Composite Photocatalysts of CNTS-TiO₂: An Efficient Photocatalyst for the Degradation of Ammonia Nitrogen Pollutant in Mariculture Wastewater under UV Light Irradiation

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Abstract. In this study, composite photocatalyst of CNTS-TiO₂ is employed to degrade ammonia nitrogen pollutant in mariculture wastewater under UV light irradiation. The photocatalyst was prepared by a sol-gel method and was characterized by SEM and XRD analysis.The photocatalytic degradation efficiency of ammonia nitrogen was analysed by various experimental parameters namely dosage, initial concentration of ammonia nitrogen, pH value, the concentration of H_2O_2, illumination timeand calcination time. The degradation of ammonia nitrogen pollution in mariculture wastewater was optimized by orthogonal experiment. According to the results, the best effect exists when the dose of catalysts was 60 mg, initial concentration of ammonia nitrogen was 10 mg/L, pH value was 9, concentration of H_2O_2 was 0.5 g/L, illumination time was 2.5 h, and calcination time was 1h. The removel rate of ammonia nitrogen can reach 75.78%.

1. Introduction

With the development of marine aquaculture, an increasing number of mariculture wastewater have exacerbated the deterioration of coastal aquatic environment. Deterioration of water quality and decreased transparency were due to the oxidation of NH_4^+-N. The excessive nitrogen content and multiplication of algous led to eutrophication rapidly. Fish poisoning infected with harmful bacteria which had a pernicious effect on human health indirectly [1, 2]. Therefore, dealing with mariculture wastewater in a high-efficiency and secure way which has received a great attention nowadays. Nano TiO_2 has been used extensively for the advantage of non-toxic, low expense, high stability, no secondary pollutant, strong redox property and the ability to decompose organic pollutants effectively and thoroughly [3-5]. The utilization of solar energy was reduced by the width of band gap and it has a high recombination rate, but low quantum efficiency as an eletron [6], which limited its practical application. Certain adsorbability of CNTS increases the concentration of surface organic compounds which shows its special pore structure and specific surface area. Electrons were transferred by good conductors of electricity so that accumulated electrons have a reduction in   CNTS-TiO₂ Composites. A large amount of agglomerated particles of TiO_2 was absorbed, limiting the recombination of electron-hole pair, which enhanced the photocatalytic activity of TiO_2 [7, 8]. Comprehensive studies of CNTS-TiO₂ Composite photocatalysts were prepared by sol-gol process at present. In this study, a composite photocatalyst of CNTS-TiO₂ is employed to degrade ammonia nitrogen pollutant in mariculture wastewater under UV light irradiation in order to provide a green environmental protection method for the treatment of mariculture wastewater.

2. Materials and Methods

2.1. Materials

The main experimental chemicals included $C_{16}H_{36}O_4Ti$, CH_3COOH, HNO_3, $HO(CH_2CH_2O)_nH$, $NaClO$, C_6H_5OH, $Na_3C_6H_5O_7 \cdot 2H_2O$, $(NH_4)_2SO_4$ solution and absolute ethanol. The apparatus consisted of an ultrasonic cleaner, a drying oven, a UV-visible spectrophotometer, an X-ray diffraction, a muffle furnace and some magnetic stirrers.

2.2. Preparation of the Composite Photocatalyst

A series of CNTS-TiO$_2$ samples were prepared by a sol-gol method according to the following procedure: First, 1 g carbon nanotubes and amount of 50 mL concentrated HNO_3 solution was added to the reflux device. Then decanted them into the suction filter after 2 h at 120°C and washed with deionized water until solution achieved neutral. Second, 35 ml $C_{16}H_{36}O_4Ti$ and 200 mL anhydrous ethanol was stirred evenly which was labeled as solution A. A certain amount of deionized water, CH_3COOH and absolute ethanol was prepared. A prescribed amount of pretreated carbon nanotubes was dissolved to form the mixed solution, a small amount of $HO(CH_2CH_2O)_nH$ was added to the solution and mixed by ultrasonic dispersion for about 1 h labeled as solution B. Drop solution B into solution A and then dried at 80°C and ground to powder, next the powder was calcinated at an optimum temperature of 500°C for 2 h. After the muffle furnace cooled down to room temperture, the samples were taken out and ground to form CNTS-TiO$_2$ composite photocatalyst.

