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Experimental Study on Continuous Degradation of Simulated Wastewater Containing Complex Black WAN with Nano TiO_2 Photocatalyst Prepared at Low Temperature

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Abstract

Nano TiO_2 photocatalyst has been prepared by the two-step microwave-assisted process at low temperature. The characterization results reveal that the product is titanium dioxide with a pure anatase crystal structure, and has a large specific surface area. In addition, a small size circulated photocatalytic reactor has been designed and developed. This paper investigates the activity of the above-mentioned photocatalyst by the orthogonal experiment on the degradation of simulated wastewater containing complex black, and studies the operation process of the self-made reactor.

Keywords: Microwave, Preparation at low temperature, Nano titanium dioxide, Circulated photocatalytic reactor

Preface

As is well known, TiO_2 is the best photocatalyst applied in the current photocatalysis technology (Gao et al, 2002). However, high temperature of 400 ℃ at the last stage of the traditional process for preparing TiO_2 photocatalyst, which converts TiO_2 into anatase phases of photocatalytic activity, not only leads to the particle agglomeration which has an adverse effect on the dispersion of TiO_2, but also results in the dehydroxylation of the crystal surface which causes a remarkable decline of the specific surface area and the hydroxylation degree, and makes the electron-hole pair separation more difficult, in turn has an adverse effect on the absorption of pollutants on the surface of catalyst, then leads to the decline of the catalytic activity. Moreover, high temperature always causes side reactions which lead to the decrease of the production efficiency, decline of the selectivity of carrier, and increase of the production cost. Therefore, to develop a nano anatase photocatalyst and compounds therefrom plays an important role in the study of photocatalysis technology. In recent years, there has been a big progress in the research and development of nano anatase photocatalyst, such as hydrothermal reaction at low temperature (Langlet, M et al, 2003, p. 3945-3953), sol-gel process (Kotani, Y et al, 2001, p. 2144-2149), and hydrolytic precipitation at low temperature (Yamabi, S H et al, 2003, p. 86-93).

Microwave-assisted chemical synthesis is a newly developed method for preparing materials. Its process, as well as microstructure and quality of the obtained product, have incomparable advantages. Its reaction mechanism is very different from that of the traditional method. It is not clear if there is non-thermal effect in microwave-assisted reaction. In 1988, Baghurst et al (1988, p. 829-830) prepared a superconducting ceramics by microwave-assisted process. At present, many research achievements indicate that microwave-assisted process not only avoids the high temperature calcinations and saves energy, but also controls the crystal size and growth orientation (Wang, J et al, 2005, p. 1405-1408; Yang, H M et al, 2007, p. 1357-1363; Newalkar, B L et al, 2008, p. 271-276), and favors the preparation of nano TiO_2 photocatalyst at low temperature. There have been quite a few reports on the preparation of nano TiO_2 photocatalyst at low temperature (Yang, Shenghong et al, 2000, p. 354; Chen, Wenxin et al, 2004, p. 661-663; Zhou, Xiaoming et al, 2005, p. 277-279; Peiro, A M et al, 2002, p. 185-191).

Photocatalytic reactor is very different from traditional reactor. In photocatalytic reactor, light irradiation should be strong enough to activate the photocatalyst, photocatalyst can be easily separated from the reaction system and reused, light source is barrier-free, light utilization efficiency is high, processing capacity is large, and etc. Based on the modification of traditional reactor by the two-phase separation and precipitation process, as well as the wastewater recycling process, nano TiO_2 photocatalyst has been prepared by the microwave-assisted process at low temperature, which in turn accelerates the progress in industrialization of energy-saving photocatalysis oxidation technology.

