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STUDY ON PREPARATION AND APPLICATION OF N-TIO₂/ACF COMPOSITE

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ARTICLE DETAILS

ABSTRACT

Article History:

Received 26 June 2018 Accepted 2 July 2018 Available online 1 August 2018 The modification of N-doping on TiO₂ and preparation method of N-TiO₂/ACF composite was studied to solve the problems of application under narrow wavelength range, difficult recovery, easy loss and suspension in the water treatment system. This composite was tested on the treatment of simulated waste water (methyl orange solution). The best removal rate of more than 95 % was performed by using this composite material, which is very ideal for this application.

KEYWORDS

TiO₂, N-Doping, Composite materials, Water treatment.

1. INTRODUCTION

Water environmental problems caused by refractory organics are becoming more and more serious with the rapid economic development. Waste water components are becoming more and more complex, which are resistant to photolysis or anti-oxidation, thus making the wastewater treatment more and more difficult [1,2]. TiO2 is recognized as the most effective semiconductor catalyst because of low cost, large supply channels, high performance, safety, and significant potential for industrialscale engineering applications in water or atmospheric purification [3]. Activated carbon fiber (ACF) is a kind of porous adsorption material. Microspores of more than vol. 90% are directly distributed on the surface of fibers, which make ACF own large specific surface area, strong adsorption force, large adsorption capacity and absorption. When TiO_2 is supported on the surface of ACF, TiO2 degrades the organic matter adsorbed on ACF, thus realizing the in-situ regeneration capability of ACF and increasing its adsorption capacity. On the other hand, ACF uses its own adsorption capacity to enrich and concentrate organics, increase local concentrations, capture intermediate products and improve removal rates at the same time. However, it can only act in ultraviolet light, and for its reaction in visible light, TiO2 is usually doped and modified to reduce the forbidden band width of TiO2, inhibit the recombination center of electrons and holes on the surface of TiO2, increase the lattice defects of TiO2 and reduce the specific surface area of TiO2, thus achieving the purpose of changing the properties of TiO2 [4,5]. Therefore, it is of great significance to study the use of nitrogen-doped titanium dioxide for photocatalytic reactions to improve the efficiency of photocatalytic reactions and to address future environmental issues [6]. The preparation and comparative study of TiO₂/ACF and N-TiO₂/ACF composite materials were carried out for efficiently remove refractory organics in this paper.

2. EXPERIMENT

2.1 **Materials and Reagents**

Butyl titanate (A.P); glacial acetic acid (A.P); anhydrous ethanol; urea; hydrochloric acid; methyl orange (A.P); ACF, etc.

2.2 **Experimental Instruments and Equipment**

BL-GHX-V photochemical reaction instrument; 721 spectrophotometer; constant temperature heating magnetic stirrer; electric blast drying box; muffle furnace; ultrasonic cleaning instrument, etc.

2.3 **Experimental Methods**

2.3.1 Preparation of N-TiO₂/ACF composites

Wet sol of N-TiO₂ was prepared by sol-gel method [1]. 0.05 g of ACF was immersed in the wet sol with ultrasonic loading (or leaching) of 15 min, and then taken out and dried at 90°C subsequently. Same steps for twice or three times were repeated as needed. Finally, this substance were placed in a muffle furnace and calcined at 450°C for 4 hr to obtain a supported N-TiO₂/ACF composite material.

2.3.2 Photocatalytic degradation of methyl orange.

The N-TiO₂/ACF composite was placed in a quartz reactor, 50 ml of methyl orange solution (50 mg/L) poured subsequently. Reaction was performed for 80min in the photochemical reaction instrument. The absorbance of methyl orange solution after photocatalysis was measured by the 721 spectrophotometer. The distilled water was used as a reference. The wavelength was selected as 460 nm. The absorbance values before and after reactions were recorded and the removal rate of methyl orange was then calculated.

2.4 Characterization of N-TiO₂/ACF Composites

FTIR spectroscopy was used to qualitatively analyze the prepared N-TiO₂/ACF composites and detect functional groups and molecular structure characteristics.

3. RESULTS AND DISCUSSION

3.1 Effect of N-doping on TiO2/ACF

Photocatalytic experiments on TiO₂/ACF and N-TiO₂/ACF with different leaching times under ultraviolet irradiation were carried out in order to investigate the influence of N-doping. The results are shown in figure 1.

