

An Experimental Study on the Degradation of Methyl Orange by Combining Hydrodynamic Cavitation and Chlorine Dioxide Treatments

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The degradation of methyl orange, an important pollutant from the dyeing industry, has been enhanced by combining hydrodynamic cavitation with chlorine dioxide oxidative treatment, using an orifice-plate type hydrodynamic cavitation reactor device. The effects of inlet pressure, solution temperature, solution pH, chlorine dioxide concentration, and reaction time on the methyl orange degradation rate were analyzed. An optimal degradation rate of 90.5% was achieved at an inlet pressure of 0.4 MPa, temperature of 35 °C, chlorine dioxide concentration of 8 mg/L, and reaction time of 90 min, which is 4.9 and 2 times higher than that obtained with hydrodynamic cavitation or chlorine dioxide treatment alone (degradation rates of 18.5% and 45.8%, respectively), and enhancement factor f is 3.625. This combined technique is insensitive to the solution pH, and the good degradation effect could be achieved when pH varies from 3 to 9. The combined technique effectively degrades the methyl orange according to the changes of UV-Vis spectrum.

1. Introduction

Rapid developments in the printing and dyeing industry in recent times have brought about great improvements in the quality of life of people. However, the wastewater generated by this industry has also resulted in significant levels of water pollution, posing serious threats to human health and social development (Weisburger, 2002). The wastewater from the printing and dyeing industry is characterized by its deep color, complex pollutant composition, high variation in water quality, high BOD and COD contents, and poor biodegradability (Ochoa, 2016). They are also difficult to treat and pose severe environmental hazards. In view of this, the development of energy-efficient solutions for the degradation of this type of wastewater has become a focus area for research.

Methyl orange (or Sodium 4-[(4-dimethylamino) phenyldiazenyl] benzenesulfonate) is a common azo dye with features of both a dye and an acid-base indicator in aqueous solutions. Since methyl orange does not degrade easily in the conventional manner, the treatment of methyl orange in the effluent is a major challenge for the dyeing industry (Jing and Guo et al. 2009). In treating the printing and dyeing wastewater, methyl orange of a certain concentration is selected as a typical degradation compound.

Currently, various advanced oxidation processes (AOPs) are either used individually or in various combinations for the degradation of methyl orange (Guin et al., 2017). Many researchers have studied the application of various methods including electrochemical techniques, photocatalytic oxidation technology, Fenton technology, and ultrasonic technology for the degradation of methyl orange. While all of these techniques degrade methyl orange partially, they also have certain disadvantages (Pilla and Gupta, 2015; Luo et al., 2016; Pang et al., 2011). In order to overcome the limitations of any single oxidation method in actual applications, some researchers have adopted the use of a combination of AOPs for efficiently degrading methyl orange (Khunphonoi and Grisdanurak, 2016; Mohammadi and Mohammadi, 2016; Hassanpour and Safardoust, et al., 2016). However, these combined degradation techniques still face the following problems: 1) the catalysts are often difficult to prepare; 2) reaction conditions are very rigorous; and 3) they are still in the experimental stage and are yet to be commercialized.

A novel type of AOP called hydrodynamic cavitation (HC) is useful for degrading complex organic and poisonous substances effectively, (Gogate, 2002; Gogate and Bhosale, 2013). However, the use of HC on its own has disadvantages such as low degradation rate for organic substances and poor cost efficiency in industrial applications (Huang et al., 2013). An environmental friendly compound—chlorine dioxide, which is characterized by energy efficient and less undesired disinfection by-products (Ayyildiz et al. 2009; Huang and Wu, 2013), could degrade organic substances effectively. So in this context, for the first time, we explore the application of HC technology in combination with chlorine dioxide oxident for the degradation of simulating dyeing-wastewater—methyl orange, in an attempt to find a simple and cost-effective technology. The effectiveness of combined HC-ClO₂ treatment in degrading methyl orange was compared to individual treatments by the two methods. Additionally, in the case of the combined treatment, the effects of inlet pressure, solution pH, chlorine dioxide concentration, and reaction time on the methyl orange degradation rate were analyzed. In addition, the reaction kinetics and degradation intermediates were also investigated. Improvement of wastewater treatment method is beneficial to the development of industry and it is also a necessary part of environmental protection. So it becomes imperative to do this research.

2. Materials and method

2.1 materials and experimental setup

This part is in accordance with another paper called Degradation of Methyl Orange Using Hydrodynamic Cavitation Technology Combined with Chlorine Dioxide oxidation: Optimization using Box – Behnken design (BBD) written by Sijing Yang and Riya Jin et al.

