

Treatment of printing and dyeing wastewater by catalytic wet hydrogen peroxide oxidation of honeycomb cinder as carrier catalyst

D H Zhang^{1,3}, H M Yang¹, Y J Ou¹, C Xu¹ and J C Gu^{2,4}

¹ Architecture and Civil Engineering, Xihua University, Chengdu, 610039, China

² Food and Biological Engineering, Xihua University, Chengdu, 610039, China

³ E-mail: 475352785@qq.com

⁴ E-mail: gu6471@163.com

Abstract. Under the condition of 35 °C, honeycomb cinder was used as the carrier, nickel as the active ingredient, impregnated for 2h, and calcined at 300 °C for 2h. The catalyst was used to Catalytic Wet Peroxide Oxidation of methylene blue simulated printing and dyeing wastewater. The effect of the amount of catalyst, the amount of catalyst, the reaction temperature and the reaction time on the treatment efficiency and the effect of the self-made catalyst on the simulated wastewater with different concentration gradient were studied in the experiment. The results showed that when the reaction conditions were H₂O₂ 8ml/L, catalyst 12g/L and reaction time 1h, the degradation rate of methylene blue reached more than 77% for the wastewater with concentration ranging from 40 mg/L to 200 mg/L. In addition, at a temperature of 30 DEG C, the wastewater, the concentration was 80mg/L, degradation rate was up to 85.70%.

1. Introduction

Printing and dyeing wastewater with high chroma, high COD, poor biodegradability, water quality and water changes largely, is recognized as one of the refractory industrial wastewater [1-2]. In recent years, with the rapid development of the industry, the textile printing and dyeing industry will emit 14.13×10⁸ t of wastewater every year [3]. According to estimates, the production of 1T dyes is accompanied by about 744m³ wastewater discharge. Meanwhile, in the dye production and use process, 10% to 20% of the dye is released into the water [4]. Therefore, more and more attention has been paid to solve the problem of printing and dyeing wastewater treatment.

Azo dyes are the most used dyes in dyeing and printing industry [5-6], and the Methylene Blue is one of azo dye, with anti-light degradation and antioxidant properties [7]. As a typical organic pollutant in printing and dyeing wastewater, Methylene Blue is mainly derived from chemical indicators, dyes, biological dyes and drugs [8-10]. Catalytic Wet Peroxide Oxidation (CWPO), as an effective method to deal with toxic high concentrations of pollutants, has received much attention in the field of wastewater treatment [11-13]. It has the characteristics of high treatment efficiency, fast reaction speed, mild reaction conditions and so on [14-16]. Honeycomb cinder is a solid waste discharged from the combustion of honeycomb. Its main components are silicon, aluminum, iron and calcium oxide. The structure is characterized by its porous material with certain specific surface and adsorption activity [17]. Therefore, in this study, Honeycomb cinder was used as the catalyst carrier to treat the dyeing wastewater.



2. Experiment

2.1. Materials and instrument

Sulfuric acid (AR), hydrogen peroxide (AR), potassium dichromate (PT), mercury sulfate (AR), ammonium ferrous sulfate (AR), silver sulfate (AR), silver nitrate (AR), methylene blue (PT), pH test paper, distilled water.

Electronic balance, COD125 COD digestion instrument, THZ-82B gas bath thermostats oscillator, TU-1901 ultraviolet and visible spectrophotometer, DHG-9240A electric thermostat blast drying box, SZ-93 automatic dual water distiller, SX2-5-12 Yifeng electric furnace, B11-2 thermostat magnetic stirrer.

2.2. Experiment and analysis methods

2.2.1. Preparation of catalyst. In this experiment, the catalyst was prepared by the impregnation method, which was prepared by pretreatment, impregnation, drying and roasting.

The collected Honeycomb cinder was crushed, placed in a beaker, soaked with distilled water, fully stirred, washed and changed repeatedly until the water is clear. And placed in oven at 105 DEG C, drying, grinding, over 100 standard sieve. Taked a certain amount of pretreated honeycomb cinder and soaked it in an excess of metal salt solution. After a period of time, the honeycomb cinder was removed, washed and dried at 105 DEG C, and then baked in a box type resistance furnace. In the existing research support (under the relevant conditions optimization of catalyst preparation), the optimum preparation conditions were determined as follows: under the condition of 35 DEG C, the use of 0.2mol/L Ni (NO₃)₂ solution impregnation 2h, impregnated carrier filtering and drying, the box type resistance furnace roasting 2H under 300 DEG C. Under the condition of 35 DEG C, the carrier was soaked in 0.2mol/L Ni (NO₃)₂ solution of 2h, and then the carrier was filtered and dried after the impregnation, and baked by a box type resistance furnace at the temperature of 300 2h.

