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Degradation of Methyl Orange using Hydrodynamic Cavitation Technology Combined with Chlorine Dioxide Oxidation: Optimization using Box–Behnken Design (BBD)

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In the present work, the hydrodynamic cavitation technology combined with chlorine dioxide oxidation was proved to be an effective method to degrade the methyl orange (MO). The influencing factors in the main experimental process such as solution temperature (25-45 °C), inlet pressure (0.2-0.6 Mpa), reaction time (20-60min) were investigated. Response surface methodology (RSM) based on Box-Behnken design (BBD) experiments were employed to optimize the experimental methods. The best performance of combined process for degradation of chlorine dioxide was achieved at temperature of 38.13°C, inlet pressure of 0.4 Mpa and reaction time of 60min and the optimal degradation rate was 82.97% which was very close to the actual experimental result of 82.8% under the same experimental condition. The experimental results showed that BBD could optimize the experimental results well with high accuracy which may simplify the experimental step and a better experimental result could obtained.

1. Introduction

Hydrodynamic cavitation is an advanced oxidation process (AOPs) which have a wide range of application in many fields, including the destruction of microbial cells, the delignification of wheat for paper manufacturing, the preparation of biodiesel and the hydrolysis of fatty acids (Badve et al., 2014; Huang et al., 2013). In recent years, hydrodynamic cavitation has been applied to degrade a majority of hardly-decomposed organic compounds (Zupanc et al., 2013; Kanthale et al., 2008). This technique mainly depends on the generation of the hydroxyl radicals induced by water decomposition and hydroxyl radicals are powerful oxidants. However, when applied cavitation individually always provides lower rates of the degradation, but the efficiency of cavitation can be significantly enhanced by combining it with other advanced oxidation processes such as Fenton process, photofenton, photolytic, photocatalytic process and some oxidizing agents (O_3, H_2O_2, etc.) (Raut-Jadhav et al., 2013).

The common devices for hydrodynamic cavitation (HC) contain the orifice plate and the venturi tube (Gogate and Pandit, 2005). Orifice plate is characterized by simple structure, easy adjustment and could induce stronger cavitation effect than venturi tube could do. For these reasons, many scholars choose orifice plate as cavitation devices to take advantage of cavitation effect induced by it. The cavitation process is as followed: when the fluid flows through the throttling area, the changed flow quantity makes flow velocity after the cavitation device increase rapidly, which contribute to the formation of high-speed jets and the decrease of outlet pressure. In the meanwhile, a number of microbubbles（vaporous cavities）are generated as the outlet pressure drop below saturated vapor pressure. Subsequently, the microbubbles collapse due to expansion of liquid jet and pressure recovery (Wang et al., 2008). Therefore, an effective equipment of HC with multi-hole orifice plate as its element is built in order to find the basic rule which affected it. Many scientific researchers have found that the structure and relevant parameters of cavitator is a dominant factor of the efficiency of cavitation (Gogate and Pandit, 2001; Kanthale et al., 2008). Parsa (2013) select the operational parameters such as Initial dye concentration, pH, inlet and back-pressures and characteristics of orifice plates to research the effect on the cavitation effect and utilize SISs as a cost effective catalyst to improve the performance of

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HC make this research unique. Therefore, three dominant factors are chosen as object of study to research the effect on the degradation of MO with combined technique.

Response surface methodology (RSM) is used to get the optimal value of unknown response surface. By means of establishing a mathematical model, RSM could be used to predict the response of a system to any new condition (Dariush and Aligholi, 2012). This technology has been successfully used in many researches to optimize the practical experimental problem. For instance, Tak Bong Yul et al., (2015) used the Box-Behnken design and response surface methodology to investigate the effects of major operating variables and optimization conditions in the removal of color and COD from livestock wastewater by electrocoagulation (EC) process using Al electrodes. The predicted values of responses obtained using the response function agree well with the experimental data. Khemakhem et al., (2013) used the Box-Behnken design to optimize the extraction and purification of a maltogenic amylase from fenugreek (Trigonella foenum graecum) seeds. An overall purification of about 239-folds with an activity yield of 47% was achieved. However, RSM has still not been used as a modeling and optimization tool for HC process to treat a type of wastewater. Hence, in this study, Box–Behnken response surface design (BBD) was adopted to optimize the experimental conditions with MO as degradation object. The influencing factors in the main experimental process such as solution temperature (25-45 °C), inlet pressure (0.2-0.6 Mpa), reaction time (20-60min) were investigated and the degradation rate of MO was chosen as response value. The optimum reaction conditions and the best response value could be obtained in the experimental process. Finally, a verification test was conducted to verify the results of BBD.

