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Improvement of Biodegradability of Synthetic Amoxicillin Wastewater by Photo Fenton Process

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Abstract: Antibiotics are emerging contaminants in the aquatic environment because of their adverse effects on aquatic life and humans. Antibiotics wastewater has high COD and very low BOD_5 and hence is difficult to treat biologically. The objective of this research was to study the effect of operating conditions (reaction time, pH, H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio) of the photo Fenton process in improving the biodegradability of a synthetic amoxicillin wastewater. In addition, study the degradation of amoxicillin by photo Fenton process under optimum conditions. These conditions have a great effect on biodegradability ratio improvement. The optimum biodegradability ratios were 0.51, 0.51, 0.55 and 0.53 at reaction time 45 min, H_2O_2/COD molar ratio 2:1, H_2O_2/Fe^{2+} molar ratio 50:1 and pH 3, respectively. Under optimum operating conditions, complete degradation of amoxicillin was achieved in one minute. The photo Fenton process is considered a suitable pretreatment method to improve the biodegradability of antibiotics wastewater.

Key words: Antibiotics wastewater · Amoxicillin · Biodegradability · photo Fenton

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. In recent years, the incidence of antibiotic resistant bacteria has increased and many people believe the increase is due to the use of antibiotics [1]. Advanced oxidation processes (AOPs) have proved to be highly effective in degradation of most pollutants in wastewaters [2]. Photo Fenton is known to be able to improve the efficiency of dark Fenton reagent by means of the interaction of radiation with the Fenton's reagent [3]. Hydroxyl radicals are produced by the decomposition of hydrogen peroxide when reacting with ferrous ions in presence of UV light, which contributes an additional pathway to the generation of free radicals, increasing the concentration of hydroxyl radicals [4]. Amoxicillin is semi-synthetic penicillin obtaining its antimicrobial properties from the presence of a beta-lactam ring. Some authors have found amoxicillin in wastewater [5-6]. There are a few researches on treatment of real amoxicillin formulation wastewater by AOPs [7-9]. Some authors studied the reaction kinetics of amoxicillin ozonation [10]. This paper aims at studying the effect of operating conditions (reaction time, pH, H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio) of the photo Fenton process on biodegradability improvement of amoxicillin wastewater.

MATERIALS AND METHODS

Chemicals and Antibiotics: Hydrogen peroxide (30% w/w) and ferrous sulphate ($FeSO_4$. $7H_2O$) were purchased from R & M Marketing, Essex, U.K. Analytical grade of amoxicillin (AMX) was purchased from (Sigma) to construct HPLC analytical curves for the determination and quantification of amoxicillin. AMX used to prepare simulated antibiotics wastewater was obtained from a commercial source (Farmaniage Company). The commercial products were used as received without any further purification. Sodium hydroxide and sulfuric acid were purchased from HACH Company USA. Potassium dihydrogen phosphate (KH_2PO_4) was purchase from Fluka and acentonitrile HPLC grade from Sigma.

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Analytical Methods: Antibiotics concentration were determined by High Performance Liquid Chromatograph (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 Chemistation Software. The detection column was ZORBAX SB-C18 (4.6 mm x 150 mm, 5 μm). The column temperature was 60 C°. Mobile phase was 55% buffer solution (KH_2PO_4 0.025 M in ultra purified water) and 45% acentonitrile. Chemical oxygen demand (COD) was determined by the Hach method at 600 nm (for a COD range 0-1500 mg/L with a HACH DR2800 instrument). If the wastewater sample contains hydrogen peroxide (H_2O_2), the COD test will be interfered since the dichromate ions react with H_2O_2 in an acidified solution [11-13]. Because of this reason, pH was increased to above 10 to decompose hydrogen peroxide to oxygen and water [13]. pH measurements were performed 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 bacterial seed for BOD_5 test was obtained from a municipal wastewater treatment plant.

Synthetic Antibiotics Wastewate: The simulated antibiotics wastewater was prepared by dissolving the specific amounts of amoxicillin in distilled water. Simulated antibiotics wastewater was prepared weekly and stored at 4°C.