3. Results and Discussion

3.1. SEM and XRD Analysis of the Photocatalyst

3.1.1. Characterization of SEM. The CNTS-TiO$_2$ composite photocatalyst was characterized by SEM and XRD methods, and the results were shown in figure 1.
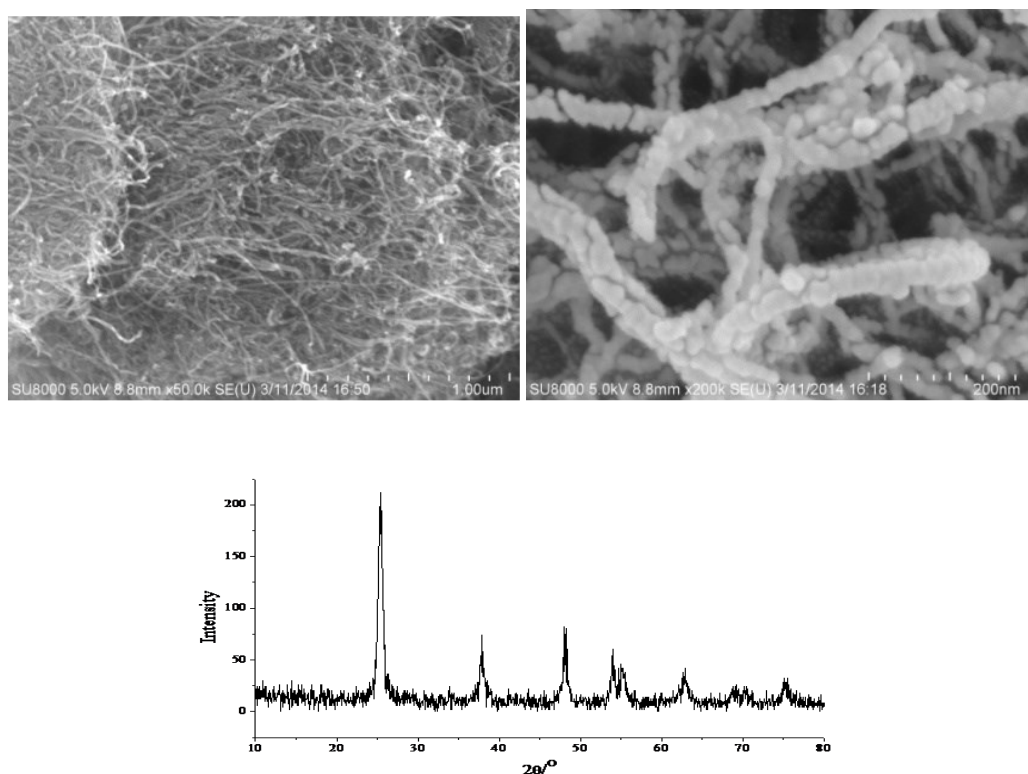

Figure 1. The SEM images and The XRD images of prepared CNTS-TiO$_2$ composite photocatalysts

   Scanning electron microscopy (SEM) can be employed to study the crystallization of nanomaterials, observe the morphology and dispersion of nanoparticles and measure or sevaluate the particle size of nanoparticles. It can be recognizabled that the CNTS-TiO$_2$ composite photocatalystsexhibite tubular morphology with a partical size approximately 20-50 nm and distributes uniformly according to the scanning electron microscope images, which in accordance with that calculated by Scherrer formula.

3.1.2. Characterization of the photocatalyst by X-ray diffraction technique. The qualitative analysis of the phase can be obtained by comparing the diffraction peak with the JCPDS card to obtain the corresponding lattice constant and related parameters according to the X-ray diffraction (XRD) that was shown in figure 1. The CNTS-TiO$_2$ composites sample has obvious peaks at 2θ of 64.1°which is similar to the standard card (JCPDS 21-1272).Calculating the particle size is 26.2 nm on the basis of Scherrer[9] formula, in conformity with that obtained by scanning electron microscopy approximately.
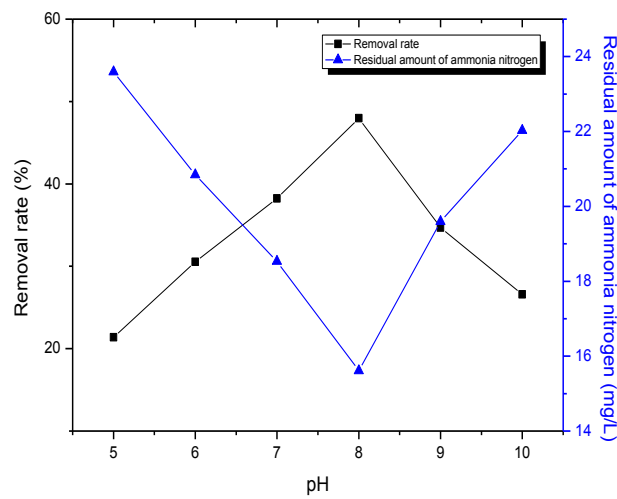
3.2. Photocatalytic Degradation of a Model Pollutant

