Photocatalytic degradation of chlortetracycline hydrochloride in marine aquaculture wastewater under visible light irradiation with CuO/ZnO

Jinghua Liu, Xiaocai Yu, Liping Wang, Meicen Guo, Wanting Zhu and Siyao Tian

ABSTRACT

A CuO/ZnO photocatalyst nanocomposite was successfully prepared by co-precipitation and characterized by investigating its chemical and physical properties by X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, UV-vis diffuse reflectance spectroscopy and photoluminescence spectroscopy. The average particle size of CuO/ZnO composite was found to be around 80 nm. The degradation of chlortetracycline hydrochloride pollutants in marine aquaculture wastewater using ZnO and CuO/ZnO was compared and it was found that CuO/ZnO nanocomposite is more efficient than ZnO. The effects of external factors on the photocatalytic effectiveness of nanocomposite were investigated under visible light. Also, the photocatalytic conditions for the degradation of chlortetracycline hydrochloride by the nanocomposite were optimized. Based on both ability and efficiency of degradation, and on the cost and availability, 10:2 molar ratio of Zn^{2+}/Cu^{2+} and 0.7 g/L nanocomposite, was found to be optimal, in which case the average photocatalytic degradation rate of chlortetracycline hydrochloride reached 91.10%.

Key words | aquaculture wastewater, chlortetracycline hydrochloride, CuO/ZnO, photocatalytic degradation, ZnO

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INTRODUCTION

Chlortetracycline hydrochloride, a widely used broad-spectrum antibiotic, could promote fish growth and prevent disease in aquaculture. Extensive farming techniques produce a large amount of aquaculture wastewater which is directly discharged into the natural world, causing serious pollution to the environment. Photocatalytic technology has the characteristics of low energy consumption, low cost and environmental friendliness, and has been applied to the treatment of wastewater containing organic pollutants (Marques *et al.* 2016; Regmi *et al.* 2017; Yu *et al.* 2018). However, photocatalytic treatment of organic pollutants has rarely been reported in the seawater environment. In order to accelerate the application of photocatalytic technology in seawater environments, CuO/ZnO composite photocatalyst will be used for the first time in this study to treat antibiotic pollution in marine culture wastewater.

ZnO has a wide band gap (3.2 eV), and has been studied by many scholars due to its characteristics of high stability, low cost (Look 2001; Zhang *et al.* 2002; Özgür *et al.* 2005), non-toxicity and environmental protection. However, the application and development of ZnO are limited by certain conditions, such as very strong energy that is required to excite ZnO, low visible light efficiency, and photochemical corrosion that is prone to occur (Zhang *et al.* 2001; Janotti & Van de Walle 2007). To overcome the above-mentioned disadvantages, in this work we introduced CuO to the surface of ZnO by co-precipitation method. At present, CuO has attracted much attention due to its unique performance, and its application has been extended to many fields such as solar cells (Langmara *et al.* 2018), sensors (Wang & Cho 2018), electro-catalytic water oxidation (Zhou *et al.* 2018), wastewater treatment (Scuderi *et al.* 2017), and even photocatalytic application (Wang *et al.* 2016). In particular, photocatalysis research has made good progress. Many researchers have complexed CuO with other catalysts to produce Au-TiO_2-CuO (Akashi *et al.* 2016), CuO/SnO_2/TiO_2 (Golestanbagh *et al.* 2018) and CuO-Pb_2O_3 (Kamaraj *et al.* 2018). These composite catalysts have exhibited excellent

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catalytic effect. For this reason, we introduced CuO to the surface of ZnO. CuO has a band gap of 1.7 eV and can absorb visible light and also increase light utilization efficiency, which significantly increases photocatalytic activity. We expect that antibiotic contamination in marine aquaculture wastewater can be degraded by the composite CuO/ZnO photocatalyst.

In this study, the composite CuO/ZnO photocatalyst was analyzed by some methods, including X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis diffuse reflectance spectra, elemental analysis, and photoluminescence (PL) spectra.