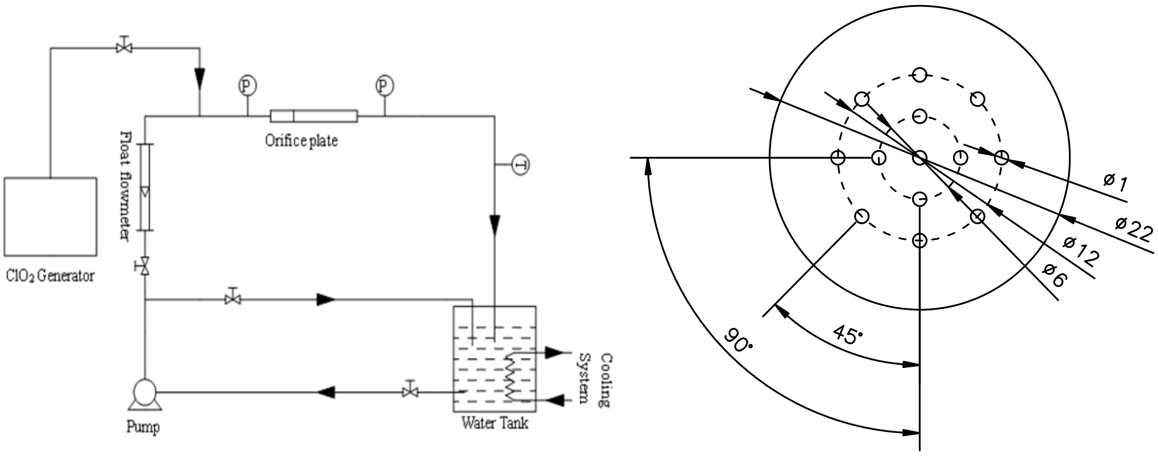
2. Materials and method

2.1 Materials

Methyl orange, Sodium hydroxide and Sulfuric acid(98%) were obtained from Hengxing Chemical Reagent(analytical reagent), the solid preparation of chlorine dioxide put into the ClO_2 generator was made by our own lab(the preparation of the chlorine dioxide contains tablet A and tablet B.

2.2 Experimental setup

The experimental apparatus assembled in our lab is shown in Figure. 1a and the geometric specifications of the orifice plate are shown in Figure 1b. The methyl orange solution was placed in the water tank and the orifice plate in the hydrodynamic cavitation reactor was placed in the main pipe line. ClO_2 Generator was assembled before the hydrodynamic cavitation reactor. The bypass regulation was controlled to adjust the water circulation pressure at the inlet of the orifice plate. A solidification device was utilized to control the solution temperature, as the temperature of the reaction solution will not be constant when the pump is turned on. The temperature will also be increased by the cavitation reaction. The orifice plate that exhibited the best cavitation effect in the previous work was chosen for the combined experiments. This orifice plate has 13 holes with an annular distribution. The diameter of the pores is 0.5mm and the thickness of the plate is 5mm.



(a) (b)

Figure 1: (a) Scheme of experimental setup; (b) Geometrical specifications of orifice plate

2.3 Experimental methods

In this paper, the degradation rate of MO with ClO_2-HC system was optimized using RSM with BBD. By this means, the effect of key parameters on the degradation rate and the maximum degradation rate could obtained with a response surface of three level BBD in Design-Expert software (Stat-Ease, Inc., USA). In this study, the temperature (A), inlet pressure (B), reaction time (C) were selected as independent variables, and the degradation rate of MO was selected as response variable.

