Optimizing Removal of COD from Water by Catalytic Ozonation of Cephalexin Using Response Surface Methodology

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Summary: Response surface methodology (RSM) has been used to optimize the effect of circulation rates, ozone supply, cephalexin (CEX) concentration, and granular activated carbon (GAC) dose on removal of COD from solution. According to statistical analysis, all of the input variables exerted significant influence on COD removal, however, the effect of interaction variables was not found to be significant on comparative basis. Further, the developed quadratic regression model based on obtained results emphasized the significance of individual terms and little of interaction terms. The values of r^2 (0.959), adjusted r^2 (0.902) obtained by analysis of variance (ANOVA) indicates the significance of quadratic model in predicting desired response. The maximum of 70% of COD was removed in these experiments and optimized value according to main effect of variables was 60%.

Key words: Ozonation; Granular activated carbon; Cephalexin; COD; Response surface methodology.

Introduction

Catalytic ozonation is amongst the tertiary treatment technologies to treat micro pollutants from water resources. Ozone based technologies are promising techniques to kill micro pollutants during drinking water treatment. Catalytic ozone is helpful to enhance overall biodegradability of water from effluents of wastewater treatment plants. Literature reflects numerous studies on catalytic ozonation of micro pollutants such as pharmaceuticals, antibiotics, dyes, or pesticides [1-4]. The decomposition of micro pollutants during ozonation depends upon their reactivity with ozone and other reactants. The overall decomposition rate and decrease in toxicity level can vary depending on the type of parent compound. Therefore, it is often useful to explore more about behavior of micro pollutant compounds by catalytic ozonation process.

CEX antibiotic is widely prescribed for treatments of bacterial diseases [5-6]. Liu et al [7] investigated removal of CEX from water solution by adsorption using activated carbon. Their experimental results show that 66 mg/g, 75 mg/g and 78 mg/g of CEX was adsorbed onto activated carbon, Fe/activated carbon, and Cu/activated carbon, respectively. They also observed that, increase in removal CEX in case of Fe/AC or Cu/Ac was attributed due to interactive adsorption. Wang et al [8] separated cephalexin from electrolyte solution using polybenzimidazole (PBI) nanofilteration membrane and analyzed the effect of pH of solution during separation. Guo et al [9] reported removal of CEX via sonochemical degradation. They reported 50% removal in CEX and significant removal of COD of solution depending upon ultrasonic power and pH of solution. In the present study, the removal of CEX is investigated by ozonation in the presence of GAC catalyst using circulating batch reactor. Furthermore, the circulating reactor has been used to enhance ozone mass transfer, resulting into removal of CEX.

In this research, effect of four operating parameters has been investigated on COD removal by using response surface methodology (RSM). The four operating parameters include circulation rates, Q (L/min), ozone supply (mg/L), CEX concentration (mg/L), and GAC dose (g/L). The removal of cephalexin is measured in terms of COD removal. A quadratic model is developed; using regression analysis and is justified by analysis of variance (ANOVA). The graphical response is discussed for effects of main and interaction variables on response surface.

Results and Discussion

A Description about COD Removal

We selected four parameters due to their importance in removal of cephalexin from solution

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via ozonation. Circulation flow rate (X_1) induces synergic effect during ozonation processes. Zhang and Wang [10] reported increase in the rate of decolorization of dye solution at high liquid circulation. The ozone gas (X_2) is well-known destructor of organic pollutants in solution. Cephalexin concentration (X_2) and GAC catalyst (X_4) is considered to estimate their significance on COD removal. Table-1 describes the values for observed and predicted responses for removal of COD from solution. It is clear from Table-1 that 35 mg/L of ozone concentration was necessary to achieve >70% of COD removal irrespective of the values of other parameters. This suggested ozone concentration as the single most influencing variable. The centre point values of circulation rates, influent ozone, and CEX concentration were sufficient to remove COD in the range of 53 to 67%, depending on GAC dosage. Therefore, GAC exerted 15% variations in overall COD removal. The change in circulation rates from 1.5 to 10.5 L/min induced 21% variations in COD removal at centre point values of other parameters (runs 17 and 18, Table-1). Similarly, the changing CEX concentration (20-100 mg/L) resulted into 18% decrease in overall COD removal. This discussion showed the significant effect of all variables on desired response.