EXPERIMENTAL

Materials

Zinc nitrate hexahydrate (AR, $Zn(NO_3)_2{\cdot}6H_2O$) and copper nitrate (AR, $Cu(NO_3)_2{\cdot}3H_2O$) were produced by Shenyang Fifth Reagent factory in China. Cetyltrimethylammonium bromide (AR, CTMAB), hydrogen peroxide (AR, H_2O_2), sodium hydroxide (GR, NaOH) and absolute ethanol (AR, CH_3CH_2OH) were purchased from Tianjin Ke Miou Chemical Reagent Co., Ltd. Chlortetracycline hydrochloride (USP, $C_{22}H_{23}ClN_2O_8{\cdot}HCl$) was produced by Beijing Solarbio, China.

Preparation of CuO/ZnO nanocomposite

A CuO/ZnO photocatalyst nanocomposite was prepared by co-precipitation. The preparation method has been published previously by Ranit and colleagues (Ranit *et al.* 1999). Briefly, $Zn(NO_3)_2$ and $Cu(NO_3)_2$ were mixed in a 250 mL beaker and the molar ratio of Zn^{2+}/Cu^{2+} was 10:1, 10:2, 10:3, 10:4, 10:5 and 10:6. Then, CTMAB was added and mixed by ultrasonic dispersion for 2 h. Next, NaOH was added and mixed for another 1 h. The mixture was alternately washed with absolute ethanol and deionized water three times and was finally dried at 105 °C in an oven for 12 h. The powder was calcined in a muffle furnace for 2 h.

Photocatalytic measurements

The photocatalytic activity of the CuO/ZnO was assessed by the degradation of chlortetracycline hydrochloride under visible light (20 W fluorescent light). The photo-degradation was carried out at room temperature. Different qualities of chlortetracycline hydrochloride and photocatalyst were added into the reactor according to the experimental conditions. At the end of the experiment, 5 mL of the suspension was taken and centrifuged and then the absorbance of chlortetracycline hydrochloride was measured. Specific experimental conditions are shown in Table 1.

The concentrations of chlortetracycline hydrochloride in the reaction solutions were determined by UV-vis spectroscopy at a wavelength of 275 nm. The photocatalytic efficiency for chlortetracycline hydrochloride degradation was calculated using the following formula: $\eta = (C_0 - C_t)/C_0$, where η is the photocatalytic degradation rate of chlortetracycline hydrochloride, C_0 is the concentration of reactant before illumination; and C_t is the reactant concentration after illumination for time t.

RESULTS AND DISCUSSION

Characterization of the CuO/ZnO nanocomposite

Figure 1 shows the XRD patterns of the prepared ZnO and CuO/ZnO. Each sample exhibited strong diffraction peaks at $2\theta = 31.737°$, $34.379°$, $36.215°$, $47.484°$, $56.536°$, $62.777°$, $67.868°$ and $69.009°$. The diffraction peaks are corresponding to a standard JCPDS card (76-0704) of ZnO. The

Table 1 | Experimental conditions

Zn^{2+}/Cu^{2+} molar ratio (°C)	Calcination temperature (g/L)	H_2O_2 mass concentration (g/L)	Dosage (g/L)	Chlortetracycline hydrochloride initial concentration (h)	Illumination time
10:1–10:6	500	0.3	0.4	0.02	2.0
10:2	350–600	0.3	0.4	0.02	2.0
10:2	400	0.0–0.5	0.4	0.02	2.0
10:2	400	0.3	0.2–0.7	0.02	2.0
10:2	400	0.3	0.4	0.010–0.035	2.0
10:2	400	0.3	0.4	0.02	1.5–4.0

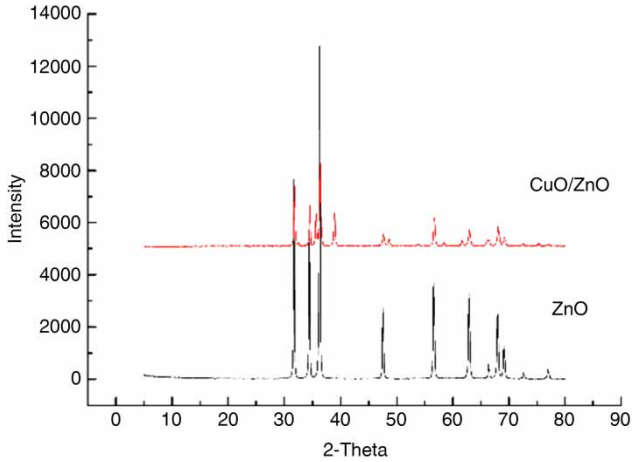

Figure 1 | XRD of ZnO and CuO/ZnO.

