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Photosynthetic Synergistic Fe(II)Y-H₂O₂ Heterogeneous Fenton for Degradation of Ciprofloxacin

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Abstract. The Fe(II) was loaded to the NaY to prepare FeY, and together with H₂O₂ constitutes a heterogeneous Fenton oxidation system. The photodegradation of ciprofloxacin by FeY-H₂O₂ heterogeneous Fenton was studied. The effects of H₂O₂ volume, FeY dosage, initial concentration of ciprofloxacin and pH on the degradation rate were studied by single factor experiment and orthogonal experiment. This study showed all the factors have an effect on the degradation rate of ciprofloxacin under the experimental conditions. The influential strengths are that: initial concentration of ciprofloxacin solution > the volume of 1:100 H₂O₂ > the value of pH > the dosage of FeY. Under the condition of 20W UV lamp irradiation, the optimal degradation conditions is that the dosage of FeY is 0.2g, the initial concentration of ciprofloxacin is 30ug/mL, the volume of 1:100 H₂O₂ is 5mL, the value of pH is 4.0; and under this condition, the degradation rate of ciprofloxacin was up to 96.6%.

1. Introduction

Antibiotics are chemicals that interfere with cell developmental functions, because humans abuse the antibiotics, which caused environmental pollution, and posed a safety hazard human being. At present, antibiotic treatment technologies mainly include biological treatment, physical treatment, and chemical degradation [1]. Ciprofloxacin is a synthetic third-generation quinolone antibiotic with broad-spectrum antibacterial activity and bactericidal activity, but it is difficult to biodegrade. The best way to treat that is to use advanced oxidation technology. Fenton method is a deep oxidation technology, which uses the chain reaction between Fe and H₂O₂ to catalyze the formation of OH radicals [2]. ·OH radicals have strong oxidizing properties and can oxidize various toxic and difficult to degrade organic compounds to achieve the purpose of removing contaminants[3]. The heterogeneous Fenton reaction can overcome many shortcomings of the homogeneous Fenton reaction, it can make the reaction in a wide pH range, and the catalyst can be used repeatedly. In this paper, we employ Fe(II) immobilized on NaY molecular sieves to prepare FeY, and then added to H₂O₂, and then added to H₂O₂, which constituted a heterogeneous Fenton oxidation system. And the photodegradation of ciprofloxacin by FeY-H₂O₂ heterogeneous Fenton was studied [4, 5].



2. Experiment part

2.1. Reagents and instruments

Reagents: NaY molecular sieve, ammonium ferrous sulfate, EDTA, hydrogen peroxide, ciprofloxacin hydrochloride.

Instruments: WFZ-26A UV-visible spectrophotometer (Tianjin Tuopu Instrument Co., Ltd.), SHB-III circulating multi-purpose vacuum pump (Zhengzhou Changcheng Branch Industry and Trade Co., Ltd.), HY-2 speed multi-purpose oscillator (Changzhou Guohua Electric) Ltd.), 78WH-1 thermostatic magnetic stirrer (Hangzhou Instrument Motor Co., Ltd.), AL204 electronic balance (METTLER TOLEDO Instrument (Shanghai) Co., Ltd.), 320 pH meter (METTLER TOLEDO Instruments (Shanghai) Ltd.), X-15A self-filtering UV lamp (American Specronics (sp) company), 101-ZAB electric heating constant temperature blast drying oven (Tianjin Taisite Instrument Co., Ltd.).

2.2. Fe(II) load

NaY type molecular sieve pretreatment: The NaY type molecular sieve was washed three times with a dilute hydrochloric acid solution having a pH of 2.0, then rinsed with distilled water for 3-5 times, and dried at low temperature for use.

Fe(II) immobilization: Weigh a certain amount of pretreated NaY molecular sieve into a 500mL beaker, add a certain amount of Fe²⁺ solution, and mix Fe²⁺ with NaY molecular sieve with fully stirred. After about 3 hours, the prepared Fe(II) molecular sieve washed 2~3 times with distilled water and then placed in an oven at a low temperature (<60°C) for drying in an oven.

2.3. Degradation experiment

Take 0.30g FeY molecular sieve in a 250mL beaker, add 3mL of 1:100 H₂O₂ solution, the beaker is placed on a magnetic stirrer, turn on the UV lamp (20W), react for 2 hours, measure the concentration of the remaining ciprofloxacin solution in the reaction, The degradation rate of ciprofloxacin was calculated according to the formula (1)

$$\eta\% = \frac{c_0 - c}{c_0} \times 100 \quad (1)$$

Where: η is the degradation rate of ciprofloxacin; c_0 is initial concentration of ciprofloxacin, ug/ml; c is the residual of the solution after degradation, ug/ml.

