Study on Nano ZnO Photocatalytic Treatment of Chlortetracycline Hydrochloride Pollution in Aquaculture Waste Water

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Abstract. The Nano ZnO photocatalyst has been successfully prepared and characterized by XRD, SEM and other testing methods. A self-made nano ZnO was successfully used for the photocatalytic treatment of chlortetracycline hydrochloride pollution in aquaculture waste water. The effects of six factors such as dosage of photocatalysts，calcining temperature of photocatalysts, calcining time of photocatalysts, H_2O_2 concentration, reaction time and initial concentration of chlortetracycline hydrochloride under UV irradiation were discussed. The optimal experimental conditions for photocatalytic treatment of chlortetracycline hydrochloride pollution in aquaculture waste water which was determined by orthogonal experiments are as follows: when the concentration of chlortetracycline hydrochloride in the ultraviolet light was 0.01 g/L, calcining temperature of nano ZnO at 250 ℃, calcining time at 1h, dosage of nano ZnO at 0.5 g/L, H_2O_2 concentration at 0.4 g/L and reaction time at 4 h, the optimized removal rate of chlortetracycline hydrochloride in aquaculture waste water occurred , which can reach 79.10%.

1. Introduction

In recent years, seafood has become more and more popular among people and aquaculture industry has been greatly developing. Large doses of antibiotics are added to the aquaculture environment to prevent fish diseases and promote fish growth and development[1]. But only a small percentage of the antibiotics put into aquaculture can be absorbed and transformed by the fish themselves, most of which are released into the natural environment with excrement[2]. Tetracycline antibiotics, mainly including soxytetracycline, chlortetracycline, tetracycline and some synthetic antibiotics[3], are often used in aquaculture field, which has produced a large amount of aquaculture waste water containing antibiotics, causing some harm to the environment[4].

The bandgap of ZnO is narrow, so it can make good use of ultraviolet light to generate photo-induced electron-hole pairs, which possesses strong redox ability to decompose inorganic and organic pollutants into simple non-toxic inorganic substances. Besides, there is no secondary pollution in the process of degradation. ZnO is an environment-friendly photocatalyst and plays an important role in the governance of environmental pollution[5]. ZnO is used to degrade amoxicillin, ampicillin, chlorcellicillin and benzazepine in water with a good effect by scholars[6-7]. Li Di and

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Shi Weidong have found that photocatalytic treatment of antibiotics has good prospects[8]. In this paper, Nano ZnO was employed to carry out a photocatalytic degradation study on chlortetracycline hydrochloride which was extensively used in aquaculture. This paper is aimed at providing a scientific and effective way to treat antibiotics in aquaculture waste water.

2. Experimental

2.1. Experimental apparatus

Muffle furnace, centrifuge, magnetic stirrer, oven, 752 UV-Vis spectrophotometer, SU8010 scanning electron microscope, D/MAX-2500 X ray diffractometer, indoor UV visible photocatalytic device. Due to the wide bandgap of ZnO, the illumination used was completely UV light source, which can provide a stronger light energy to excite ZnO to generate photoelectron electron-hole pairs, thereby generating more hydroxyl radicals and superoxide radicals on the degradation of chlortetracycline hydrochloride.

2.2. Experimental reagents

Zinc nitrate (AR), sodium hydroxide (AR), 30% H_2O_2 (AR), absolute ethanol (AR) and chlortetracycline hydrochloride (USP).

2.3. Preparation of Nano ZnO photocatalyst

Nano ZnO can be prepared by a precipitation method[9-10]. A certain amount of zinc nitrate hexahydrate was dissolved in pure water and stirred. Then, a certain concentration of sodium hydroxide solution was slowly added dropwise to the zinc nitrate solution to produce a uniform zinc hydroxide precipitate, which was centrifuged, washed with anhydrous ethanol and pure water for several times, and dried in an oven at 105 ℃. The dried solids were ground and finally calcined at different temperatures in a muffle furnace to obtain nano-ZnO photocatalysts. The prepared photocatalyst was characterized by SEM, XRD and other testing methods.

