Experimental study on single factor effect of divergent ultrasonic degradation of methylene blue in water

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Abstract: The study of divergent ultrasonic degradation of methylene blue in water was carried out by exploring the ultrasonic intensity of the methylene blue, the initial concentration and the degradation rate of the solution pH. The test results show that the degradation rate of methylene blue decreases with the increase of ultrasonic power. The initial concentration of methylene blue solution is in the range of 0.00-10.00 mg/L. The degradation rate of methylene blue increases as the concentration of the solution increases. When the concentration is greater than 10.00 mg/L, the concentration increases, and the ultrasonic degradation rate decreases. When the pH value is higher, the degradation rate of the methylene blue solution increases with the increase of pH, and the degradation rate reaches a maximum of 77.89%. The region where the ultrasonic degradation of methylene blue occurs is mainly at the junction of gas-liquid two phases, and is degraded by forming hydrogen peroxide in the cavitation bubbles and decomposing into various highly active radicals. Ultrasound has the advantages of fast, low energy consumption and environmental friendliness.

Since the 21st century, China's industrialization has been continuously strengthened, and industries such as fine chemicals, pharmaceuticals, printing and dyeing have developed rapidly. However, a large amount of organic polluted wastewater has been produced. Among them, organic dye wastewater accounts for a large proportion\textsuperscript{1}. China's printing and dyeing wastewater discharges approximately 4.0×10\textsuperscript{6} tons per day. These wastewaters contain many polar groups such as -SO\textsubscript{3}Na, -NH\textsubscript{2}, and chromogenic groups such as -N=N-, -N=O. It has toxic pollutants which are difficult to be degraded biologically containing such groups as phthalic acid, nitrobenzene, aniline, etc., which are also benzene ring, azo, amine group, etc., and are also carcinogenic substances present in wastewater. At present, the proportion of printing and dyeing wastewater to water environment pollution is becoming more serious, and the treatment of printing and dyeing wastewater is more difficult\textsuperscript{2,3}.

Methylene blue (M=373.9, molecular formula C\textsubscript{16}H\textsubscript{18}ClN\textsubscript{3}S•3H\textsubscript{2}O). It is a trihydrate compound with a slightly dark green bronze luster crystal, soluble in water and ethanol, and insoluble in ethers\textsuperscript{4}. Methylene blue is more stable at room temperature, while methylene blue solution is generally toxic and alkaline. Methylene blue is not only a blue-based basic dye reagent, but also a frequently used redox indicator. It is used biologically to judge the dyeing of certain reagents and certain bacteria. It is also used in cotton, wool and other cotton. In the dyeing of fibers, the untreated methylene blue solution can seriously pollute the environment of natural waters\textsuperscript{5,6}.

This experiment explores the influencing factors of divergent ultrasonic degradation of methylene blue in water, in order to maximize the degradation rate, making it more economical and efficient in practical applications.

1 Experimental method

1.1 Drawing of standard curve

Determine the scanning wavelength: Prepare C=3.0mg/L methylene blue solution, and put it into the UV-5500PC UV-visible spectrophotometer for spectral scanning. The scanning result shows that the absorption peak is at 664nm, so 664nm is used as the specified scanning wavelength.

Preparation of standard solution: Pipette 5.00mL, 6.00mL, 7.00mL, 8.00mL, 9.00mL, 10.00mL, 11.00mL, 12.50mL, 15.00mL of methylene blue mother liquor in 9 volumetric flasks, add water to the 50mL mark. The cuvette thickness was 2.0 cm, the scanning wavelength was 664 nm measured in the previous part of the experiment, and the reference solution was selected as deionized water, and the absorbance (A) was measured. Taking the measured absorbance A as the ordinate, the concentration C (mg/L) of the methylene blue solution is plotted on the abscissa.
1.2 Single factor test of trough ultrasonic degradation of methylene blue in water

The methylene blue powder was accurately weighed and solventized with deionized water to prepare a certain concentration of methylene blue reaction solution. We determined the reaction time and reaction temperature by using the control variable method, ultrasonic power, initial concentration and pH value. We also studied the effect of each factor on the degradation rate of methylene blue.

The solution after precise measurement was placed in a brown 50 mL volumetric flask, and deionized water was added to prepare a solution whose absorbance fell in the regression equation. The absorbance value was measured at a UV absorption wavelength of 664 nm, and substituted into a standard curve to obtain a reaction. The concentration of methylene blue in the liquid is then calculated according to the formula.

Degradation rate (%) = (methylene blue concentration before degradation - methylene blue concentration after degradation) / methylene blue concentration before degradation x 100%

2 Results and analysis

2.1 Drawing of standard curve

Taking the measured absorbance A as the ordinate and the concentration C (mg/L) of the methylene blue solution as the abscissa, the regression curve is drawn, and the regression equation is obtained: A=0.271C -0.0171, the correlation coefficient is greater than 0.99 and close to 1.00, ie R² =0.9997, the results are shown in Figure 1 below, demonstrating a good linear relationship between methylene blue concentration C and absorbance A, which can be used to calculate the degradation rate of this test.