3. Results and discussion

3.1. Single factor experiment

3.1.1. *Effect of H₂O₂ volume on degradation rate.* The effect of hydrogen peroxide volume on the degradation rate of ciprofloxacin was shown in Figure 1:

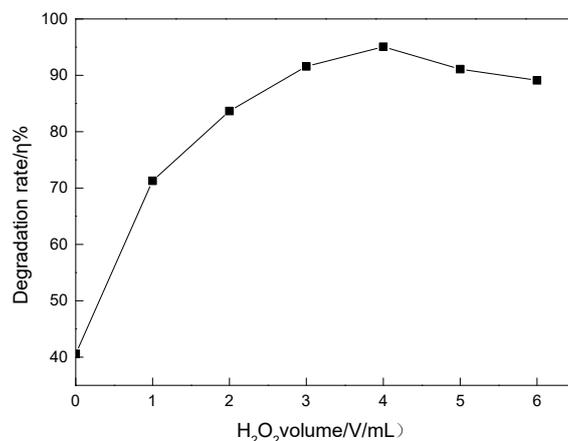


Figure 1. Effect of H₂O₂ volume on the degradation rate.

It can be seen from Fig 1 that when the amount of H₂O₂ is under 4mL, the degradation rate of ciprofloxacin increases with the increase of H₂O₂ volume; after over 4mL, the degradation rate decreases slightly. This is due to the increase in volume of H₂O₂, the amount of •OH increases in the solution increases, and the oxidation effect increases. When the volume of H₂O₂ is excessive, H₂O₂ will eliminate free radicals and reduce the degradation rate of ciprofloxacin.

3.1.2. The effect of FeY dosage on degradation rate. The effect of the dosage of FeY on the degradation rate was shown in Figure 2:

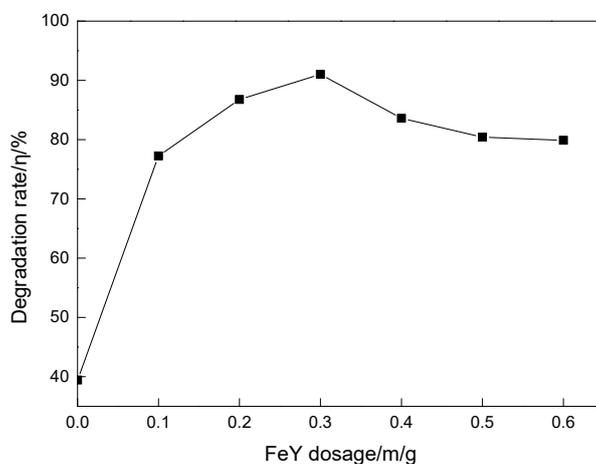


Figure 2. Effect of FeY dosage on the degradation rate.

It can be seen from Fig 2 that the degradation rate of ciprofloxacin is only 39.43% without catalyst, and the degradation rate of ciprofloxacin increases with the increase of the dosage of FeY. Under the UV/H₂O₂/FeY molecular sieve reaction system the degradation rate of ciprofloxacin reached 90.59% when the dosage of FeY was 0.3g.

3.1.3. Effect of initial concentration of ciprofloxacin on degradation rate. The effect of initial concentration of ciprofloxacin on degradation rate was shown in Figure 3.

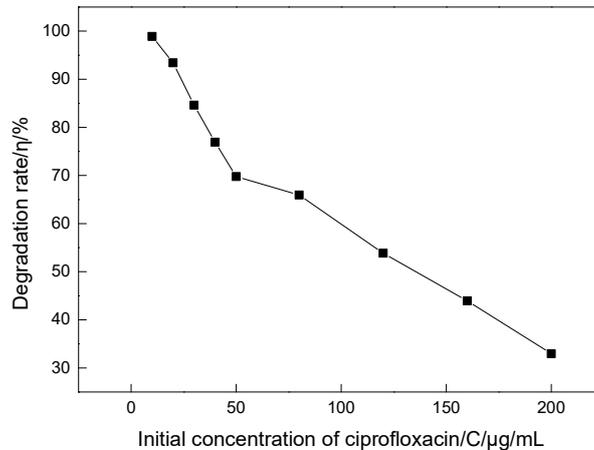


Figure 3. Effect of initial concentration of ciprofloxacin on the degradation rate.

The degradation rate of ciprofloxacin concentration decreased rapidly in 0~50μg/mL and then decreased slowly.

3.1.4. Effect of pH value on degradation rate. The effect of pH value on the degradation rate was shown in Figure 4.

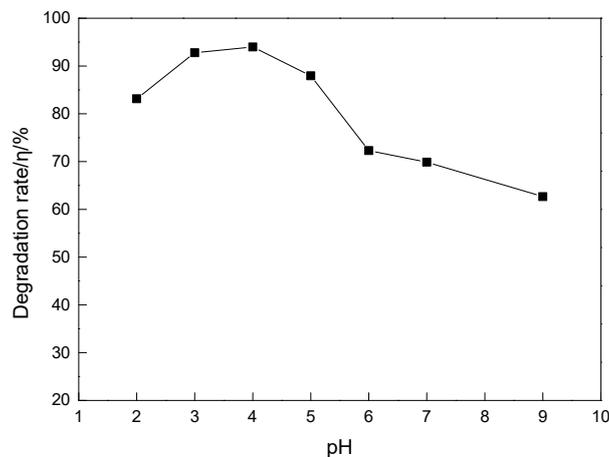


Figure 4. Effect of pH value on the degradation rate.

