, that would have considerable effects on the oxidation rate, reaction mechanism and ozone absorption rates during ozonation. Hence, two separate control experiments were conducted where effluent samples buffered at pH = 7.0 and pH = 11.5 were also ozonated for 60 min at otherwise identical conditions. In these separate control experiments, the pH value was kept at the desired pH value by adding proper amounts of KH_2PO_4 and NaOH for pH = 7.0, as well as Na_2HPO_4 and NaOH for pH = 11.5, respectively [25]. Phosphates are known to react with OH^\bullet radicals at relatively slow rates ($k_{OH^\bullet, PO_4^{3-}} = 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) as compared with other inorganic salts [26]. Hence, they have been selected as the most suitable pH buffering agents. As expected, the pH of the buffered reaction solutions remained stable (maximum changes in pH < 0.2 units). In parallel to this observation COD removal rates did not slow down and were improved appreciably as compared to the unbuffered effluent samples. At pH = 7.0, for instance, a COD reduction similar to that at pH = 11.5 for the sample with no buffer could be achieved, and the highest COD removal rate (86%) was obtained for the pH = 11.5-buffered sample. Again, ozone absorption rates for the control experiments

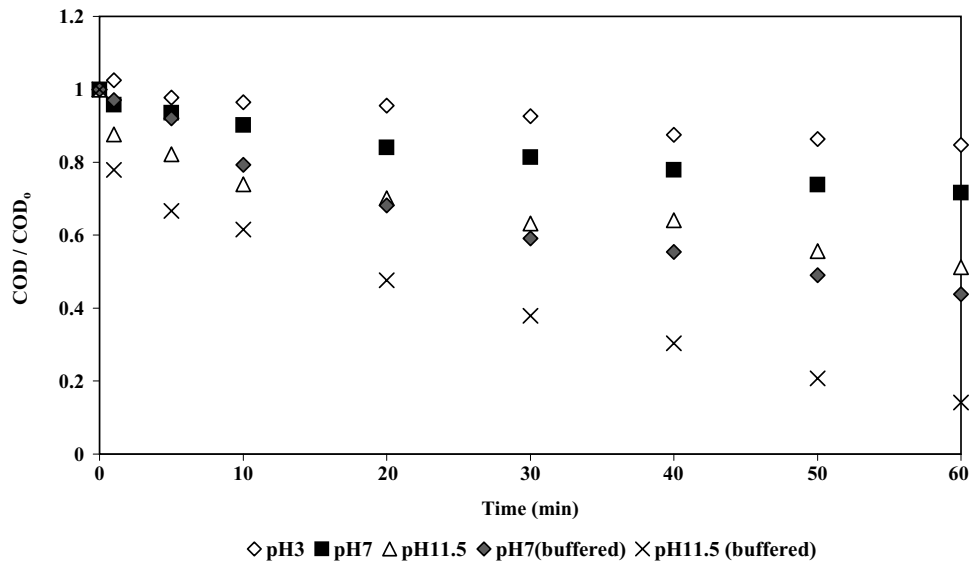


Fig. 2. Normalized COD abatement kinetics for ozonation of penicillin formulation effluent at varying pH. Applied ozone dose after 1 h = 2750 mg/L.

were found relatively high (64 and 79%) in comparison to ozonation at acidic pH, speaking for a shift in the reaction mechanism from a rather selective, molecular ozone oxidation to a faster, non-selective free radical chain reaction [27–29]. Release and successive oxidation of elemental sulfur was apparently in strong correlation with COD abatement profiles. During ozonation, an almost instantaneous increase in the “free” sulfur content followed by a rapid decrease thereafter, was observed being speculatively indicative of the release and subsequent oxidation of the S-moieties resulting. It is also worth mentioning that sulfur concentrations as high as 3 and 4.8 mg/L were found after 5 and 10 min ozonation at pH = 11.5, respectively (with unbuffered samples).