2.4. Experimental methods

To simulate the preparation of aquaculture waste water containing chlortetracycline hydrochloride: the sea water was taken from the Dalian Ocean University, and suctioned by filtration. Different quantities of chlortetracycline hydrochloride were prepared according to the experiment needs and dissolved in sea water. The content of chlortetracycline hydrochloride was estimated by UV spectrophotometry.

A certain amount of simulated aquaculture waste water was taken into the reaction vessel. Chlortetracycline hydrochloride, Nano ZnO dosage, H_2O_2 concentration and reaction time were adjustable according to the experimental conditions. The experiment was carried out under the condition of magnetic stirrer and UV irradiation. Before the photocatalytic reaction was carried out, it was stirred for one hour in the dark to bring it to equilibrium after adsorption. The light source is then turned on for photocatalytic reaction. After the reaction, the supernatant was taken to measure the absorbance at a wavelength of 275 nm with a UV-visible spectrophotometer and the degradation rate of chlortetracycline hydrochloride was calculated.

3. Results and discussion

3.1. X-ray diffraction characterization (XRD) and scanning electron microscopy (SEM)

The XRD and SEM characterization results were shown Figure 1.

It could be concluded from the analysis of Figure 1 that the peak value was obvious when 2θ was 31.7348°, 34.3994°, 36.2102°, 56.5351°, 61.7981° or 47.4826°, and the sample was a hexagonal wurtzite structure in comparison with the standard JCPDS card (JCPDS 36-1541). The average

crystallite size of nanometer ZnO photocatalyst could be calculated by Scherrer formula. The lattice constants a, b and c of ZnO were 3.2539Å, 3.2539Å and 5.2098Å, respectively. By calculating the (111) diffraction peak, the average crystallite size of the nanometer ZnO photocatalyst was 34.14 nm, which was similar to the partical size of ZnO in SEM image.

It could be observed from the scanning electron micrograph image that the ZnO crystal presented an elliptical structure with uniform distribution and good particle dispersion while the particle size was consistent with the characterization result of XRD pattern.