XRD pattern of CuO/ZnO exhibited the characteristic peaks of CuO at $2\theta = 35.558°$, 38.759° and 48.704°. The diffraction peaks are corresponding to a standard JCPDS card (89-5899) of CuO. Since the tight binding of CuO and ZnO inhibits the growth of ZnO, the diffraction peaks at 1.737°, 34.379° and 36.215°, 47.484°, 56.536°, 62.777°, 67.868° and 69.009° were lower in intensity than that of pure ZnO. The result showed that CuO grew on the surface of the ZnO, which further illustrated the successful formation of CuO/ZnO composite material. Subsequently, with the Scherrer formula, the mean diameters of ZnO and CuO/ZnO were calculated to be 41.998 and 80.552 nm, which were in line with the requirements of nano materials.

The composition and microstructure of the prepared photocatalysts were analyzed by SEM and energy dispersive spectroscopy (EDS). In Figure 2(a), ZnO particles with a diameter of 40 nm were obtained by precipitation of sodium hydroxide and zinc nitrate hexahydrate. Figure 2(b) shows that in CuO/ZnO, the ZnO particles were tightly bound to CuO, which mainly exhibited a rod-like structure with an average diameter of 80 nm. After hybridization with pure ZnO, rod-like CuO and ZnO were fully combined

