Optimization of Process Parameters for Enhanced Degradation of Methylene Blue by Trough Ultrasonic

Yong-guang Bi¹,³, Yu-hong Zheng³, Li Tang³, Juan Guo²,⁴,*, and Shao-qi Zhou¹,⁵,*

¹School of Environment and Energy, South China University of Technology, Guangzhou 510006, Guangdong, China
²College of Food Science, Guangdong Pharmaceutical University, Zhongshan 528458, China
³School of Pharmacy, Guangdong Pharmaceutical University, Guangzhou 510006, Guangdong, China
⁴GDPU-HKU Zhongshan Biomedical Innovation Platform, Zhongshan, 528400, China
⁵Guizhou Academy of Sciences, Guiyang 550001, Guizhou, China

*Corresponding author
ygb@gdpu.edu.cn

Abstract. Due to the complex quality and the large discharge of printing and dyeing wastewater, it will pollute the environment and affect human health. Therefore, how to use efficient and inexpensive treatment methods to treat printing and dyeing wastewater has become an urgent problem to be solved. At present, most printing and dyeing wastewater contains methylene blue pollutants. Based on the previous research in this article, the process conditions for the enhanced degradation of methylene blue by trough ultrasound are optimized. Orthogonal test results show that the optimal process parameter for the degradation of methylene blue by trough ultrasonic is pH 12.70, and the initial concentration of 10.00mg/L and an ultrasonic power of 200W, under the above optimal process conditions, the degradation rate of methylene blue is 77.95%; Ultrasound improves the rapid degradation of methylene blue through mechanisms such as cavitation, thermal and mechanical effects. This process can be used for the industrial degradation of methylene blue. The application provides a research basis.

Keywords: Methylene Blue, Ultrasound, Degradation, Process Optimization.

1. Introduction

Methylene blue, with the chemical formula C₁₆H₁₈N₃ClS, is a phenothiazine salt, dark green bronze shiny crystal or powder, It is soluble in water and ethanol, but insoluble in ethers. Methylene blue is relatively stable in the air, and its aqueous solution is alkaline and toxic [1-3]. Methylene blue is widely used in the chemical industry, clothing dye industry, biological colorants and medicines [4].

It is well known that methylene blue (MB) is a highly carcinogenic thiazide pollutant. At present, it is used in many industries, and it has a wide range of uses, such as: dyeing of fabrics, cotton and wool, etc. According to reports, people have studied the removal of MB in industrial waste through enzymatic, photodegradation, ionization chemical removal, chemical mixing, biomembrane filtration and physicochemical adsorption. At present, the most researched removal method is the adsorption
method. The number of published documents has more than tripled in the past 10 years [5,6]. The adsorption process is simple, uses low-cost, abundant adsorbents, and can maintain a high MB removal efficiency, and can also prevent the formation of secondary pollutants.

At present, with the rapid development of society and economy, people have higher and higher requirements for beauty and color, which has promoted the vigorous development of the printing and dyeing industry. However, in the printing and dyeing process, the amount of industrial wastewater is large and the composition is complex, which causes certain harm to the ecological environment. When treating these wastewater pollution, conventional adsorbents have certain limitations. For example, activated carbon, which is currently widely used as a material, has a large specific surface area and good adsorption performance, but its separation is difficult and costly [7]. At present, chemical methods can be used to make it Magnetized, so as to have the ability to quickly separate. The output of sludge from urban sewage treatment plants is large and the composition is complex. People have been discussing how to realize the recycling and harmless treatment of sludge. Using sludge to burn activated carbon can not only treat printing and dyeing wastewater, but also realize the resource-free and harmless treatment of sludge, achieving two goals with one stone.

At present, the industrial treatment methods for wastewater containing methylene blue generally include ultrasonic method and oxidation method. Among them, the oxidation method has strong oxidizing ability, easy to operate and easy to control, but the amount of oxidant is large and the cost is high. The harm of secondary pollution. With the development of sonication in recent years, N. Mariguchi discovered in 1934 that ultrasonic waves can enhance the electrolysis of water, enabling the research and application of ultrasonic technology. Ultrasonic method has the natural advantages of no secondary pollution, wide application range and strong oxidation ability [8,9]. It can also be used alone or in combination with other wastewater treatment technologies, which is in line with the current sustainable development requirements. In addition, organic dye wastewater generally has a darker chromaticity, and the penetration ability of ultraviolet light to non-transparent substances is very low, but ultrasonic waves do not have this problem, and the penetration ability of ultrasonic waves is stronger [10,11].