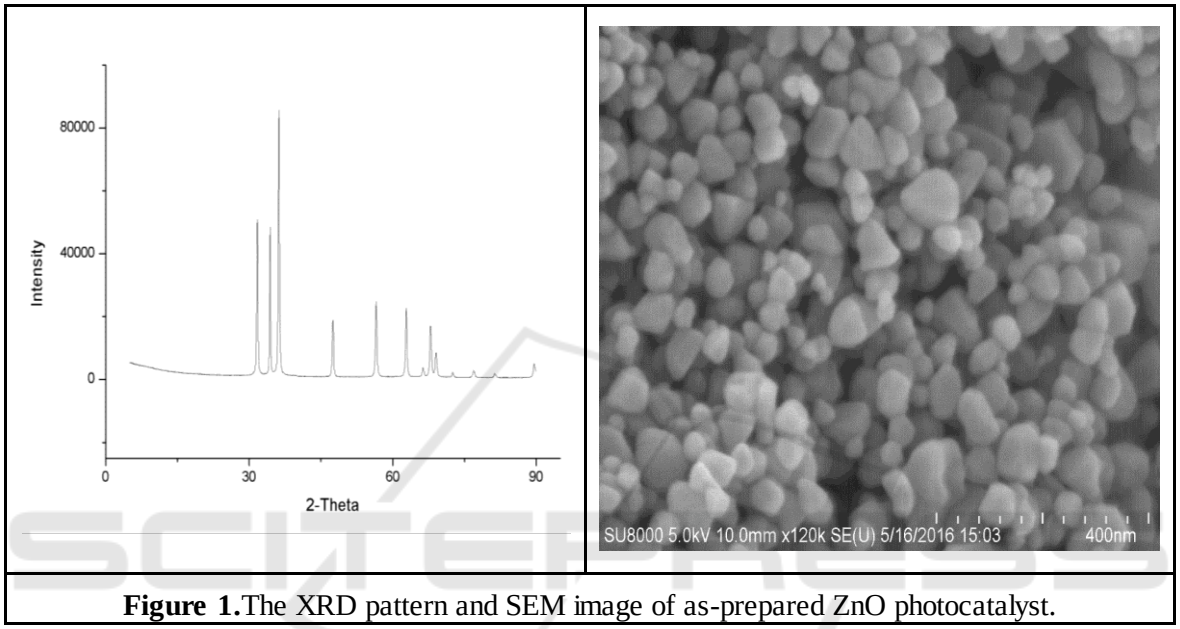
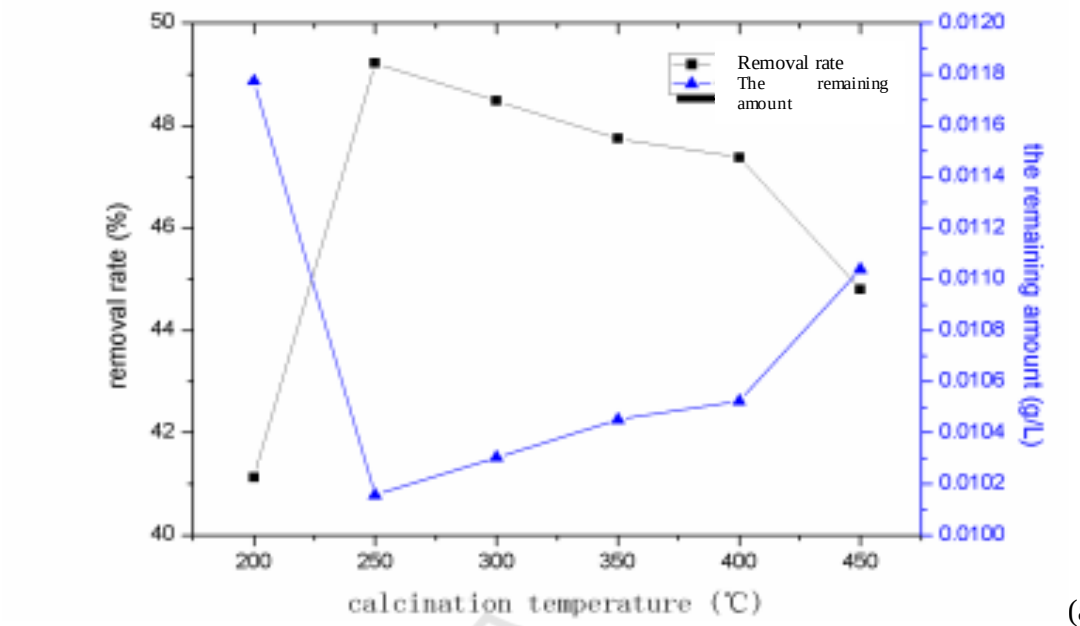