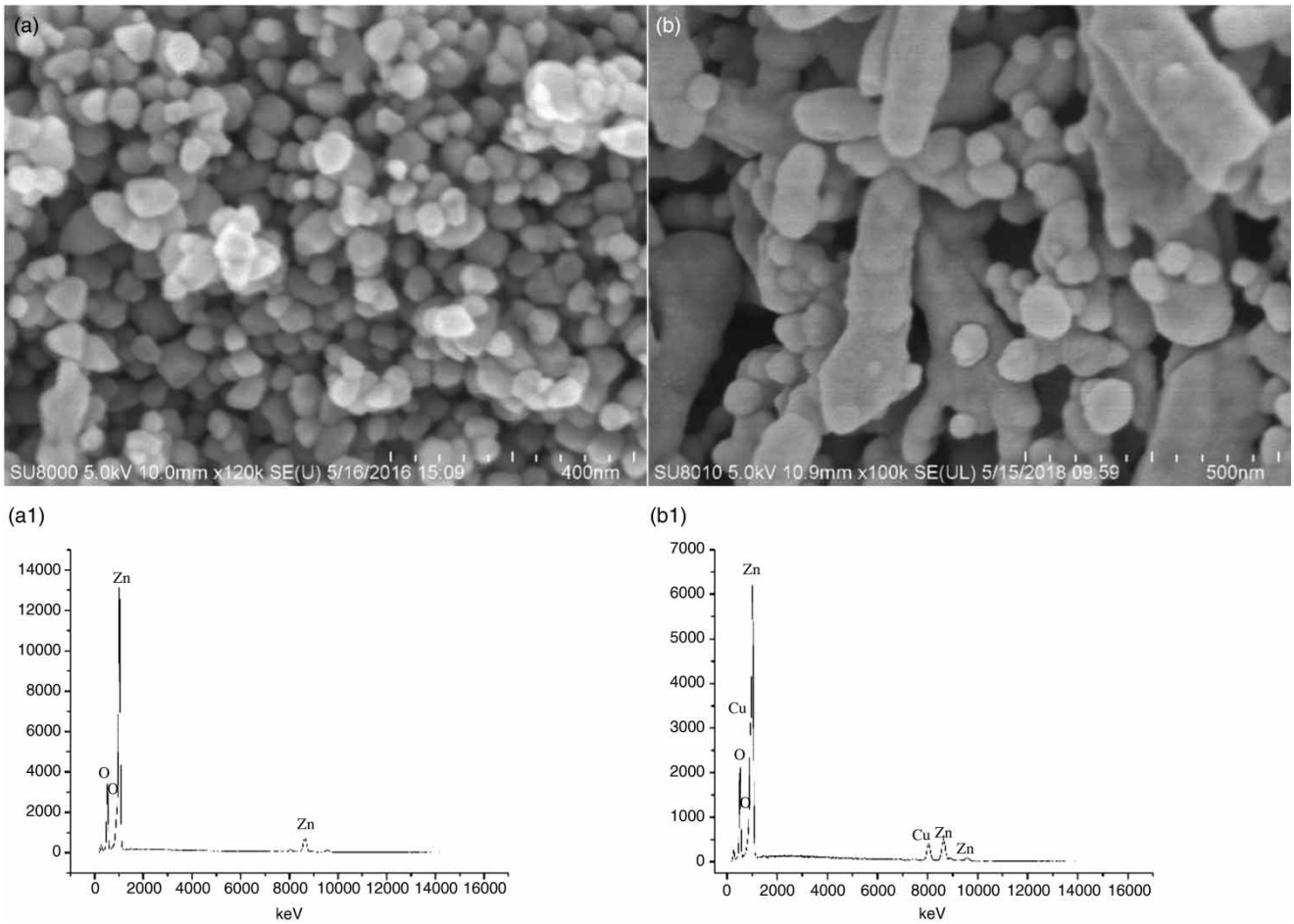

Figure 2 | SEM and EDS of pure ZnO (a, a_1) and CuO/ZnO (b, b_1).

to facilitate the transfer of photo-carriers and improve photocatalytic activity. The SEM result further illustrated that the prepared material contains CuO. In Figure 2(a1), the EDS characterization result of the ZnO sample showed the existence of Zn and O elements. As for CuO/ZnO (Figure 2(b1), the results showed that Cu element was also detected besides Zn and O elements, which further indicated that the sample consisted of CuO and ZnO.

In Table 2, the molar ratio of Zn/O in the ZnO sample was 1:1, indicating the successful preparation of ZnO. In the CuO/ZnO sample, the molar ratio of Zn/O was decreased, and the molar ratio of (Cu + Zn)/O was 1:1, further illustrating the successful preparation of CuO/ZnO composites.

PL analysis was used to evaluate the separation and recombination efficiency of photo-generated electron–hole pairs of photocatalysts. In Figure 3, ZnO showed luminescence in the range of 400–700 nm with an excitation wavelength of 328 nm. It was shown that the ZnO photo-generated electron–hole pairs were separated and recombined. In addition, the PL intensity of CuO/ZnO was significantly lower than that of ZnO, which indicated that the recombination rate of CuO/ZnO photo-generated electron–hole pairs was slower and the photocatalytic efficiency was enhanced. The results showed that after the combination of CuO and ZnO, the photocatalytic photoelectron–hole pairs were effectively separated and the recombination rate of photo-generated electron–hole pairs slowed down.

In Figure 3(b), is shown that pure ZnO could absorb ultraviolet light ($\lambda < 400$ nm) but had a low absorption of visible light. CuO/ZnO exhibited a significant absorption in the visible ($\lambda > 400$ nm) region with red shift. One possible reason is that CuO composite on the surface of ZnO expands the absorption wavelength of the material from ultraviolet light to visible light, changes the material band gap and increases the absorption range of light. According to the energy formula ($E = h\nu$, where E is energy, h is Planck's constant, ν is light wave frequency), the band gaps of ZnO and CuO/ZnO were calculated to be 3.2 and 1.2 eV, respectively.