1. Nano TiO_2 photocatalyst prepared by microwave-assisted process at low temperature

1.1 Materials, equipments and methods

Nano TiO_2 photocatalyst has been prepared by microwave-assisted hydrolysis process. Microwave initiates the vibration of O—H in H_2O, and results in a large amount of heat, which, in one hand, accelerates the hydrolysis of Ti^{4+} into a local supersaturated solution of TiO_2, and in other hand, increases the temperature of this supersaturated solution rapidly in a very short time, and results in a large amount of crystal nucleus. Nano-scale TiO_2 can be obtained only when the nucleus-forming speed is greater than the crystal-forming speed.

(1) Methods

Weigh a certain amount of $Ti(SO_4)_2$ into a premixed H_2SO_4 (HCl) solution with pH of 2 to obtain a 100 g/L acid solution of $Ti(SO_4)_2$. Regulate pH to 8 by adding concentrated ammonia drop-by-drop into the solution under the condition of strongly stirring. Irradiate the obtained solution for a certain period in an experimental microwave oven under different microwave conditions. Age, wash, remove part of water, and then irradiate for the second time in the microwave oven. The temperature is lower than 200 ℃ throughout the experiment.

(2) Equipments

ML08S-1 experimental microwave oven is from Nanjing Huiyan Microwave Co., Ltd.; DHS-25 pH meter is from Shanghai REX Instrument Factory. The crystal structure of the obtained TiO_2 is identified with X'pert PRO X-Ray Diffractormeter (Co target, Kα radiation, 30 mA tube current, 30 kV tube voltage, scan range of 10~90 °, step width of 0.0334 °) which is from PANalytical of Holland. The internal structure of crystal of the obtained TiO_2 is imaged with G^2F20 HRTEM from PHILIPS TECNAI.

(3) Materials

Main reagents: absolute ethanol, ammonia water, sulfuric acid, hydrochloric acid, titanium sulfate, barium chloride, potassium chloride, methyl orange solution and etc. All of them are analytical reagents.

1.2 Analysis on experimental results

Based on the previous investigations, it is determined to improve the crystal size and crystallinity of nano TiO_2 powder by increasing irradiation power and lengthening irradiation time under the pulsed microwave irradiation. The titled nano TiO_2 photocatalyst has been prepared under the conditions of using sulfuric acid, continuous microwave irradiation for the 1st time, pulsed microwave irradiation for the 2nd time, and power of 700 W. Figure 1 exhibits the XRD spectrum of nano TiO_2 obtained after 15 minutes of two-step microwave irradiation.

Figure 1 indicates that the self-made sample is a pure anatase of low crystallinity, which has an average diameter of 4.72 nm (calculated with Scherrer formula), and specific surface area of 225 m^2/g. It proves that the self-made sample has a small particle size and large specific area, which are favorable for the formation of hole/electron pair through electron transition, and form much more active reaction centers for the absorptions of pollutants during photocatalysis reaction.

Figure 2 exhibits the HRTEM images of nano TiO_2 obtained after 15 minutes of two-step microwave radiation. It reveals that the self-made sample is composed of 6~9 nm stout prismatic crystals which have irregular edges, obvious lattice defects, and severe agglomeration. The characterization results indicate that the reaction system releases a large amount of heat rapidly in a very short time under the action of microwave irradiation. As a result, the nucleus-forming speed is much greater than the crystal-forming speed, which results in evenly distributed small crystal particles. What's more, the crystallization degree is further improved by the two-step microwave-assisted process which makes the concentrated solution supersaturated. Therefore, as far as the crystal-forming effect is concerned, the two-step microwave-assisted process works the same way as the high temperature calcinations. However, high frequency vibration of reactant molecule initiated by the microwave irradiation results in much more irregular edges and lattice defects, which are favorable for the formation of hole/electron pair through electron transition, and accelerate the photocatalysis reaction.

2. Continuous degradation equipment of simulated wastewater containing complex black WAN

2.1 Continuous degradation equipment

Figure 3 exhibits the continuous degradation equipment of simulated wastewater.