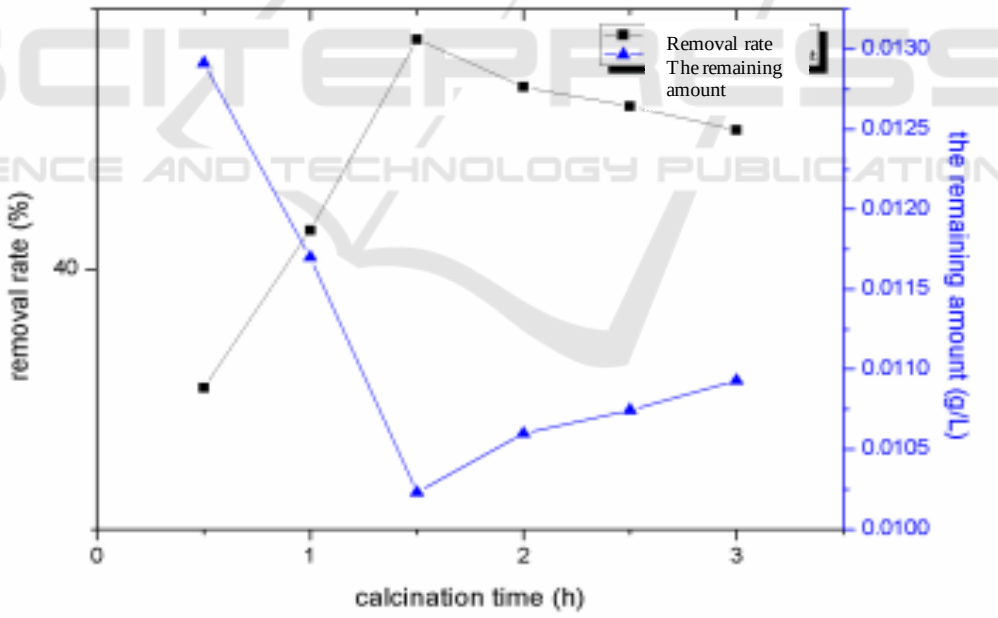
Figure 1. The XRD pattern and SEM image of as-prepared ZnO photocatalyst.

3.2. Photocatalytic degradation of antibiotic pollution in aquaculture wastewater with Nano –ZnO photocatalyst

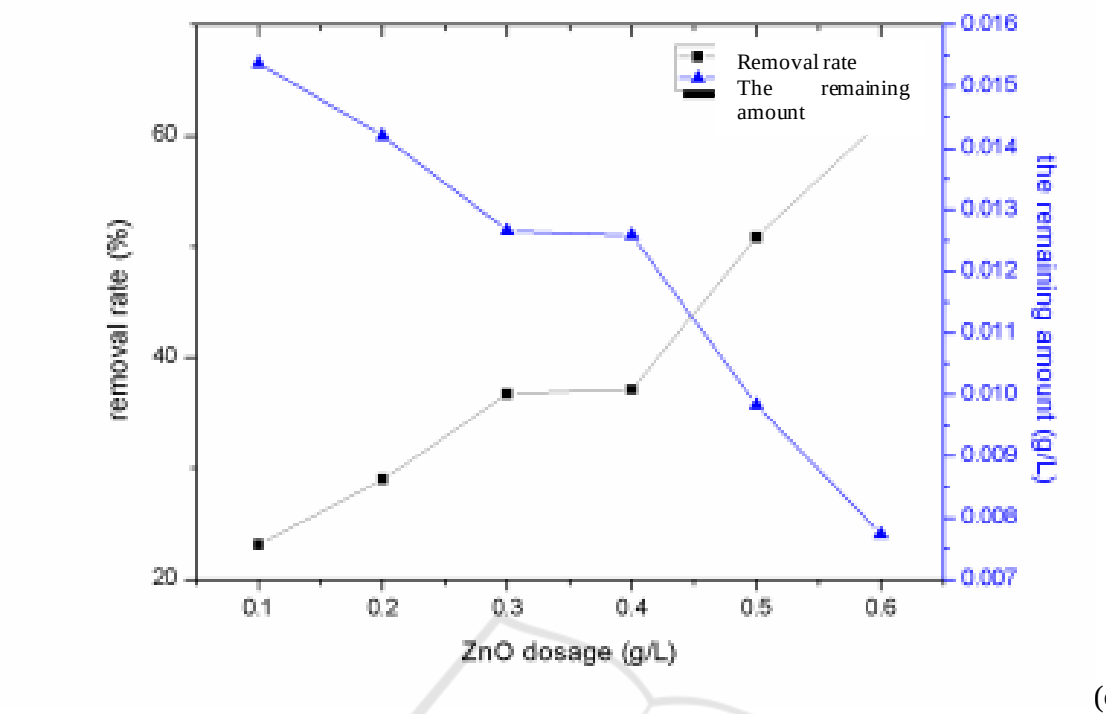
Each reaction vessel was added 50 mL simulated aquaculture wastewater， calcination temperature at 250 ℃, calcination time at 1.5 h,dosage of ZnO at 0.4 g/L, concentration of chlortetracycline hydrochloride at 0.02 g/L and concentration of H2O2 at 0.3 g/L. The reaction lasted two hours under ultraviolet light illumination.