Table 2 | Element composition of samples

Sample	Zn (%)	O (%)	Cu (%)
ZnO	49.98	49.95	0
CuO/ZnO	33.34	49.96	16.62

Exploring the optimum conditions for photocatalytic degradation of chlortetracycline hydrochloride by CUO/ZNO

The effect of Zn^{2+}/Cu^{2+} molar ratio on photocatalytic reaction

The photocatalytic degradation rate of chlortetracycline hydrochloride is maximum when the molar ratio of Zn^{2+}/Cu^{2+} is 10:4 (Figure 4(a)). The doping of CuO promoted the transfer of photo-generated electrons and holes in CuO/ZnO composite photocatalyst, and the photocatalytic performance was improved. However, when CuO was excessively doped, CuO/ZnO composite photocatalyst formed a new recombination center of photo-generated electron–hole, which accelerated the recombination rate of

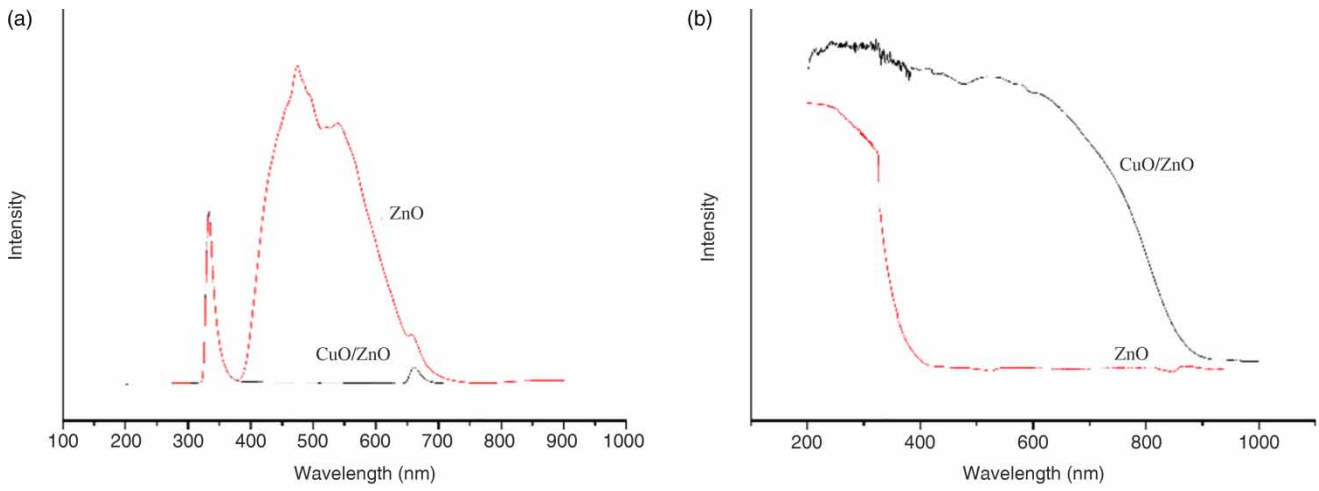

Figure 3 | PL spectra (a) and UV-vis diffuse reflectance spectra (b).