It can be seen from Figure 4 that when the pH is between 2 and 5, the degradation rate of ciprofloxacin is large, and the degradation rate changes little with the increase of pH. When the pH is more than 5, the degradation rate of ciprofloxacin shows a large downward trend. This is because the oxidizing ability of $\bullet\text{OH}$ is weak in a weakly acidic solution, Buxton et al. proposed that when the pH is between 2.0 and 3.0, the redox potential of $\bullet\text{OH}$ is 2.8V; and when the pH tends to be neutral, the $\bullet\text{OH}$ redox potential is reduced to 1.9V; in addition, when the pH is higher, Fe^{2+} will precipitate as an oxide and lose its catalytic ability.

3.1.5. The effect of UV lamp power on degradation rate. The effect of UV lamp power on degradation rate was shown in Figure 5.

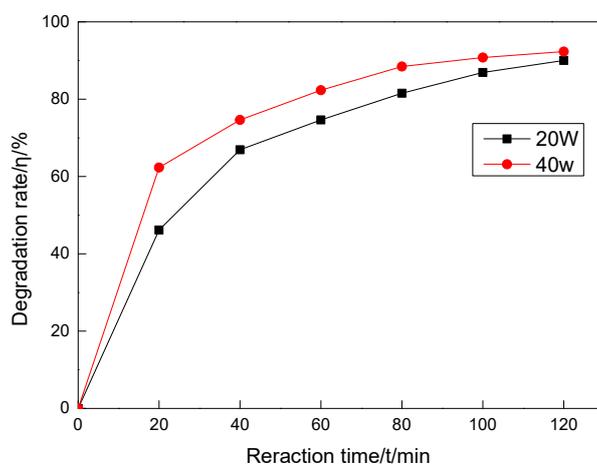


Figure 5. Effect of light power on the degradation rate.

Under the UV/H₂O₂/FeY molecular sieve reaction system, the degradation rate of ciprofloxacin is 82.31% with the irradiation of 40W UV lamp, while the degradation rate is 74.62% under the irradiation of 20W UV lamp. After two hours of UV lamp, the degradation rate of ciprofloxacin was basically the same.

3.2. Orthogonal test

On the basis of single factor experiment, four factors including the initial concentration of ciprofloxacin, FeY dosage, H₂O₂ volume and pH value were selected for four-factor and three-level orthogonal experiments. The experimental results were shown in Table 1.

Table 1. Orthogonal test table for degradation of ciprofloxacin by UV/H₂O₂/FeY.

Column number Test number	Ciprofloxacin initial concentration c_0 / μ g/mL	FeY quality m/g	H ₂ O ₂ volume V/mL	pH	Degradation rate $\eta/\%$
1	20	0.2	3	3.0	93.66%
2	20	0.3	4	4.0	90.93%
3	20	0.4	5	5.0	93.28%
4	30	0.2	4	5.0	83.21%
5	30	0.3	5	3.0	83.88%
6	30	0.4	3	4.0	92.03%
7	40	0.2	5	4.0	72.84%
8	40	0.3	3	5.0	62.00%
9	40	0.4	4	3.0	49.38%
I	2.78	2.50	2.48	2.27	
II	2.59	2.37	2.24	2.56	
III	1.84	2.35	2.50	2.38	
I/3	92.62%	83.24%	82.56%	75.64%	
II/3	86.37%	78.94%	74.51%	85.27%	
III/3	61.41%	78.23%	83.33%	79.50%	
Level difference R	31.22%	5.01%	8.83%	5.77%	
Due to the order of influence	initial concentration of ciprofloxacin solution > H ₂ O ₂ volume > initial solution pH > the dosage of FeY				

It can be seen from Table 1 that the influencing factors of each factor are that: initial concentration of ciprofloxacin solution > the volume of 1:100 H₂O₂ > the value of pH > the dosage of FeY. The optimal process conditions for photo-assisted heterogeneous Fenton degradation of ciprofloxacin solution is that: 3 the dosage of FeY is 0.2g, the initial concentration of ciprofloxacin is 30ug/mL, the volume of 1:100 H₂O₂ is 5mL, the value of pH is 4.0. The optimum process conditions were not included in the 9 groups of experiments. In a separate experiment, the degradation rate of ciprofloxacin under the optimal conditions was 96.6%.

4. Conclusion

(1) The UV/H₂O₂/FeY system has a good degradation effect on ciprofloxacin. The optimized process condition is that the dosage of FeY is 0.2g, the initial concentration of ciprofloxacin is 30ug/mL, the volume of 1:100 H₂O₂ is 5mL, and the value of pH is 4.0. Under this condition, the degradation rate of ciprofloxacin was about 96.6%.

(2) The factors affecting the degradation of ciprofloxacin are that: initial concentration of ciprofloxacin solution > the volume of 1:100 H₂O₂ > the value of pH > the dosage of FeY.

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