Quadratic Model

The quadratic model obtained after performing regression analysis is given in the following model equation (1) which determines the % COD removal.

$$\begin{aligned}\%\ COD\ removal \\ &= -34.3115 + 11.7266\,X_1 - 0.8168\,X_1^2 + 2.8015\,X_2 - 0.0167\,X_2^2 - 0.3897\,X_3 + 0.0016\,X_3^2 \\ &\quad + 11.5578\,X_4 - 0.0661\,X_4^2 - 0.0469\,X_1X_2 - 0.0041\,X_1X_3 - 0.3569\,X_1X_4 + 0.0011\,X_2X_3 \\ &\quad - 0.1769\,X_2X_4 - 0.0067\,X_3X_4\end{aligned} \tag{1}$$

Table-1: Design of experiment for input parameters and desired response.

Runs	Input variables matrix (DOE)				COD removal	
	Circulation (L/min) (X_1)	O_3 (mg/L) (X_2)	CEX (mg/L) (X_3)	GAC(g/L) (X_4)	Experimental	RSM
1	3.5 (-1)	16(-1)	60 (-1)	2 (-1)	33.02	36.43
2	3.5 (-1)	16(-1)	60 (-1)	4 (+1)	47.46	49.78
3	3.5 (-1)	16(-1)	140 (+1)	2 (-1)	27.58	30.32
4	3.5 (-1)	16(-1)	140 (+1)	4 (+1)	43.33	42.61
5	3.5 (-1)	35(+1)	60 (-1)	2 (-1)	71.43	71.13
6	3.5 (-1)	35(+1)	60 (-1)	4 (+1)	77.78	77.77
7	3.5 (-1)	35(+1)	140 (+1)	2 (-1)	66.06	66.68
8	3.5 (-1)	35(+1)	140 (+1)	4 (+1)	71.52	72.25
9	8 (+1)	16(-1)	60 (-1)	2 (-1)	38.10	45.98
10	8 (+1)	16(-1)	60 (-1)	4 (+1)	52.38	56.13
11	8 (+1)	16(-1)	140 (+1)	2 (-1)	33.33	38.40
12	8 (+1)	16(-1)	140 (+1)	4 (+1)	40.61	47.48
13	8 (+1)	35(+1)	60 (-1)	2 (-1)	82.54	84.70
14	8 (+1)	35(+1)	60 (-1)	4 (+1)	85.71	88.12
15	8 (+1)	35(+1)	140 (+1)	2 (-1)	76.36	78.76
16	8 (+1)	35(+1)	140 (+1)	4 (+1)	81.82	81.12
17	1.5(-1.68)	21(0)	100 (0)	3 (0)	32.72	32.60
18	10.5(+1.68)	21(0)	100 (0)	3 (0)	53.95	45.46
19	6 (0)	2(-1.688)	100 (0)	3 (0)	16.80	12.30
20	6 (0)	40(+1.68)	100 (0)	3 (0)	88.44	86.80
21	6 (0)	21(0)	20 (-1.68)	3 (0)	78.95	72.96
22	6 (0)	21(0)	180 (+1.68)	3 (0)	62.58	58.91
23	6 (0)	21(0)	100 (0)	1 (-1.68)	53.20	46.04
24	6 (0)	21(0)	100 (0)	5 (+1.68)	67.07	64.58
25	6 (0)	21(0)	100 (0)	3 (0)	60.14	55.57

