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Optimization of Fenton process for treatment of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution

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ABSTRACT

The study examined the effect of operating conditions of the Fenton process on biodegradability improvement and mineralization of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution. In addition, degradation of amoxicillin, ampicillin and cloxacillin under optimum operating conditions were evaluated. The optimum operating conditions for an aqueous solution containing 104, 105 and 103 mg/L amoxicillin, ampicillin, and cloxacillin, respectively were observed to be COD/H_2O_2/Fe^{2+} molar ratio 1:3:0.30 and pH 3. Under optimum operating conditions, complete degradation of amoxicillin, ampicillin and cloxacillin occurred in 2 min. In addition, biodegradability improved from ~0 to 0.37 in 10 min, and COD and DOC degradation were 81.4% and 54.3%, respectively in 60 min. Maximum biodegradability (BOD_5/COD ratio) improvement was achieved in 10, 20 and 40 min at antibiotics concentration 100, 250 and 500 mg/L, respectively for each antibiotic in aqueous solution. Increase in nitrate and ammonia concentration were observed due to mineralization of organic nitrogen, concentration of nitrate increased from 0.3 to 10 mg/L and concentration of ammonia increased from 8 to 13 mg/L in 60 min. The study indicated that Fenton process can be used for pretreatment of amoxicillin, ampicillin and cloxacillin wastewater for biological treatment.

1. Introduction

Among all the pharmaceutical drugs that cause contamination of the environment, antibiotics occupy an important place due to their high consumption rates in both veterinary and human medicine. Problem that may be created by the presence of antibiotics at low concentrations in the environment is the development of antibiotic resistant bacteria [1]. In fact, bacteria have been observed to transfer their resistance in laboratory settings as well as in the natural environment [2]. Furthermore, the presence of antibiotics in wastewaters has increased in recent years and their abatement will be a challenge in the near future. Amoxicillin, ampicillin and cloxacillin are semi-synthetic penicillin obtaining their antimicrobial properties from the presence of a beta-lactam ring. They are widely used in human and veterinary medicine. Some authors have found amoxicillin and cloxacillin in wastewater [3,4].

Advanced oxidation processes (AOPs) have proved to be highly effective for the removal of most of the pollutants in wastewaters [5]. Oxidation with Fenton's reagent is based on ferrous ions, hydrogen peroxide and hydroxyl radicals produced by the catalytic decomposition of hydrogen peroxide in acidic solution [6]. Fenton's reagent has been reported to be effective in the treatment of refractory industrial wastewaters –>95% decolorization of three dyes in aqueous solution were achieved [7] and 95% COD removal was achieved for carpet dyeing wastewater and semiconductor wastewater [8,9].

There have been studies on treatment of amoxicillin wastewater and penicillin formulation effluent by AOPs [10–12]. Reaction kinetics of amoxicillin ozonation has been studied [13]. However, no studies on degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution have been reported.

This study examined the effect of operating conditions (H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio, pH, reaction time and antibiotics concentration) of the Fenton process on biodegradability improvement and mineralization of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution (simulated antibiotics wastewater). In addition, degradation of amoxicillin, ampicillin and cloxacillin antibiotics under optimum operating conditions was also evaluated.

2. Materials and methods

2.1. Chemicals and antibiotics

Hydrogen peroxide (30%, w/w) and ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) were purchased from R & M Marketing, Essex, U.K. Analytical grade of amoxicillin (AMX) and ampicillin (AMP) were purchased from Sigma and cloxacillin (CLX) from Fluka to

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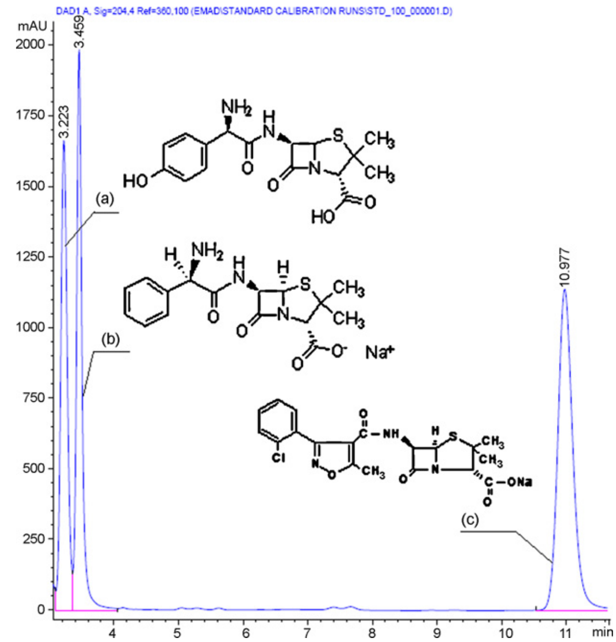

Fig. 1. Chemical structure and HPLC chromatography of the organic pollutants: (a) amoxicillin, (b) ampicillin sodium, and (c) cloxacillin sodium.

construct HPLC analytical curves for the determination and quantification of these antibiotics. AMX, AMP and CLX used to prepare simulated antibiotics wastewater were obtained from a commercial source (Farmaniage Company). The commercial products were used as received without any further purification. Sodium hydroxide and sulphuric acid were purchased from HACH Company USA. Potassium dihydrogen phosphate (KH_2PO_4) was purchased from Fluka and acentonitrile HPLC grade from Sigma. Fig. 1 shows the chemical structure and HPLC chromatograph for AMX, AMP and CLX.

