Research on Catalytic Oxidation Pretreatment of Organic Pesticide Wastewater with High Concentration

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Abstract: Pesticide wastewater has the characteristics of high organic pollutant, high concentration, deep color and high toxicity, which has become difficult to treat the organic wastewater with high concentration at home and abroad. This article uses three methods of US(ultrasonic), Fenton(Fe^{2+}&H_2O_2) and combination of US&Fenton were used in the comparative research on the treatment of organic pesticide wastewater with high concentration. **Experimental conditions:** time of 130 min, ultrasonic power of 280W, frequency of 418kHz, pH value of 3.5, H_2O_2 concentration of 0.3mol/l; dosing mode: two thirds was added at 0 min, the rest one third was added at 65 min. The results showed that the treatment effect of the combination of US&Fenton was significantly better than that of independent US and independent Fenton; after the treatment on the organic pesticide wastewater with high concentration, the degradation rate of COD reached 85%, the chromaticity degradation rate reached 99%; the ratio of COD/BOD was about 1.4, with better biodegradability, which has provided a good condition for the subsequent biochemical treatment. Solved the problem of pesticide wastewater was difficult and expensive to degradation.

1. Introduction

With the wide application of pesticide, pesticide wastewater discharged in the process of pesticide production has become a potential environmental hazard. This kind of industrial wastewater has become one of the pollutions which are the most seriously and the most difficultly treated in China. Advanced oxidation technology usually refers to the treatment technology which oxidizes and degrades organic pollutants by producing high-reactivity hydroxyl radicals (HO) under ambient temperature and pressure, including the photocatalytic oxidation, O_3 oxidation, Fenton reagent oxidation as well as the combinations of oxidation technology. The application of advanced oxidation technology to treat landfill leachate, pesticide wastewater and dye wastewater has been reported in the literature [1-5]. However, due to the characteristics of pesticide wastewater, the application of advanced oxidation technology is not yet common in practice.

The composition of pesticide wastewater is complex, containing a large number of toxic and harmful substances, resulting in its poor biodegradability; the use of traditional biochemical treatment method is generally difficult to get good treatment results, so it is needed to strengthen the pretreatment of wastewater [6, 7].

The combination of Fenton method and ultrasonic method was used to pre-treat the organic pesticide wastewater with high concentration, and the effect of the process conditions on US&Fenton treatment system was discussed.

2. Experiment

2.1 Experimental materials

Wastewater used in the experiments is from a chemical plant in Chengdu, the wastewater is reddish brown, with strong pungent odor, and poor biodegradability. According to the report of wastewater detection, the water mainly contains dimethyl phthalate, tributyl phosphate, etc.

Experiment reagents:$FeSO_4 \cdot 7H_2O$（analytical reagent AR）, 30%H_2O_2（analytical reagent AR）, $K_2Cr_2O_7$（analytical reagent AR）

Experimental apparatus: Visible spectrophotometer 721G (Shanghai Precision Scientific Instrument Co., Ltd.), JY92 - II ultrasonic instrument (Ningbo scientz Biotechnology Co., Ltd.), PHS-3B digital precision pH meter (Shanghai Leici Instrument Factory).

2.2 Experimental methods

Put wastewater in the reactor, add a certain amount of ferrous sulfate and hydrogen peroxide, turn on the ultrasound instrument, and add H_2O_2 according to a certain way under the condition of aeration rate of 150 L/h. After a period of time of reaction, adjust the pH

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value to 10, and then wait 1h, finally take the supernatant for the index measurement.

The initial concentration of water sample COD was 2253 mg/L, the ultrasonic frequency was418kHz, the power was 280W, the pH value was 3.5, the concentration of Fe^{2+} was 25mmol/L, the concentration of H_2O_2 was 0.3mol/L, and the three kinds of treatment methods of independent Fenton, independent US and combination of US&Fenton were used to treat wastewater for 130min.

2.3 Analysis method

Potassium dichromate method was used to determine wastewater COD [8]; Fe^{2+} concentration and total iron concentration were measured according to HJ/T345-2007 "*Water Quality Determination of the Iron Phenanthroline Spectrophotometric Method"* [9].