Experimental Procedure: In batch experiments, 250 ml of synthetic amoxicillin wastewater were placed in a 300 ml Pyrex reactor and mixed by a magnetic stirrer. Thereafter, the required amount of the Fe^{2+} in the form of $FeSO_4$ $7H_2O$ was added to the wastewater and well mixed, followed by pH adjustment to the required value by H_2SO_4 or NaOH. Finally, the necessary amount of H_2O_2 was added to the solution and the ultraviolet lamp was switched on at the same time. The time at which the H_2O_2 Was added to the solution was considered as the beginning of the experiment. Samples were taken at pre-selected time using syringe. The separated samples were filtered through 0.45 μm membrane filter for chemical oxygen demand (COD), biological oxygen demand (BOD_5) measurement and filtered through 0.20 μm membrane filter for antibiotics measurement by high performance liquid chromatography (HPLC).

Photo Fenton Reactor: Photo Fenton processes were preformed in 300 ml Pyrex glass reactor. Stirring plate and stirrer bar were used to make the solution inside the reactor homogenous. The source of UV light was UV lamp (spectroline model EA-160/FE 230 volts 0.17 Amps Spectronics Corporation, New York U.S.A) with nominal power of 6 W emits radiation at 365 nm and was placed above the reactor.

RESULTS AND DISCUSSION

Effect of Reaction Time: Figure 1 shows the effect of reaction time on amoxicillin degradation in terms of COD and BOD_5. The operation conditions were pH 3, initial amoxicillin concentration 500 mg/L, initial COD 790 mg/L, H_2O_2/COD molar ratio 2 and H_2O_2/Fe^{2+} molar ratio 50. The results showed that COD decreased to 243 and 85mg/L after 15 and 75 min, respectively. Initial BOD_5 was 4 mg/L and increased to 90 mg/L after 30 min, then decreased to 51 mg/L after 75 min. Increase in BOD_5 during the first 30 min of reaction and decreasing thereafter is presumably due to the degradation of the active substance into less toxic intermediate byproducts.

COD degradation percents and biodegradability ratios (BOD_5/COD) at various reaction times are shown in Fig. 2. COD degradation percent was 69.2, 82.7 and 89.2% after 15, 45 and 75 min, respectively and BOD_5/COD ratio was 0.36, 0.51 and 0.60 after 15, 45 and 75 min, respectively. Based on the results we can consider 45 min as optimal reaction time because a BOD_5/COD ratio of 0.40 is considered adequate for biological treatment [15]. This agrees well with other studies on the oxidation of organic compounds in wastewaters such as textile dyes by photo Fenton process [16].

Effect of H_2O_2/COD Molar Ratio: Figure 3 shows the effect of H_2O_2/COD molar ratio on amoxicillin degradation

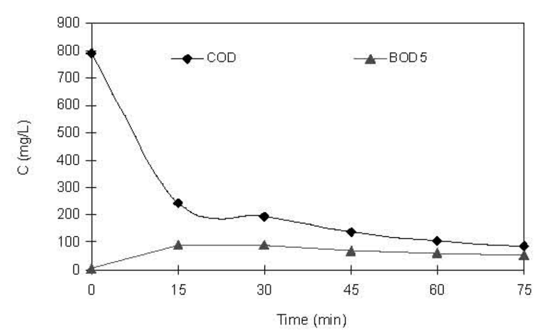

Fig. 1: Effect of reaction time on amoxicillin degradation in term of COD and BOD_5

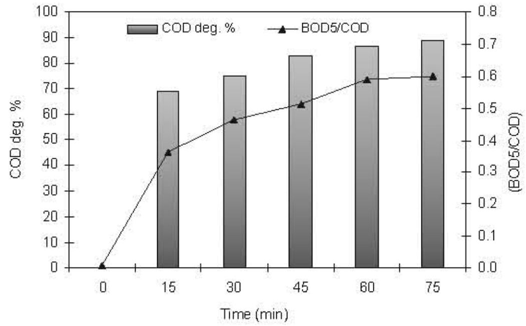

Fig. 2: Effect of reaction time on amoxicillin degradation in terms of COD degradation and BOD_5/COD ratio