2.2. Analytical methods

Antibiotics concentration was determined by HPLC (Agilent 1100 Series) equipped with micro-vacuum degasser (Agilent 1100 Series), quaternary pumps, diode array and multiple wavelength detector (DAD) (Agilent 1100 Series) at wavelength 204 nm. The data was recorded by a chemistation software. The detection column was ZORBAX SB-C18 (4.6 mm × 150 mm, 5 μm). The column temperature was set at 60 °C. Mobile phase was made up of 55% buffer solution (0.025 M KH_2PO_4 in ultra purified water) and 45% acentonitrile.

Chemical oxygen demand (COD) was determined according to the Standard Methods [14]. If the sample contained hydrogen peroxide (H_2O_2), to reduce interference in COD determination pH was increased to above 10 to decompose hydrogen peroxide to oxygen and water [15–17]. pH measurements were measured using a pH meter (HACH sension 4) and a pH probe (HACH platinum series pH electrode model 51910, HACH company, USA). Biodegradability was measured by 5-day biochemical oxygen demand (BOD_5) test according to the Standard Methods [14]. DO was measured using YSI 5000 dissolved oxygen meter. The seed for BOD_5 test was obtained from a municipal wastewater treatment plant. TOC analyzer (Model 1010 O & I analytical) was used for determining dissolved organic carbon (DOC).

2.3. Antibiotics aqueous solution

Antibiotics aqueous solution was prepared by dissolving the specific amounts of amoxicillin (AMX), ampicillin (AMP) and cloxacillin (CLX) in distilled water. It was prepared weekly and stored at 4 °C.

2.4. Experimental procedure

Batch experiments were conducted in a 600 ml Pyrex reactor with 500 ml of the antibiotics aqueous solution. The required amount of iron in the form of $FeSO_4 \cdot 7H_2O$ was added to the aqueous solution and mixed by a magnetic stirrer to ensure complete homogeneity during reaction. Thereafter, necessary amount of hydrogen peroxide was added to the mixture simultaneously with pH adjustment to the required value using H_2SO_4 or NaOH. The time at which hydrogen peroxide was added to the solution was considered the beginning of the experiment. Samples were taken at pre-selected time intervals using a syringe. The samples were then filtered through 0.45 μm membrane filter and tested for chemical oxygen demand (COD), biological oxygen demand (BOD_5), dissolved organic carbon (DOC) and filtered through 0.20 μm membrane filter for measurement of antibiotics concentration by HPLC.

3. Results and discussion

3.1. Effect of H_2O_2/COD molar ratio

To determine the optimal H_2O_2/COD molar ratio, initial H_2O_2 concentration was varied in the range 15–54 mM at constant initial COD 520 mg/L (16.25 mM). The corresponding H_2O_2/COD molar ratios were 1, 1.5, 2, 2.5, 3 and 3.5. Initial AMX, AMP and CLX concentrations were 104, 105 and 103 mg/L, respectively. The other operating conditions were fixed at pH 3 and H_2O_2/Fe^{2+} molar ratio 50. Figs. 2–4 show the effect of H_2O_2/COD molar ratio on AMX, AMX and CLX degradation in terms of COD degradation, BOD_5/COD ratio and DOC degradation. COD degradation percent after 60 min reaction time was 25.6, 44.6, 54.6, 60.2, 62.1 and 60.9 at H_2O_2/COD molar ratio 1, 1.5, 2, 2.5, 3 and 3.5, respectively (Fig. 2). BOD_5/COD ratio after 60 min reaction time was 0.05, 0.07, 0.21, 0.28, 0.31 and 0.29 at H_2O_2/COD molar ratio 1, 1.5, 2, 2.5, 3 and 3.5, respectively (Fig. 3). DOC degradation percent after 60 min reaction time was 13.3, 19.8, 30.1, 34.4 and 35.6 at H_2O_2/COD molar ratio 1, 1.5, 2.0, 2.5, 3.0 and 3.5, respectively (Fig. 4). A statistical analysis (one-way ANOVA) performed on the results at a 5% level of significance indicated that, COD degradation was significantly affected by H_2O_2/COD molar ratios (Table 1). Maximum COD degradation, biodegradability (BOD_5/COD ratio) improvement and DOC degradation for simulated AMX, AMP, and CLX wastewater was achieved at H_2O_2/COD molar ratio 3.