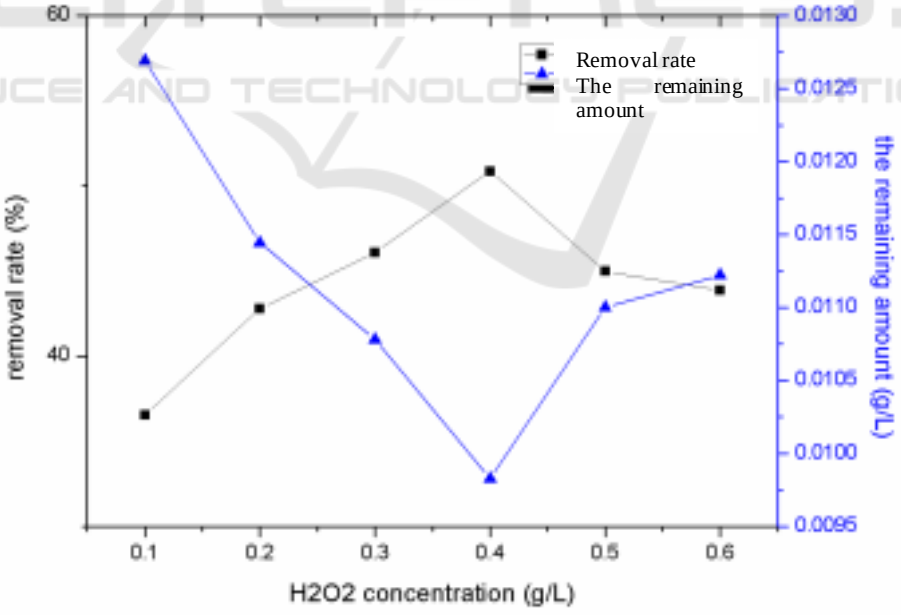
(a)



(b)



(c)



(d)