The principle of trough ultrasound is to transform the sound power with electrical energy into a strong mechanical vibration effect, so that the solvent in the ultrasound trough can obtain uniform power ultrasound. Due to the power ultrasonic radiation on each surface of the ultrasonic tank, many tiny bubbles in the liquid in the tank vibrate strongly back and forth under the action of ultrasonic waves. When the sound power density or sound pressure reaches a certain amount, the tiny bubbles in the liquid will expand rapidly, and then suddenly close after a short period of time. Therefore, the bubble will generate a strong shock wave after being expanded to close, causing a pressure of up to 1000 Pa and a temperature of several thousand K around the bubble. This is the strong pressure generated by the ultrasonic wave after the cavitation effect, which continuously washes away the dirt and decomposes them in the solution. In addition, when the ultrasonic wave propagates in the solution, it will produce strong positive and negative sound pressure, forming a powerful micro-jet, so as to continuously perform impact cleaning on its surface. After washing back and forth several times, the dirt surface gets a strong cleaning force, so as to clean the dirt. the goal of. If a chemical cleaning agent is added to the solution, the ultrasonic cavitation effect can produce high-speed micro-jets at the solid-liquid interface [12]. These micro-jets have a strong power to destroy dirt, and can accelerate the dissolution and decomposition of dirt and improve the chemical cleaning agent. The cleaning effect. Therefore, ultrasonic technology synergistically strengthens the object to be processed through mechanisms such as cavitation, mechanical, and thermal effects.

The principle of ultrasonic degradation is to achieve the degradation of refractory organic waste through ultrasonic cavitation, which is an extremely complex process in which the powerful energy of the sound field is gathered and the energy is released instantaneously. The whole process of ultrasonic degradation also includes oxidation reaction and degradation reaction. Generally speaking, ultrasonic cavitation means that the tiny bubble nuclei in the organic solution are excited Under the combined action of the mechanical and cavitation effects of ultrasonic waves, it is mainly manifested in a series
of processes such as vibration, growth, closure, contraction, and explosion of tiny bubbles. When ultrasound is emitted in the liquid, the tiny bubbles in the liquid will rapidly expand and become larger. After a certain degree, the bubbles will explode, resulting in instantaneous high temperature, high pressure and strong shock waves. In this way, cavitation As a result, the water vapor in the bubble core undergoes a thermal decomposition reaction, which produces free radicals such as ·OH, HO₂⁻ and ·O⁻· have strong oxidizing power and can decompose and destroy organic matter, and this part of the free radicals is again Will combine into H₂O₂ [13]. At the same time, the energy generated by the collapse of the cavitation bubble is sufficient to break the difficult-to-break chemical bonds, and the mass transfer process of the organic solution is accelerated during the reaction, which directly reduces the activation energy of the degradation reaction and accelerates the explanation rate. Under the high-pressure and high-temperature environment produced by ultrasonic cavitation and the action of free radicals with strong oxidation, organic pollutants in the water can be decomposed in a large amount.

In the early stage, we discussed the factors that affect the degradation of methylene blue by trough ultrasonic. Based on the previous research [14], this manuscript is mainly engaged in the follow-up research work, that is, using the orthogonal test method to optimize the process conditions for the ultrasonic degradation of methylene blue. The research results can provide a reference for the industrial application of ultrasonic degradation.

2. Test Equipment and Reagents

2.1 Apparatus
Desktop CNC ultrasonic cleaner, ultraviolet-visible spectrophotometer (UV-5500PC), electronic balance (SOPTOP), pH meter (PHS-3C), vacuum drying oven, etc.

2.2 Reagents
Methylene blue, sodium hydroxide and concentrated sulfuric acid, the above reagents are evenly divided into analytical grades.

3. Experimental Method
Due to the experimental methods and procedures involved in this manuscript, the authors have done the relevant foundation and reports [14].

4. Orthogonal Test Results
Nine experiments were selected to conduct orthogonal design experiments on three factors: ultrasonic power, initial concentration of methylene blue, and pH value. The results are shown in Table 1 and Table 2.
Table 1. Orthogonal Design Table

| No. | Ultrasonic power A (W) | pH B | The initial concentration C (mg/L) | Degradation rate (%) |
|-----|------------------------|------|-----------------------------------|----------------------|
| 1   | 200                    | 6.10 | 10.00                             | 27.42                |
| 2   | 200                    | 10.65| 20.00                             | 26.09                |
| 3   | 200                    | 12.70| 50.00                             | 68.96                |
| 4   | 280                    | 6.10 | 20.0                              | 23.86                |
| 5   | 280                    | 10.65| 50.0                              | 20.54                |
| 6   | 280                    | 12.70| 10.0                              | 74.89                |
| 7   | 360                    | 6.10 | 50.0                              | 23.29                |
| 8   | 360                    | 10.65| 10.0                              | 30.32                |
| 9   | 360                    | 12.70| 20.0                              | 63.61                |
| K1  |                        |      |                                   |                      |
| K2  |                        |      |                                   |                      |
| K3  |                        |      |                                   |                      |
| k1  |                        |      |                                   |                      |
| k2  |                        |      |                                   |                      |
| k3  |                        |      |                                   |                      |
| Range R |                  |      |                                   |                      |
| Optimal conditions | 200 | 12.70 |                                   | 10                   |

It can be seen from Table 1 that the order of magnitude affecting the degradation rate of methylene blue solution is: B>C>A, that is, pH>initial concentration>ultrasonic power. Therefore, through experiments, it can be known that the comprehensive optimization process parameter of each factor is B3C1A1. The process parameters are as follows: the initial concentration of the solution is 10.00mg/L, pH is 12.70 and ultrasonic power is 200W. The resulting analysis of variance table is shown in Table 2.