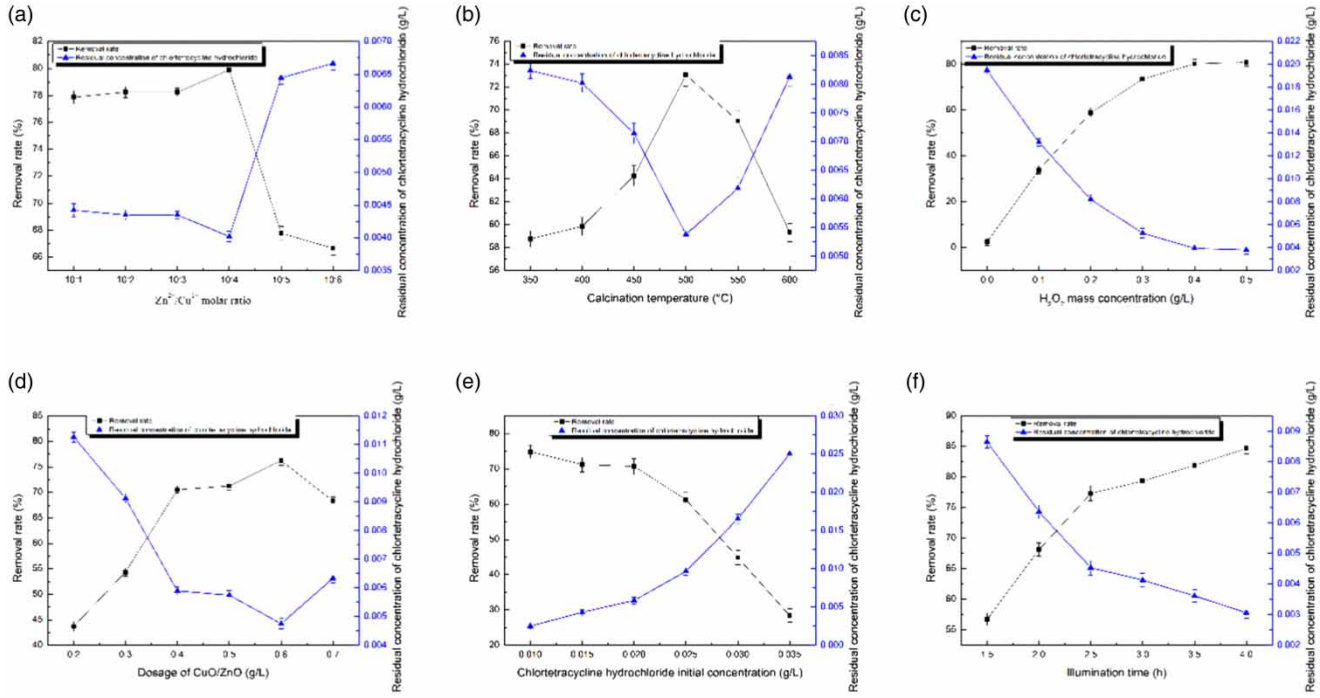

Figure 4 | Effects on chlortetracycline hydrochloride removal of Zn^{2+}/Cu^{2+} molar ratio (a), calcination temperature (b), H_2O_2 mass concentration (c), dosage (d), chlortetracycline hydrochloride initial concentration (e), and illumination time (f).

photo-generated electrons and holes, and the photocatalytic degradation rate of chlortetracycline hydrochloride decreased evidently.

The effect of calcination temperature on photocatalytic reaction

The calcination temperature is a key factor that will affect the growth of the photocatalyst crystal. The CuO/ZnO photocatalyst has the highest photocatalytic degradation rate of chlortetracycline hydrochloride at the calcination temperature of 500 °C (Figure 4(b)). If the CuO/ZnO crystal was not fully matured, CuO and ZnO could not be combined completely, and the electron orbit was not easy to obtain. When calcination temperature was too high, the CuO crystal grew excessively, it destroyed the crystal structure of ZnO and reduced photo-generated electron–hole pairs, which led to low removal rate of chlortetracycline hydrochloride.

The effect of H_2O_2 mass concentration on photocatalytic reaction

From Figure 4(c), it could be seen that the photocatalytic degradation rate of chlortetracycline hydrochloride by CuO/ZnO is obviously improved after adding H_2O_2. The reason is that H_2O_2 can promote the generation of $\cdot O_2^-$ groups and ·OH radicals with CuO/ZnO photocatalysts, and then improve photocatalytic efficiency. The photocatalytic ability was determined by the properties of the photocatalytic material. With the increasing of the mass concentration of H_2O_2, the photocatalytic degradation rate of chlortetracycline hydrochloride is not significantly enhanced.

The effect of catalyst dosage on photocatalytic reaction

The photo-generated electron–hole pairs excited by the photocatalyst are positively correlated with the dose of photocatalysts. Figure 4(d) shows that by increasing the dose of CuO/ZnO, the quantities of photo-generated e^--h^+ pairs grew, and thus increased the photocatalytic degradation rate of chlortetracycline hydrochloride. The photocatalytic degradation rate decreased when the addition of CuO/ZnO is continuously increased. Due to the addition of excessive CuO/ZnO particles, diffuse reflection of light occurred in the reaction solution, and thus the availability ratio of light lowered, which reduced the removal efficiency of chlortetracycline hydrochloride.

