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Optimization of Fenton treatment of amoxicillin and cloxacillin antibiotic aqueous solution

Augustine Chioma Affam, Malay Chaudhuri*

Department of Civil Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Tronoh, Perak 31750, Malaysia
Tel. +60 12 510 3547; Fax: +60 5 365 6716; email: malaychaudhuri@yahoo.com

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ABSTRACT

Response surface methodology was used to optimize the Fenton treatment of amoxicillin and cloxacillin antibiotic aqueous solution. Under optimum operating conditions (hydrogen peroxide (H_2O_2)/chemical oxygen demand (COD) molar ratio 2, H_2O_2/Fe^{2+} molar ratio 76, and reaction time 90 min at pH 3), 78.98, 72.96, and 81.18% removal of COD, total organic carbon, and ammonia–nitrogen, respectively were achieved. Experimental removal efficiency and model prediction were in close agreement (<0.4% error). Fourier transform infrared spectra indicated degradation of the beta-lactam bond of the antibiotics. Biodegradability (BOD_5/COD ratio) improved from zero to 0.33, indicating that Fenton treated antibiotic aqueous solution was amenable to biological treatment.

Keywords: Fenton process; Amoxicillin; Cloxacillin; Optimization; Response surface methodology

1. Introduction

Pharmaceuticals are emerging chemicals of concern [1] because of their increasing use in human and veterinary medicine and as growth promoter in aquaculture and livestock operations [2]. Pharmaceuticals may be discharged into the environment during manufacturing processes and through consumption or disposal of used and discarded drugs [3]. Although the concentration of antibiotics in domestic wastewater and streams are very low, usually at the μg/L and ng/L level, their transformation products may result in the development of antibiotic-resistant bacteria [4]. Degradation of antibiotics in antibiotic-manufacturing wastewater is a current challenge, especially as the conventional wastewater treatment plants are not designed to remove them [5].

Oxidation with Fenton's reagent is based on hydroxyl radical ($OH^\cdot$) produced by catalytic decomposition of hydrogen peroxide (H_2O_2) in reaction with ferrous ion (Fe^{2+}) [6]. In the photo-Fenton process, additional reactions occur in the presence of light that produce $OH^\cdot$ radicals or increase their production rate [7], thus enhance the efficiency of the process. The $OH^\cdot$ radicals react with organics and oxidize (degrade) them. The initiation reaction is shown in Eq. (1) [8].

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^\cdot \tag{1}$$

To regenerate Fe^{2+} from Fe^{3+}, the solution needs to be acidified to $pH < 5$ [9], as shown in Eq. (2) [8].

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*Corresponding author.

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

If the Fenton oxidation is carried to completion, the organics break down into CO_2 and H_2O; otherwise, the organics will be oxidized to intermediates as shown in Eq. (3) [8].

$$\text{Organics} + OH^{\cdot} \rightarrow H_2O + \text{intermediates} \rightarrow CO_2 + H_2O \quad (3)$$

The Fenton process has been applied as pretreatment of antibiotic aqueous solution for biological treatment [10,11]. Other recent studies on antibiotic degradation in wastewater include treatment by advanced oxidation process (AOP) [12–19], combined AOP and biological processes [20–24] and combined AOP and reverse osmosis treatment [25], and artificial neural network modeling of chemical oxygen demand (COD) removal from antibiotic aqueous solution by the Fenton process [26]. However, statistical optimization of the Fenton process for the treatment of antibiotic aqueous solution by response surface methodology (RSM) has not been reported.

In the present study, Fenton treatment of amoxicillin (AMX) and cloxacillin (CLX) antibiotic aqueous solution was optimized by RSM for the removal of COD, total organic carbon (TOC), and ammonia–nitrogen (NH_3-N). Antibiotic degradation was estimated by Fourier transform infrared spectroscopy (FTIR). Improvement in biodegradability was measured by BOD_5/COD ratio.

2. Materials and methods

2.1. Chemicals and antibiotics

Hydrogen peroxide (35% w/w) and ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) were purchased from R&M Marketing, Essex, UK. AMX and CLX were obtained from a commercial source. The commercial antibiotics were used as received without any additional reformulation. Fig. 1 shows the chemical structure of the antibiotics.