Thereafter, the sulfur content of the reaction solution fell down rapidly to practically non-detectable levels (not shown data).

3.2. H_2O_2 /UV-C experiments

UV-C only (direct UV-C photolysis) and H_2O_2 /UV experiments conducted using two different H_2O_2 doses (30 and 40 mM) at pH = 7 are shown in Fig. 3. H_2O_2 concentrations were selected considering the optimum H_2O_2 range found as 25–50 mM for different raw and biologically pre-treated industrial effluents [30]. These applied H_2O_2 doses correspond to 35% (30 mM) and 47% (40 mM) of the COD equivalent

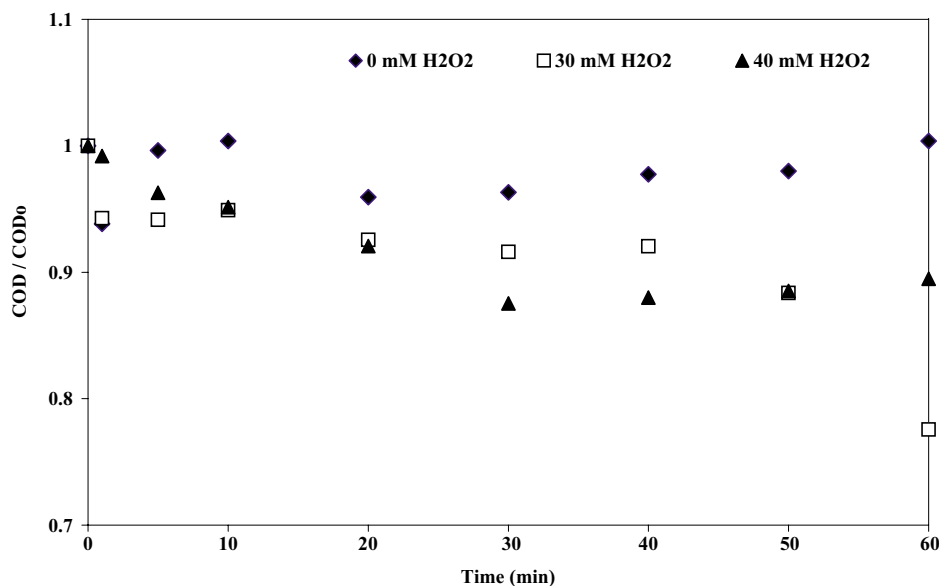


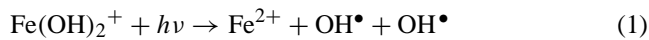
Fig. 3. Normalized COD abatement kinetics for direct UV-C photolysis, H_2O_2 /UV-C oxidation of penicillin formulation effluent with 30 and 40 mM H_2O_2 at pH 7.

H₂O₂ oxidant requirement of the penicillin formulation effluent. From the UV-C only experiment performed without H₂O₂ addition and displayed in Fig. 3 it is evident that the effluent was not degraded at all via direct UV photolysis. In addition to this observation, no increase in color being measured at $\lambda = 436$ nm was obtained for mere UV-C photolysis speaking for the absence of any significant degradation, though the abrupt build-up of a pale pink color (appearance of an absorption band at $\lambda = 525$ nm) instead delineates at least structural modifications, i.e. the possible formation of polymerization products, and hence probable changes in effluent composition. The addition of H₂O₂ only slightly improves the overall COD removal rates up to 22% for 30 mM, which is relatively speaking to the ozonation experiments a rather poor oxidation rate. Speculatively, the high UV absorbance (aromaticity) of the effluent competes with H₂O₂, having a low absorption coefficient of only $19 \text{ M}^{-1} \text{ cm}^{-1}$ at 254 nm wavelength, for UV light, thus hindering effective H₂O₂ photolysis required for the generation of OH[•] [14,15]. For this reason, generally large amounts of H₂O₂ have to be added to the wastewater making this treatment option rather impractical. On the other hand, increasing the H₂O₂ dose to 40 mM resulted in a significant inhibition of the COD abatement rate resulting in 11% COD removal because H₂O₂ acts as an OH[•] scavenger when overdosed depending upon the reaction conditions [26]. After treatment, a substantial fraction of added oxidant usually remains in the water without having reacted [5]. In fact, only 25 and 30% of the introduced H₂O₂ could be used in the present study.