The effect of chlortetracycline hydrochloride initial concentration on photocatalytic reaction

The concentration of the contaminants also affected the photocatalytic efficiency of the photocatalyst. It can be seen from Figure 4(e) that, with the initial concentration of chlortetracycline hydrochloride increasing, the photocatalytic degradation rate of chlortetracycline hydrochloride by CuO/ZnO gradually reduced. The reason was that with the increasing of the initial concentration of chlortetracycline hydrochloride, the surface of CuO/ZnO was covered by an excessive amount of chlortetracycline hydrochloride, thereby leading to the restriction of solar transmission, Hence the photo-generated electron–hole pairs should not be excited easily. Thus the removal ratio of CuO/ZnO on chlortetracycline hydrochloride decreased obviously.

The effect of illumination time on photocatalytic reaction

The photocatalytic degradation rate of chlortetracycline hydrochloride on CuO/ZnO was gradually improved with irradiation. When the illumination time was 3.5 h, the photocatalytic degradation rate of chlortetracycline hydrochloride was 81.92% (Figure 4(f)). The photocatalytic degradation rate of chlortetracycline hydrochloride rose gently with the increase of the illumination time. The results showed that the effective contact between CuO/ZnO and chlortetracycline hydrochloride is limited due to the decrease of the residual concentration of chlortetracycline hydrochloride as the reaction progresses. Ability is eventually weakened.

Optimize experimental conditions

Experiments were conducted under varying conditions, as follows: the dose of CuO/ZnO was 0.3–0.7 g/L, the initial concentration of chlortetracycline hydrochloride was 0.010–0.030 g/L, the molar ratio of Zn^{2+}/Cu^{2+} was 10:1–10:5, the calcination temperature was 350–550 °C, the concentration of H_2O_2 was 0.1–0.5 g/L, and the reaction time was 2.0–4.0 h to study the interaction between variable factors and the photocatalyst (Table 3).

The experiments varying the CuO/ZnO photocatalytic conditions indicated the optimization conditions of chlortetracycline hydrochloride degradation were: the dose of CuO/ZnO was 0.7 g/L, the initial concentration of chlortetracycline hydrochloride was 0.01 g/L, the molar ratio of Zn^{2+}/Cu^{2+} was 10:2, the calcination temperature was 500 °C, the concentration of H_2O_2 was 0.5 g/L, and the reaction time was 3.5 h (Experiment 17). Under the conditions above, a verification test was repeated five times. The results showed that photocatalytic degradation rates of chlortetracycline hydrochloride were 92.52%, 91.87%, 90.99%, 90.33% and 89.78%, respectively. And the average photocatalytic degradation rate was 91.10%. The influence of these factors on the photocatalytic degradation rate was: H_2O_2 mass concentration > CuO/ZnO dosage > chlortetracycline hydrochloride initial concentration > illumination time > calcination temperature > Zn^{2+}/Cu^{2+} molar ratio.

CONCLUSIONS

A CuO/ZnO photocatalyst was developed on the base of ZnO. The study was a simple way to combine CuO and ZnO and to establish a reaction model with chlortetracycline hydrochloride. The results showed that CuO/ZnO can absorb visible light to promote the utilization efficiency of light, thereby enhancing the photocatalytic activity. The reason for the enhancement of photocatalytic activity is that the addition of CuO can effectively separate photo-generated electron–hole pairs, promote the transmission of photo-generated electrons, slow down the photo-electron–hole pair recombination, and generate more hydroxyl radicals for degradation of chlortetracycline hydrochloride. The study proposes a modification method that enables ZnO to make better use of visible light, and provides a theoretical basis for photocatalytic technology in the treatment and recovery of environmental pollution. The results are as follows.