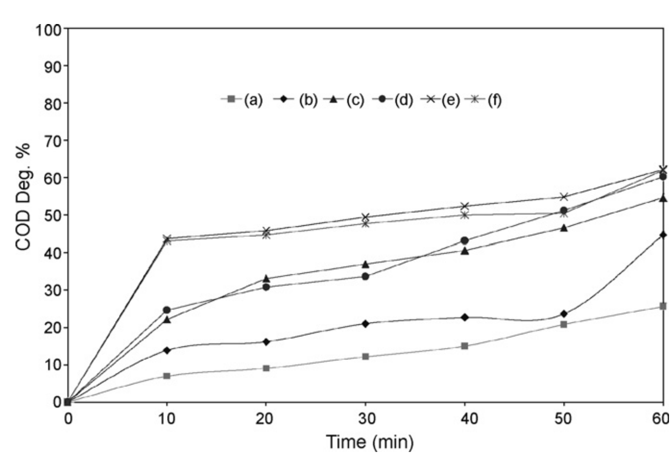

Fig. 2. Effect of H_2O_2/COD molar ratio on AMX, AMP and CLX degradation in terms of COD degradation: (a) 1.0, (b) 1.5, (c) 2.0, (d) 2.5, (e) 3.0, and (f) 3.5.

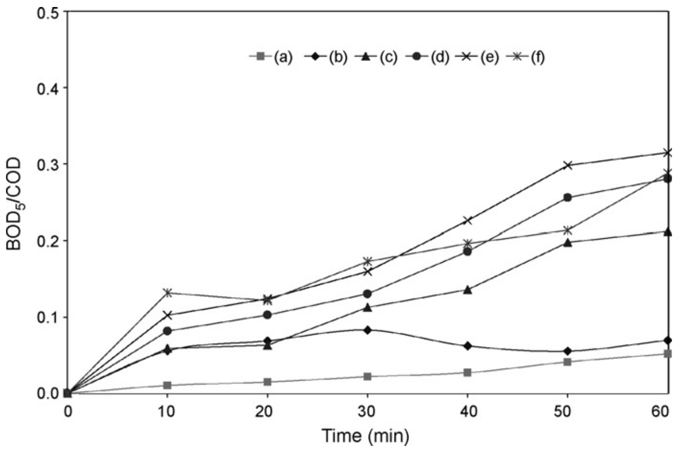

Fig. 3. Effect of H_2O_2/COD molar ratio on AMX, AMP and CLX degradation in terms of BOD_5/COD ratio: (a) 1.0, (b) 1.5, (c) 2.0, (d) 2.5, (e) 3.0, and (f) 3.5.

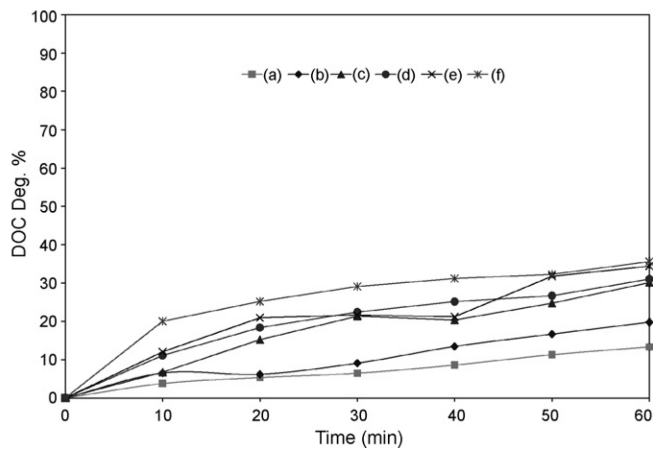

Fig. 4. Effect of H_2O_2/COD molar ratio on AMX, AMP and CLX degradation in terms of DOC degradation: (a) 1.0, (b) 1.5, (c) 2.0, (d) 2.5, (e) 3.0, and (f) 3.5.

The results show that increasing of COD degradation, BOD_5/COD ratio and DOC degradation at H_2O_2/COD molar ratio 1–3 and further increasing in H_2O_2/COD did not improve the degradation. This may be due to auto-decomposition of H_2O_2 to oxygen and water and scavenging of $OH^\bullet$ by H_2O_2 as in reactions (1) and (2) [18]. Moreover, the excess H_2O_2 reacts with ferric ions to form hydroperoxyl radical as in reaction (3) [19]:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (1)$$

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \quad (3)$$

3.2. *Effect of H_2O_2/Fe^{2+} molar ratio*

In Fenton process, iron and hydrogen peroxide are two major chemicals determining the operation cost as well as efficiency. To determine the optimal H_2O_2/Fe^{2+} molar ratio, experiments were conducted at constant H_2O_2 concentration (46.87 mM) and varying Fe^{2+} concentration in the range 0.32–24.3 mM. The corresponding H_2O_2/Fe^{2+} molar ratios were in the range 2–150. Initial AMX, AMP and CLX concentrations were 104, 105 and 103 mg/L, respectively. The operating conditions were pH 3, H_2O_2/COD molar ratio 3 and initial COD 520 mg/L (16.25 mM). Figs. 5–7 show the effect of H_2O_2/Fe^{2+} molar ratio on AMX, AMP and CLX degradation terms of COD degradation, BOD_5/COD ratio and DOC degradation. COD

Table 1
One-way ANOVA for COD degradation at different H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio, pH and antibiotics concentration.