2.2. Analytical methods

COD and BOD_5 were determined according to the Standard Methods [27]. If the sample contained hydrogen peroxide (H_2O_2), to reduce interference in COD and BOD_5 determination, pH was increased to above 10 to decompose H_2O_2 to oxygen and water [28,29]. NH_3–N was measured according to the Water Analysis Handbook [30]. TOC analyzer (Model 1010; O & I Analytical) was used for determining TOC. The bacterial seed for BOD_5 test was obtained from a municipal wastewater treatment plant. DO was measured using YSI 5000 dissolved oxygen meter. FTIR spectra of the antibiotic aqueous solution were taken by Shimadzu FTIR-8400S.

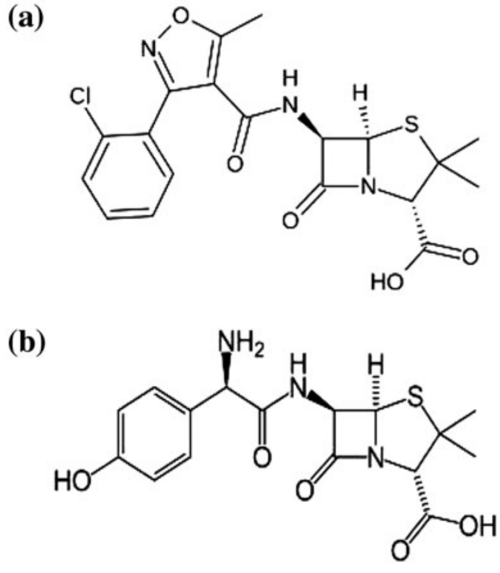

Fig. 1. Chemical structure of the antibiotics (a) AMX and (b) CLX.

2.3. Antibiotic aqueous solution

The antibiotic aqueous solution was 300 mg/L of the antibiotics (150 mg/L of AMX and 150 mg/L of CLX) in distilled water. Concentration of penicillin in penicillin-manufacturing wastewater has been reported to be up to 400 mg/L [31]. The antibiotic aqueous solution was prepared weekly and stored at 4°C. The characteristics of the antibiotic aqueous solution were COD 390 mg/L, TOC 168.8 mg/L, and NH_3–N 20.6 mg/L.

2.4. Experimental procedure

Batch experiments were conducted using a 600 mL conical flask. A known amount of $FeSO_4 \cdot 7H_2O$ was added to 500 mL of the antibiotic aqueous solution and the solution pH was adjusted to 3.0 with sulfuric acid [9,32]. This was followed by hydrogen peroxide addition with mixing by a magnetic stirrer for complete homogeneity. Samples were withdrawn at various time intervals, filtered through 0.45 μm membrane filter and tested for COD, BOD_5, and TOC, and filtered through 0.20 μm syringe filter for FTIR spectra.

2.5. Optimization and response surface modeling

Design expert software Version 6.0.7 [33] was used for statistical design of experiment and data analysis. Central composite design (CCD) of the RSM was used to optimize the operating conditions (variables) of the treatment because it is well suited for fitting a quadratic surface and is the experimental design mostly utilized for the development of analytical procedures as against three-level factorial design which is limited to optimization of two variables [34].

The variables were simultaneously changed in a central composite circumscribed design. The coded values of the variables H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio, and reaction time were set at five levels: $-\alpha$ (minimum), −1 (low), 0 (central), +1 (high), and $+\alpha$ (maximum) and 20 experiments were performed to give a statistical consistency to the mathematical model. For Fenton treatment of antibiotic aqueous solution, optimum H_2O_2/COD molar ratio 3, H_2O_2/Fe^{2+} molar ratio 10, and reaction time of 60 min have been reported [10]. In the present study, the variables H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio, and reaction time were studied in the range of 1.0–3.0, 2–150, and 60–120 min, respectively. Table 1 shows the experimental design range—actual and coded values of the variables. Chosen response parameters were the removal of COD, TOC, and NH_3–N. Regression analysis, response surface plots, and analysis of variance (ANOVA) were carried out using the design expert software. The optimum operating variables were identified from the response surface plots and the response equation, simultaneously. The following response equation

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \quad (4)$$

was used to assess the predicted result (Y) as a function of the variables H_2O_2/COD molar ratio (A), H_2O_2/Fe^{2+} molar ratio (B), and reaction time (C), and calculated as the sum of a constant (β_0), three first-order effects (A, B and C), three second-order effects (A^2, B^2 and C^2), and three interaction effects (AB, AC, and BC).