3. Results and discussion

In previous studies, using hydrodynamic cavitation method in conjunction with dioxide is proved to be an efficient and sound method for degradation of MO. Therefore, considering the advantages of RSM analytical method such as a reduction in the number of experiments that need to be executed, a three level designs called Box-Behnken design (BBD) was used to optimize the reaction process by providing optimum parameters and statistical significance of the factor effects in the experiment conditions. The MO and chlorine dioxide concentrations were fixed at 10 mg/L and 8 mg/L, respectively. In this section, the effect of temperature, inlet pressure and reaction time on the degradation of MO was evaluated with the method of RSM with BBD. Based on the design principles, three factors were set as three levels with the code of -1, 0, 1 and the response value was degradation rate. The experimental design, variables, and corresponding values are shown in Table 1.

Table1: The Box-Behnken experimental design for ClO2-HC with three independent variables and the corresponding experimental results.

Trial NO.	Temperature /□		Inlet pressure /Mpa		Reaction time /min		Degradation rate /%	
	A	Code	B	Code	C	Code	Predicted	Actual
1	25	-1	0.2	-1	40	0	16.16	15.96
2	45	1	0.2	-1	40	0	20.04	20.08
3	25	-1	0.6	1	40	0	21.86	21.82
4	45	1	0.6	1	40	0	38.43	38.63
5	25	-1	0.4	0	20	-1	30.34	26.91
6	45	1	0.4	0	20	-1	34.55	30.88
7	25	-1	0.4	0	60	1	59.30	62.97
8	45	1	0.4	0	60	1	75.53	78.96
9	35	0	0.2	-1	20	-1	9.82	13.45
10	35	0	0.6	1	20	-1	17.05	20.52
11	35	0	0.2	-1	60	1	39.97	36.5
12	35	0	0.6	1	60	1	56.84	53.21
13	35	0	0.4	0	40	0	70.48	71.28
14	35	0	0.4	0	40	0	70.48	70.6
15	35	0	0.4	0	40	0	70.48	69.55

Table 2: Model summary statistic tested for the response R

Model	Std. Dev.	R^2	R^2_{Adj}	R^2_{Pred}	PRESS	Remark	CV	Adeq. Precision	Mean
Linear	20.57	0.3875	0.2204	0.0045	7566.91				
2FI	23.86	0.4006	-0.0490	-0.8626	14157.21				
Quadratic	4.53	0.9865	0.9622	0.7870	1619.21	Suggested	10.76	17.774	42.09
Cubic	0.87	0.9998	0.9986	N/A	N/A	Aliased			

Std. Dev. = standard deviation; R^2_{Adj}= adjected-R^2; R^2_{Pred}= predicted-R^2; CV=coefficient variation; Adeq. Precision=adequate precision.

In order to investigate effects of independent factors on the responses, fifteen experimental sets need to be conducted as the experimental design required. As can be seen from the experimental results, both temperature and inlet pressure had the best value ranges, and the degradation rate was enhanced over reaction time. The sequential model sum of squares was carried out to find an adequate type of regression model for further optimization steps, the results are listed in Table 2. The comparative results showed that both Linear type model and 2FI type model were not significantly relative to the noise, in addition, the cubic type model was found to be aliased because of lacking in runs to support a full cubic model in case of a BBD. While a quadratic type model was recommended for it had lower standard deviation of 4.53, which revealed that the predicted values would be more accurate and closer to the actual value. Besides, the ratio of adequate precision is 17.774(greater than 4 is desirable), which indicates that adequate signals for the models can be used to navigate the design space. Subsequently, the experimental results can be analyzed with the quadratic type model accurately and the detailed results are showed in Table 3: the calculated model *F*-value is 40.64 and P-value is 0.0004. These results imply that the model and the model terms were significant. On the basis of the ONOVA results, the final quadratic regression model for the degradation of MO (Eq.(1)) was obtained to fit the experimental data of degradation of MO:

$$Y = 70.48 + 5.11A + 6.02B + 17.49C + 3.17AB + 3.01AC + 2.41BC - 13.67A^2 - 32.68B^2 - 6.87C^2 \quad (1)$$

Where A, B, C, and Y are temperature(°C), inlet pressure (Mpa), reaction time(min), and degradation rate(%),respectively.