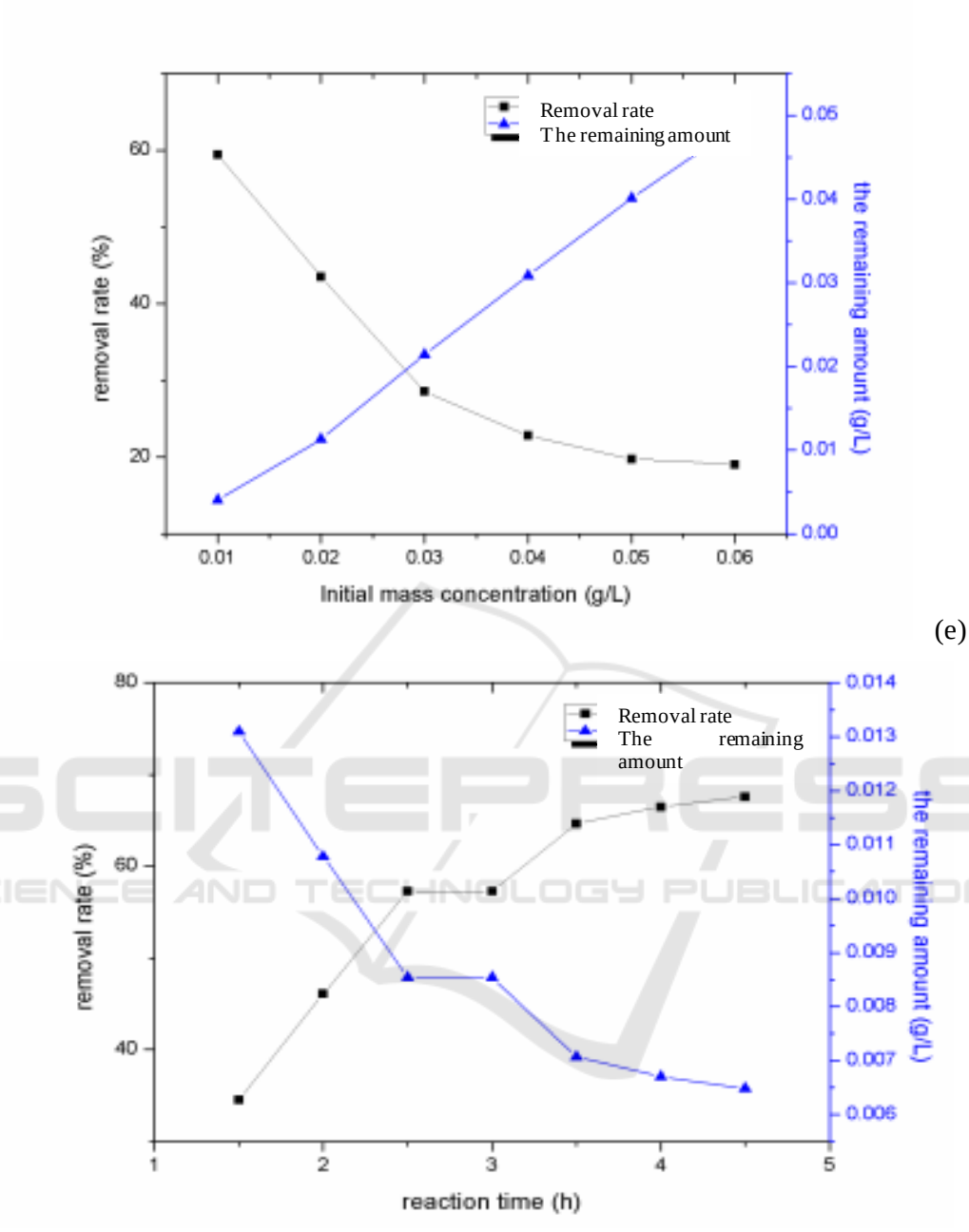


Figure 2. Effects of calcination temperature (a), calcination time (b), dosage (c), concentration of H_2O_2 (d), initial chlortetracycline hydrochloride concentration (e), and illumination time (f) on photocatalytic degradation.

3.3. Effect of calcination temperature of nanometer ZnO photocatalyst on the degradation of antibiotic pollution in aquiculture wastewater

The results were shown in Figure 2 (a). When the calcination temperature of nano-ZnO increased gradually, the removal rate of chlortetracycline hydrochloride increased first and then decreased, indicating that the crystal phase of nanometer ZnO has not been fully matured at a low calcination temperature. As the calcination temperature increased with the gradual maturity of crystal phase of

nanometer ZnO, the sites of photosensitizing adsorption to chlortetracycline hydrochloride increased. Thus, the removal rate of chlortetracycline hydrochloride increased continuously when the calcination temperature was from 250 ℃ to 450 ℃. When the calcination temperature was 250 ℃, the removal rate reaches the maximum of 49.22%. Higher calcination temperature was not conducive to the formation of nano-ZnO crystals for the reduction of the photosensitive adsorption sites to chlortetracycline hydrochloride.

3.4. Effect of calcination time of nanometer ZnO photocatalyst on the degradation of antibiotic pollution in aquiculture wastewater

The results were shown in Figure 2(b). When the calcination time of nano-ZnO increased dgradually, the removal rate of chlortetracycline hydrochloride first increased and then decreased, indicating that the degree of maturity of nano-ZnO crystalline was affected by the calcination time. With the gradual growth of calcination time, the crystalline phase of nano-ZnO became more mature, and the photo-adsorption sites of nano-ZnO as well as the photocatalytic kinetic energy gradually increased when the calcination time was from 0.5 h to 3 h. When the calcination time reached 1.5 h, the photocatalytic activity of the catalyst was the optimal. An increase of calcination time was not conducive to the formation of the catalyst, weakening the photocatalytic degradation of chlortetracycline hydrochloride.