2.2.2. Experimental method. A certain amount of oxidant H₂O₂ and the self-made catalyst were added to the simulated wastewater of methylene blue, and then Catalytic wet hydrogen peroxide oxidation reaction was carried out, with temperature and time were controlled. And explored the self-made catalyst for oxidation of methylene blue in wastewater during the reaction agent dosage, catalyst dosage, reaction temperature, reaction time 4 factors on treatment effect. The optimum reaction conditions and treatment effect of the catalyst were found out.

2.2.3. Analytical methods. The removal efficiency of methylene blue was used as the evaluation index. The UV absorbance of methylene blue was obtained, and the maximum absorbance was 664nm. According to Beer-Lambert's law, the concentration of methylene blue was measured by UV Vis spectrophotometer.

The formula of the removal rate:

$$W = [(A_1 - A_2) / A_1] \times 100\%$$

Formula: A1 for The absorbance of methylene blue solution before treatment.;

A2 for The absorbance of methylene blue solution after treatment.

3. Results and discussion

3.1. Effect of oxidant dosage

100ml methylene blue simulation wastewater was placed in a conical flask at a concentration of 120mg / L, and 1g self-made catalyst and a certain amount of hydrogen peroxide were added, and then reacted at 30 °C for 1h. The effect of different H₂O₂ dosage on the removal efficiency of methylene blue in simulated wastewater was compared. The results were shown in Figure 1.

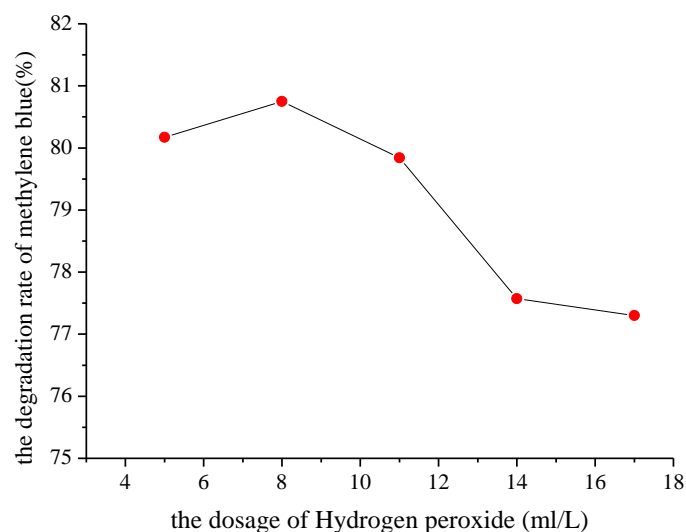
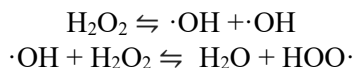


Figure 1. Effect of oxidant dosage on reaction.

As shown in Fig. 1, the methylene blue degradation rate increased first and then decreased with the increase of the amount of oxidant. When the dosage was 5mg / L, the degradation rate of methylene blue reached 80.17%, and the degradation rate increased when the dosage was increased to 8 mg / L. And then the degradation rate of methylene blue decreased with the further increase of oxidant. When the dosage of H_2O_2 was 17 mg / L, the degradation rate was 77.30%. This is because, with the increase of the amount of H_2O_2 added, the formation of hydroxyl radical ($\cdot OH$) and the generation of chain reaction are accelerated by the action of metal ions Ni in the catalyst, resulting in an increase in the generation of $\cdot OH$. And the further reacted can be occurred between H_2O_2 and $\cdot OH$, finally to generate $HOO\cdot$, the reaction process is as follows:



The simulated wastewater was degraded by $\cdot OH$ and $HOO\cdot$, and the degradation rate of methylene blue was increased. However, due to the above reactions are reversible, when H_2O_2 increased to a certain amount, a large number of $\cdot OH$ generated in the water, so that some $\cdot OH$ has not been involved in the degradation reaction to collide with each other to regenerate H_2O_2 . And on the one hand, H_2O_2 is a free radical adsorbent, more H_2O_2 will consume $\cdot OH$; On the other hand, Under the condition of large amount of H_2O_2 , the decomposition of organic compounds is intensified, which is not conducive to the catalytic oxidation reaction. So the degradation rate of methylene blue was decreased.

Therefore, the best oxidant dosage is 8mg/L.