3.3. Fenton and photo-Fenton experiments

Among the AOPs, dark and photo-assisted Fenton reactions have been considered as the most promising industrial wastewater pre-treatment processes with regard to their high COD removal efficiencies and rates observed for a variety

of refractory organic pollutants [31–33]. Former investigations have demonstrated that upon irradiation of the “spent” Fenton solution by UV and even near-UV-Vis light, Fe(III) species can be photoreduced to Fe(II) and thereby OH[•] is simultaneously formed. Fe(OH)₂⁺ being the dominant form of the ferric iron source at pH = 3, is photoreduced as follows [34]:



Consequently, the introduction of UV-light promotes oxidation of organic compounds in two ways, namely by supplying additional OH[•] and recycling ferrous iron to continue the Fenton reaction until all H₂O₂ is consumed. These are the major reasons why the Fenton process requires more Fe(II) salt and the reaction is usually incomplete.

Fig. 4 displays changes in COD during Fenton and Fenton-like reaction conducted with 20 mM H₂O₂ + 1 mM Fe²⁺ (Fenton process) and Fe³⁺ iron (Fenton-like process) at pH = 3. Closer inspection of the figure reveals that the oxidation rate is appreciably faster than for ozonation and H₂O₂/UV processes and that the reaction rate levels off within the first 10–15 min. This observation is typical for Fenton reactions being indicative of a direct and fast OH[•] oxidation step that slows down as soon as Fe³⁺ starts to accumulate. This is due to the fact that the Fenton-like process mainly proceeds via HO₂[•], the product of Fe³⁺ reacting with H₂O₂ and HO₂[•] is known to react 10³ to 10⁴ times slower with contaminants than OH[•]. As is obvious from Fig. 5, the Fenton process is considerably enhanced in terms of COD removal rates upon the introduction of UV-C light. The assisting effect of UV light introduction is pronounced for the Fenton-like process involving Fe(III)-salt that is in complete agreement with the aforementioned photo-Fenton-like chemistry. Moreover, comparing the initial reaction rates $R_{\text{COD},i}$ (in terms of COD removal kinetics) of the Fenton and Fenton-like reactions in the absence