![Fig.1 Standard curve of methylene blue](image1)

2.2 Single factor test of trough ultrasonic degradation of methylene blue

2.2.1 Effect of trough ultrasonic power on the degradation rate of methylene blue solution

The solution was prepared to contain 10 mg of methylene blue per 1 L (measured pH=6.10), 80 mL of each reaction was taken, and placed in a special long tube ultrasonic glass, and the outer layer was covered with a black plastic bag to protect from light, placed in a trough ultrasound reaction. The ultrasonic frequency of the fixed reaction was 40 kHz and the time was 20 min. The output power of the ultrasonic wave was set to 200 W, 240 W, 280 W, 320 W, 360 W, respectively, and the measured degradation rate is as shown in Fig.2.

![Fig.2 Effect of power on the dissolution rate of methylene blue](image2)

It can be seen from Fig.2 that the degradation rate is 17.63% when P=200W, 13.99% when P=240W, and the degradation rate is minimized when P is increased to 360W. It is 12.39%. The degradation rate of the methylene blue solution decreases as the ultrasonic power increases. This is because the minimum power of 200W in the test has reached a threshold of ultrasonic power, and then the power is amplified, so that the cavitation bubbles in the ultrasonic field are formed too fast and prematurely broken, so that the methylene blue in the water body is not fully obtained. Oxidation, the degradation rate will decrease as the power increases.

2.2.2 Effect of initial concentration of methylene blue on its degradation rate

A methylene blue mother liquor having a concentration of C=50 mg/L was prepared with deionized water. Pipette 8.00mL, 16.00mL, 24.00mL, 32.00mL, 80.00mL, and prepare the same reaction solution with a concentration of 80.00mL of 5.00mg/L, 10.00mg/L, and 15.00mg/L. 20.00 mg/L, 50.00 mg/L of methylene blue initial solution. The output power of the trough ultrasonic wave is set to 200W, and the reaction time is 20 min. The degradation rate is shown in Figure 3 below.
Fig. 3 Effect of initial concentration of methylene blue solution on degradation rate

It can be seen from Fig. 3 that when $C=5.00$ mg/L, the degradation rate is 18.66%; when $C=10.00$ mg/L, the degradation rate is 25.72%, which is the maximum degradation rate. The initial concentration of methylene blue solution is in the range of 0.00-10.00 mg/L. The higher the concentration, the higher the ultrasonic degradation rate; when the concentration is greater than 10.00 mg/L, the concentration increases, and the ultrasonic degradation rate decreases. This is because high-activity free radicals such as hydroxyl radicals in the cavitation nucleus between 0.00-10.00 mg/L remain, so the greater the initial concentration in this interval, the higher the degradation rate. However, when the critical point exceeds 10.00 mg/L, the increase of the initial concentration necessarily requires more highly active free radicals to support the reaction, but at this time, the $H_2O_2$ in the system has reached a constant state, and the generated free radicals such as $OH\cdot$ It is constant, so the increase in the initial concentration at this time causes the degradation rate to decrease.

2.2.3 Effect of pH value of methylene blue solution on its degradation rate under trough ultrasonic

The solution was formulated into 10 mg of methylene blue per 1 L, and the methylene blue solution with pH=2.30, 3.65, 6.10, 10.65, and 12.70 was adjusted by using the diluted $H_2SO_4$ solution and the dissolved NaOH solution, respectively, and placed in a trough ultrasonic reactor for 20 min, ultrasonication. The output power is selected to be 200W. Among them, the difference between the three adjustment measurements when adjusting the pH does not exceed ±0.2, and the last used pH value is the average value.

Fig. 4 Effect of pH value of methylene blue solution on its degradation rate

It can be seen from 4 that the degradation rate is 19.26% at pH=2.30; the degradation rate is slowly increased to 22.03% at pH=3.65; the degradation rate is 29.12% at pH=6.10; the degradation rate is 34.80% at pH=10.65. At pH=12.70, the degradation rate reached a maximum of 77.89%. When the pH is higher, the degradation rate of the methylene blue solution increases with increasing pH.

3 Conclusion

The test results show that the stronger the output power of the trough ultrasonic, the lower the degradation rate of the methylene blue solution. The initial concentration of methylene blue solution is in the range of 0.00-10.00 mg/L. The higher the concentration, the higher the ultrasonic degradation rate; when the concentration is greater than 10.00mg/L, the concentration increases, and the ultrasonic degradation rate decreases. When the pH value is higher, the degradation rate of the methylene blue solution increases with the increase of pH, and the degradation rate reaches a maximum of 77.89%.

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