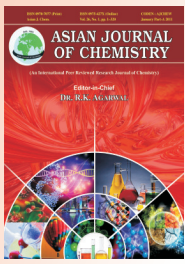
Asian Journal of Chemistry; Vol. 26, No. 15 (2014), 4845-4848

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16257



Degradation of Rhodamine B by Ultrasound/Fenton-Like Reagent

PENG ZHANG*, WEI ZHANG, XUE ZHANG, BOZHI REN, HONGPU MA and ZHENGHUA WANG

College of Civil Engineering, Hunan University of Science and Technology, Xiangtan 411201, Hunan Province, P.R. China

*Corresponding author: Tel: +86 18673218500, E-mail: zhangpeng388@126.com

Received: 30 August 2013; *Accepted*: 11 December 2013; *Published online*: 16 July 2014; AJC-15584

The catalytic oxidation of Rhodamine B using the ultrasound/Fenton-like process was investigated. 11.3 % of Rhodamine B using the ultrasound process and 50.1 % of Rhodamine B using Fenton-like process were obtained in 90 min. While the degradation of of Rhodamine B using ultrasound/Fenton-like process was 99.2 % obtained in 90 min. During the ultrasound/Fenton-like process, parameters affecting ultrasound degradation degree such as reaction time, pH, dosage of H_2O_2 and the dosage of Cr^{6+} were examined under the sound power was 250 W and the ultrasound frequency was fixed at 45 kHz. The results showed that after 90 min, the degradation degree could reach 98.1 % under the optimum conditions, when the initial pH value of the model dye was 3, the dosage of H_2O_2 was 11 uL and the dosage of Cr^{6+} was 0.8 mmol. In addition, the importance of the parameters on degradation degree was investigated by the model. The degradation degree was enhanced significantly as listed herein decreasing order of effectiveness: H_2O_2 dosage > Cr^{6+} dosage > Time > pH.

Keywords: Degradation, Rhodamine B, Synergistic effect, Ultrasound, k-Means clustering algorithm.

INTRODUCTION

De-coloration of wastewater containing dyes in industrial effluents has been a key issue for a long time. This is mainly because of that these organic molecules pose a direct or indirect threat to the environment due to their chemical nature[1]. The disposal of wastewater containing azo dyes is an environmental concern since the associated color is quite noticeable to the public and some dyes may have carcinogenic and/or teratogenic effects on human[2]. Many researchers have been forward to handle the clean-up of effluents containing these chemicals.

Advanced oxidation processes (AOPs), based on the chemical, photochemical and photo-catalytic production of •OH radicals which acts as strong oxidizing agents have emerged as a promising technology for the degradation of organic pollutants[3-7].

Fenton reaction and Fenton-like reaction are advanced oxidation process based on the generation of •OH radical[8,9]. In recent years, Fenton process was widely focused on the treatment of high color dye wastewater because of the powerful oxidation of •OH. And now, more and more research have focus on the synergistic effect of Fenton-like reaction with other methods.

The purpose of this paper is to assess the respective and interactive effects of operating parameters (*e.g.* pH, hydrogen peroxide, Cr^{6+} dosage, *etc.*) on the degradation degree.

EXPERIMENTAL

Analytically pure sodium hydroxide and sulfuric acid of concentration 0.50 mol/L reagents were used for regulating the pH of dye wastewater. The other reagents used in the study include a solution with 30 % H_2O_2 and analytically potassium dichromate.

The instruments used in the experimental setup are as follows: KQ-250VDB ultrasound generator supplied by Kunshan Ultrasound Instrument Co. Ltd from Jiangshu, China. The generator had a fixed frequency of 28 kHz and a fixed output power of 250 W; pH meter: DELTA 320 pH meter supplied by Mettler Toledo Instruments Co., Ltd., from Shanghai, China; TU-1810 UV-visible spectrophotometer supplied by Purkinje General Instrument Co. Ltd from Beijing, China; Micro-injector supplied by Zhenhai Glass Instrument Factory from Ningbo, China.

Water sample: Rhodamine B was used without further purification. A reference solution (1000 mg/L) of the simulation dye wastewater was prepared with deionized water and further diluted to various concentrations.