The ANOVA is performed to justify the adequacy and significance of individual terms in the model. The individual terms with p-value < 0.05 are called adequate for 95% significance interval. The F-values give the significance of individual terms. Higher the F-value, more significant is the individual term [11]. The p-value of four linear terms and one quadratic term was < 0.05; hence, these five terms fell within adequacy limit of ANOVA analysis. The order of significance of these terms according F-value is X_2 [O_3 dosage] > X_1 [Circulation rate] > X_3 [CEX conc.] > X_1X_2 [Circulation rate with O_3 dosage] > X_4 [GAC dose]. The other measures for adequacy obtained from Table-2 r^2 (0.959), adjusted r^2 (0.902) were close to 1 within 90% confidence interval. The values of both r^2 and adjusted r^2 show that model predictions may deviate from the experimental data within acceptable limit. The predicted r^2 (0.9505) also shows the prediction ability of model within 10% error. The insignificant terms seldom cause any influence on adequacy of model to desired response. Therefore, the improved model after elimination of insignificant terms as given in equation (2):

$$\%\ \text{COD removal} = -34.3115 + 11.7266\, X_1^2 + 2.8015\, X_2 - 0.3897 X_3 + 11.5578\, X_4 - 0.0469\, X_1X_2 \quad (2)$$

Table-2: ANOVA table for removal of COD during four-parameter optimization of CEX.

Term	Sum of Square (SS)	Degree of Freedom	Mean Square	F-value	p-value
X_1	490.35	1	490.350	11.82	0.0063
X_1^2	221.67	1	221.666	5.34	0.0433
X_2	6508.67	1	6508.66	156.96	0.0000
X_2^2	35.93	1	35.933	0.86	0.3738
X_3	248.70	1	248.69	5.99	0.0343
X_3^2	86.08	1	86.084	2.07	0.1801
X_4	357.27	1	357.26	8.61	0.0149
X_4^2	0.06	1	0.056	0.0014	0.9713
X_1X_2	17.22	1	17.21	0.41	0.5338
X_1X_3	2.20	1	2.202	0.05	0.8223
X_1X_4	10.36	1	10.35	0.24	0.6280
X_2X_3	2.93	1	2.927	0.07	0.7958
X_2X_4	48.54	1	48.54	1.17	0.3046
X_3X_4	1.15	1	1.150	0.027	0.8710
Error	414.66	10	41.46		
Total SS	10155.45	24			

The Graphical Response

The Pareto chart is a graphical explanation of the ANOVA results and illustrates the t-distribution values. The length of Pareto bars measures the magnitude of variables (either individual or interaction). Fig. 1 contains synergistically influencing variables (dark color bars) and agonistically influencing variables (blank bars) [12]. The order of significance for positively influencing terms is: $X_2 > X_1 > X_4 > X_3^2 > X_1X_2 > X_2X_3$. However, terms X_1, X_2, and X_4 are significant according to F-values whereas all other terms are insignificant. The order for the effect of agonistic variables is $X_1^2 > X_3 > X_2^2 > X_1X_4 > X_4^2 > X_3X_4 > X_1X_3$. However, except X_3, all other terms are insignificant and can be eliminated from quadratic model.

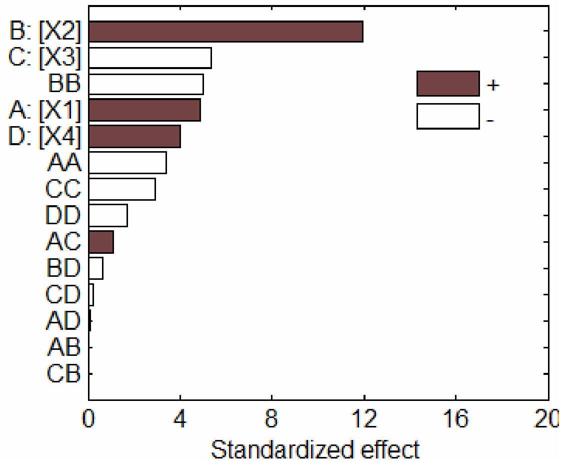

Fig. 1: The Pareto chart for effect of variables on removal of cephalexin from solution.

