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Preparation of Husk-Based Porous Carbon-TiO_2 Composites for Adsorption-Photocatalytic Degradation of Toluene in Aqueous Solution

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Abstract. In this study, PC-nanoTiO_2 and PC-P25 were prepared via chemical-deposition and mixture-calcination methods, respectively. Both of PC-nanoTiO_2 and PC-P25 were employed to adsorb and photocatalytic degrade toluene in aqueous solution. The characterization results show that distribution of TiO_2 nanoparticles in PC-nanoTiO_2 and PC-P25 were different, but their binding force between PC and TiO_2 were both chemical bonds. Due to synergy of adsorption and photocatalytic degradation, both PC-nanoTiO_2 and PC-P25 exhibit good effect in removing toluene in aqueous solution, and both PC-nanoTiO_2 and PC-P25 could be utilized for treating wastewater generated from hazardous chemicals leakage accidents emergency.

1. Introduction

Now a day, environmental pollutions frequently appear in a variety of forms in the context of the rapid development of chemical, fossil energy and other related industries [1]. Chemical pollutions caused by leakage accidents [2] would bring very serious harm to human health and natural environment, and about 1/3 accidents were leakage of liquid benzene series [3-5]. At present, benzene series emergency treatment mainly include foam covering method, plugging method, spraying method, burning method and adsorption method domestic and foreign [6, 7]. Though all above methods would reduce the benzene series concentration immediately, secondary pollution would be probably caused if follow-up treatment was inappropriate. Adsorption [8] was the most effective method of treating a large number of chemical leakages rapidly, meanwhile, controls hazardous chemical pollutants diffusion. Porous Carbon [9, 10] (PC), carbon materials with large specific surface area and plenty of macro- and meso-porous structure, was one of the most promising adsorbent for rapid adsorption for hazardous chemicals leakage [11]. Wang [12] has prepared PC from corncob and investigated its property of liquid benzene adsorption. Despite a large quantity of hydrophobic leakage would be adsorbed on PC, the mishandled saturated PC could also be a threat to either environment or to human health. Photocatalytic degradation is a technology could completely decompose organic hazardous chemicals, but unfortunately, performance of photocatalytic degradation is limited by many factors, thus it is difficult to be applied in such an emergency of leakage accidents. In this study, rice husk char (RHC) was selected as raw material, and PC-nanoTiO_2 and PC-P25 were prepared via chemical-deposition and mixture-calcination methods, respectively. The effects of preparation methods of composites on the structural properties and photocatalytic degradation performance were investigated.

2. Experimental

2.1. Materrials
RHC was obtained from Changlv gardening Co., Ltd. Other chemicals used in the experiment are the following: P25 (Shanghai best more Industrial Co., Ltd), corn starch (Sinopharm Chemical Reagent Co., Ltd, China), tetrabutyltitanate (TBT, Tianjin No. 3 Chemical Reagent Factory, China), toluene (Tianjin Kermel Chemical Reagent Co., Ltd. China), ethanol (Tianjin No. 1 Chemical Reagent Factory, China), and all these chemicals were used as received.

2.2. Preparation of RHC-TiO2 Composites
The preparation process of PC is as follows: 9g corn starch were added into 91 ml deionized water, then stirred for 10min at 100 ℃; 3g RHC powder was mixed with the above mixture under stirring for 30 min to obtain a homogeneous paste; after solidified in oven at 110 ℃ for 4 h, obtained solid were carbonized at 400 ℃ with flowing nitrogen for 20min.

Chemical deposition process was show as follow: 35 ml ethanol mixed with 32.4mL deionized water, and TBT solution (35mL TBT, 23mL ethanol and 70 mL acetic acid) was added at 26℃, then stirring for 100 min before aging for 18 h; 18 g obtained gel and 2 g PC were hydrothermal treated under 180℃ for 2h, and then PC-nanoTiO_2 was obtained after washing and drying.

The preparation of RHC-TiO_2 composites in mixture-calcination method was similar with preparation process of PC, the only difference is the thick starch paste composed of 9g corn starch, 91 ml deionized water and 1g P25, and obtained composite was termed PC-P25.

2.3. Characterizations
Morphology of samples and raw materials were examined by scanning electron microscopy (SEM) (ZEISS EVO 18). The crystal structure was characterized using X-ray powder diffraction (XRD) (Rigaku D/Max 2400 diffractometer using CuK/radiation (40 kV, 100 mA, k=1.5406A°)). Surface functional groups were investigated by Fourier transform infrared spectrometer (FT-IR, Vector 22, Brook).

2.4. Adsorption and photocatalytic degradation of toluene in aqueous solution
The experimental detail of toluene removing shows as follow: 0.1g photocatalyst added into 200 mL toluene solution (50 mg/L); after stirring in dark for 0.5h, the solution was irradiated by a 1500-W Xe lamp with a 340-nm cutoff filter. At fixed time point, 3 mL of pure reaction liquid was taken for testing toluene concentration and then calculating removal rate.

3. Results and Discussion

3.1. Surface morphology

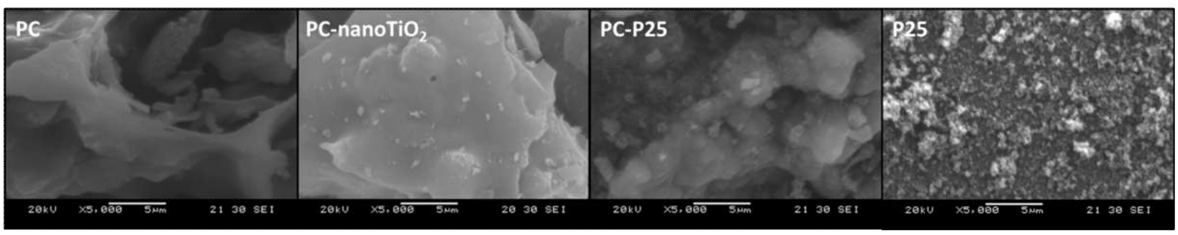

Figure 1. SEM of PC, PC-nanoTiO2, PC-P25 and P25

As shown in Figure 1. PC is composed of mostly lamellar, and it endow with well-developed pore structure with smooth pore wall surface. The micromorphology of PC-nanoTiO_2 is fine and smooth. In the SEM of PC-P25, because of the uniform embedding of P25, surface of PC-P25 exposes both the

P25 and PC, thus is relatively rough. SEM of P25 particles reveals it good dispersibility and uniformity.