TiO_2-contained wastewater flows from the raw solution tank into reactor, and then the three-phase fluidized photocatalysis reaction occurs in the reactor with gas flowing from gas distributor. The obtained liquid flows into the settling pond, and the supernatant outflows into the inner circulation self-dilution system. The continuous inner circulation reactor has the following features: (1) the treated wastewater can be reused as the circulation diluents; (2) the inner circulation self-dilution technology ensures the effective reutilization of nano TiO_2 photocatalyst; (3) based on the above-mentioned process, the continuous multi-level reaction system can be designed to increase the output and the comprehensive indexes of the treated wastewater.

2.2 Experimental method and result analysis

Formulate the complex black WAN-contained simulated wastewaters of different initial concentrations based on the practical industrial applications. Design a 3-factor-3-level orthogonal table (see table 1).

Measure the absorption (A) of the formulated complex black WAN-contained simulated wastewaters with UV-752 UV-Vis Spectrophotometer at wavelength of 740 nm, and calculate the decoloration rate (X) of above solutions. Measure the total organic carbon (TOC) of the degraded simulated wastewaters with TOC-5000A TOC detector.

$L_9(3^4)$ is used to schedule 9 operation conditions of orthogonal experiment, with the three factors being initial concentration of wastewater, feed flow rate and circulation flow rate. The effects of these factors on the chromaticity and TOC of the simulated wastewaters are investigated by the orthogonal experiment (see table 2).

Table 2 reveals that nano TiO_2 has a remarkable effect on the degradation of complex black WAN-contained simulated wastewater, which indicates that nano TiO_2 photocatalyst prepared by the microwave-assisted process at low temperature has good photocatalytic activity.

Figure 4 exhibits the changes of average value of the above-investigated factors at different levels. From figure 4, we can see that both COD_{Cr} removal rate and TOC removal rate change a little at the level of C_2 and circulation flow rate, however, decrease with the rise of feed flow rate. It indicates that the circulation photocatalytic reactor can achieve a better photocatalytic effect by regulating the feed flow rate. However, the circulation flow rate can be set in an easy-to-handle range since its effect on the degradation is little. The process should be further studied to develop a multi-level recycling processing equipment, which can increase the tolerance of equipment for processing wastewater. Therefore, the method studied here is valuable for broader applications.

3. Conclusion

(1) Nano TiO_2 photocatalyst has been prepared by the two-step microwave-assisted process at low temperature. The characterization results reveal that the obtained product has a larger specific surface area and much more crystal defects which favor the photocatalytic reaction.

(2) A small size circulated photocatalytic reactor has been designed and developed. The effects of the obtained nano TiO_2 photocatalyst on the degradation of simulated wastewater are investigated by the orthogonal experiment on the initial conditions of wastewater and operation process. The results indicate that the low feed flow rate favors the degradation of wastewater.

(3) The major task in the future study is to optimize the conditions for preparing nano TiO_2 photocatalyst by two-step microwave-assisted process at low temperature, increase its photocatalytic activity, develop the multi-level continuous processing equipment based on the method studied here, and figure out the way of reutilization of catalyst.

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Table 1. Factor/level of orthogonal experiment

Levels	Factors		
	A (Initial concentrations of simulated wastewater)	B (Feed flow rate)	C (Circulation flow rate)
1	C_1	Q_1 (0.01625 mL/s)	Q_1 (1.5015 mL/s)
2	C_2	Q_2 (0.03250 mL/s)	Q_2 (1.7745 mL/s)
3	C_3	Q_3 (0.04875 mL/s)	Q_3 (2.0475 mL/s)

- C_1 represents the wastewater containing 100 mg/L complex black WAN, 50 mg/L α-naphthol and 15 mg/L NaCl, which has COD_{Cr} of 176 and TOC of 52.87.
- C_2 represents the wastewater containing 200 mg/L complex black WAN, 100 mg/L α-naphthol and 30 mg/L NaCl, which has COD_{Cr} of 326 and TOC of 104.1.
- C_3 represents the wastewater containing 250 mg/L complex black WAN, 150 mg/L α-naphthol and 40 mg/L NaCl, which has COD_{Cr} of 456 and TOC of 132.5.
- The amount of photocatalyst is 1 g/L, and UV radiation time is 2 h.