Table 1
Actual and coded values for the independent variables of the CCD design

Independent variable	Unit	Coded value −1	0	+1
		Actual value		
A: H_2O_2/COD	molar ratio	1.0	2.0	3.0
B: H_2O_2/Fe^{2+}	molar ratio	2.0	76	150
C: Reaction time	min	60	90	120

3. Results and discussion

3.1. Statistical analysis

The experimental design and observed removal (response) are shown in Table 2. Presumably, difference in removal is due to statistical variations of repeated experiments. The responses were analyzed by ANOVA to assess the "goodness of fit". The models for COD, TOC, and NH_3–N removal (Y_1, Y_2 and Y_3) were significant by the F-test at 95% confidence level. The following fitted regression models (equations in terms of coded values) were obtained to quantitatively investigate the effects of H_2O_2/COD molar ratio (A), H_2O_2/Fe^{2+} molar ratio (B), and reaction time (C) on COD, TOC, and NH_3–N removal, respectively.

COD removal

$$Y_1 = 78.98 + 7.13A + 5.44B + 1.93C - 5.99A^2 - 6.11B^2 + 3.27C^2 - 2.11AB - 3.21AC + 3.65BC \quad (5)$$

TOC removal

$$Y_2 = 72.96 + 6.83A + 7.00B - 0.78C - 6.70A^2 - 4.90B^2 + 2.23C^2 - 3.84AB - 46.92AC + 4.45BC \quad (6)$$

NH_3–N removal

$$Y_3 = 81.18 + 10.16A + 4.36B - 3.66C + 1.94A^2 - 6.74B^2 + 1.59C^2 - 8.25AB - 0.58AC - 4.37BC \quad (7)$$

In Eqs. (5)−(7), the values of the sum of a constant β_0 (78.98, 72.96, and 81.18) represent the percentage removal of COD, TOC, and NH_3–N, respectively. The positive sign indicates that the variable is directly proportional to the response parameter, and the negative sign indicates that the variable is inversely proportional to the response parameter. Table 3 shows the ANOVA using the results of the experiments performed from the design. Adequate precision (A.P.) compares the range of the predicted values at the design points to the average prediction error. Ratios greater than four indicate adequate model discrimination and can be

Table 2
Experimental design and observed removal

Experimental design			Removal (%)		
H_2O_2/COD Molar ratio (A)	H_2O_2/Fe^{2+} Molar ratio (B)	Reaction Time (min) (C)	COD	TOC	$NH_{3.}N$
2.0 (0.0)	76.0 (0.0)	90.0 (0.0)	78.69	75.09	93.0
0.32 (−1.68)	76.0 (0.0)	90.0 (0.0)	48.51	42.93	74.57
2.0 (0.0)	76.0 (0.0)	90.0 (0.0)	74.36	71.58	86.54
2.0 (0.0)	76.0 (0.0)	90.0 (0.0)	80.51	67.86	72.41
2.0 (0.0)	76.0 (0.0)	90 (0.0)	78.97	72.11	77.57
1.0 (−1.0)	150.0 (1.0)	60.0 (−1.0)	72.85	58.89	79.11
2.0 (0.0)	76.0 (0.0)	90.0 (0.0)	73.79	71.43	82.54
2.0 (0.0)	8.45 (1.68)	90.0 (0.0)	69.62	67.51	66.32
2.0 (0.0)	76.0 (0.0)	39.55 (1.68)	82.31	74.8	90.45
3.0 (1.0)	150.0 (1.0)	120.0(1.0)	96.64	69.2	68.88
1.0 (−1.0)	150.0 (1.0)	120.0 (1.0)	89.23	75.58	74.78
3.68 (1.68)	76.0 (0.0)	90.0 (0.0)	75.64	50.31	100.0
3.0 (1.0)	150.0 (1.0)	60.0 (−1.0)	82.9	75.48	100.0
3.0 (1.0)	2.0 (−1.0)	120.0 (1.0)	57.9	50.31	100.0
2.0 (0.0)	76.0 (0.0)	90.0 (0.0)	81.67	75.48	78.45
1.0 (−1.0)	2.0 (−1.0)	60.0 (−1.0)	40.28	44.35	59.78
3.0 (1.0)	2.0 (−1.0)	60.0 (−1.0)	68.95	79.88	89.2
2.0 (0.0)	200.45 (1.68)	90.0 (0.0)	82.56	73.52	72.23
1.0 (−1.0)	2.0 (−1.0)	120.0 (1.0)	52.26	45.94	48.45
2.0 (0.0)	76.0 (0.0)	140.0(1.68)	94.23	84.25	82.15