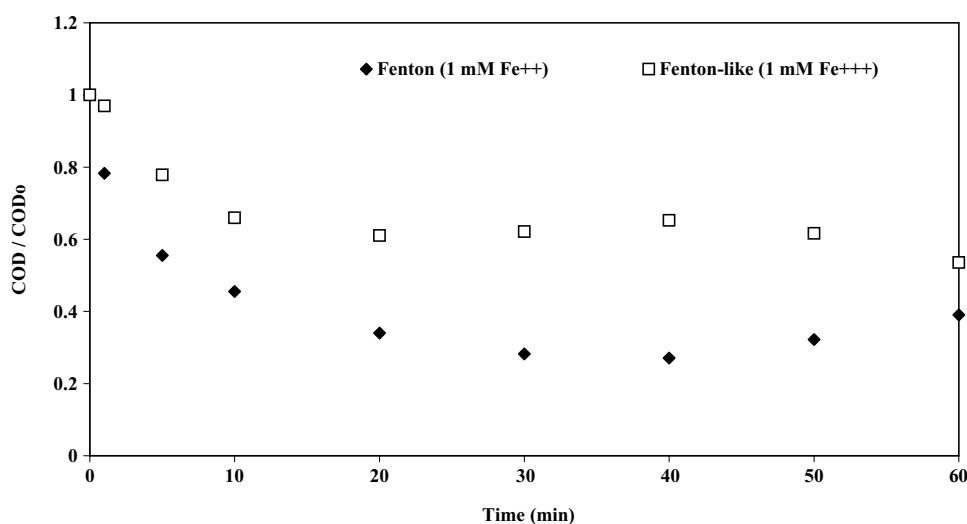


Fig. 4. Normalized COD abatement kinetics for Fenton and Fenton-like oxidation of penicillin formulation effluent with 1 mM Fe(II) or Fe(III) and 20 mM H₂O₂ at pH 3.

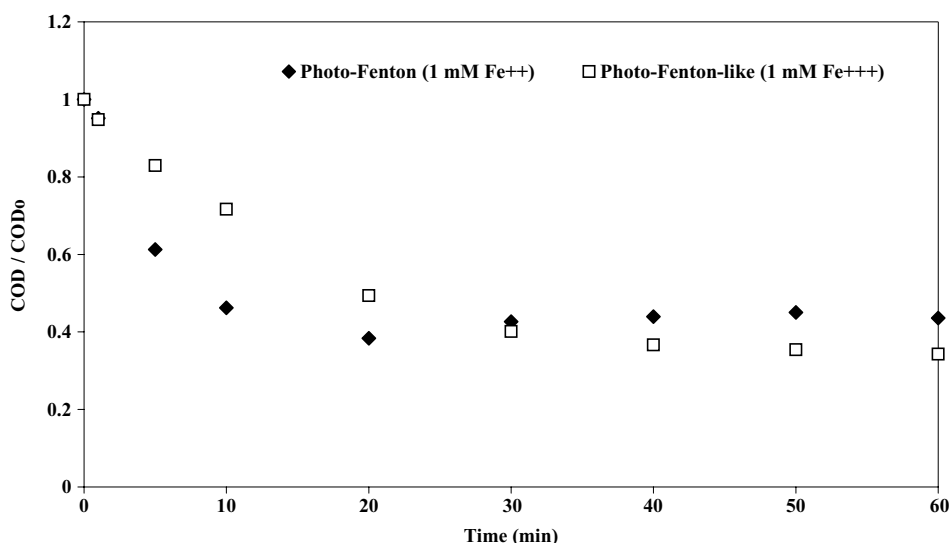


Fig. 5. Normalized COD abatement kinetics for photo-Fenton and photo-Fenton-like oxidation of penicillin formulation effluent with 1 mM Fe(II) or Fe(III) and 20 mM H₂O₂ at pH 3.

(Fig. 4) and presence (Fig. 5) of UV-light it can be clearly seen that the reactions involving Fe²⁺ are approximately 3 times faster than those involving Fe³⁺-iron ($R_{\text{COD},i,\text{Fe}^{2+}}$ in the range of 108–130 mg/L COD/min). In terms of overall COD abatement rates, however, the photo-Fenton process initiated with Fe³⁺-iron reaches the COD removal efficiency of the photo-Fenton process 20–30 min faster than during dark Fenton/Fenton-like reactions. Residual H₂O₂ measurements have demonstrated that during the Fenton and photo-Fenton reactions H₂O₂ was completely used up at the end of the experiments.

3.4. Changes in biodegradability

Ozonation and advanced oxidation may enhance the biocompatibility of industrial wastewater significantly [35]. No positive BOD₅ value of the untreated formulation effluent could be determined and hence was accepted as practically “zero”. This was also demonstrated in experimental studies of Kümmerer et al. who tested the biodegradability of some clinically important antibiotic drugs [3]. The antibiotics they have tested using a closed bottle test [36] were also found non-biodegradable. However, they recommended the assessment of different wastewater bacteria species, i.e. a broader spectrum of bacteria that would enable a more reliable simulation of STP conditions. In the present study a mixed bacterial culture adapted to synthetic, municipal domestic wastewater was used as the inoculum for the BOD₅ measurements. However, only slight improvements of the biodegradability expressed as BOD₅ were obtained after pre-oxidation with different, optimized AOPs (Fig. 6).