Parameter	No. of groups	*F*	*P*-value	*F* crit
H_2O_2/COD	6	3.662	0.009	2.477
H_2O_2/Fe^{2+}	7	3.162	0.012	2.324
pH	5	2.862	0.012	2.690
Antibiotic concentration	3	0.088	0.917	3.555

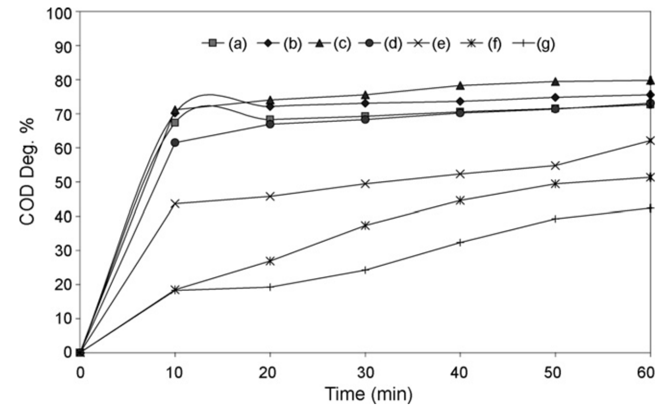

Fig. 5. Effect of H_2O_2/Fe^{2+} molar ratio on AMX, AMP and CLX degradation in terms of COD degradation: (a) 2.0, (b) 5.0, (c) 10.0, (d) 20.0, (e) 50.0, (f) 100, and (g) 150.

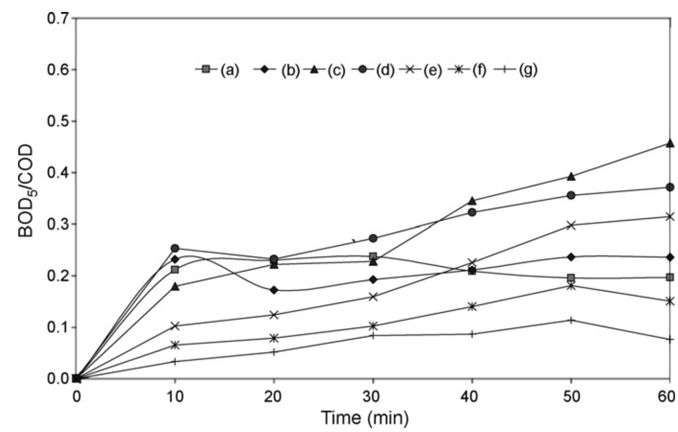

Fig. 6. Effect of H_2O_2/Fe^{2+} molar ratio on AMX, AMP and CLX degradation in terms of BOD_5/COD ratio: (a) 2.0, (b) 5.0, (c) 10.0, (d) 20.0, (e) 50.0, (f) 100, and (g) 150.

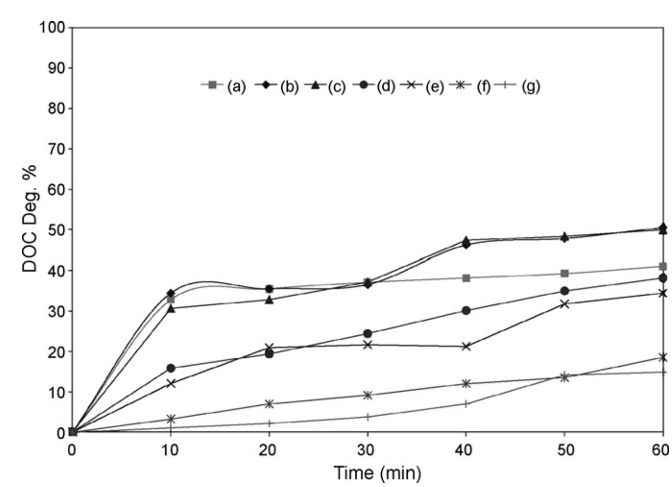

Fig. 7. Effect of H_2O_2/Fe^{2+} molar ratio on AMX, AMP and CLX degradation in terms of DOC degradation: (a) 2.0, (b) 5.0, (c) 10.0, (d) 20.0, (e) 50.0, (f) 100, and (g) 150.

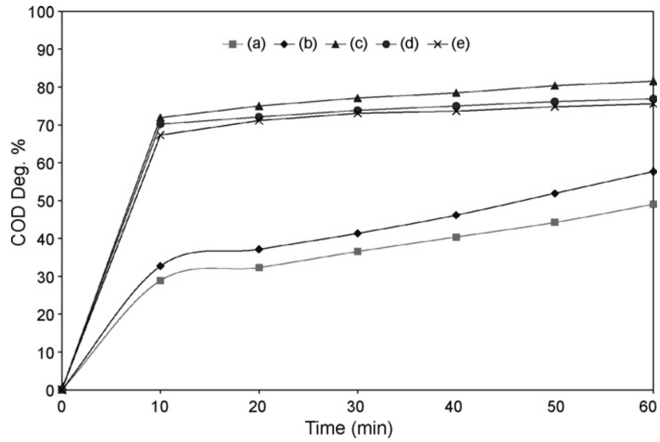

Fig. 8. Effect of pH on AMX, AMP and CLX degradation in terms of COD degradation: (a) 2.0, (b) 2.5, (c) 3.0, (d) 3.5, and (e) 4.0.

