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Synthesis, Surface Characterization and Photocatalytic Activity of TiO_2 Supported on Almond Shell Activated Carbon

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Three types of photocatalysts were synthesized by metal organic chemical vapor deposition and impregnation methods using the almond shell activated carbon as support. These photocatalysts denoted by (TiO_2/ASAC (V), TiO_2/ASAC (I1) and TiO_2/ASAC (I2)) were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), diffuse reflectance spectroscopy (DRS) and nitrogen adsorption−desorption isotherms. SEM observation shows that TiO_2 was deposited on activated carbon surface. XRD results confirm that TiO_2 existed in a mixture of anatase and rutile phases. The DRS spectra show the characteristic absorption edge of TiO_2 at approximate 380 nm corresponding to the optical band gap of 3.26 eV. Besides, FTIR spectrum indicated the presence of (Ti−O) groups. The specific surface area of photocatalysts decreased drastically in comparison with the original activated carbon. The catalysts were very efficient for the photodegradation of total organic carbon (TOC) from industrial phosphoric acid solution under UV irradiation. The kinetics of photocatalytic TOC degradation was found to follow a pseudo-first-order model. The prepared TiO_2/ASAC showed high photoactivity for the photodegradation of TOC in the following order: TiO_2/ASAC (V) > TiO_2/ASAC (I1) > TiO_2/ASAC (I2) > ASAC > TiO_2 (P25).

KEY WORDS: Almond shell activated carbon; Photocatalyst; Vapor deposition; Impregnation; Total organic carbon

1. Introduction

Activated carbon is used mostly for adsorption in industry because of its large adsorption capacity, fast adsorption kinetics and relative ease of regeneration[1−5]. Activated carbons are commonly prepared from coal, wood[6,7], peat and coconut shells[8]. However, the demand for novel and more efficient adsorbents initiated research for low-cost, locally available and renewable materials as potential alternative precursors in activated carbon production. For this purpose, many materials such as fruit stones[9], pyrolyzed coffee residues[10], date stones[11], pomace ashes[12], and rice husks[13] were studied.

Photocatalysis is an important industrial process in wastewater treatment, heavy metal remediation, air purification, sterilization, etc. Titanium dioxide (TiO_2) is the most widely used photocatalyst owing to its efficiency, low-cost and chemical stability[14]. TiO_2 powders such as DEGUSSA P25 have been commercially available for several years. Nevertheless, after degradation tests, photocatalysts in the form of powders must be removed from the suspension and this step is an important factor that may cause some problems in industrial applications[15−17]. To solve these problems, photocatalysts (e.g. TiO_2) have been immobilized on various supports such as silica[18,19], silicon carbide[20], clay[21], fly ash[22], zeolites[23] and activated carbon[24−27].

The advantages of using the activated carbon as a support, are summarized as follows. (1) The support adsorbs a high amount of pollutants around the loaded TiO_2. Then the rate of photo-oxidation is improved[28,29]. (2) The adsorbed pollutants (organic substances) are oxidized at the surface of the photocatalyst, and resulting intermediates are also adsorbed and then further oxidized. Toxic intermediates, if formed, are not released in the air atmosphere and/or in solution phase, thus preventing secondary pollution. (3) Since the pollutants are finally oxidized into CO_2, the lifetime of the hybrid photocatalysts is long[30]. Presently, several preparation methods for TiO_2/activated carbon composites, such as hydrothermal[31], sol−gel[30], boil deposition[32], dip coating[33], metal organic chemical vapor deposition

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(MOCVD)[34], and impregnation[35] have been reported. Although TiO_2/activated carbon has been extensively used for the degradation of pollutants, such as phenol[36], substituted phenol and dyes[30,37], there is no available literature for the photodegradation of organic moieties from Tunisian industrial phosphoric acid by TiO_2 supported on activated carbon.

The phosphoric acid is manufactured using different processes, among which the thermal and wet-processes are the most commonly used. Concerning the wet-process, it is used in Tunisia to produce phosphoric acid from phosphate minerals[38]. However, this process leads to an acid with a high impurities level, including organic pollutants[3,4,39] which are n-dibutyl phthalate, humic and fulvic acids[40,41]. Hence, the removal of these organic pollutants seems to be an important step for the production of phosphoric acid with a high purity level.

The purpose of the present work is to load TiO_2 on the surface of active carbon by using two techniques (MOCVD and impregnation). Both techniques are compared in terms of textural and structural properties as well as the amount of loaded TiO_2 in anatase form. In this aim, three photocatalysts were prepared by the deposition of TiO_2 on the surface of almond shell activated carbon. These photocatalysts were employed not only for the adsorption of total organic carbon (TOC) from industrial phosphoric acid solution, but also for determining their catalytic efficiency for industrial applicability.