3.5. Active oxidant and oxidant requirements

Generally speaking it is possible to achieve high levels of COD and even TOC removals by AOPs. As has been

mentioned before, AOPs involve high electrical energy and chemical oxidant (H₂O₂, O₃) requirements. For this reason it is important to determine the relative Ox and AOx demands as to estimate the most efficient and hence practically feasible options. In the present section applied molar-based Ox and (theoretical) AOx values required for molar-based TOC and COD removals obtained after the application of different optimized oxidation processes have been determined in the following manner:

$$\text{Ox} = \frac{\text{moles of oxidant applied per mole of COD or TOC removed during treatment}}{\quad} \quad (2)$$

$$\text{Aox} = \frac{\text{moles of active oxidant (i.e. OH}^\bullet\text{) theoretically formed from the moles of applied oxidant (i.e. O}_3\text{ or H}_2\text{O}_2\text{) per mole of COD or TOC removed during treatment}}{\quad} \quad (3)$$

For this purpose the molar concentrations of the applied oxidants and moles of OH[•] theoretically expected to be formed from these chemicals (=Aox; i.e. 2 mol of OH[•] are theoretically formed from 1 mol of H₂O₂ used) were considered and used in these calculations. Results in terms of TOC and COD removal are given in Table 3. From Table 3 it is apparent that highest COD and TOC removal efficiencies per used AOx and Ox were achieved for the photo-Fenton and dark Fenton/Fenton-like processes closely followed by the O₃/pH 11.5 process. Here it should be noted that the ozonation experiments run in buffered solutions and results obtained for advanced oxidative treatment of active ingredients were not included due to the fact that these experiments have been conducted to demonstrate “real case” experimental results.

Table 4 summarizes final TOC, COD and BOD₅/COD values as well as respective TOC and COD removal efficiencies