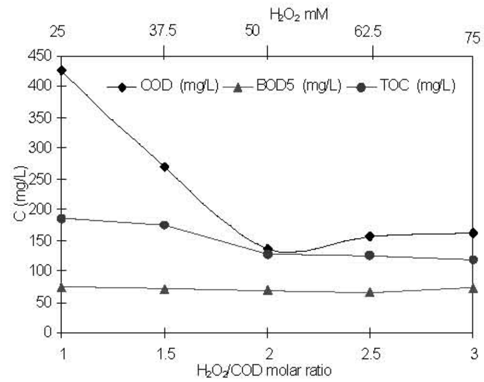

Fig. 3: Effect of hydrogen peroxide concentration and H_2O_2/COD molar ratio on amoxicillin degradation in term of COD and BOD_5

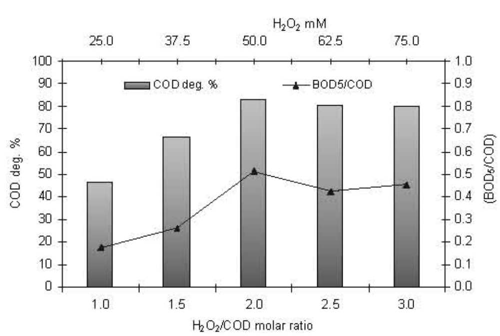

Fig. 4: Effect of hydrogen peroxide concentration and H_2O_2/COD molar ratio on amoxicillin degradation in terms of COD degradation and BOD_5/COD ratio

in terms of COD and BOD_5. The operating conditions were pH 3, initial COD 790 mg/L (24.68 mM), initial amoxicillin concentration 500 mg/L, reaction time 45 min and H_2O_2/Fe^{2+} molar ratio 50. Initial H_2O_2 concentration was varied in the range 25 mM-75 mM. The corresponding H_2O_2/COD molar ratios were 1, 1.5, 2, 2.5 and 3. It was expected that as the molar ratio of H_2O_2/COD increased, more hydroxyl radicals would be available to attack the substrate and therefore the degradation would increase. The results showed that COD concentration deceased from 427 mg/L at H_2O_2/COD molar ratio 1 to 137 mg/L at H_2O_2/COD molar ratio 2, then slightly increased at H_2O_2/COD molar ratio 2-3. BOD_5 varied from 66-74 mg/L at H_2O_2/COD molar ratio 1-3.

The effect of H_2O_2/COD molar ratio on COD degradation percent and biodegradability ratio (BOD_5/COD) are shown in Fig. 4. COD degradation percent was 46.6, 66.3, 82.9, 80.4 and 79.7 at H_2O_2/COD molar ratios 1, 1.5, 2.0, 2.5 and 3.0, respectively. BOD_5/COD ratio was 0.17, 0.26, 0.51, 0.42 and 0.45 at H_2O_2/COD molar ratios 1, 1.5, 2.0, 2.5 and 3.0, respectively.

The results demonstrated that COD degradation and biodegradability improved with increasing H_2O_2/COD molar ratio. Addition of H_2O_2 in excess of H_2O_2/COD molar ratio 2 did not improve the degradation. This is presumably due to auto-decomposition of H_2O_2 to oxygen and water and the recombination of $OH^{\bullet}$ radicals as in reactions 1, 2.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad \text{Reaction 1}$$

$$OH\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet \qquad \text{Reaction 2}$$

Since the $OH^{\bullet}$ radical reacts with H_2O_2, the H_2O_2 *per se* contributes to the $OH^{\bullet}$ scavenging [17]. Based on these results, it may be considered that optimal H_2O_2/COD molar ratio is two for biodegradability improvement.