Dosage, initial concentration of ammonia nitrogen, pH value, the concentration of H$_2$O$_2$, illumination time, calcination temperature and calcination time are employed as single variables studied by 'control variable method'. The effect of a variable examination was shown by the range of the variable changing in the photocatalytic reaction.
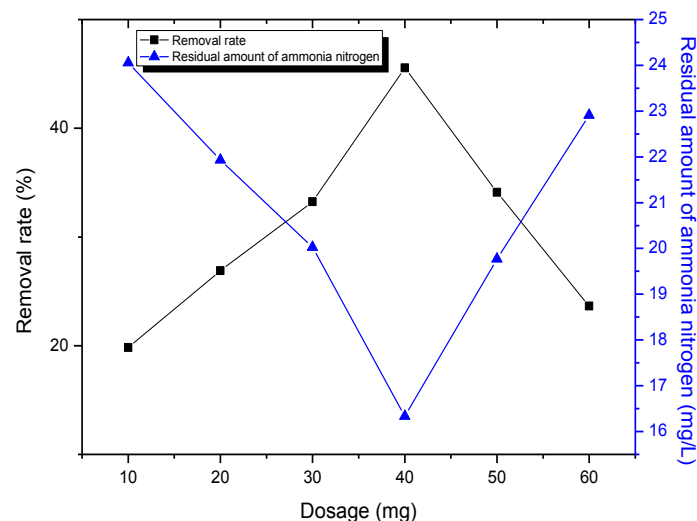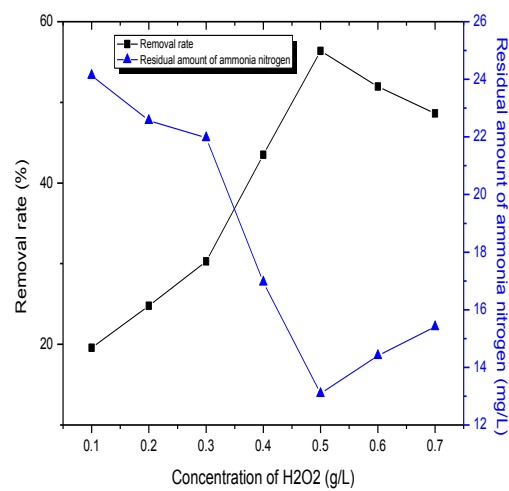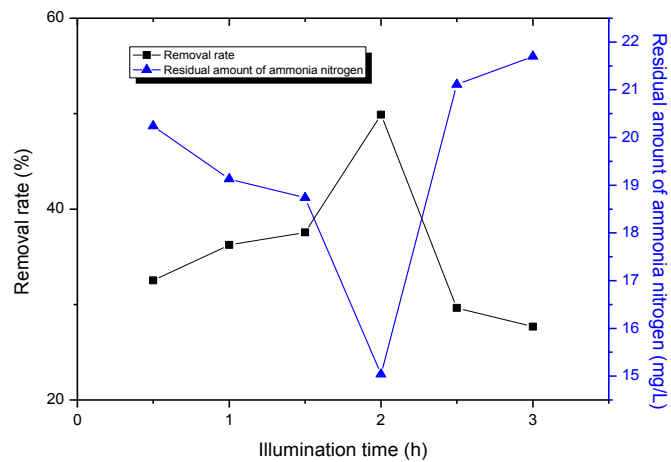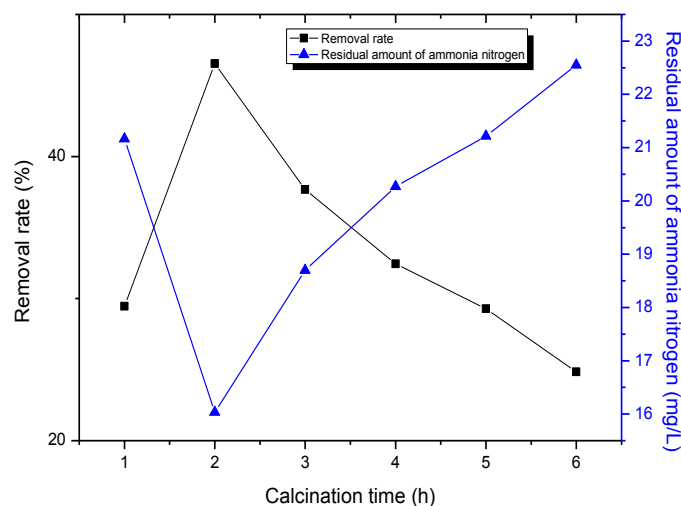