1. EDS and elemental analysis showed that the sample consisted of CuO and ZnO, and the composite material was determined that to be CuO/ZnO. XRD determined that the average particle diameter of CuO/ZnO was 80.552 nm. From the SEM images, it can be seen that CuO/ZnO and ZnO have good dispersion. The characterization of PL indicated that CuO/ZnO can effectively promote the separation of photo-generated electron–hole pairs and slow down the recombination rate of photo-generated electron–hole pairs. From the UV-vis diffuse reflectance spectrum, the light absorption of CuO/ZnO ranges from ultraviolet light to visible light, which enhances the absorption of the composite in the visible region to promote the utilization efficiency of light.
2. The results showed that CuO/ZnO photocatalyst could effectively degrade chlortetracycline hydrochloride in marine aquaculture wastewater under visible light. For optimized photo-degradation, the dose of CuO/ZnO was 0.7 g/L, the initial concentration of chlortetracycline

Table 3 | Orthogonal experiment

Experiment	Calcination temperature (°C)	Zn^{2+}/Cu^{2+} molar ratio	Dosage of CuO/ZnO (g/L)	H_2O_2 mass concentration (g/L)	Chlortetracycline hydrochloride initial concentration (g/L)	Illumination time (h)	Degradation rate (%)
1	350	10:1	0.3	0.1	0.010	2.0	39.14
2	350	10:2	0.4	0.2	0.015	2.5	62.46
3	350	10:3	0.5	0.3	0.020	3.0	71.92
4	350	10:4	0.6	0.4	0.025	3.5	72.16
5	350	10:5	0.7	0.5	0.030	4.0	66.31
6	400	10:1	0.4	0.3	0.025	4.0	75.54
7	400	10:2	0.5	0.4	0.030	2.0	39.73
8	400	10:3	0.6	0.5	0.010	2.5	88.75
9	400	10:4	0.7	0.1	0.015	3.0	42.87
10	400	10:5	0.3	0.2	0.020	3.5	47.48
11	450	10:1	0.5	0.5	0.015	3.5	84.76
12	450	10:2	0.6	0.1	0.020	4.0	31.31
13	450	10:3	0.7	0.2	0.025	2.0	50.55
14	450	10:4	0.3	0.3	0.030	2.5	17.19
15	450	10:5	0.4	0.4	0.010	3.0	82.14
16	500	10:1	0.6	0.4	0.030	3.0	56.76
17	500	10:2	0.7	0.5	0.010	3.5	89.12
18	500	10:3	0.3	0.1	0.015	4.0	38.95
19	500	10:4	0.4	0.2	0.020	2.0	50.42
20	500	10:5	0.5	0.3	0.025	2.5	62.75
21	550	10:1	0.7	0.4	0.020	2.5	81.47
22	550	10:2	0.3	0.5	0.025	3.0	73.92
23	550	10:3	0.4	0.1	0.030	3.5	68.88
24	550	10:4	0.5	0.2	0.010	4.0	64.13
25	550	10:5	0.6	0.3	0.015	2.0	77.41
K1	311.99	337.67	216.68	221.15	363.28	257.25	
K2	294.37	296.55	339.44	275.05	306.44	312.63	
K3	265.95	319.05	323.29	304.80	282.62	327.60	
K4	297.99	246.77	326.39	332.25	334.91	362.40	
K5	365.82	336.09	330.32	402.86	248.87	276.24	
R	99.87	90.90	122.76	181.71	114.41	105.15	

K*i* (*i* = 1, 2, 3, 4 and 5) represents the sum of the removal rates of experiment *i*. R represents the difference between the maximum value and the minimum value of K1–K5.

hydrochloride was 0.01 g/L, the molar ratio of Zn^{2+}/Cu^{2+} was 10:2, the calcination temperature was 500 °C, the concentration of H_2O_2 was 0.5 g/L, and the reaction time was 3.5 h. Under these conditions, the average photocatalytic degradation rate of chlortetracycline hydrochloride could reach 91.10%.

3. The sequence of importance of the factors influencing photocatalytic degradation of chlortetracycline hydrochloride in marine aquaculture wastewater by CuO/ZnO photocatalyst was: H_2O_2 mass concentration > CuO/ZnO dosage > chlortetracycline hydrochloride initial concentration > illumination time > calcination temperature > Zn^{2+}/Cu^{2+} molar ratio.

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