Effect of H_2O_2/Fe^{2+} Molar Ratio: In the photo 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 by varying the H_2O_2/Fe^{2+} molar ratio in the range 10-100. The operating conditions were initial COD 790 mg/L (24.68 mM), initial amoxicillin concentration 500 mg/L, pH 3, H_2O_2/COD molar ratio 2 and reaction time 45 min. Figure 5 shows the effect of H_2O_2/COD molar ratio on amoxicillin degradation in terms of COD and BOD_5. COD concentration deceased from 159 mg/L at H_2O_2/Fe^{2+} molar ratio 10 to 130 mg/L at H_2O_2/Fe^{2+} molar ratio 50, then increased to 341 mg/L at H_2O_2 / Fe^{2+} molar ratio 100. BOD_5 varied from 87 mg/L at H_2O_2 /Fe^{2+} molar ratio 10 to 69 mg/L at H_2O_2/Fe^{2+} molar ratio 100.

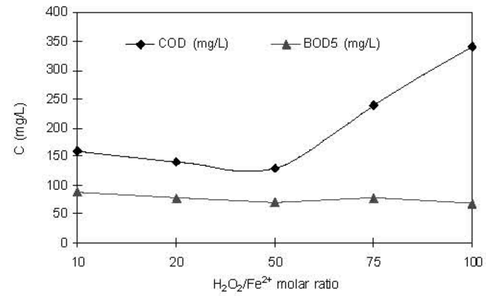

Fig. 5: Effect of H_2O_2/Fe^{2+} molar ratios on amoxicillin degradation in term of COD and

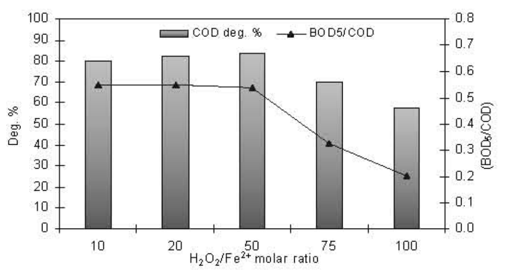

Fig. 6: Effect of H_2O_2/ Fe^{2+} molar ratio on amoxicillin degradation in term of COD degradation and BOD_5/COD ratio

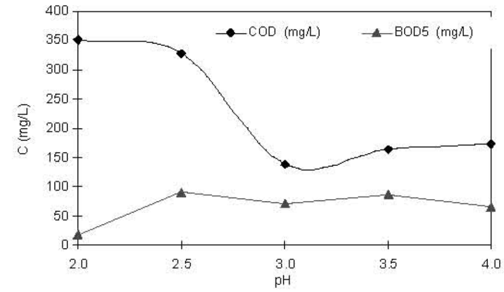

Fig. 7: Effect of pH on amoxicillin degradation in term of COD and BOD_5

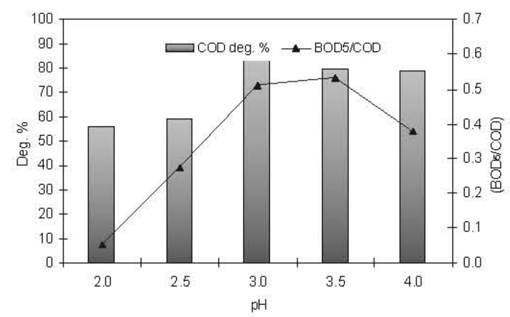

Fig. 8: Effect of pH on amoxicillin degradation in term in term of COD degradation percent and BOD_5/COD ratio