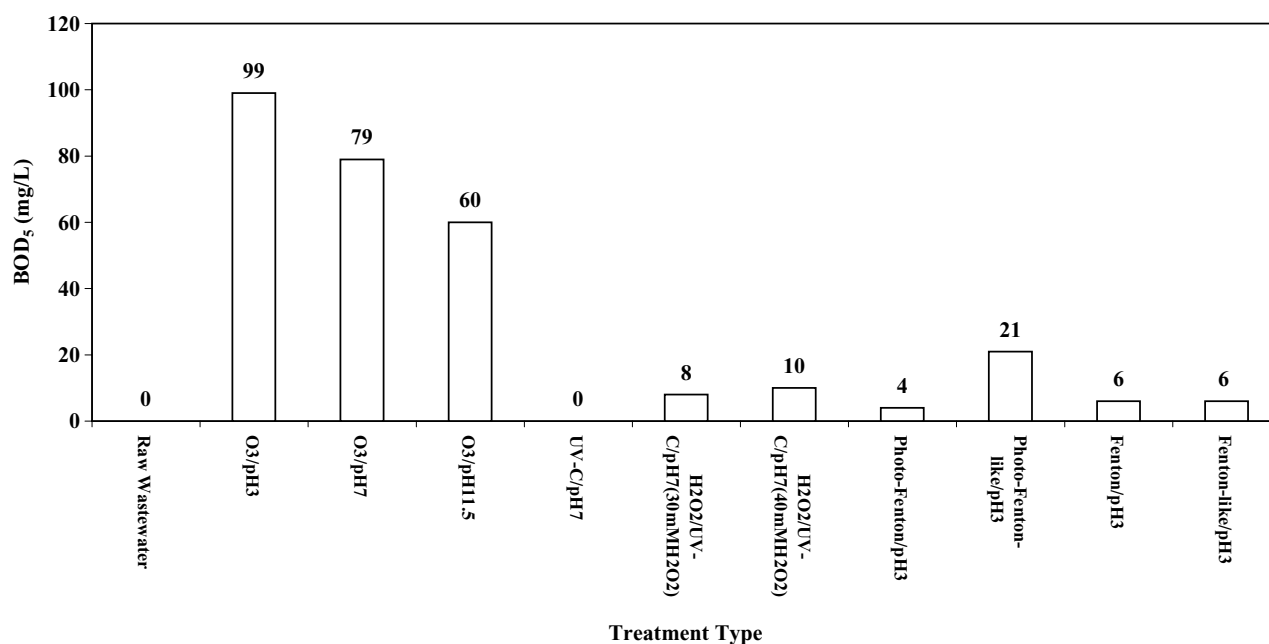


Fig. 6. Initial and final BOD₅ values obtained for penicillin formulation effluent before and after application of different AOPs for 1 h.

Table 3

COD and TOC removal per applied active oxidant (AOx) and oxidant (Ox) for different oxidation processes on molar basis

Oxidation process	ΔCOD (mol)	ΔCOD/Aox (mol/mol)	ΔCOD/Ox (mol/mol)	ΔTOC (mol)	ΔTOC/Aox (mol/mol)	ΔTOC/Ox (mol/mol)
O ₃ /pH 3	0.0067	0.12	0.12	0.0017	1.07	0.03
O ₃ /pH 7	0.0121	0.26	0.21	0.0178	0.10	0.31
O ₃ /pH 11	0.0228	0.61	0.40	0.0400	0.37	0.70
H ₂ O ₂ /UV/pH 7 (40 mM H ₂ O ₂)	0.0041	0.05	0.10	0.0078	0.07	0.19
H ₂ O ₂ /UV/pH 7 (30 mM H ₂ O ₂)	0.0057	0.10	0.19	0.0043	1.95	0.14
Photo-Fenton/pH 3	0.0246	1.23	1.23	0.0389	1.61	1.95
Photo-Fenton-like/pH 3	0.0279	1.40	1.40	0.0323	1.07	1.61
Fenton/pH 3	0.0230	1.15	1.15	0.0256	1.28	1.28
Fenton-like/pH 3	0.0245	1.23	1.23	0.0142	0.71	0.71

obtained for the oxidative pre-treatment processes. The findings given in Table 4 reveal that photo-Fenton, dark Fenton/Fenton-like reactions and the O₃/pH 11.5 process are the most promising candidates for penicillin formulation effluent pre-treatment.

3.6. Advanced oxidation of penicillin active substance (active ingredient)

Separate treatability studies with 400 mg/L active substance of the antibiotic formulation effluent have been

Table 4

Results obtained for advanced oxidation of penicillin formulation effluent

Oxidation process	BOD ₅ /COD	Final COD (mg/L)	COD removal (%)	Final TOC (mg/L)	TOC removal (%)
Raw wastewater	0.000	1395	0	920	0
O ₃ /pH 3	0.083	1196	15	900	2
O ₃ /pH 7	0.080	985	28	707	23
O ₃ /pH 11	0.078	771	49	440	52
Direct UV photolysis/pH 7	0.000	1333	0	920	0
H ₂ O ₂ (40 mM)/UV/pH 7	0.009	1106	11	827	10
H ₂ O ₂ (30 mM)/UV/pH 7	0.007	1220 ^a	22	869	6
Photo-Fenton/pH 3	0.007	608	56	453	51
Photo-Fenton-like/pH 3	0.045	466	66	533	42
Dark Fenton/pH 3	0.010	570	61	613	33
Dark Fenton-like/pH 3	0.008	726	46	750	18

^a Final COD is unexpectedly high, because the initial COD value was higher.