Experimental procedure: The spectral absorbance curve of Rhodamine B wastewater was obtained by using UV-visible spectrophotometer and the peak absorption was found at a wavelength of 554 nm. A series of reference solutions of Rhodamine B were prepared from the 1000 mg/L reference

solution by using the UV-visible spectrophotometer at a wavelength of 554 nm, the absorbance of standard solutions was determined to produce a calibration curve.

Ultrasound was carried out using a slotted reactor made of stainless steel and several ultrasound transducers positioned under the bottom of the tank. The ultrasound frequency was fixed at 45 kHz and the fixed output power was 250 W. During ultrasound, the reaction temperature was controlled at about 30 °C by a combination of the external circulation pump and water flow into the water bath. The sonochemical degradation for different systems (pH, H_2O_2 dosage, Cr^{6+} dosage) was determined by taking samples at 90 min interval and measuring the absorbance by a UV-visible spectrophotometer at a wavelength of 554 nm. Using the calibration curve, the degradation degree (q) of Rhodamine B was calculated using the expression:

$$q = \frac{C_0 - C_e}{C_0} \times 100\ \%$$

where C_0 and C_e are the initial concentration and concentration obtained for the corresponding time, respectively.

RESULTS AND DISCUSSION

Synergistic reaction of ultrasound and Fenton-like: The purpose of experiment was to investigate the degree of degradation with and without ultrasound by using Fenton-like prosess. The concentration of Rhodamine B was 50 mg/L, pH value was 3, the dosage of H_2O_2 was 11 μL and the dosage of Cr^{6+} was 0.8 mmol/L.

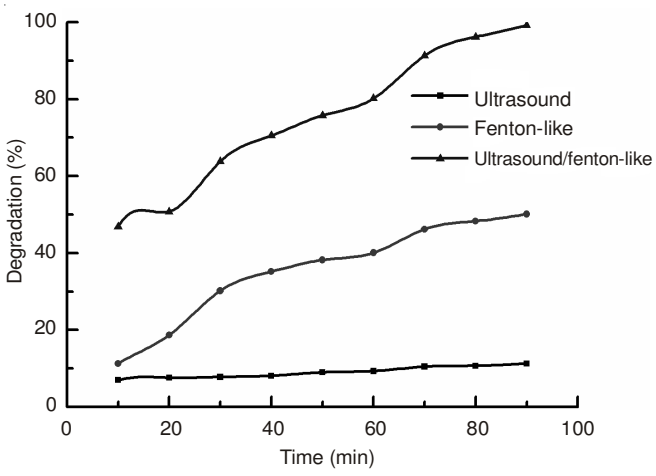


Fig. 1. Removal of Rhodamine B under different conditions

Fig. 1 showed that the degradation degree was up to 11.3 and 50.1 %, respectively by using single ultrasound treatment and Fenton-like process in 90 min. During the ultrasound/Fenton-like process, 99.2 % degradation of Rhodamine B was achieved in 90 min. This means that the degradation efficiency of ultrasound/Fenton-like process was not only higher than single ultrasound process, but higher than Fenton-like process owing to the synergistic reaction of ultrasound and Fenton-like process lead to generate more •OH radicals. This may be because of ultrasound can generate ultrasound cavitation effect and mechanical effect. This can produce strong oxidizing hydroxyl radicals, with clean surface of the catalyst, strengthen the role of mass transfer, thus enhancing the degradation rate.

Effect of pH on the degradation degree: The pH is an important parameter for degradation of Rhodamine B. It affects the formation of •OH and the concentration of Cr^{6+} and Cr^{3+}. Therefore the purpose of this experiment is to investigate the effect of the pH value on the degradation of Rhodamine B. The concentration of Rhodamine B was 50 mg/L, the dosage of H_2O_2 was 11 μL and the dosage of Cr^{6+} was 0.8 mmol/L.

Fig. 2 showed that as the increase of the initial pH values from 1 to 3, the degradation degree of Rhodamine B was up to 97.5 %. However, with the increase of pH from 3 to 5, the degradation degree decreased range from 97.5 to 58.3 %. The maximum removal rate of 97.5 % was obtained at pH 3. Hence, pH 3 was adopted as the optimum pH based on ultrasound/Fenton-like process. The Fenton-like reagent play a role influence a lot by pH value. When the pH value is higher, on the one hand, it will inhibit the production of •OH radicals and the Cr^{6+} and Cr^{3+} will be precipitate as the form of hydroxide, which lead to the reduction of catalytic activity. On the other hand, H_2O_2 could decomposition of invalidation in alkaline conditions, lead to the low utilization rate of H_2O_2. When the pH value is too low (< 3), the conversion of Cr^{6+} and Cr^{3+} will be inhibited. The reaction can not proceed smoothly, which could made the degradation rate decrease.