Effect of H_2O_2/Fe^{2+} molar ratios on COD degradation percents and biodegradability ratios (BOD_5/COD) are shown in Fig. 6. COD degradation percent was 80.1, 82.5, 83.8, 70.1 and 57.4 at H_2O_2/Fe^{2+} molar ratio 10, 20, 50, 75 and 100, respectively. BOD_5/COD ratio was 0.55, 0.55, 0.54, 0.53 and 0.20 at H_2O_2/COD molar ratio 10, 20, 50, 75 and 100, respectively. The results showed that COD concentration decreased with increase in H_2O_2/Fe^{2+} molar ratio till H_2O_2/Fe^{2+} molar ratio 50 (Fig. 5). Increasing H_2O_2/Fe^{2+} molar ratio over 50 produced high COD and low BOD_5 concentration also, COD degradation percent and biodegradability ratio (BOD_5/COD) decreased (Fig. 6). This may be due to direct reaction of OH- radical with metal ions at high concentration of Fe^{2+} as in reaction 3 [18].

$$Fe^{2+} + OH \rightarrow Fe^{3+} + HO^{-} \qquad \text{Reaction 3}$$

Based on these results, we can consider that 50 is the optimal H_2O_2/Fe^{2+} molar ratio to get optimal biodegradability improvement.

Effect of pH: Generation of hydroxyl radicals and the oxidation efficiency is influenced by pH. To determine the optimal pH, experiments were conducted by varying the pH in the range 2-4. The operating conditions were COD 790 mg/L, H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 50 and reaction time 45 min. Figure 7 shows the effect of pH on amoxicillin degradation in terms of COD and BOD_5. COD concentration deceased from 350 mg/L to 137 mg/L at pH 3 and increased to 172 mg/L at pH 4. BOD_5 varied from 18 mg/L at pH 2 to 65 mg/L at pH 4.

Figure 8 shows the effect of pH on COD degradation percent and biodegradability ratio (BOD_5/COD). Maximum improvement in BOD_5/COD ratio and COD degradation occurred in the pH range 3.0-3.5.

The results agree well with those of other studies on oxidation of organic substances in wastewater such as creosol [19], p-chlorophenol [20], methomyl [21] and dimethyl phthalate [22]. The degradation decreased at pH > 3.5, because of decrease in dissolved iron [19]. In addition, oxidation rate of hydroxyl radical decreases with increasing pH [21]. Also, lower COD degradation at pH < 3 is due to the dissociation and auto-decomposition of H_2O_2 [22]. At low pH, hydrogen peroxide can stay stable, probably because it solvates a proton to form an oxonium ion ($H_3O_2^+$). An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion [20]. Therefore, amount of hydroxyl radicals would decrease at pH < 3, thereby decreasing the degradation rate of amoxicillin.

Degradation of Antibiotics under Optimum Conditions: To study the degradation of amoxicillin (AMX) antibiotic, an experiment was conducted under selected operating condition (H_2O_2/COD molar ratio 2, H_2O_2/Fe^{+2} molar ratio 50 and pH 3.0) and initial AMX was 500 mg/L. Complete degradation of AMX was observed after 1.0 min. This agree well with results reported by Trovo et al [23] on degradation of amoxicillin (AMX), bezafibrate (BZF) and paracetamol (PCT) in aqueous solutions by the photo-Fenton process. They observed 90 and 89% of AMX oxidation in one minute of irradiation in distilled water and in STP effluent, respectively. We can see a difference between required reaction time to achieve complete degradation (1 min) and optimum reaction time (45 min) to achieve suitable biodegradability ratio for biological treatment. This is may be due to the toxicity effect of early intermediates produced by photo Fenton reaction. Hence, the biodegradability ratio of the intermediates at early time of photo Fenton reaction is low.

CONCLUSIONS

Effects of operating conditions (reaction time, H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio and pH) of the photo Fenton process on biodegradability improvement of antibiotics wastewater contains 500 mg/L amoxicillin were studied. The maximum biodegradability ratio (BOD_5/COD) was achieved at H_2O_2/COD molar ratio 2:1, H_2O_2/Fe^{2+} molar ratio 50:1 and pH 3-3.5. The optimum reaction time was observed to be 30-45 min to achieve a suitable biodegradability ratio (>0.40). Under optimum operating conditions, complete degradation of amoxicillin was achieved in one minute. The study indicated that the photo Fenton process can be used as a pretreatment system for improvement of the biodegradability of amoxicillin wastewater.

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