3 Results and Discussion

3.1 Degradation of COD with different methods and color contrast

It can be known from Fig 1 that the degradation effect of independent US on water sample COD was not obvious, it was only 15%, the maximum value was reached at 90min. The degradation effect of independent Fenton on water sample COD was 65%, the maximum value was reached at about 90min. The degradation effect of combination of US&Fenton on water sample COD was up to 85%, which was more than the degradation sum of independent US and independent Fenton, and it reached the maximum value at 130 min, and tended to be stable, proving US and Fenton have synergistic effect, and its degradation effect on water sample COD was obvious. The COD value of water sample reduced from 2253 to 338, the ratio of COD/BOD was about 1.4, the biodegradability was better, which have achieved the pretreatment effect of pesticide wastewaters with high concentration.

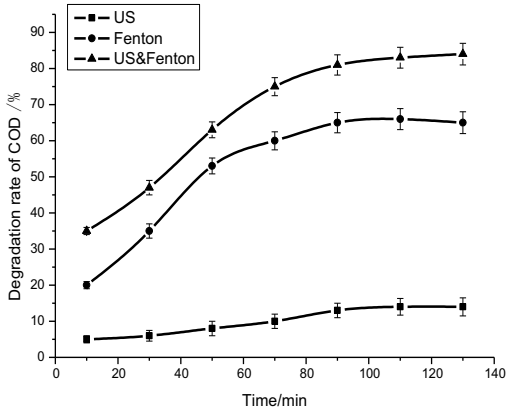

Figure 1. COD degradation with different methods

Figure 2 shows the degradation rate contrast of 3 methods for the water samples in the experiments. The degradation rate of US on experimental water sample was 30%, and the highest value was reached at 90min. The degradation rate of Fenten was 74%, and the highest value was reached at 90min. The degradation rate of US&Fenten on the chromaticity in experimental water sample reached 99%, the highest value was reached in 110 min; the reaction process was more durable, the treatment effect was significantly higher than those of the US and Fenten. The pretreatment effect of the combination of US&Fenten on organic pesticide wastewater with high concentration was obvious, achieved the goal of the wastewater pretreatment, which has provided favorable conditions for follow-up biochemical treatment.

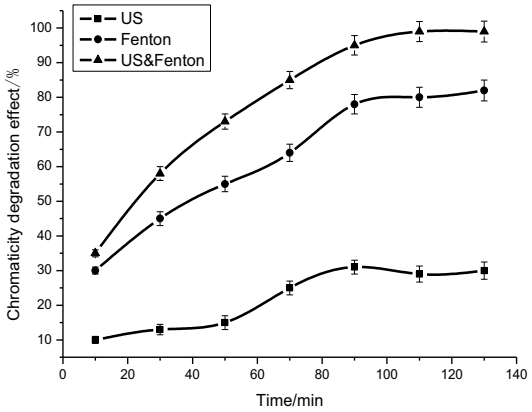

Figure 2. Chromaticity degradation effect with 3 different methods

3.2 Effect of pH value on degradation rate

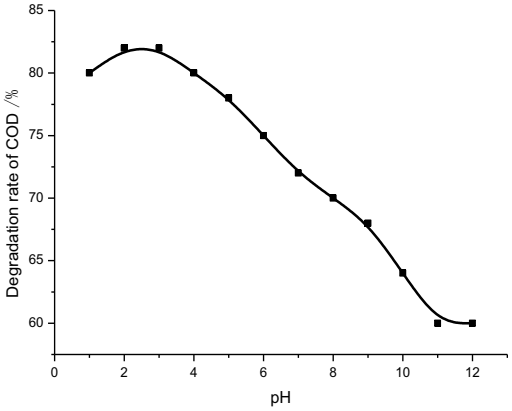

Figure 3. Effect of pH value on COD degradation rate

With the combination treatment method of US&Fenten, it can be seen from Figure 3 that the experimental conditions were as follows: the initial concentration of experimental water samples COD was 2253 mg/L, ultrasonic frequency was 418 kHZ, the power was 280W, the concentration of Fe^{2+} was 25 mmol/L, the concentration of H_2O_2 was 0.3 mol/L. it can be seen from Fig 4 that when the pH value is 2 ~ 5, the degradation efficiency of COD was higher; when the pH value was 3, the degradation rate of COD had its peak value, and the degradation efficiency decreased with the increase of pH value. Therefore, it is concluded that the optimum condition is the pH value of 3.5. This is because when the pH value is less than 3, $[Fe(Ⅱ)(H_2O)_6]^{2+}$ will be produced in the system, the reaction rate of the compound with H_2O_2 is lower than

that of[Fe(Ⅱ)(OH)$(H_2O)_5$]$^+$, thus, reducing the production of OH, affecting the effect of catalytic oxidation reaction [10]. And when the pH value is much higher, it not only inhibits the production of OH, but also makes Fe^{2+} and Fe^{3+} in the solution subside in the form of hydroxide precipitation and lose catalytic ability; at the same time, the higher pH value will make the H_2O_2 produce invalid decomposition, reducing the utilization rate of H_2O_2 [11].