Table 2. $L_9(3^4)$ orthogonal experiment

Samples	After 2 hours of reaction		
	Decoloration rate	COD removal rate	TOC removal rate
1	1	0.913	0.922
2	1	0.855	0.917
3	1	0.835	0.850
4	1	0.938	0.905
5	0.97	0.904	0.893
6	1	0.966	0.952
7	0.96	0.922	0.907
8	0.971	0.956	0.929
9	0.97	0.938	0.911

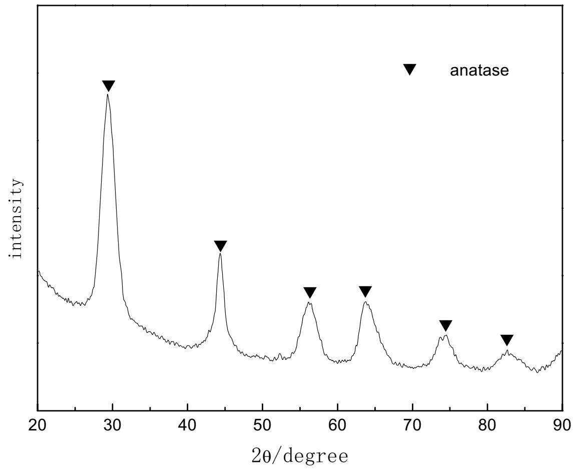


Figure 1. XRD spectrum of nano TiO_2 obtained after 15 minutes of two-step microwave radiation at different conditions

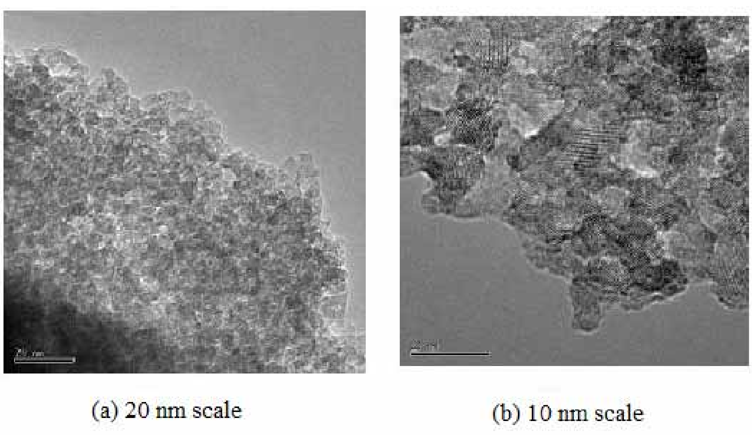
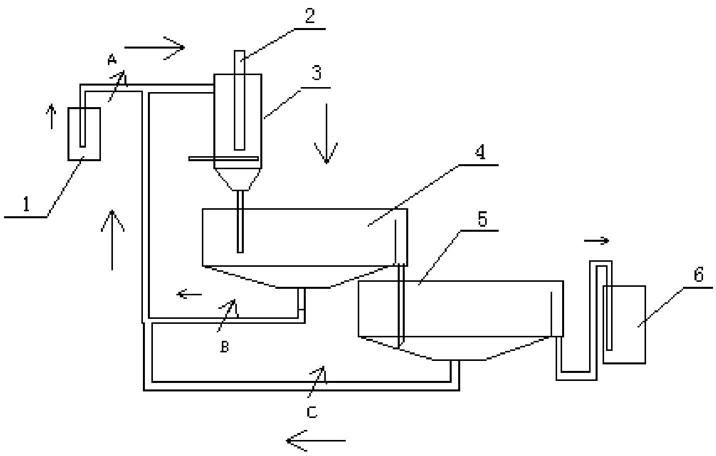
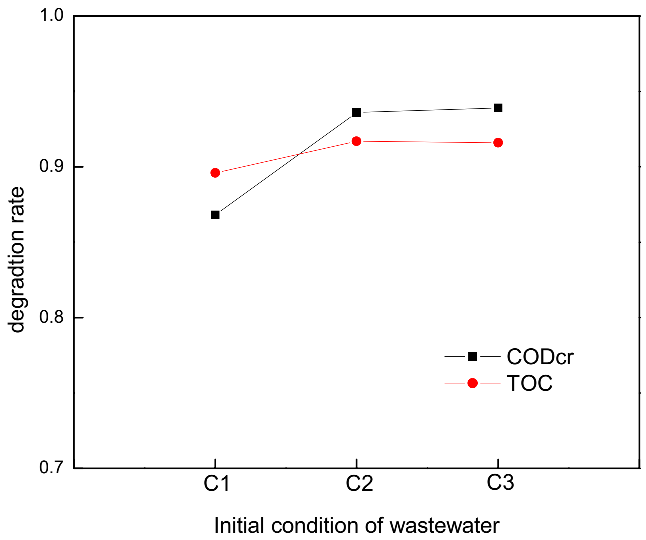