Fig. 2 illustrates the main effect of variables on desired response. The coded values of input variables were used within a range of ±2. The effect of each input variable was determined by varying its value within coded interval. All of the other variables were assigned centre point value (0). The circulation rate exerted synergetic effect on removal of COD within -2 to 0 intervals and agonistic effect within 0 to +2 intervals. Therefore, centre point value of Q is regarded as optimum value. The decrease in COD removal at very excessive circulation rates is attributable to the flooding of ozone gas that actually decreases the ozone mass transfer. The decrease in ozone mass is plausible by degasification of dissolved ozone at excessive turbulence. The COD removal continuously increased from 18 to 90% by changing ozone concentration O_3 within (-2 to +2) i.e. the O_3 was the single most influencing variable for desired response. The influence of ozone is well documented during ozonation of organic compounds. The cephalexin concentration CEX, decreased overall COD removal by 20% approximately within interval (-2 to +2) exerted agonistic effect on desired response. The effect of GAC dosage was synergetic as well. The COD removal increased by 15% approximately for GAC variation interval (-2 to +2).

This represents GAC as significant variable. The order of influence of main effects for synergetic variables was O_3 > Q > GAC. Consequently, the CEX exhibited agonistic effects.

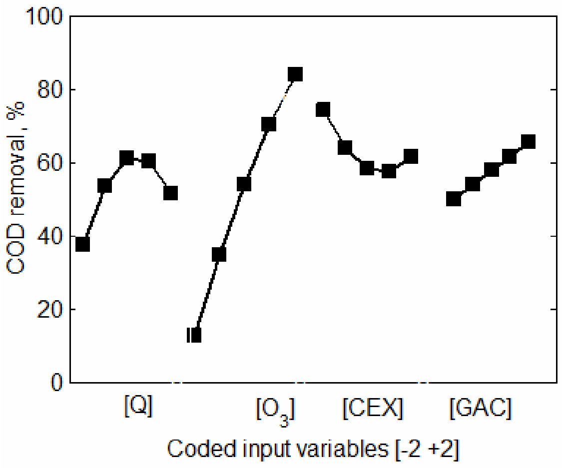

Fig. 2: The main effect of variables on removal of COD from solution.

3D Surface Curves and Contours

The 3D response surface offers direct explanation about the effect of interaction variables on desired response. Fig. 3a estimates the effect of GAC and ozone concentration on COD removal. Because, both variables exert synergetic effect, the COD removal increased as a function of their supply. The removal of COD was more sensitive to variations in ozone supply. Ozone supply within 5-40 mg/L interval exerted 90% variations in COD removal. Whereas, GAC exerted 28% variations on response within GAC dosage range. The maximum of 92% of COD was achieved at extreme values of input variables. For COD removal, usually concentrated supply of ozone is required [13-15]. Therefore, ozone concentration more than 35 mg/L and 4-5 g/L of GAC is necessary to remove COD in short time duration (typically < 20 min). Fig. 3b illustrates the role of CEX concentration and circulation rates on COD removal. The CEX concentration slightly decreased the overall COD removal by 30% within 50-200 mg/L concentration range. The effect of CEX concentration is therefore agonistic. The circulation flow rate increased COD removal within 2-8 L/min interval. The maximum 70% of COD removal was achieved at 8 L/min and 50 mg/L of CEX. For 8-12 L/min of circulations rates, COD of solution actually decreased. Excessive turbulence may be the plausible reason at high circulations rates that degasify dissolved ozone. Therefore, the mass of ozone dissolved may decrease and as a result can reduce COD removal. Based on this research, it has also been observed that the optimum value of circulation ~~rates~~ is 8 L/min at any CEX concentration. Fig. (3a, 3b) show the dominance of ozone supply as input variable followed by circulation rates, GAC supply, and CEX concentration.