3.2. Effect of catalyst dosage

100ml methylene blue simulation wastewater was placed in a conical flask at a concentration of 120mg / L, according to the existing experimental data, each water sample was added to 0.8ml hydrogen peroxide, the concentration of 8ml/L, and a certain amount of self-made catalyst was added, and next reacted at 30 °C for 1h. The effects of different catalysts on the degradation of methylene blue in simulated wastewater. The results are shown in Figure 2.

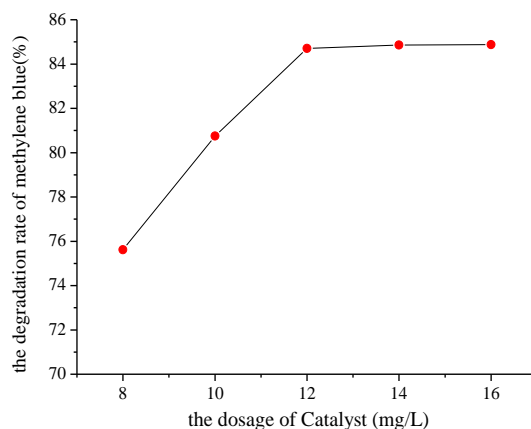


Figure 2. Effect of catalyst dosage on the reaction.

As shown in Figure 2, when the dosage was 8g/L, the degradation rate of methylene blue reached 75.62%, then continue to increase the dosage, the degradation rate of methylene blue increased with dosage increasing. until the dosage was 12g/L, the degradation rate reached 84.71%. Further increased the dosage of catalyst, the increase of the degradation rate of methylene blue was not obvious, when the dosage were 14g/L and 16g/L, the degradation rates were 84.86% and 84.88%, respectively. This is because with the addition of catalyst, the active ingredient was increased, and the contact probability between the reactant and the active ingredient increased; The active ingredient in the catalyst accelerates the formation of $\cdot\text{OH}$ and the chain reaction, leads the formation of $\cdot\text{OH}$ increases. At the same time, the active ingredient also increases the rate of hydroxyl radical initiation and propagation, which made the reaction efficiency higher and the degradation rate of methylene blue increased. When the catalyst dosage further increased, on the one hand, the catalyst active ingredient and reactant contact rate continues to increase, the reaction efficiency was improved; On the other hand, the active ingredient of catalyst was too much, and the anti-catalytic reaction can inhibit the oxidation reaction, so the reaction efficiency was reduced. Because of these two aspects, the degradation rate of methylene blue gradually stabilized.

Considering the overall economy, the optimal dosage of catalyst is 12g/L.

3.3. Effect of reaction temperature

Combined with the existing experimental data, the simulated wastewater was added with self-made catalyst and H_2O_2 , and the reaction time was 1h. The effect of different temperature conditions on the degradation rate of methylene blue in simulated wastewater was studied. The results are shown in Figure 3.

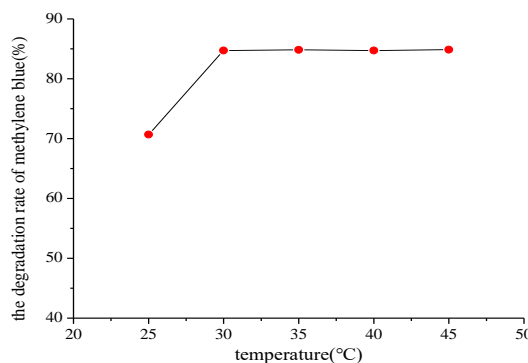
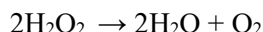


Figure 3. Effect of temperature on the reaction.

As shown in Figure 3, when the reaction temperature was 25 DEG C, the degradation rate of methylene blue was about 70.68%, and then the reaction temperature was increased, and the degradation rate of methylene blue in wastewater increased with the increase of temperature. When the reaction temperature was 30 DEG C, the degradation rate was up to 84.71%. With the increase of the reaction temperature, the degradation rate of methylene blue increased little with the increase of reaction temperature, and the degradation rate was 84.82%, 84.71% and 84.85%, respectively, when the dosage was about 35 DEG C, 40 DEG C and 45 DEG C. This is because, From the aspect of dynamics, when the temperature rises, increasing the number of active molecules in the reactant activation, methylene blue and H₂O₂ molecules movement rate is also improved, so the mass transfer process among reactants, resultants and the active site quickly, so as to improve the efficiency of the reaction and the degradation rate of methylene blue was improved; When the temperature continued to rise, still below 30 DEG C, the "positive" effect of temperature continued. However, from the analysis of thermodynamics, methylene blue oxidation process and catalyst surface adsorption process was exothermic reaction, the temperature rise is not conducive to the oxidation reaction and adsorption, moreover, H₂O₂ has obvious thermal instability, When the temperature increases, H₂O₂ self-disproportionation accelerated, the chemical reaction is as follows:



Therefore, when the temperature is higher than a certain temperature, the degradation rate is not increased. Considering economic efficiency and energy saving, the optimum reaction temperature is 30 DEG C.