3.5. Effect of dosage of ZnO on the degradation of antibiotic pollution in aquaculture wastewater treatment

The results were shown in Figure 2(c). The removal rate of chlortetracycline hydrochloride showed a positive correlation with the dosage of nano-ZnO. When the concentration of pollutants was constant, the increase of the dosage of nano-ZnO improved the photo-absorption sites of nano-ZnO under UV light , and enhanced the utilization rate of photo-generated electrons and promotes the generation of hydroxyl radicals and oxidation of substances[11-13], so as to improve the removal rate of chlortetracycline hydrochloride. Due to the concentration of chlortetracycline hydrochloride was constant, when the dosage of nano-ZnO was too large, the particles would have diffuse reflection to light and the the photosensitive adsorption site utilization of nano-ZnO was too low to improve the removal of hydrochloric chlortetracycline.

3.6. Effect of H_2O_2 concentration on the degradation of antibiotic contamination in aquaculture wastewater

The results were shown in Figure 2(d). When the H_2O_2 concentration gradually increased, the removal rate of chlortetracycline hydrochloride first increased and then decreased. The effect of adding H_2O_2 was to promote photogenerated electron-hole pairs of ZnO photocatalysts to generate more hydroxyl radicals and superoxide radicals and improve the degradation rate of chlortetracycline hydrochloride. But excessive H_2O_2 was not conducive to the reaction.

3.7. Effect of initial chlortetracycline hydrochloride concentration on the degradation of antibiotic contamination in aquaculture wastewater

The results were shown in Figure 2(e). The removal rate of chlortetracycline hydrochloride and the initial concentration of chlortetracycline hydrochloride were negatively correlated. When the dosage of nano-ZnO was constant the photo-sensitive adsorption sites on the photocatalyst remained unchanged. The initial concentration of chlortetracycline hydrochloride gradually increased and the photo-adsorption sites on the photocatalyst gradually saturated, which affected the further removal of chlortetracycline hydrochloride. Besides, too much chlortetracycline hydrochloride would cover the surface of the nano-ZnO, producing shading and diffuse effect to the ultraviolet light[8]. It would

have effect photocatalysts on the utilize of ultraviolet light and weaken the removal of chlortetracycline hydrochloride .

3.8. UV irradiation reaction time on the treatment of aquaculture wastewater antibiotic contamination

The results were shown in the Figure 2(f). The results showed that with the increase of reaction time, the removal rate of chlortetracycline hydrochloride increased gradually. The removal rate reached 66.49% when the reaction time was 4 h. The removal rate tended to be gentle when the reaction time was longer than 4 h. The results also showed that the effective contact with ZnO was low when the residual concentration of chlortetracycline hydrochloride was low, and the photocatalytic activity of nanometer ZnO was weak. It was difficult for ZnO to remove a very low concentration of chlortetracycline hydrochloride. The removal rate tended to be stable.

3.9. Optimization of photocatalytic treatment of chlortetracycline hydrochloride wastewater

Six factors and five levels table was designed. The orthogonal experimental data was shown in Table 1.

Table 1. Design matrix and experimental results for orthogonal array.