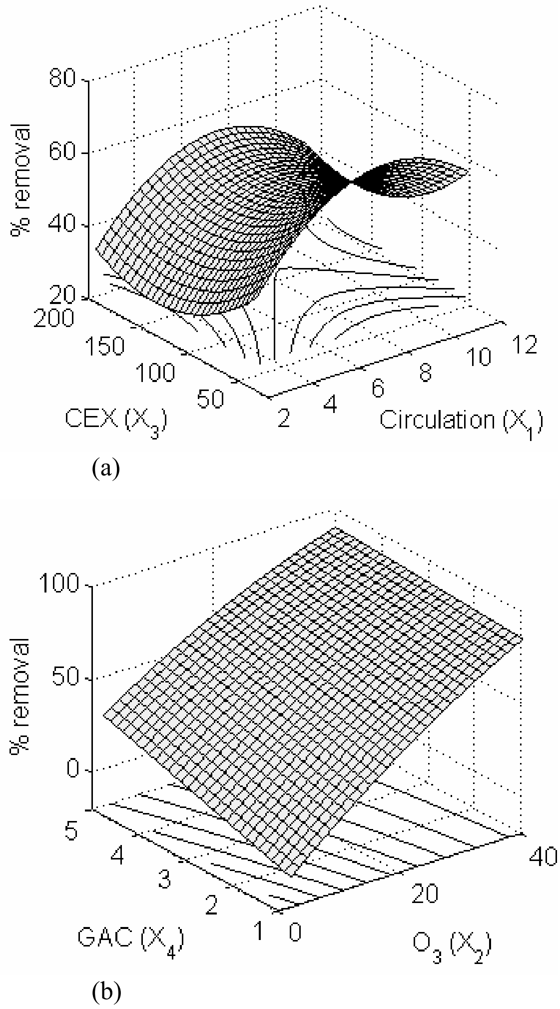

Fig. 3: 3D responses for effect of input variables on removal of COD from solution (a) Effect of circulation rates and CEX concentration, (b) O_3 concentration and GAC dosage.

Experimental

Materials

Various chemicals were purchased from Merek (acetonitrile, methanol, HPLC grade), QreC (NaOH, HCl, and acetic acid), Hach (COD reagent, high range), and Pharmaniaga Bhd (cephalexin antibiotic). Nylon membrane filters (0.45 μm) from Satorius.

Methods

A circulating batch type reactor was used for ozonation studies. The circulating batch reactor is two-column; each of length 18 cm and 6 cm (internal diameter). A connecting column was joined at the top of the two columns so that water can flow from first to second column. Ozone gas passes through reactor via venturi mixer and bubble diffuser. The water was allowed to circulate across the reactor columns by centrifugal pump. The solution of CEX was prepared according to the DoE experiments from deionized water. Initial pH was adjusted to 6-6.5 using ammonia solution and/or acetic acid. For every run, fixed 1100 mL of cephalexin solution was fed to reactor and was circulated across the reactor by using centrifugal pump. The ozone gas was generated from pure oxygen supply with the help of ozone generator (Ozonia Lab 2B). The mixer of O_3/O_2 was injected via fine bubble diffuser and venturi mixer. The samples were drawn after 15 min of ozonation and were analyzed for Hach analysis according to equation (3).

$$\text{Removal efficiency} = \frac{C_i - C_f}{C_i} \times 100 \qquad (3)$$

Conclusions

The ozonation of cephalexin from solution has been investigated in a circulating reactor using response surface methodology. The effect of circulation flow rate, ozone supply, CEX concentration, and GAC dose is optimized for desired response (COD removal). The maximum of 72% of COD was removed under optimized conditions. The ozone supply, circulation rates and GAC influenced the COD removal synergistically while that of CEX concentration agonistically. The influence of various variables under consideration in this study, can be expressed in the form of highest to lowest as follows; i.e., ozone supply has the highest influence, then comes circulation rates, later is the GAC dose, while the CEX concentration, has least influence. The quadratic model was able to predict desired response within 95% confidence interval. The values of r^2 (0.959), and adjusted r^2 (0.902) indicates the adequacy of the developed quadratic model. Furthermore, the results of response surfaces show that removal of COD from 50-100% was possible depending upon the input conditions. However, optimized response according to main effect of variables suggested the values of 60-70% of COD removal were more probable.

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Nomenclature

CEX	Cephalexin Antibiotic
C_i	Initial Concentrations of COD (mg/L)
C_f	Final Concentrations of COD (mg/L)
COD	Chemical Oxygen Demand
GAC	Granular Activated Carbon
O_2	Oxygen
O_3	Ozone gas
RSM	Response Surface Methodology
r^2	Root Mean Square

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