degradation percent after 60 min reaction time was 72.7, 75.6, 79.8, 73.1, 62.1 and 42.3 at H_2O_2/Fe^{2+} molar ratio 2, 5, 10, 20, 50, 100 and 150, respectively (Fig. 5). BOD_5/COD ratio after 60 min reaction time was 0.20, 0.29, 0.38, 0.37, 0.31, 0.15 and 0.08 at H_2O_2/Fe^{2+} molar ratio 2, 5, 10, 20, 50, 100 and 150, respectively (Fig. 6). DOC degradation percent after 60 min reaction time was 41, 50.5, 50, 38.2, 34.4, 18.5 and 14.9 at H_2O_2/Fe^{2+} molar ratio 2, 5, 10, 20, 50, 100 and 150, respectively (Fig. 7).

The results show that COD degradation, BOD_5/COD ratio and DOC degradation percent increased with the decrease of H_2O_2/Fe^{2+} molar ratios by 10. Further decrease in H_2O_2/Fe^{2+} molar ratios below 10 did not improve the degradation of antibiotics. This may be due to direct reaction of $OH^•$ radical with metal ions at high concentration of Fe^{2+} [20] as in reaction (4):

$$Fe^{2+} + HO^• \rightarrow Fe^{3+} + HO^- \quad (4)$$

A statistical analysis (one-way ANOVA) performed on the results at a 5% level of significance indicated that, COD degradation was significantly affected by H_2O_2/Fe^{2+} molar ratio (Table 1). Maximum COD degradation, biodegradability improvement and DOC degradation for simulated AMX, AMP, and CLX wastewater was achieved at H_2O_2/Fe^{2+} molar ratio 10.

This result agree well with the reported results for different pollutants – the optimum H_2O_2/Fe^{2+} molar ratio was 10 and 40 for chlorophenol and chlorinated aliphatics [5,22], 6.5 for cresols destruction [19], 5–40 for degradation of aromatic amines [21] and 1.9–3.7 for degradation of trihalomethanes [23]. In the present study COD and DOC degradation and BOD_5/COD ratio improvement for low H_2O_2/Fe^{2+} molar ratio is higher than that for high H_2O_2/Fe^{2+} molar ratio. This may be explained taking into consideration the intermediates formed during reaction. Lower H_2O_2/Fe^{2+} molar ratio causes a high removal of the target compound and formation of early intermediates [5,24].

3.3. Effect of pH

The pH value influences the generation of hydroxyl radicals and hence the oxidation efficiency. To determine the optimum pH, experiments were conducted by varying the pH in the range 2–4. Initial AMX, AMP and CLX concentrations were 104, 105 and 103 mg/L, respectively. The operating conditions were H_2O_2/COD molar ratio 3, H_2O_2/Fe^{2+} molar ratio 10 and initial COD 520 mg/L.

Figs. 8–10 show the effect of pH on COD degradation, BOD_5/COD ratio and DOC degradation. COD degradation percent after 60 min reaction time was 49.0, 57.7, 81.5, 76.9 and 75.6 at pH 2, 2.5, 3, 3.5 and 4, respectively (Fig. 8). BOD_5/COD ratio after 60 min reaction

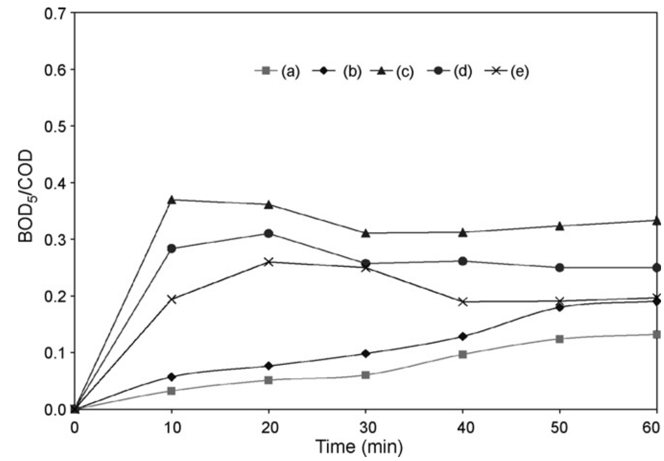

Fig. 9. Effect of pH on AMX, AMP and CLX degradation in terms of BOD_5/COD: (a) 2.0, (b) 2.5, (c) 3.0, (d) 3.5, and (e) 4.0.

time was 0.13, 0.19, 0.33, 0.35, 0.25 and 0.20 at pH 2, 2.5, 3, 3.5 and 4, respectively (Fig. 9). In addition, DOC degradation percent after 60 min reaction time was 33.9, 43.5, 54.3, 50 and 48.4 at pH 2, 2.5, 3, 3.5 and 4, respectively (Fig. 10). A statistical analysis (one-way ANOVA) performed on the results at a 5% level of significance indicated that, COD degradation was significantly affected by pH (Table 1). Based on the results, the optimum pH for treatment of simulated AMX, AMP, CLX wastewater is 3.0.