Table 3
ANOVA

Parameter	A.P.	PLOF	C.V.	R^2
COD	15.619	0.001	6.20	0.9484
TOC	12.547	0.001	6.37	0.9396
NH_3–N	8.454	0.0138	10.44	0.8023

used to navigate the design space defined by the CCD [35]. The A.P. for all the response parameters was greater than four. The probability of lack of fit (PLOF) describes the variation of the data around the fitted model. This is significant at 95% confidence level when PLOF < 0.05. The PLOF for all the response parameters were <0.05. The coefficient of variance (C.V.) is the ratio of the standard error of estimate to the mean value of the observed response parameters and defines reproducibility of the model. A model normally can be considered reproducible if its C.V. is not greater than 10% [34,36]. The C.V for NH_3–N was >10%, and thus fell slightly short of reproducibility. The coefficient of determination (R^2) is the proportion of variability in a data set which indicates whether the empirical model is good enough for the quadratic fit to navigate the design space defined by the CCD [33]. The R^2 values were 0.9484, 0.9396, and 0.8023 for COD, TOC, and NH_3–N, respectively.

3.2. Process analysis

Visualization of the predicted model equation can be obtained by the response surface and contour plots [37]. The response surface plot is the theoretical three-dimensional plots showing the relationship between the response parameters and the variables. The two-dimensional display of the surface plot is called contour plot and in the contour plot, lines of constant response are drawn in the plane of the variable [37]. The contour plot helps to visualize the shape of a response surface. When the contour plot displays ellipse or circle, the center of the system refers to a point of maximum or minimum response. Sometimes, contour plot may display hyperbolic or parabolic system of the contours [38]. Figs. 2–4 depict the response surface plots for COD, TOC, and NH_3–N removal. Maximum COD, TOC, and NH_3–N removal were 78.98, 72.96, and 81.18% at H_2O_2/COD molar ratio 2.0, H_2O_2/Fe^{2+} molar ratio 76, and reaction time 90 min, respectively.

Three confirmatory experiments were performed under the optimum operating conditions to verify the

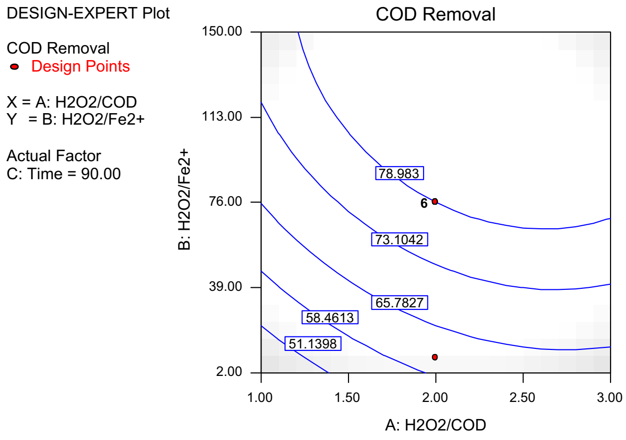

Fig. 2. Response surface plot for COD removal.

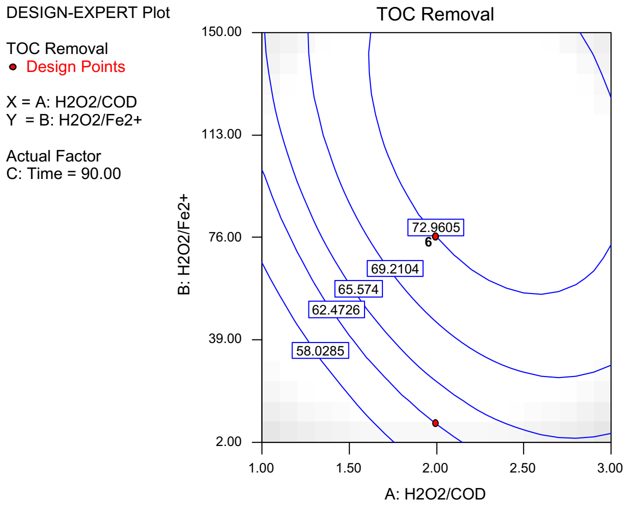

Fig. 3. Response surface plot for TOC removal.