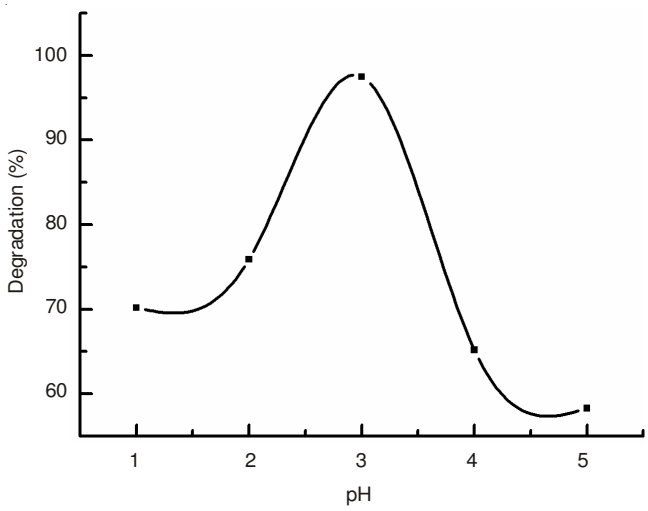


Fig. 2. Effect of pH on the degradation degree

Effect of H_2O_2 dosage on the degradation degree: In ultrasound/Fenton-like process, H_2O_2 concentration affects the degradation of Rhodamine B and its optimal concentration may also reduce the operating cost. In order to study the effect of H_2O_2 concentration level on the formation of •OH radicals, another set of experiments were conducted. In these experiments, the concentration of Rhodamine B was 50 mg/L, pH value was 3 and the dosage of Cr^{6+} was 0.8 mmol/L.

Fig. 3 showed that after a reaction time of 90 min, 92.8 % of Rhodamine B was degradated when H_2O_2 was 10 μL, while more than 99.0 % was degradated at H_2O_2 11 μL, H_2O_2 is one of the reactantd and more •OH radicals are expected to form as H_2O_2 concentration increase. However, when H_2O_2 concentration was raised from 11.0 to 14.0 μL, the degradation of Rhodamine B dropped down. This reason behind this may be attributed to the fact that the scavenging of •OH radicals will

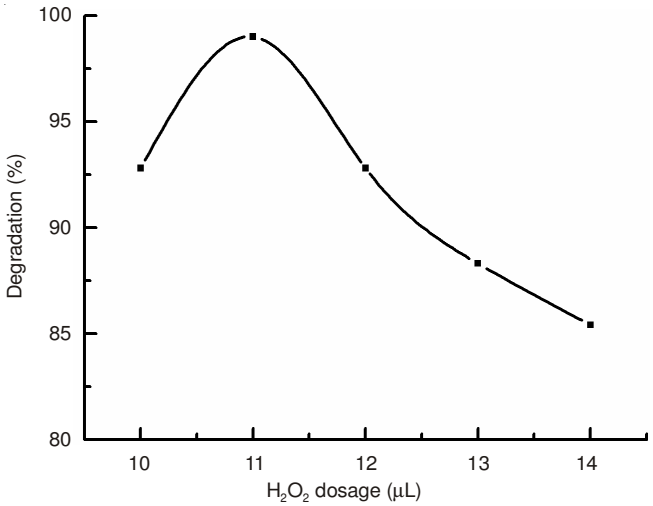


Fig. 3. Effect of H_2O_2 dosage on the degradation degree

occur at a higher H_2O_2 concentration as expressed by the following equation:

$$^{\bullet}OH + H_2O_2 \longrightarrow H_2O + HO_2^{\bullet} \quad (1)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \longrightarrow H_2O + O_2 \quad (2)$$

$$^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2 \quad (3)$$

The scavenging effect decreased the number of $^{\bullet}OH$ radicals in the reaction system. As a result, degradation rate was significantly decreased. This means that the initial concentration of H_2O_2 has to be optimized for a certain Fenton-like process in order to achieve a better degradation rate. Hence, 11 μL of H_2O_2 dosage as a result of its higher degradation rate.