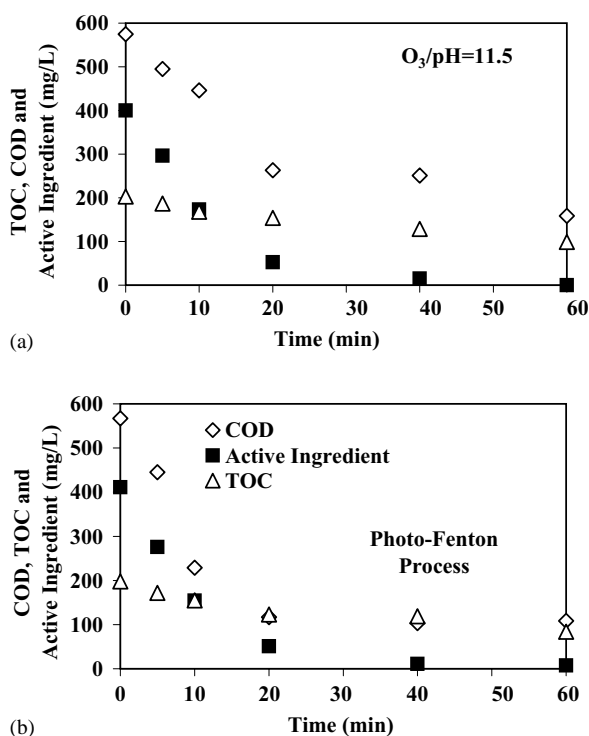


Fig. 7. Abatement of penicillin active ingredient (target substance), COD and TOC during advanced oxidation of amoxicillin trihydrate with (a) ozone (pH = 11.5; applied ozone dose = 2750 mg/L) and (b) photo-Fenton's reagent (pH = 3; 1 mM Fe^{2+} ; 20 mM H_2O_2).

conducted to confirm that amoxicillin, the target substance of the present work, was actually removed during the selected AOPs. Fig. 7 provides evidence that amoxicillin could be completely eliminated after 40 min treatment with ozone at pH = 11.5 (a) and photo-Fenton's reagent at pH = 3 (b) under optimized process conditions. Due to the fact that 400 mg/L is the practically highest expected concentration of active ingredient in the formulation effluent (=penicillin formulation + rinse water + detergents), it can be inferred that its complete elimination should also be expected for real penicillin formulation wastewater. Active ingredient abatement was accompanied by 72% COD–51% TOC (O_3/pH 11.5) and 81% COD–58% TOC (photo-Fenton/pH 3) removal.

4. Summary and conclusions

The following conclusions can be drawn from the present study:

- Ozonation of the penicillin formulation effluent was pH-dependent and the highest COD and TOC reductions occurred for alkaline ozonation as a result of enhanced ozone decomposition to reactive radicals (OH^\bullet) at elevated pH values.
- $\text{H}_2\text{O}_2/\text{UV-C}$ treatment is a relatively less effective method for the advanced oxidation of penicillin formulation

effluent. This is at least partially attributable to the fact that H_2O_2 photo-dissociation is seriously inhibited in the presence of other strong UV absorbers such as the penicillin formulation effluent.

- Relatively higher COD and TOC removal rates were obtained with the dark $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{pH}$ 3 process when compared with dark Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{pH}$ 3) reactions as a direct consequence of Fenton's chemistry. The presence of UV-C light only slightly improved the treatment performance. Highest removal efficiency in terms of TOC could be achieved via photo-Fenton's reagent, whereas COD removal was higher for the photo-Fenton-like process.
- A rather poor improvement in biodegradability of the oxidized effluent could be obtained. A more detailed investigation of the acclimatization of penicillin formulation effluent as well as its fate in the activated sludge process is currently under progress in our laboratory.
- In separate treatability experiments conducted with aqueous amoxicillin solution at the highest, practically expected concentrations it could be demonstrated that the penicillin active substance can be completely removed at the selected experimental conditions accompanied by effective oxidation (i.e. 51–58% TOC and 72–81% COD removal).

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