Table 2. Analysis of variance

| Source of Variance | sum of square | Free difference | Mean square | F value | Table value | Significance |
|--------------------|---------------|-----------------|-------------|---------|-------------|--------------|
| A                  | 4.66          | 2               | 2.33        | 0.25    | F_{0.25(2,4)}=2.00 |              |
| B                  | 3855.36       | 2               | 1927.68     | 205.07  | F_{0.01(2,4)}=18.00 | **           |
| C                  | 84.21         | 2               | 42.10       | 4.48    | F_{0.1(2,4)}=4.32 | *            |
| Error e            | 37.60         | 4               | 9.40        |         |             |              |

It can be seen from Table 2 that among the three factors, the effect of solution pH on the degradation rate of methylene blue has reached a highly significant level. On the contrary, the effect of ultrasonic power on the degradation rate of methylene blue is minimal and not significant. It can be seen from the test results that when the methylene blue solution is formulated to a certain concentration (10 mg methylene blue per 1 liter of solution), under the above optimal process conditions and three parallel experiments, the final methylene blue degradation rate is 77.95%.

5. Conclusion
In this paper, the orthogonal test method is used to optimize the process parameters of the ultrasonic degradation of methylene blue. The test results show that: at an ultrasonic power of 200W, an initial
concentration of 10.00mg/L, a pH of 12.70, and an ultrasonic action time of 20min, the degradation rate of methylene blue is 77.95%. It shows that the effect of ultrasound on the removal of methylene is very obvious. The next step can be based on the results of small-scale and pilot scale-up experiments to provide process parameters for large-scale applications.

Acknowledgements
This work is financially supported by Guizhou Science and Technology Department Science and Technology Project (No.[2017]-5409-2), Zhongshan Social Welfare and basic research program (No.2020B2005) and National key R&D Program of China (No.2016YFC0400707-4).

References
[1] Rafatullah M, Sulaiman O, Hashim R, et al. Adsorption of methylene blue on low-cost adsorbents: A review [J]. J. Hazard. Mater., 2010, 177(1-3): 70
[2] Guo J Y,Gan P F,Chen C,et al. Preparation of magnetic chitosan and its application in the treatment of methylene blue wastewater [J]. Chin. Environ. Science., 2019, 39(6): 2422
[3] Crini G, Lichtfouse E, Wilson L D, et al. Conventional and non-conventional adsorbents for wastewater treatment [J]. Environ.Chem. Lett., 2019, 17:195
[4] Yao Y J, Xu F F, Chen M, et al. Adsorption behavior of methylene blue on carbon nanotubes [J]. Bioresource Technol., 2010, 101(9):3040
[5] Zhou L, Gao C, Xu W J. Magnetic dendritic materials for highly efficient adsorption of dyes and drugs [J]. Acs. Appl. Mater. Inter.,2010, 2(5): 1483
[6] Altenor S, Carene B, Emmanuel E, et al. Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation [J]. J. Hazard. Mater., 2009, 165(1-3): 1029
[7] Lu N, He G, Liu J X, et al. Combustion synthesis of graphene for water treatment [J]. Ceram. Int., 2018, 44(2): 2463
[8] Xiao W Q,Huang H,Chen L, et al. Preparation and heat treatment of nanocomposites of PBT/graphene oxide [J]. Chin. J. Mater.Res., 2019, 33(02): 95
[9] Din M I , Khalid R , Najeeb J , et al. Fundamentals and Photocatalysis of Methylene blue dye using various nanocatalytic assemblies-A Critical Review[J]. Journal of Cleaner Production, 2021:126567.
[10] Kumar K , Chitkara M , Sandhu I S , et al. Photocatalytic, optical and magnetic properties of Fe-doped ZnO nanoparticles prepared by chemical route[J]. Journal of Alloys &Compounds, 2014, 588:681-689.
[11] Es A , Re A , Yk A , et al. Review on recent advances of carbon based adsorbent for methylene blue removal from waste water[J]. Materials Today Chemistry, 2020, 16:100233.
[12] Yi J, Christian P, T. David W, Sonolysis of 4-chlorophenol in aqueous solution: Effects of substrate concentration, aqueous temperature and ultrasonic frequency[J] Ultrasonic Sonochemistry 2006.13(5):425-422.
[13] Bo Lai, et al, Removal of high concentration p-nitrophenol in aqueous solution by zero valent iron with ultrasonic irradiation(US-ZVI) [J]. Journal of Hazardous Materials. 2013, 250-251(15):220-228.
[14] Yong-guang Bi, Xin-ting Zhang, Shao-qi Zhou. Experimental study on single factor effect of divergent ultrasonic degradation of methylene blue in water. E3S Web of Conferences, 2019,118: 03051.