These results show that pH significantly influences COD degradation, biodegradability (BOD5/CODratio) improvement and DOC degradation. Decrease in COD and DOC degradation and biodegradability improvement at pH higher than 3 may be due to the decrease in dissolved iron, decrease in oxidation rate of hydroxyl radical and due to the dissociation and auto-decomposition of H_2O_2 [19,25,26]. Further, hydrogen peroxide is stable at low pH probably because it solvates a proton to form an oxonium ion (H_3O^+). An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion [27]. Therefore, amount of hydroxyl radicals would decrease at low pH, decreasing degradation of antibiotics intermediate. Also, the calculated average oxidation state (AOS) using Eq. (1) given by Bowers et al. [28] reflects the degree of change in antibiotics structure after oxidation. AOS of the treated antibiotics solution at pH 2 and 3 is 0.76 and 2.3, respectively:

$$AOS = \frac{4(DOC - COD)}{DOC} \quad (1)$$

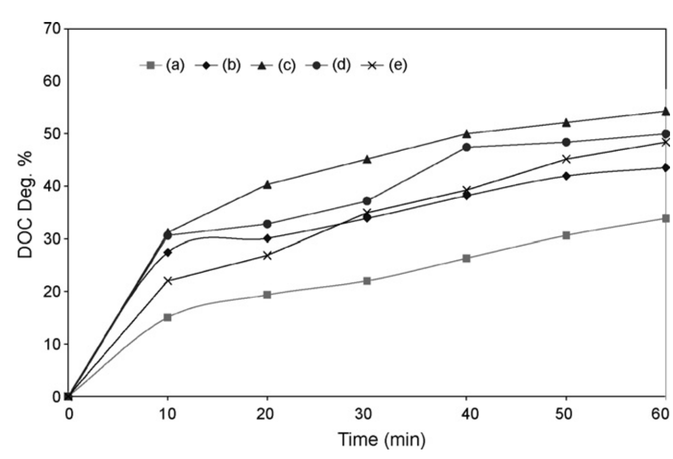

Fig. 10. Effect of pH on AMX, AMP and CLX degradation in terms of DOC degradation: (a) 2.0, (b) 2.5, (c) 3.0, (d) 3.5, and (e) 4.0.

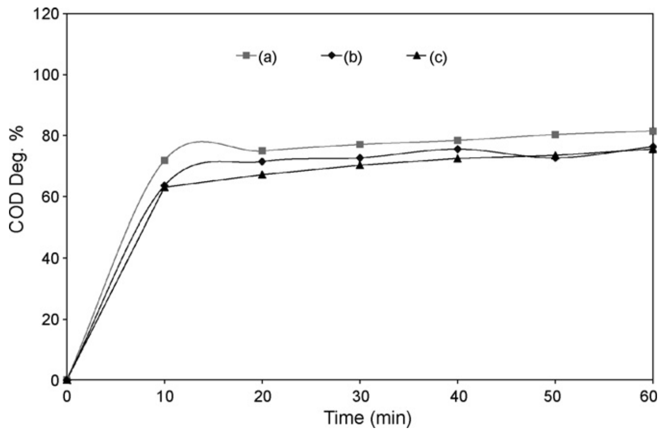

Fig. 11. Effect of initial antibiotics concentration on AMX, AMP and CLX degradation in terms of COD degradation: (a) 100, (b) 250, and (c) 500 mg/L.

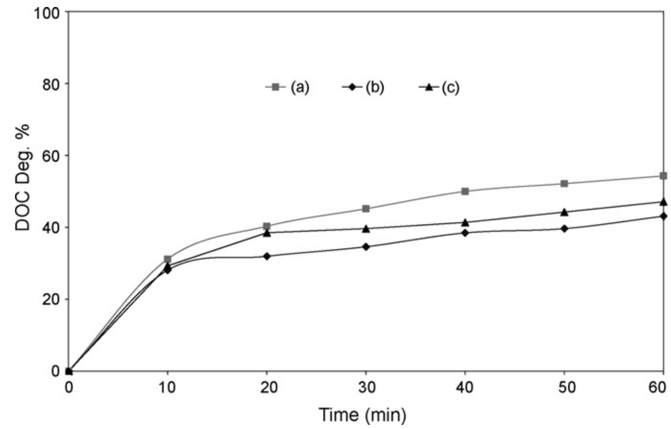

Fig. 13. Effect of initial antibiotics concentration on AMX, AMP and CLX degradation in terms of DOC degradation: (a) 100, (b) 250, and (c) 500 mg/L.

where COD is expressed in moles O_2 per liter and DOC in moles C per liter.

The high AOS value of the treated antibiotics solution at pH 3 indicates that the byproducts formed during the oxidation of antibiotics are highly biodegradable and less toxic [19]. These results agree well with the reported results of oxidation of organic substances in wastewater such as creosol [19], methomyl [25], dimethyl phthalate [26], p-chlorophenol [27] and p-nitroaniline [29].