(a)
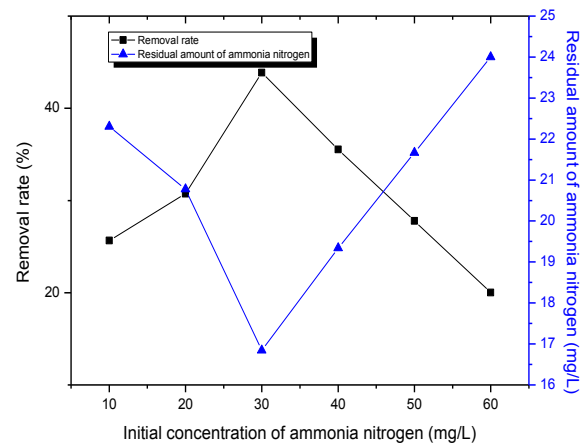
(b)

(c)

(d)

(e)

(f)

Figure 2. Effects of dosage (a), initial concentration of ammonia nitrogen (b), pH value(c), concentration of H_2O_2 (d), illumination time (e), and calcination time (f) on photocatalytic degradation

3.2.1 The effect of dosage on photocatalytic efficiency. The dosage of catalysts varied from 10 mg to 60 mg in order to determine the optimum amount of composite photocatalyst to degrade a known concentration of ammonia nitrogen. The results shown in figure 2(a) indicated that with the dosage increasing, the degradation increases initiatively and then decreases and the degradation rate reaches maximum (45.55%) when the dosage is 40 mg. When minor catalyst was added to mariculture wastewater, a large amount of CNTS-TiO$_2$ particles were participated in the procedure with the increase of dosage, leading to the incremental of removal effect. But increased continuously would enhance scattering of light to CNTS-TiO$_2$ composite photocatalyst in solution when dosage of photocatalyst in seawater reaches a certain concentration [9], thereby decreasing the utilization of solar energy and the concentration of photo-generated electrons and electron holes [10]. Therefore, an overdose of the catalyst not only increases expenditure, but also mitigates the removal efficiency.

3.2.2 The effect of initial concentration of ammonia nitrigen on photocatalytic efficiency. Variation of initial concentration of ammonia nitrigen from 10 mg/L to 60 mg/L were conducted to investigate the

degradation capacity of the photocatalyst. The results shown in figure 2(b) which makes a clear indication that when the initial concentration of ammonia nitrogen was 30 mg/L, the removal rate reached 43.86%. On account of restricted capacity of CNTS-TiO$_2$ composite photocatalyst to pollutants from mariculture wastewater in adsorption, which effected the ammonia nitrogen degradation directly. Therefore, the degradation rate of ammonia nitrogrn was in decline when the concentration of ammonia nitrogen above or below 30 mg/L.

3.2.3 *The effect of pH value on photocatalytic efficiency.* pH values were performed between 5 and 10 in the studies of ammonia nitrogen degradation and the results are shown in figure 2(c). The result confirms that the removal rate can reach high efficiency in neutral or weakly alkaline environmental condition, which reaches 47.98%. The amount of hydroxyl effected by H+in water under acidic conditions and produced high pH value with excessive hydroxyl, which inhibited the photocatalytic reaction [11, 12]. It illustrates that photocatalyst has a positive effectiveness when pH value equals to 8, which is suitable for the ammonia nitrogen degradation in mariculture wastewater.