2.2 Calculation of methyl orange degradation rate

The methyl orange concentration could be calculated based on the absorbance value and its degradation rate could be calculated using the changes in the absorbance values. The degradation rate was computed as Equation(1) and (2):

$$A = 0.072C_{MO} - 0.004 \quad (1)$$

$$\omega_{MO} = \frac{\Delta A}{A_0 + 0.004} \quad (2)$$

In which, A_0 is initial absorbance of the solution; ΔA is difference value of solution absorbance before and after the cavitation; ω_{MO} is the degradation rate of methyl orange.

3. Results and Discussion

3.1 Effect of inlet pressure and solution temperature with HC technique

An orifice plate was added to the main pipeline and the solution temperature was varied from 20 °C to 40 °C (20, 25, 30, 35, 40 °C) via adjusting the cooling system. According to the bypass regulation, the inlet pressure varied from 0.2 to 0.6 MPa (0.2, 0.3, 0.4, 0.5, 0.6 MPa) at each solution temperature, respectively. Figure 2 showed the dependence of methyl orange degradation rate on the inlet pressure and solution temperature.

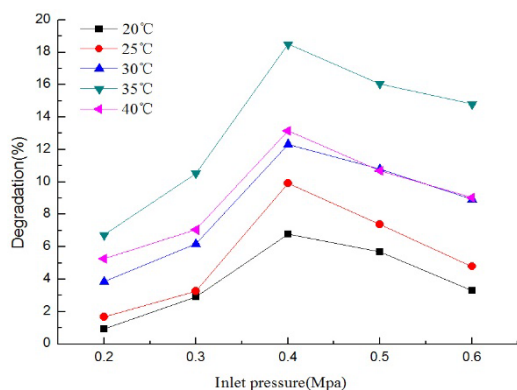


Figure 1: Effect of inlet pressure and solution temperature on methyl orange degradation with HC technique

As shown in the Figure 1, the optimal inlet pressure is 0.4Mpa, for the lower and higher pressure have negative effect on the hydrodynamic cavitation, leading to the decrease to the degradation rate of methyl orange. The solution temperature influences the saturated vapor pressure of the liquid and an increase in the solution temperature results in an increase in the saturated vapor pressure (Gogate et al. 2003). The pressure behind the orifice plate may easily be reduced below the saturated vapor pressure, which favors the cavitation effect. Therefore, the degradation efficiency of methyl orange increases with increase in the solution temperature to a certain extent (20~35 °C). Meanwhile, increase in the solution temperature intensifies the molecular movements and accelerates the chemical oxidation between chlorine dioxide and methyl orange. When the solution temperature exceeds 35 °C, chlorine dioxide gas escapes from the liquid, thereby suppressing the oxidative degradation of methyl orange. The similar results can be seen in the degradation experiment of 2, 4-dinitrophenol and andalochlor (Tao and Cai, et al. 2016), the optimal temperature are 35 °C and 30-40 °C, respectively. The degradation rate of the pollutants both offered upgrade firstly than descending latter tendency with the change of temperature.

Based on these results, we conclude that an inlet pressure of 0.4 Mpa and solution temperature of 35 °C are optimal for maximizing the degradation rate of methyl orange in the hydrodynamic cavitation treatment process.

3.2 Effect of chlorine dioxide concentration and solution pH with HC-CIO₂ technique

Under optimum pressure of 0.4 MPa and optimum temperature of 35 °C, adjusting pH value of solution at 3.2, 5.4, 7.2, 8, 9.2. Chlorine dioxide (concentration: 2 to 10 mg/L) was combined with hydrodynamic cavitation to degrade methyl orange of different pH in an aqueous solution. Fig.4 showed the dependency of solution pH and chlorine dioxide concentration to the degradation rate of methyl orange.

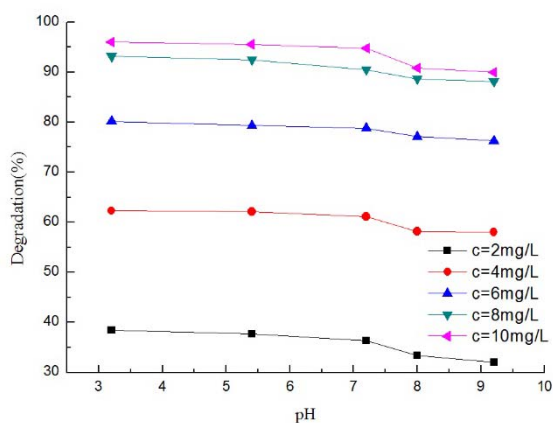


Figure 2: Effect of temperature and concentration of chlorine dioxide on methyl orange degradation with combined experiment