3.2. Material surface properties

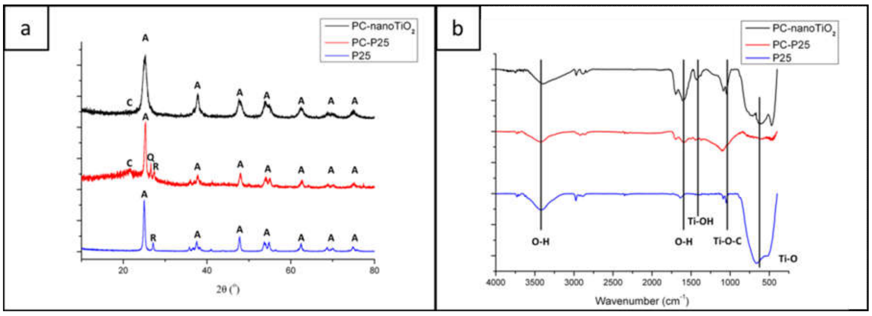

Figure 2. XRD patterns of PC-nanoTiO2, PC-P25 and P25 (a); FT-IR spectrum of PC-nanoTiO2, PC-P25 and P25 (b)

The XRD patterns are presented in Figure 2 a. A sharp peak at 25.28° reveals that nanoTiO_2 distributed onto PC-nanoTiO_2 was mainly anatase (A); Broad peak appear at 21-27.5° supports that PC are the combination of many turbostratic carbon domains. XRD patterns of P25 proved that P25 is a mixed crystalline composed of anatase and rutile (R, 2θ=27.16°). Crystalline composition of PC-P25 is rather complex: it is characterized by anatase, rutile, quartz (Q) and amorphous carbon (C). All above three samples have anatase crystallization phase, which ensure their high photocatalytic degradation potential. The most notable absorption band of infrared absorption in Figure 2 b is located at 1040 cm^{-1}, which was evidence for existence of Ti-O-C bonds, it ensures the bonding force between TiO_2 and carbon materials as chemical bonds. Such infrared absorption of Ti-O-C bonds could obviously find in the spectra of both PC-nanoTiO_2 and PC-P25, as it illustrates Ti-O-C bonds could formatted either in hydrothermal reactions or high temperature calcination. In addition, formation of Ti-O-C bonds would prevent some nanoTiO_2, including P25, from dispersing into aqueous. In this view, PC-nanoTiO_2 and PC-P25 would prevent TiO_2 nanoparticles dispersion to a certain extent, hence both have good application prospects due to avoid the nanoTiO_2-secondary pollution.

3.3. Performance analysis of adsorption and photocatalytic degradation of toluene

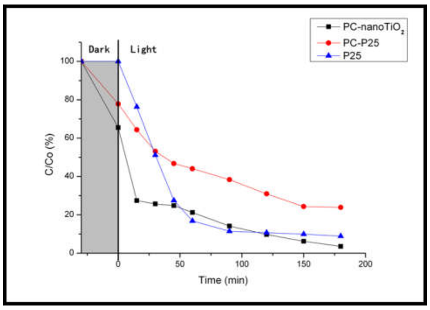

Figure 3. Effect of toluene removing of PC-nanoTiO2, PC-P25 and P25

In Figure 3, before UV irradiation, both PC-nanoTiO_2 and PC-P25 show obvious adsorption effect on toluene, and the PC-nanoTiO_2 was more effective, meanwhile, no enrichment effect was found in P25. When the UV lamp turned on, concentration of toluene begins to decrease, and 3h later, toluene removal efficiency of PC-nanoTiO_2, PC-P25, and P25 were 96.46%, 76.14% and 91.1%, respectively. Both PC-nanoTiO_2 and PC-P25 have good removing effect on toluene in aqueous solution, and the main reason lying on synergistic effect existed between porous carbon and TiO_2. So we could infer that PC-nanoTiO_2 can be applied to benzene series leakage emergency, and then photocatalytic degrade the adsorbed organic pollutant later. Although there is no big gap of photocatalytic properties between P25 and PC-nanoTiO_2, P25 is still will rarely to be applied in treating organic pollution in aqueous, because of the enormous difficulty in removing dispersing P25 from water bodies.

4. Conclusion

In this study, PC-nanoTiO_2 and PC-P25 were prepared in chemical-deposition and mixture-calcination methods for investigating their performance of removing toluene in aqueous. The results of revealed that both of PC-nanoTiO_2 and PC-P25 have rough surface and porous structure; the main components of two composites are both PC and TiO_2, but the surface of PC-nanoTiO_2 appears mainly anatase; infrared absorption of Ti-O-C bonds could obviously find in the spectra of both PC-nanoTiO_2 and PC-P25, and it ensure the bonding force between TiO_2 and carbon materials. Toluene removal efficiency of PC-nanoTiO_2 was 96.46%, even 5.88% higher than P25. Thus, PC-nanoTiO_2 can be applied to toluene leakage emergency, and then photocatalytic degrade the adsorbed organic pollutant later.

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