2. Experimental

2.1. Materials

Activated carbon (ASAC) was prepared from the physical activation of almond shell, which was obtained from a local company in Sfax (Tunisia). Ammoxidation process was used to modify the activated carbon surface using a method described previously[4]. The textural properties of the material are listed in Table 1.

Titanium isopropoxide (Ti $(OPr^i)_4$, TTIP, Sigma-Aldrichs, purity: 97%) and commercial TiO_2 (Degussa P25, Degussa Chemical) were used as titanium source for the preparation of photocatalysts. Industrial phosphoric acid solution (54% P_2O_5) produced by the SIAPE society was used to evaluate the photocatalytic efficiency of synthesized photocatalysts. This phosphoric acid contains $(578 \pm 5) \times 10^{-6}$ of TOC. The details of this industrial product are found in a previous research study[4].

2.2. Synthesis of TiO_2/ASAC photocatalysts

2.2.1. MOCVD method. To prepare the TiO_2/ASAC photocatalyst by the MOCVD method, the apparatus presented in Fig. 1 was used. A fixed amount (4.0 g) of ASAC (particle size < 63 μm) was put into a quartz reactor, and dehydrated under a stream of dry nitrogen at 400 °C for 3 h. Then, the temperature of the reactor was adjusted to 600 °C. After the reactor temperature was stabilized, the deposition of TiO_2 was initiated by evaporating TTIP contained in a flask at 100 °C under a nitrogen flow rate of 200 mL/min for 5 h. The gas line was heated to avoid the TTIP condensation. At the end of the deposition, the reactor was purged by nitrogen gas for about 15 min. The resulting deposit was removed from the reactor and kept in a hermetic bottle for subsequent use.

The photocatalyst prepared by this method, was named TiO_2/ASAC (V), with the letter (V) indicating the vapor phase.

Table 1 Textural and structural properties of the samples

Properties	Samples			
	ASAC	TiO_2/ASAC (V)	TiO_2/ASAC (I1)	TiO_2/ASAC (I2)
S_{BET} (m^2/g)	1398	695	730	580
Total pore volume (cm^3/g)	0.8	0.4	0.5	0.3
Pore diameter (nm)	2.4	3.5	3.2	3.1
Porosity, χ (%)	75	25	30	20
Crystallite size, D (nm)	–	16	19	12
Anatase content, A (%)	–	92	83	81
TiO_2 (wt%)	–	18.2	17.1	17.5
r_c (%)	0	87.57	79.25	89.55

2.2.2. Impregnation method. Two TiO_2/ASAC photocatalysts were prepared by the impregnation method. First, different weights of ASAC were added under stirring into a TTIP solution or a TiO_2 P25 aqueous suspension. When TTIP was used, the temperature of the mixing was fixed to 150 °C. After the impregnation process, the samples were filtered and dried for different times. The first series was calcined to 500 °C for 3 h in a nitrogen purged reactor tube in the furnace with a heating rate of 5 °C/min. The steps of the photocatalysts preparation were presented in Fig. 2.

The synthesized photocatalysts are named TiO_2/ASAC (I1) and TiO_2/ASAC (I2), where I1 and I2 indicate the impregnation by TTIP and TiO_2 P25, respectively.

2.3. Characterization of TiO_2/ASAC photocatalysts

Several techniques were employed for the characterization of the samples. In order to determine the crystal phase composition and the TiO_2 crystallite size in the photocatalysts, X-ray diffraction measurements were carried out at room temperature using an X-ray diffractometer (Philips® PW 1710 diffractometer, Cu $K\alpha$, 40 kV/40 mA, scanning rate of 2 degree per min). The crystallite size was calculated by X-ray line broadening analysis using Scherrer equation[42].

The micrographs of TiO_2/ASAC and original ASAC samples were examined under a scanning electron microscope (SEM, Hitachi SU-70). The structural feature of these samples was

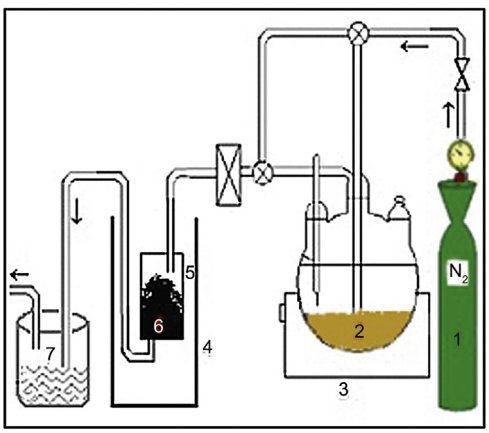

Fig. 1 Schematic diagram of the experimental setup: (1) nitrogen gas cylinder; (2) TTIP; (3) flask heater; (4) furnace; (5) quartz tube; (6) ASAC; (7) cold trap.