3.4. *Effect of initial antibiotics concentration and reaction time*

The efficiency of the Fenton process depends on the formation of hydroxyl radicals and less scavenging of hydroxyl radicals occurs as initial organic substrate concentration increases [30]. To observe the effect of initial antibiotics concentration, experiments were conducted by varying the initial concentration of AMX, AMP and CLX as 100, 250 and 500 mg/L for each antibiotic in the aqueous solution. The corresponding COD were 520, 1229 and 2440 mg/L. The operating conditions were H_2O_2/COD molar ratio 3, H_2O_2/Fe^{2+} molar ratio 10 and pH 3.

Figs. 11–13 show the effect of initial antibiotics concentration on COD degradation percent, BOD_5/COD ratio and DOC degradation percent. COD degradation percent after 60 min reaction time was 81.4, 76.4 and 75.6 at initial antibiotics concentration 100, 250 and 500 mg/L, respectively for each antibiotic in the aqueous solution (Fig. 11). Fig. 12 shows that the maximum BOD_5/COD ratio was achieved at different reaction times – it was 0.37, 0.36 and 0.36 at reaction time 10, 20 and 40 min for initial antibiotics concentration 100, 250 and 500 mg/L, respectively. This may be due to the concentration of recalcitrant byproducts is different at the same time, recalcitrant byproducts concentration in the high antibiotics concentration (case c) at 10 min is more than the concentration in case (a). DOC degradation percent after 60 min reaction time was 54.3, 43.1 and 47.1 at initial antibiotics concentration 100, 250 and 500 mg/L, respectively for each antibiotic (Fig. 13). The results indicate that a little decreasing in COD degradation with increasing of antibiotics concentration, this reveal that the selected $COD/H_2O_2/Fe^{2+}$ molar ratio (1:3:0.30) is optimum for this type of wastewater. A statistical analysis (one-way ANOVA) performed on the results at a 5% level of significance indicates no significant effect of antibiotics concentration on the COD degradation (Table 1).

3.5. *Degradation of the antibiotics in aqueous solution, biodegradability improvement and mineralization under selected operating conditions*

Fig. 14 shows the degradation of the antibiotics (AMX 104 mg/L, AMP 105 mg/L and CLX 103 mg/L) in aqueous solution (COD 520 mg/L; 16.25 mM) under optimum operating conditions ($COD/H_2O_2/Fe^{2+}$ molar ratio 1:3:0.3 and pH 3). Complete degradation of all antibiotics was achieved in 2.0 min. These results agree well with that reported by Trovo et al. [31] on degradation of amoxicillin and bezafibrate in aqueous solutions by the photo-Fenton process.

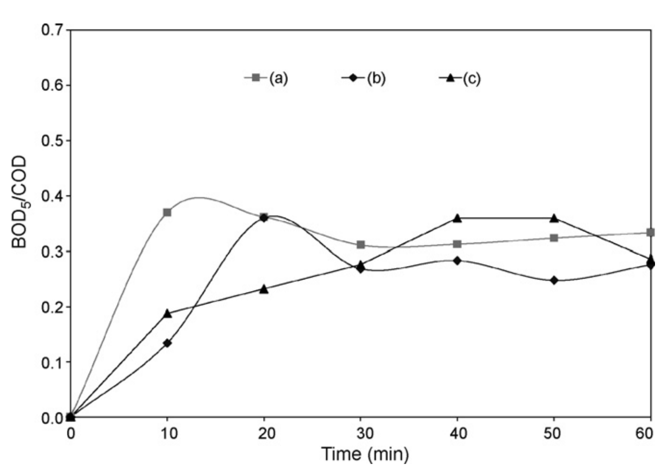

Fig. 12. Effect of initial antibiotics concentration on AMX, AMP and CLX degradation in terms of BOD_5/COD ratio: (a) 100, (b) 250, and (c) 500 mg/L.

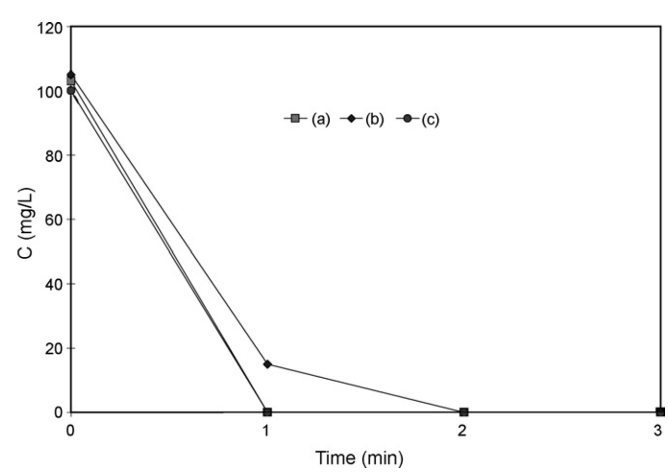

Fig. 14. Degradation of AMX, AMP and CLX under optimum operating conditions: (a) AMX, (b) AMP, and (c) CLX.