Experiment	Calcination temperature(℃)	Calcination time(h)	Dosage (g/L)	Concentration of H_2O_2 (g/L)	Illumination time(h)	Iinitial chlortetracycline hydrochloride concentration(g/L)	Removal rate (%)
1	250	1	0.2	0.1	2	0.1	54.65
2	250	1.5	0.3	0.2	2.5	0.2	65.57
3	250	2	0.4	0.3	3	0.3	47.65
4	250	2.5	0.5	0.4	3.5	0.4	52.56
5	250	3	0.6	0.5	4	0.5	52.57
6	300	1	0.3	0.3	3.5	0.5	29.67
7	300	1.5	0.4	0.4	4	0.1	69.35
8	300	2	0.5	0.5	2	0.2	52.34
9	300	2.5	0.6	0.1	2.5	0.3	38.83
10	300	3	0.2	0.2	3	0.4	18.51
11	350	1	0.4	0.5	2.5	0.4	33.91
12	350	1.5	0.5	0.1	3	0.5	27.09
13	350	2	0.6	0.2	3.5	0.1	77.44
14	350	2.5	0.2	0.3	4	0.2	56.93
15	350	3	0.3	0.4	2	0.3	28.91
16	400	1	0.5	0.4	4	0.3	71.17
17	400	1.5	0.6	0.5	2	0.4	25.83
18	400	2	0.2	0.1	2.5	0.5	5.41
19	400	2.5	0.3	0.2	3	0.1	71.19
20	400	3	0.4	0.3	3.5	0.2	62.26
21	450	1	0.6	0.4	3	0.2	58.95
22	450	1.5	0.2	0.5	3.5	0.3	35.28
23	450	2	0.3	0.1	4	0.4	22.52
24	450	2.5	0.4	0.2	2	0.5	2.84
25	450	3	0.5	0.3	2.5	0.1	57.23
K1	273	248.35	170.78	148.5	164.57	329.86	
K2	208.7	223.12	217.86	235.55	200.95	296.05	
K3	224.28	205.36	220.92	253.74	223.39	221.84	
K4	235.86	222.35	260.39	280.94	257.21	153.33	
K5	176.82	219.48	253.62	199.93	272.54	117.58	
R	96.18	42.99	89.61	132.44	107.97	212.28	

The order of these factors magnitude of effects on the removal rate was the following: initial concentration of chlortetracycline hydrochloride> hydrogen peroxide concentration> reaction time> calcination temperature> dosage of catalyst> calcination time. The optimal experimental condition for the photocatalytic degradation of chlortetracycline hydrochloride using nano-ZnO was: the chlortetracycline hydrochloride was 0.01 g/L, the calcination was 250 ℃, the calcination time was 1 h, the catalyst dosage was 0.5 g/L, the hydrogen peroxide was 0.4 g/L and the reaction time was 4 h. Verification tests under the above conditions were carried out and the removal rate reached 79.10%. The experimental results were shown in the Table 2.

Table 2. Verification test.

Experiment	Calcination temperature(℃)	Calcination time(h)	Dosage (g/L)	Concentration of H_2O_2 (g/L)	Illumination time(h)	Iinitial chlortetracycline hydrochloride concentration(g/L)	Removal rate (%)	Average removal rate(%)
1	250	1	0.5	0.4	4	0.01	77.63	
2	250	1	0.5	0.4	4	0.01	78.02	
3	250	1	0.5	0.4	4	0.01	78.92	79.10
4	250	1	0.5	0.4	4	0.01	79.91	
5	250	1	0.5	0.4	4	0.01	81.02	

4. Conclusions

(1) The nano-ZnO photocatalyst was successfully prepared. The average particle size of the nano-ZnO photocatalyst was 34.14nm. The prepared nano-ZnO can be used as a photocatalyst to degrade the chlortetracycline hydrochloride pollutants in aquaculture wastewater efficiently under the ultraviolet light with low concentration of chlortetracycline hydrochloride.

(2) The optimum reaction conditions obtained by orthogonal test were as follows: when the concentration of chlortetracycline hydrochloride was 0.01 g / L, the photocatalyst calcination temperature of nano ZnO was 250 ℃, the calcination time was 1 h, the dosage was 0.5 g / L, the concentration of H_2O_2 was 0.4g / L and the reaction time was 1 h, in which case the average removal rate reached 79.10% under ultraviolet light.

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