Values of "Prob > F" less than 0.0500 indicate that model terms are significant, nevertheless, values more than 0.1 reveal that model terms are not significant. In this case A, B, C, A^2, B^2, C^2 are significant model terms. So the interactive items can be eliminated during the computing process. The Figure 2 revealed a good relationship between predicted values and the actual values of degradation rate, they were almost on the same straight line. This model could explain up to 98.65% of the variability in response and the fit indicators of the model proposed by this study are acceptable. Moreover, the "Lack of Fit F-value" of 44.31 implies that the Lack of Fit is significant and there is only a 2.21% chance that this value could occur due to noise. As shown in Table 2, the quadratic model is suggested because of the coefficient of variation value is 10.76, which indicate that this model can be considered as a reasonable model for reproducibility. Besides, the "Predicted-R^2" of 0.7870 is in reasonable agreement with the "Adjected-R^2" of 0.9622, which shows that the proposed equation ensures the precision for the interpretation of the relationship between the independent variables and the response variable.

Table 3: the ANOVA results of variance analysis for the quadratic model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob＞F	
Model	7498.37	9	833.15	40.64	0.0004	significant
A	209.00	1	209.00	10.19	0.0242	
B	290.28	1	290.28	14.16	0.0131	
C	2445.80	1	2445.80	119.30	0.0001	
AB	40.26	1	40.26	1.96	0.2200	
AC	36.12	1	36.12	1.76	0.2418	
BC	23.23	1	23.23	1.13	0.3358	
A^2	690.19	1	690.19	33.67	0.0021	
B^2	3943.82	1	3943.82	192.37	＜0.0001	
C^2	174.50	1	174.50	8.51	0.0331	
Residual	102.51	5	20.50			
Lack of fit	100.99	3	33.66	44.31	0.0221	significant
Pure Error	1.52	2	0.76			
Cor Total	7600.87	14				

In order to analysis effects of three key parameters(temperature, inlet pressure, reaction time) on the response value(degradation rate of MO) more intuitively, three-dimensional response surfaces derived from equation(x) are showed in Figure 3(a)-(c). Three figures are showed with one independent factor being kept constant at the optimal statistic and the other two independent factors varied within the experimental range. It is obvious that a rounded ridge running diagonally along the plot, indicating that three key parameters had slight interactive effects on the response value, and each of the factors showed the great dependence on the response value. As we can see in the above figures, the maximum degradation rate of 82.97% is achieved at the peak of the surface, the corresponding experimental condition of which is temperature of 38.13 °C, inlet pressure of 0.4 Mpa and reaction time of 60min. Making a comprehensive analysis with equation(x) and

Figure 2(a)-(c), as the temperature and inlet pressure increased in a certain range, the degradation rate showed a significant growth. However, as the inlet pressure and temperature continuously increased beyond the optimal values, the degradation rate decreased on the contrary. That is to say, both the temperature and inlet pressure exist the optimized value in the experimental tests. The reasons for this phenomenon is the higher temperature and inlet pressure in a certain degree lead to an increase in the cavitation intensity (Vichare Gogate et al., 2000), then the enhanced cavitation intensity would contribute to the degradation of the target pollutions. Referring to the factor of reaction time, the degradation rate was increased with longer reaction time. Because this factor is related to the amount of ·OH induced by the hydrodynamic cavitation. The longer the reaction time is, the more cavitation events would happen. Subjected to these experimental conditions, water molecules are dissociated into ·OH radicals, and subsequently expose organic pollutants to these radicals and degrade them eventually (Saharan and Pandit et al., 2011). It also can be recognized from the P value that three influencing factors on degradation rate with importance from big to small were reaction time, inlet pressure and temperature, in order. The reaction time as the dominant factor is due to the extension of reaction time could increase the amount of ·OH leading to the higher degradation rate. It can be imagined that the degradation rate of the pollutants could reach 100% if the reaction time is long enough. In addition, the inlet pressure could largely affect the hydrodynamic cavitation intensity, for the cavitation is generated by pressure variation induced by the constrictions of orifice plates in the flow liquid (Gogate and Pandit, 2001). With regard to the temperature, it is associated with the saturated vapor pressure of the solution. The higher the solution temperature is, the higher saturated vapor pressure is. Then the high saturated vapor pressure decreased the pressure drop needed by hydrodynamic cavitation, hence, cavitation is more likely to occur. Whereas, the effect of inlet pressure is more direct than that of temperature. To sum up, the effect on the degradation rate in a descending order as: reaction time, inlet pressure, temperature.