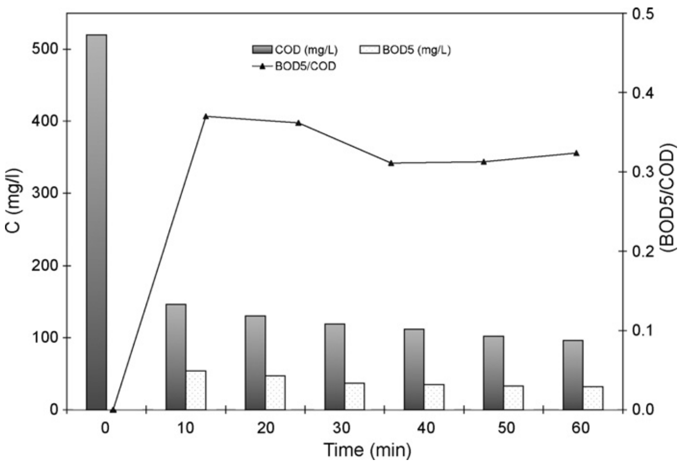

Fig. 15. Degradation of AMX, AMP and CLX in terms of COD, BOD_5 and BOD_5/COD ratio.

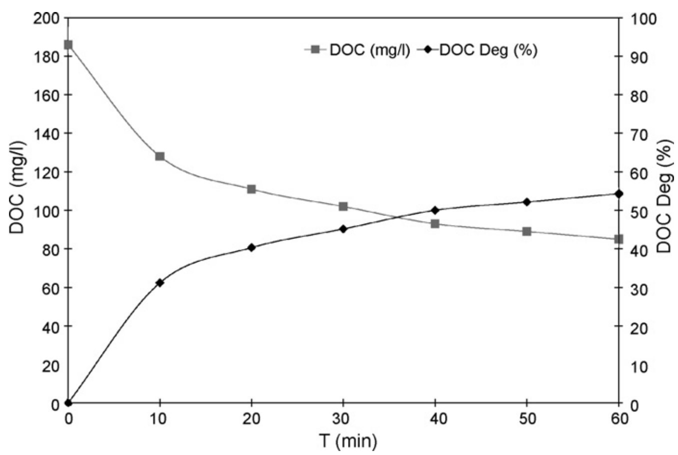

Fig. 16. Mineralization of AMX, AMP and CLX in terms of DOC concentration and degradation.

Fig. 15 shows degradation of AMX, AMP and CLX in aqueous solution in terms of COD, BOD_5 and biodegradability (BOD_5/COD ratio) improvement. COD decreased from 520 mg/L (initial value) to 146 mg/L in 10 min whereas, BOD_5 increased from 0 to 54 mg/L. The corresponding BOD_5/COD ratio is 0.37 and it is considered adequate for biological treatment as a wastewater is considered biodegradable if BOD_5/COD ratio is 0.4 [32].

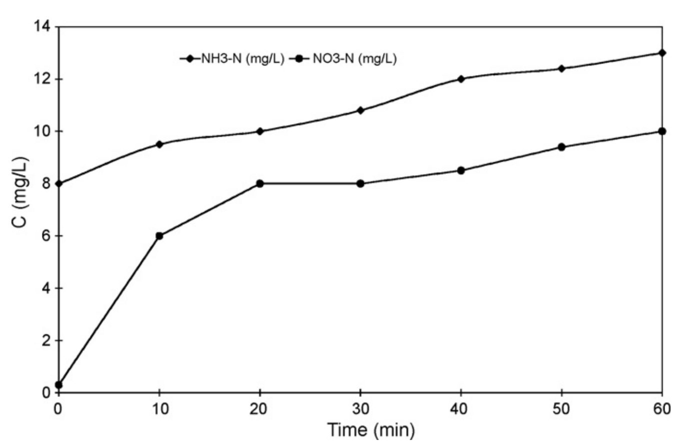

Fig. 17. Mineralization of AMX, AMP and CLX in terms of NH_3^-, NO_3 concentration.

To assess degree of mineralization, degradation of DOC and increase in nitrate and ammonia in the solution were measured. Mineralization of organic carbon and nitrogen compounds are verified by the results presented in Figs. 16 and 17. DOC degradation percent was 31.2, 40.3, 45.2, 50.0, 52.2 and 54.3 at reaction time 10, 20, 30, 40, 50, 60 min, respectively. Concentration of nitrate (NO_3^-) increased from 0.3 to 10 mg/L and concentration ammonia (NH_3) increased from 8 to 13 mg/L in 60 min.

4. Conclusions

- Fenton process is effective in the treatment of an aqueous solution of amoxicillin, ampicillin and cloxacillin.
- Under optimum operating conditions (COD/H_2O_2/Fe^{2+} molar ratio 1:3:0.30, pH 3), for an aqueous solution of amoxicillin (104 mg/L), ampicillin (105 mg/L) and cloxacillin (103 mg/L), complete degradation of the antibiotics occurred in 2 min. Biodegradability improved from ∼0 to 0.37 in 10 min, and COD and DOC degradation were 81.4% and 54.3%, respectively in 60 min. Maximum biodegradability (BOD_5/COD ratio) improvement was achieved in 10, 20 and 40 min at antibiotics concentration of 100, 250 and 500 mg/L, respectively for each antibiotic in aqueous solution. Mineralization of organic carbon and nitrogen occurred.
- Fenton process can be used for pretreatment of amoxicillin, ampicillin and cloxacillin antibiotics wastewater for biological treatment.

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