Effect of hexavalent chromium dosage on the degradation degree: The effect of different Cr^{6+} concentration on the rate of degradation has been investigate. In these experiments, the concentration of Rhodamine B was 50 mg/L, pH value was 3 and the dosage of H_2O_2 was 11 μL.

Fig. 4 showed that after a reaction time of 90 min, 30.6 % of Rhodamine B was degradated when the dosage of Cr^{6+} was 0.4 mmol/L, while more than 92.8 % was degradated at Cr^{6+} was 1 mmol/L. This is because if there was no Cr^{6+}, the decomposition of $^{\bullet}OH$ is slow from H_2O_2. While the concentration of Cr^{6+} was low, the reaction was:

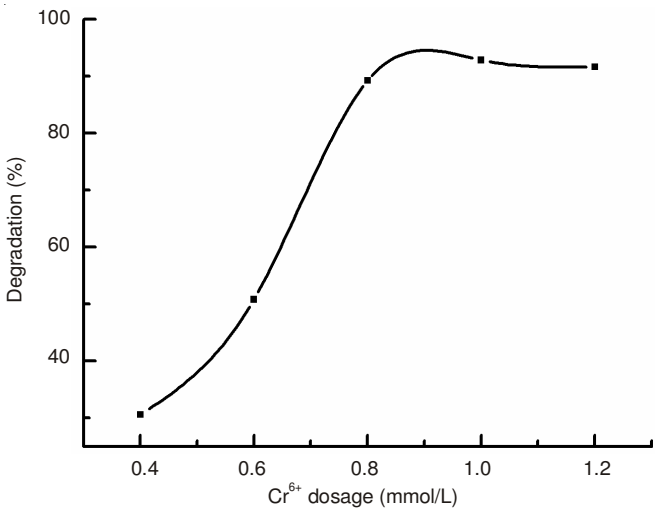


Fig. 4. Effect of Cr^{6+} dosage on the degradation degree

$$Cr^{3+} + H_2O_2 \rightarrow Cr^{6+} + {}^{\bullet}OH + OH^- \quad (4)$$

$$Cr^{4+} + H_2O_2 \rightarrow Cr^{5+} + {}^{\bullet}OH + OH^- \quad (5)$$

$$Cr^{5+} + H_2O_2 \rightarrow Cr^{6+} + {}^{\bullet}OH + OH^- \quad (6)$$

$$HO_2^{\bullet} + Cr^{6+} \rightarrow Cr^{3+} + O_2\uparrow + H^+ \quad (7)$$

From the equation of (4-7), we know that the reaction rate was very slow and the quantity of generation $^{\bullet}OH$ was small. The H_2O_2 in the thermal effect of ultrasound was decomposed to H_2O and O_2 which reduce the percentage of removal rate. While increase the dosage of Cr^{6+}, the removal rate will be increased. When the dosage was too high, the rate of decomposition was too quick, lead to the reaction between $^{\bullet}OH$, caused the decline of utilization rate of H_2O_2.

Assessment of factors importants: Cluster analysis is a statistical tool used for grouping large data sets into several categories using predefined variables[10]. k-Means clustering algorithm was developed to help classify or to group the studied objects based on attributes/features into k number of group. The grouping is done by minimizing the sum of squares of distances between data and the corresponding cluster centroid. k-Means clustering algorithm is an unsupervised learning algorithm. If the clustering sample set is defined X = [i = 1, 2, 3…,N] the C cluster centers are $z_1,z_2,\ldots,z_j$ and w_j (j = 1, 2, …,C) is set as the cluster category, then the cluster centers were given by the following form:

$$z_j = \frac{1}{N_1} \sum_{x \in w_j} x$$

The objective function takes the form:

$$J = \sum_{i=1}^{C} \sum_{j-1}^{k} d(x_i, z_j)$$

where, n is the number of the samples concluded in w_j; d is Euclidean distance; $d(x_i, z_j)$ was the distance among samples. The objective function J was the the minimum mean square error of cluster.