Figure 2. HRTEM images of nano TiO_2 obtained after 15 minutes of two-step microwave radiation

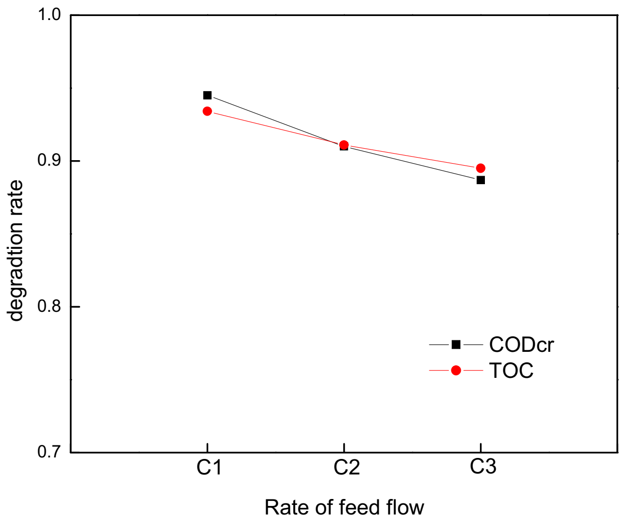


1– raw solution tank; 2– gas distributor; 3– photocatalytic reactor;
4– first solid/liquid separator; 5– second solid/liquid separator; 6– effluent tank;
A,B,C– peristaltic pump

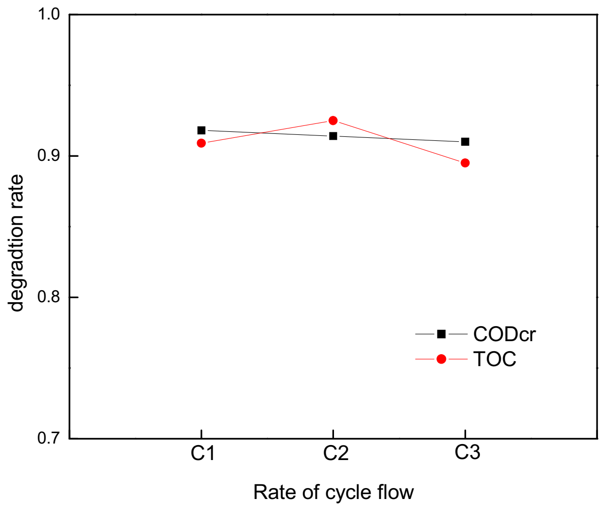
Figure 3. The continuous degradation equipment of simulated wastewater



(a)



(b)



(c)

Figure 4. The evaluation of the factors at different levels