As shown in Figure 2, at a given solution pH, the degradation rate of methyl orange increases continuously with increase in the concentration of chlorine dioxide, although the magnitude of increase diminishes. As a chlorine dioxide concentration greater than 8 mg/L, the rate of increase in the degradation efficiency obviously slows down. This indicates that further increase in the concentration of chlorine dioxide will only very slightly influence the degradation rate of methyl orange. From an economic point of view, the preferred concentration of chlorine dioxide is 8 mg/L under the present experimental conditions. Therefore, the results obtained at this concentration were analyzed. With increase in the concentration of chlorine dioxide, the oxygen content in the aqueous solution increases, thereby increasing the yield of hydroxyl radicals and degradation rate of methyl orange.

The effect of pH on the degradation rate is very slight, acidic (pH=3.2, 5.4) and neutral condition (pH=7.2) are beneficial to the degradation than alkaline condition (pH=8, 9.2), with difference no more than 3%. In the pH range of 3.2 to 9.2, the disproportionation reaction occurs in only a small proportion of chlorine dioxide, which have slightly impact on its oxidation capacity (Liu and Huang, et al. 2006). It can be seen that the effect of pH on the removal of methyl orange is weak and almost can be negligible between pH value of 3 to 9. Usually, an acid condition is favored by pollutant degradation by hydrodynamic cavitation as a result of the condition is benefit for the generation of hydroxyl radicals (Tao et al., 2016), while the introduction of chlorine dioxide may reduce the effect of solution pH.

3.3 Effect of reaction time and effect of the combination of treatments on the methyl orange degradation

Under optimal experimental conditions, the degradation of methyl orange by hydrodynamic cavitation alone, chlorine dioxide treatment alone, and a combination of the two treatment procedures are compared. The combined treatment was conducted at an inlet pressure of 0.4 MPa, solution temperature of 35 °C, solution pH of 7.2, chlorine dioxide concentration of 8mg/L, and reaction time of 90 min. On the other hand, treatment involving chlorine dioxide alone was conducted at a temperature of 35 °C, chlorine dioxide concentration in the range of 8 mg/L, and reaction time of 90 min. The hydrodynamic cavitation treatment alone was conducted at an inlet pressure of 0.4 MPa, solution temperature of 35 °C, and reaction time of 90 min. Figure 4 showed the contrast to degrading effect of three different experimental conditions.

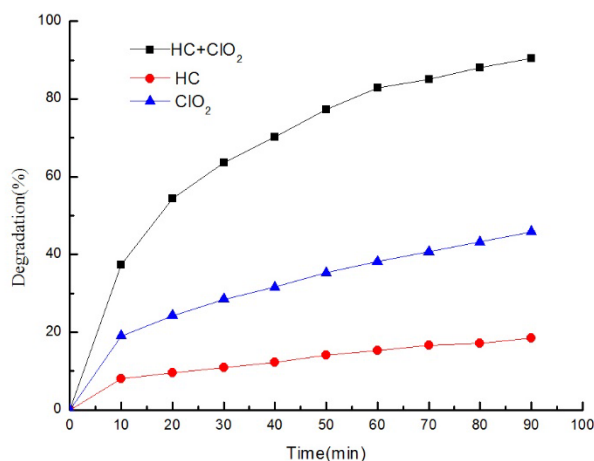


Figure 3: The contrast to degrading effect of three different experimental conditions

The relationship between methyl orange degradation and processing time under the three different treatment conditions are shown in Figure 3. As illustrated in Figure 3, the degradation rate of methyl orange increases with processing time under all the three experimental conditions. However, the degradation rate of methyl orange in the combined hydrodynamic cavitation and chlorine dioxide treatment increases most rapidly with time. Specifically, at a treatment time of 90 min, the degradation rates of methyl orange are only 18.5% and 45.8%, respectively, by hydrodynamic cavitation treatment and chlorine dioxide treatment alone. The value of degradation rate obtained by the HC-ClO₂ technique didn't equal to the sum of degradation rate of the single methods according to experimental results. So Hydrodynamic cavitation and the oxidation of chlorine dioxide promote each other and make a synergetic effect on the degradation of methyl orange in the enhanced process of HC-ClO₂ treatment.