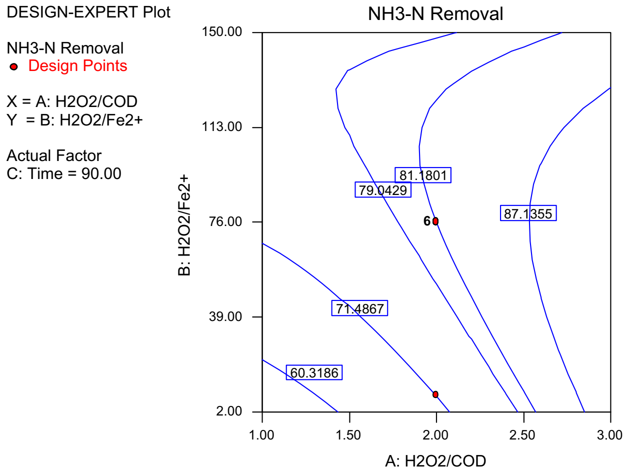

Fig. 4. Response surface plot for NH_3–N removal.

model response. As shown in Table 4, experimental removal efficiency and model prediction were in close agreement with less than 0.4% error.

The untreated and treated antibiotic aqueous solution were analyzed by FTIR spectroscopy to estimate the extent of antibiotic degradation. The characteristic band which occurred at 1637.45 cm^{-1} (Fig. 5) in the untreated antibiotic aqueous solution, shifted and modified to 1618.17 cm^{-1} (Fig. 6) in the treated solution. This can be attributed to pairing up of the organic group degradation intermediates [39].

Table 4
Experimental removal efficiency and model prediction

Parameter	Experimental	Model prediction	% Error
COD (%)	78.98	79.21, 79.15, 79.32; Av. 79.23	0.25
TOC (%)	72.96	74.0, 72.94, 72.75; Av. 73.23	0.27
NH_3–N (%)	81.18	82.55, 81.13, 81.0; Av. 81.56	0.38

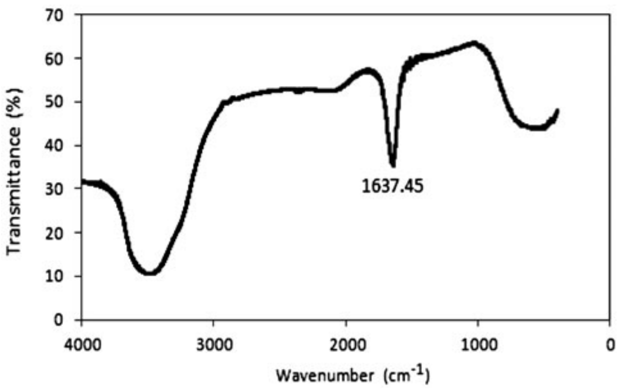

Fig. 5. FTIR spectra of untreated antibiotic aqueous solution.

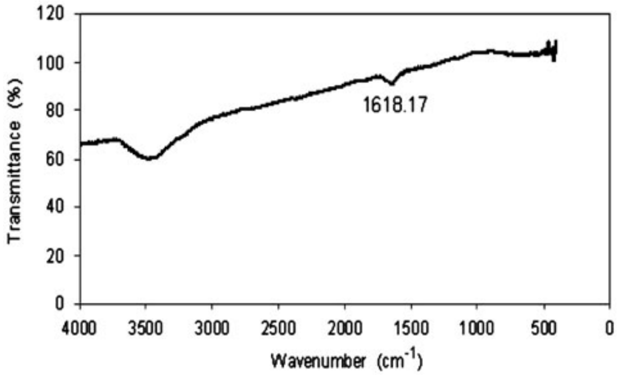

Fig. 6. FTIR spectra of treated antibiotic aqueous solution.

Biodegradability (BOD_5/COD ratio) of the antibiotic aqueous solution improved from 0 to 0.33 after treatment, indicating that the treated antibiotic aqueous solution was amenable to biological treatment [40].

4. Conclusions

The optimum operating conditions for Fenton treatment of AMX and CLX antibiotic aqueous solution at pH 3 were H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 76, and reaction time 90 min for 78.98, 72.96, and 81.18% removal of COD, TOC, and NH_3–N, respectively. Experimental removal efficiency and model prediction were in close agreement (<0.4% error). Fenton treatment led to the degradation of the beta-lactam bond of the antibiotics. Biodegradability improved from 0 to 0.33, indicating that the treated antibiotic aqueous solution was amenable to biological treatment.

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