3.3 Effect of ultrasonic parameters on the degradation rate

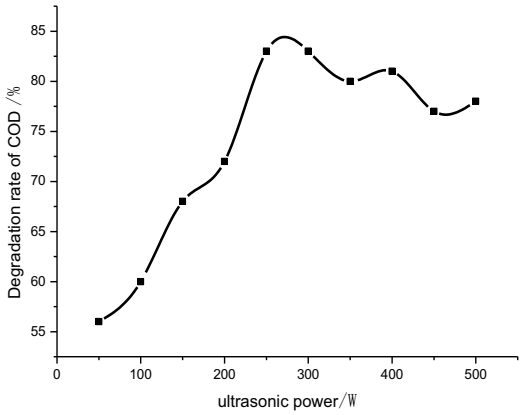

Figure 4. Effect of ultrasonic power on the COD degradation rate

With the combination treatment method of US&Fenten, the experimental conditions were as follows: the initial concentration of experimental water samples COD was 2253 mg/L, the pH value was 3.5, the concentration of Fe^{2+} was 25 mmol/L, the concentration of H_2O_2 was 0.3 mol/L. it can be seen from Figure 4 that degradation efficiency of COD increased with the increase of the power of ultrasonic power, peaked in 200 ~ 300 w; when the power is greater than 300, the degradation rate of COD decreased. Generally speaking, when the ultrasonic frequency is constant, the degradation effect should increase with the increase of power, the phenomenon in the experiment is speculated that too great power will result in the barrier effect caused by cavitation bubbles in ultrasonic larger negative phase, resulting in instable energy and attenuation, thereby reducing the utilization rate of ultrasonic energy [12, 13]. As a result, too great ultrasonic power may cause energy waste, from the perspectives of economy and treatment effect, it is determined that the best ultrasonic power is 280 W.

3.4 Effect of H_2O_2 dosage on degradation rate

With the combination treatment method of US&Fenten, the experimental conditions were as follows: the initial concentration of experimental water samples COD was 2253 mg/L, the ultrasonic power was 280W, the pH value was 3.5, the concentration of Fe^{2+} was 25 mmol/L. H_2O_2 with different concentrations was added; the organic pesticide wastewater with high concentration was treated with the combination method of US&Fenton for catalytic oxidation degradation for 130 min, the result is shown in Figure 5.

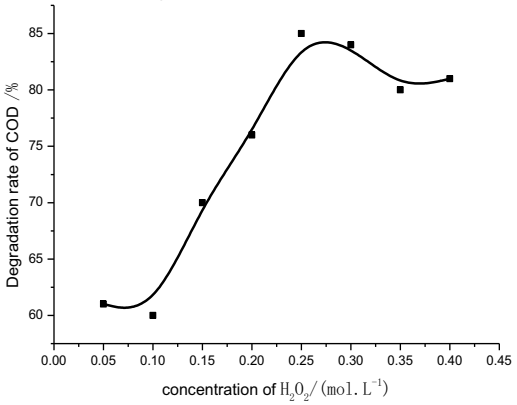

Figure 5. Effect of H_2O_2 concentration on COD degradation rate

It can be seen from the Figure, when the concentration of H_2O_2 in the solution was less than 0.25 mol/L, it increased with the concentration of H_2O_2, the degradation rate of COD in experimental sample water was increased. When the concentration of H_2O_2 in the solution increased to 0.25 ~ 0.3 mol/L, the degradation rate reached its peak; afterwards, the degradation rate of COD in experimental sample water decreased with the increase in the concentration of H_2O_2. Therefore, it is established that the best experimental concentration condition of H_2O_2 is between 0.25 ~ 0.3 mol/L.

4 Conclusions

Under the experimental conditions of 418 kHZ ultrasonic frequency, the 280W power, 3.5 pH value, 25mmol/L concentration of Fe^{2+}, 0.3mol/L concentration of H_2O_2, three methods were used to treat organic pesticide wastewater with high concentration for 130 min; the results proved that the effect of combination treatment method of US&Fenton was the best, COD degradation rate reached 85%, chromaticity degradation rate reached 99%, the ratio of COD/BOD was about 1.4, with better biodegradability, which has provided a good condition for the subsequent biochemical treatment.

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