The pseudo first-order kinetics equation listed in equation (3) was used to test the experimental datas obtained by three different degradation techniques. The linear fitting equations and associated parameters such as apparent rate constant, correlation coefficient and half-time of three different experimental conditions are showed in table1.

$$\ln \frac{c_t(A)}{c_0(A)} = -kt \quad (3)$$

Table 1: Apparent rate constants, correlation coefficient, linear fitting equation and half-time of three different experimental conditions

	HC	ClO ₂	HC-ClO ₂
Linear fitting equation	y = 0.0015x + 0.0713	y = 0.0049x + 0.1794	y = 0.0232x + 0.2967
Correlation coefficient(R ²)	0.9935	0.9953	0.9961
Apparent rate constant (K)/min ⁻¹	0.0015	0.0049	0.0232
Half-time/min	462	141.43	29.87

As shown in Table 1, it is evident that the combined treatment has the higher apparent rate constant and the shorter half-time than those of the single method. The enhancement factor *f* can be calculated as equation (4):

$$f = \frac{K_{HC-ClO_2}}{K_{HC} + K_{ClO_2}} = \frac{0.0232}{0.0015 + 0.0049} = 3.625 \quad (4)$$

Therefore, it is clear that the introduction of chlorine dioxide enhances the degradation of methyl orange by hydrodynamic cavitation. The HC-ClO₂ system could improve the degradation efficiency greatly and decrease the doses of chlorine dioxide than the single method for the same degradation rate. According to the results of the study, this simple and easily implementable method is effective for the degradation of methyl orange.

3.4 Analysis of degradation intermediates with HC-ClO₂ treatment

The presence of an azo group and benzene ring in the methyl orange molecule results in absorption peaks in the visible and ultraviolet regions, respectively. The wavelength of the absorption peak varies with the type of parent compound. Figure 5 showed the Uv-vis spectra of degrading methyl orange with combined experiment.

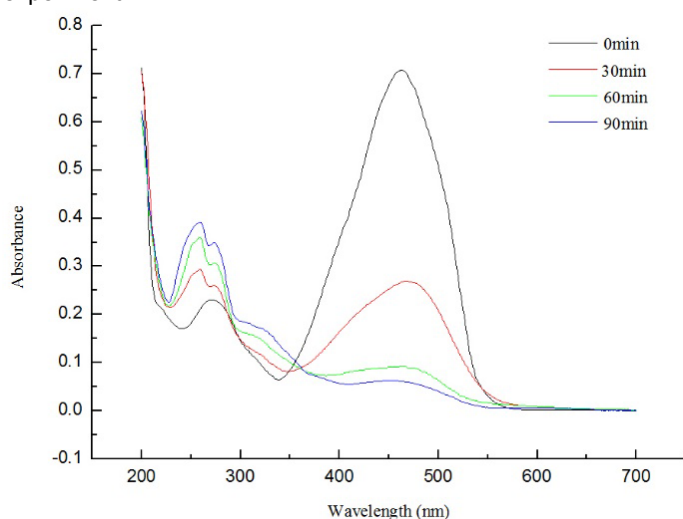


Figure 4: Uv-vis spectra of degrading methyl orange with combined experiment

The UV-vis spectra of the methyl orange solution subjected to combined treatment for 0, 30, 60, and 90min are shown in Figure 4. As shown in Figure 4, at 0 min, the methyl orange solution is undegraded. Absorption peaks are observed at 464 and 270 nm, which are generated from the chromophoric groups of methyl orange. The highest characteristic absorption peak is located at 464 nm and is generated from the chromophoric group of methyl orange. With increase in treatment time, the intensity of the peak at 464 nm decreases, indicating that the azo groups (-N=N-) in the methyl orange molecules are destroyed. In the 250-300 nm wavelength range, strong absorption peaks corresponding to aromatic substances are observed and increased with time. This spectra indicates the continuous degradation of methyl orange over time.

4. Conclusions

In this study, the combined treatment involving hydrodynamic cavitation and chlorine dioxide oxidation increases the degradation efficiency of methyl orange in aqueous solutions greatly compared to individual treatments, the enhancement factor f of which is 3.625. Compared with the single method, the HC-ClO₂ system could improve the degradation efficiency greatly and decrease the doses of chlorine dioxide. This combined technique is insensitive to the solution pH, and the good degradation effect could be achieved when pH varies from 3 to 9. The optimal conditions for the combined treatment were determined to be as follows: inlet pressure of 0.4MPa, solution temperature of 35 °C, chlorine dioxide concentration of 8mg/L, and reaction time of 90 min. The changes of UV-Vis spectrum indicated that chlorine dioxide effectively degrades the azo dyes in short time.

Acknowledgement

This work is supported by the Science and Technology Committee of Shanxi Province (2015031020).

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