3.2.4 *The effect of concentration of H$_2$O$_2$ on photocatalytic efficiency.* Different concentration of H$_2$O$_2$ from 0.1 g/L to 0.7 g/L are studied for purpose of finding a greatest result. The results are shown in figure 2(d). It clearly proves that the maximum degradation rate appears when the concentration of H$_2$O$_2$ was 0.5 g/L, the degradation rate reaches 56.36%. The H$_2$O$_2$ solution has a strong oxidizing property which acts as an electron acceptor to capture the photo-generated electrons formed on the surface of the catalyst and prevent the recombination of electron-hole pairs(e^-/h^+)[13,14]. Moreover, hydroxyl also generated by H$_2$O$_2$ self-decomposition under illumination condition, degraded ammonia nitrogen in coordination with the catalyst. Thus, moderate H$_2$O$_2$ will increase the removel rate, but excess H$_2$O$_2$ will be detrimental to the photocatalytic process.

3.2.5 *The effect of illumination time on photocatalytic efficiency.* The degradation efficiency of catalyst was researched by illumination time which transform from 0.5 h to 3 h and the results are shown in figure 2(e). It is apparent that the fastest growth rate of degradation appeared when the illumination time is 2 h. The degradation percentage first increases then decreases is due to an increasing number of hydroxyl radical. It illustrate that reactants cannot perform thoroughly in a short time, nevertheless, long-time process will increment technological cost.

3.2.6 *The effect of calcination time on photocatalytic efficiency.* The calcination time were varied from 1 h to 6 h in order to find the fastest growth rate of degradation. The results are shown in figure 2(f). It is obvious that the fastest increase in the rate of degradation exists when the calcinition time is 2 h and the degradation reaches maximum (46.55%). The formation of anatase crystalline phase is incomplete when calcination time is less than 2 h, nevertheless, continuous calcination cause particle size to increase and lower the specific surface area and activity after 2 h, reducing the removal efficiency of ammonia nitrogen consequently.

4. The Optimization of Photocatalytic Conditions of CNTS-TiO$_2$
Six factors and five levels table was designed and the orthogonal experimental data is shown in Table 1.

Table1. Design matrix and experimental results for orthogonal array

Experiment	Dosage (mg)	Initial concentration of ammonia nitrogen (mg/L)	Concentration of H_2O_2 (g/L)	Illumination time(h)	pH value	Calcination time(h)	Removal rate (%)
1	1	1	1	1	1	1	25.64
2	1	2	3	4	5	2	38.97
3	1	3	2	5	4	3	45.64
4	1	4	4	3	2	5	40.08
5	1	5	5	2	3	4	35.25
6	2	1	2	2	2	2	51.62
7	2	2	3	3	4	5	47.68
8	2	3	1	1	5	4	21.31
9	2	4	5	4	3	1	61.35
10	2	5	4	5	1	3	29.81
11	3	1	2	3	4	5	57.73
12	3	2	3	4	5	3	60.11
13	3	3	4	5	1	1	65.48
14	3	4	5	1	2	2	48.75
15	3	5	1	2	3	4	38.24
16	4	1	5	4	4	2	64.3
17	4	2	4	3	5	1	50.13
18	4	3	3	5	2	4	73.27
19	4	4	2	1	3	5	48.19
20	4	5	1	2	1	3	34.4
21	5	1	2	3	4	5	70.85
22	5	2	3	4	5	1	67.41
23	5	3	4	5	1	2	46.7
24	5	4	5	1	2	3	58.65
25	5	5	1	2	3	4	43.76
K1	185.58	270.14	163.35	202.54	202.03	270.01	
K2	211.77	267.74	274.03	203.27	272.37	250.34	
K3	270.31	252.4	287.44	266.47	226.79	228.61	
K4	270.29	257.02	232.2	292.14	286.2	211.83	
K5	287.37	181.46	268.3	260.9	237.93	264.53	
R	101.79	88.68	124.09	89.6	84.17	58.18	

5. Summary

The CNTS-TiO$_2$ composite photocatalyst was made by a sol-gol method. The SEM and XRD characterization shows that CNTS-TiO$_2$ composite particals appear as a tubular morphology with good dispersibility, the average partical size of which is 26.2 nm. The CNTS-TiO$_2$ composite photocatalyst can degrade the ammonia nitrogen in mariculture wastewater efficiently under the UV-light irradiation. The optimized effect exists when the dose of catalyst was 60 mg, initial concentration of ammonia nitrogen was 10 mg/L, pH value was 9, concentration of H$_2$O$_2$ was 0.5 g/L, illumination time was 2.5 h and calcination time was 1 h. Under these conditions, the ammonia nitrogen degradation can reach 75.78%. The order of the effect of factors on degradation rate is: concentration of H$_2$O$_2$> dosage> illumination time> initial concentration of ammonia nitrogen> pH value> calcination time.

6. Acknowledgments

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