3.4. Effect of reaction time

According to the experimental data, the experimental operation was kept under the optimal conditions, only the reaction time was changed, and the effect of reaction time on the degradation rate of methylene blue in simulated wastewater was studied. The results are shown in Figure 4.

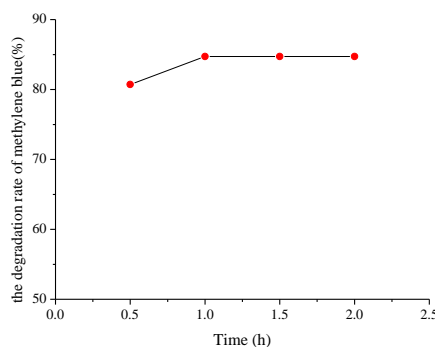


Figure 4. Effect of reaction time on reaction.

As shown in Figure 4, the degradation rate of methylene blue increased with the increase of reaction time when the reaction time below 1h. When the reaction time was 1.5h and 2H, the degradation rate increased by 0.01% and 0.02%, respectively, compared with 1h. The degradation rate of methylene blue was not obvious with the increase of reaction time. When the reaction time was less than 1h, ·OH and methylene blue molecules contact in the active site, and the oxidation reaction occurs. After 1h, the OH in liquid phase has been consumed, so oxidation reaction can not be carried out.

Based on the above experimental data, the optimal reaction time is 1h.

3.5. The degradation rate of wastewater with different concentration under the optimum reaction conditions

Based on the above experimental data, under the optimum reaction conditions, that is, H₂O₂ dosage of 8ml/L, dosage of catalyst 12g/L, reaction under the condition of 30 DEG C for 1h. The effect of the

catalyst on the treatment of wastewater with different concentrations was studied. The results are shown in Figure 5.

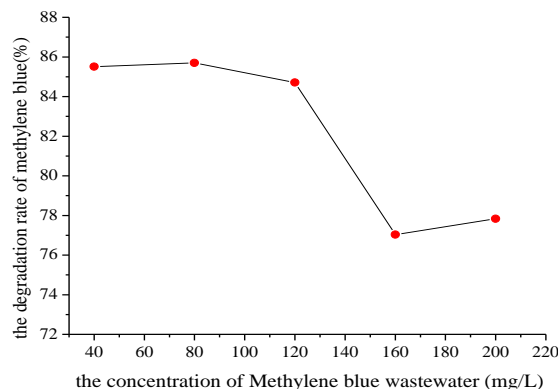


Figure 5. degradation rate of different concentration of wastewater under optimal reaction conditions.

As shown in Figure 5, when the concentration of methylene blue wastewater was 40mg/L, 80mg/L, the degradation rate was higher than 85%. When the concentration increased to 120mg/L, the degradation rate decreased slightly to 84.71%. When the concentration of wastewater increased to 160mg/L and 200mg/L, the degradation rate of methylene blue decreased obviously, but still exceeded 77%, and the methylene blue treatment continued to increase. This is because when the concentration of methylene blue wastewater is lower, the surface of the catalyst can contact the reactants continuously, and the oxidation process is not saturated; This is because when the concentration of methylene blue wastewater is lower, the surface of the catalyst can contact the reactants continuously, and the oxidation process is not saturated, moreover, the oxidation reaction can be maintained at a higher reaction rate; However, under the condition of high methylene blue concentration, the dosage of oxidant is relatively low, which makes the oxidation rate slow down. As a result, there is an optimal remove concentration of methylene blue for the catalyst.

4. Conclusion

Based on the experimental data, the self-made catalyst with honeycomb cinder as the carrier has a good effect on the treatment of methylene blue simulated wastewater. The amount of oxidant, catalyst dosage, reaction time and reaction temperature have a certain influence on the reaction, and the reaction temperature increased the remove rate significantly. From 25 to 30 DEG C, the degradation rate increased by 10%. The optimum reaction conditions were as follows: for the 80mg/L methylene blue wastewater, the honeycomb cinder catalyst 12g/L, dosage of H₂O₂ 8ml/L, under the condition of 30 DEG C for 1h, and the degradation rate was up to 85.70%; And the degradation rate of methylene blue can reach more than 77% for 40~200mg/L methylene blue wastewater.

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