After the cluster number is specified C, samples are classified and the clustering results are defined by the cluster centers. Based on the given objective function, the clustering algorithm is performed by the iterative methods.

In this research, the importance of the variables was estimated using the algorithm in digital form (Fig. 5). The higher the importance of the variable is, the greater influence of degradation degree of the Rhodamine B. At the same time, the estimated accuracy was 90.1 % after the estimation of the variables using the model. Fig. 5 shows the favorable effects on degradation degree of Rhodamine B which are listed in the following decreasing order: H_2O_2 dosage > Cr^{6+} dosage > Time > pH. It's obviously seen that the H_2O_2 dosage is the most important factor affecting the degradation degree of the Rhodamine B.

Conclusion

The ultrasound/Fenton-like process was more efficient than single ultrasound Fenton-like process. The optimum pH for both the formation of $^{\bullet}OH$ radicals and removal rate was 3. The H_2O_2 dosage was a main factor for removal rate based on ultrasound-Fenton-like process. 11 μL of H_2O_2 showed the highest removal rate. The Cr^{6+} as catalyst accelerated the

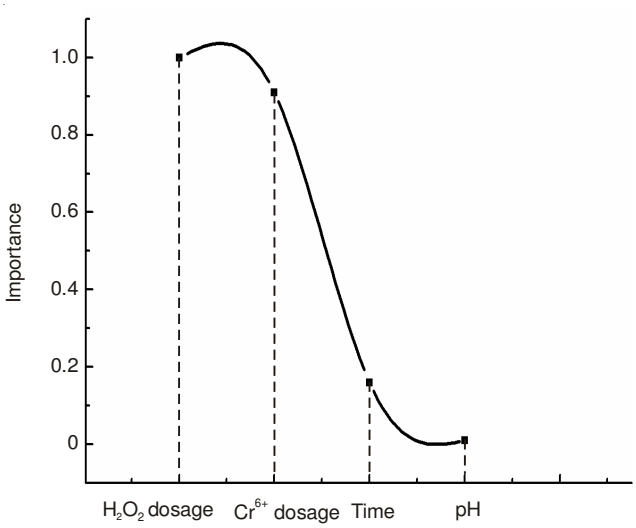


Fig. 5. Operational parameter

degradation of Rhodamine B 1 mmol/L of Cr^{6+} dosage could be used as the optimum dosage based on ultrasound/Fenton-like process.

The model was used to evaluate the importance of the parameters affecting the ultrasound/Fenton-like process, which was listed in following descending order: H_2O_2 dosage, Cr^{6+} dosage, time and pH value.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support provided by the National Natural Science Foundation of China (Project No.NSFC, 51174090), Hunan Provincial Natural Science Foundation of China (12JJ8007) and Scientific Research Fund of Hunan Provincial Education Department, China (No. 10K027).

REFERENCES

1. C. Hachem, F. Bocquillon, O. Zahraa and M. Bouchy, *Dyes Pigments*, **49**, 117 (2001).
2. H. Zhang, Y.J. Lv, F. Liu and D.B. Zhang, *Chem. Eng. J.*, **138**, 231 (2008).
3. J.T. Ge and J.H. Qu, *J. Hazard. Mater.*, **100**, 197 (2003).
4. H.L. Zheng, Y.X. Pan and X.Y. Xiang, *J. Hazard. Mater.*, **141**, 457 (2007).
5. H. Wang, F. Li, A.A. Keller and R. Xu, *Water Sci. Technol.*, **60**, 1803 (2009).
6. K. Tanaka, K. Padermpole and T. Hisanaga, *Water Res.*, **34**, 327 (2000).
7. M. Perez, F. Torrads and X. Domenech, *Water Res.*, **36**, 2703 (2002).
8. H.L. Zheng, H.Q. Zhang, X.P. Sun, P. Zhang, T. Tshukudu and G. Zhu, *Water Sci. Technol.*, **62**, 1304 (2010).
9. Z.M. Zhang and H.L. Zheng, *J. Hazard. Mater.*, **172**, 1388 (2009).
10. A.H. Omar, J.G. Won, D.M. Winker, S.C. Yoon, O. Dubovik and M.P. McCormick, *J. Geophys. Res.*, **110(D10)**, D10S14 (2005).