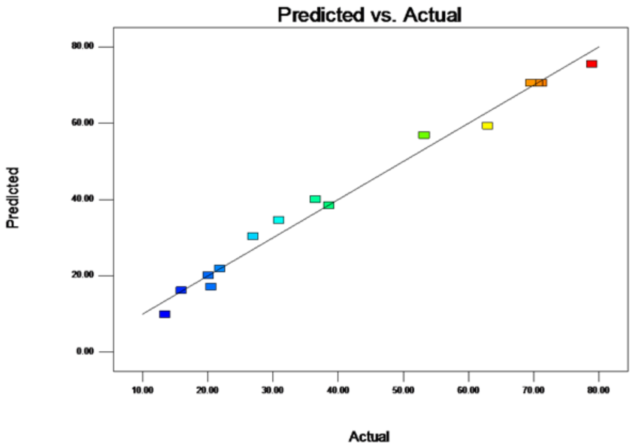
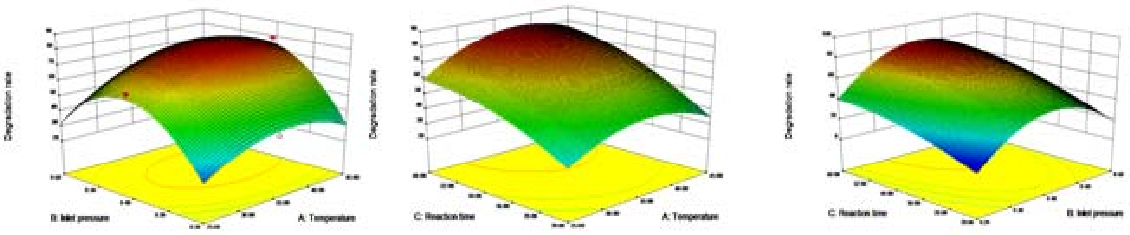


Figure 2: Predicted values versus actual values of degradation rate



(a) (b) (c)

Figure 3: Three dimensional contour plots for degradation rate: fixed at each optimum condition.(a) Reaction time of 60 min; (b) inlet pressure of 0.43 Mpa;(c) temperature of 38.14℃.

In the end, based on the BBD results, a verification test was conducted three times in order to verify the reliability of the statistically optimized conditions and the corresponding degradation efficiency. The replication experiment results show that the degradation rate of 82.8% could obtained under condition that temperature of

35~40 °C, inlet pressure of 0.4 Mpa and reaction time of 60min. This result is very close to the simulation result. So this quadratic model could simulate the actual experiment very well. In conclusion, the ClO_2-HC system proposed in this paper is a suitable way to degrade the MO in the HC system. This model simplifies the whole operation and easy to realize. The prediction shows no difference to actual measuring result.

4. Conclusion

Response surface methodology (RSM) based on Box-Behnken design (BBD) was successfully used to study the effect of three parameters including solution temperature, inlet pressure, reaction time on degradation of MO with combined technique. The polynomial model was obtained with BBD analysis. Based on the fitting data of variance analysis and residual analysis for regression equation, this model can accurately predict the degradation of methyl orange with high credibility. The prediction results showed that the maximum degradation rate of MO was obtained under the following conditions: temperature of 38.13□, inlet pressure of 0.4 Mpa, reaction time of 60min and the optimal degradation rate of 82.97% which was very close to the actual experimental result of 82.8%. It also can be recognized that three influencing factors on degradation rate with importance from big to small were reaction time, inlet pressure and temperature, in order.

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