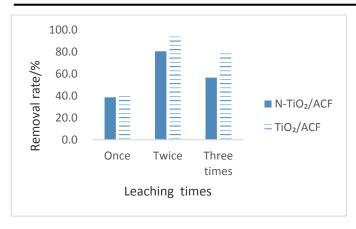


Figure 1: Comparison of removal rate of methyl orange on TiO_2/ACF and $N-TiO_2/ACF$

As seen in figure 1, removal rate of methyl orange was less than 50% on both TiO_2/ACF and N- TiO_2/ACF when leaching times is only once. However, removal rate was increased after leaching multiple times. Among them, leaching twice shows the best result. It means that the leaching times affect the loading of TiO_2 on ACF which may affect both the photocatalysis of TiO_2 and the adsorption of ACF [7]. The surface area of ACF decreased because of over coverage of TiO_2 particles so that the leaching times of should be controlled as twice.

In addition, it was found that TiO_2/ACF had better catalytic effect than N- TiO_2/ACF under ultraviolet light. The removal rate on TiO_2/ACF was 93.6 %, which is 13.4% higher than that on N- TiO_2/ACF when leaching twice. It indicates that doping modification of the catalyst cannot play a role in the ultraviolet range, but still get a high removal rate of 80.3%.

3.2 Effect of Different Light Sources

The experiment on N-TiO₂/ACF under visible light was carried out to investigate the applicability of the doped modified catalyst in the visible range. The results are compared with the data on TiO₂/ACF and shown in Figure 2.



Figure 2: Comparison of the removal rate of methyl orange on N- TiO_2 /ACF under different light sources

Comparing figure 2 with figure 1, the same conclusion can be drawn that leaching twice shows the best removal rate whether under ultraviolet light or under visible light, which confirms the former conclusion. It can also be seen from Figure 2 that the removal rate can still reach 74.2% on N-TiO₂/ACF after twice leaching although which is little lower than that under visible light [8]. The removal rate is of great practical significance for extending the applicable light range to visible light.

3.3 Effect of Load Methods

Different loading methods were tested under visible light to optimize a better preparation way of N-TiO₂/ACF. The results are shown in Figure 3.

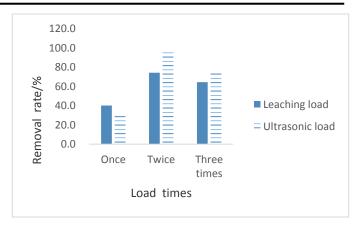


Figure 3: Effects of different loading methods on removal rate of methyl orange

As seen in Figure 3, the removal rate of methyl orange on N-TiO₂/ACF prepared by ultrasonic load method can reach over 95%, much better than those prepared by leaching load. It indicates the ultrasonic load promote the dispersion of TiO₂ on ACF.

3.4 Characterization of N-TiO₂/ACF Composites

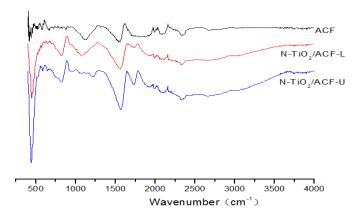


Figure 4: Infrared spectra of different composite materials

The infrared spectra of different composite materials were shown in Figure 4. Wherein, the composite materials prepared by leaching loading and ultrasonic loading were marked as N-TiO2/ACF-L and N-TiO2/ACF-U respectively. The stretching vibration of C=C at 1543-1572cm⁻¹ and the stretching vibration of unsaturated hydrocarbon group R2C=CHR at 2333cm⁻¹ belong to the characteristic peaks of ACF. Absorption peaks at 443-450 cm⁻¹ and 819-826 cm⁻¹ can be attributed to Ti-O vibration [9]. The stretching vibration peak of N-H bond is at 1739cm⁻¹. This is because urea is adsorbed on the surface of TiO2 and decomposed by heating urea to enter the TiO_2 lattice [10, 11]. The peak intensity of N-TiO₂/ACF-U is more obvious here, which is also consistent with the results of removal rate of methyl orang in the experiment. Compared with N-TiO₂/ACF-L, the stretching vibration peak of the C-O bond at the original 1094-1240 cm⁻¹ was obviously blue shifted after ultrasonic treatment. This indicates that chemical bond of C-O-Ti may be produced during the preparation process of N-TiO₂/ACF-U, which increases the stability of TiO₂ supported on the support.

4. CONCLUSION

An effective preparation method of N-TiO₂/ACF composite was improved and proposed in this study. Both Loading method and times affect the dispersion of TiO₂ on ACF, which would affect the removal efficiency of methyl orange afterwards. Higher removal rate on N-TiO₂/ACF composite material can be performed under both ultraviolet light and visible light. It is very meaningful for the application of this composite material because of the wide extension of wavelengths range.

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