



# Industrial application of photocatalysts prepared by hydrothermal and sol–gel methods



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## ARTICLE INFO

### Article history:

Received 9 November 2013

Accepted 24 February 2014

Available online 2 March 2014

### Keywords:

Almond shell activated carbon

TiO<sub>2</sub>

Hydrothermal

Sol–gel

Total Organic Carbon

## ABSTRACT

TiO<sub>2</sub>-containing almond shell activated carbons (TiO<sub>2</sub>/ASAC) with high photocatalytic activity were prepared using hydrothermal and sol–gel methods. The prepared photocatalysts were characterized by different techniques. XRD study confirmed that TiO<sub>2</sub> existed in a mixture of anatase and rutile phase. Nano-TiO<sub>2</sub> particles were dispersed on the ASAC with the size of 18–24 nm. The specific surface area of the samples decreased from 1398 m<sup>2</sup>/g to 661 m<sup>2</sup>/g indicating that the pores of activated carbon are blocked by TiO<sub>2</sub>. The photocatalyst obtained from the hydrothermal process is better than the other samples one in a comparison of the anatase content, and was also confirmed by the photocatalytic degradation of Total Organic Carbon (TOC) from industrial phosphoric acid solution under UV irradiation.

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## 1. Introduction

Titanium dioxide has been extensively studied as a promising material for environment protection for the past decade because of its excellent photocatalytic activity. Numerous studies have shown their unique performance in photodegradation of toxic components in wastewater, such as phenols, herbicides, pesticides, dyes, and surfactants, etc. [1–5]. However, there are some drawbacks to the practical use of TiO<sub>2</sub> powder during the photocatalytic process [6]: (1) separation of powder TiO<sub>2</sub> from water is difficult; (2) the suspended powder TiO<sub>2</sub> tends to aggregate especially at high concentrations. Therefore, much research has been conducted to immobilize TiO<sub>2</sub> in order to overcome these problems.

Early work mainly focused on coating TiO<sub>2</sub> on fixed supports, such as glass fibers, glass, quartz, and stainless steel, etc. [7,8]. The efficiency of pollutant degradation on TiO<sub>2</sub> particles so immobilized is usually decreased because of the mass transfer limitation. So to solve the problem, photocatalysts (e.g. TiO<sub>2</sub>) have been immobilized on various supports such as silica [9,10], perlite [11], clay [12,13], zeolites [14] and activated carbon [15–18]. After it has been used as an adsorbent in aqueous or gaseous medium [19–23],

activated carbon is employed in the process of photodegradation in recent years. The advantages of the use of the activated carbon as a catalytic support are summarized as follows: (1) the support adsorbs a high amount of pollutants around the loaded TiO<sub>2</sub>. Then the rate of photooxidation is improved [24,25]; (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, and thereby preventing secondary pollution; (3) since the pollutants are finally oxidized into CO<sub>2</sub>, the lifetime of the hybrid photocatalysts is long [26]. Also, several preparation methods for TiO<sub>2</sub>/activated carbon composites, such as hydrothermal [27], sol–gel [26], boil deposition [28], dip coating [29], metal organic chemical vapor deposition (MOCVD) [30], and impregnation [31] have been reported. Although TiO<sub>2</sub>/activated carbon has been extensively used for the degradation of pollutants, such as phenol, substituted phenol and dyes, there is no available literature for the photodegradation of organic moieties from Tunisian industrial phosphoric acid by TiO<sub>2</sub> supported activated carbon. The phosphoric acid is manufactured using different processes; the most commonly used are thermal and wet-processes. The wet-process is used in Tunisia to produce phosphoric acid from phosphate minerals [32]. Nevertheless, this process conducts to an acid with a high level of impurities, including organic pollutants

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[33]. These organic pollutants are n-dibutyl phthalate, humic and fulvic acids [34,35]. Hence, removal of these organic pollutants seems to be an important step for the production of phosphoric acid with a high level of purity.

The present study is focused on the preparation of reproducible TiO<sub>2</sub> supported activated carbon catalysts (TiO<sub>2</sub>/ASAC) by chemical routes followed by hydrothermal and sol–gel methods. The TiO<sub>2</sub>/ASAC photocatalyst was subjected to instrumental techniques in order to study its surface morphology, structural and chemical properties. The prepared catalysts were employed for the photocatalytic degradation of Total Organic Carbon (TOC) from industrial phosphoric acid solution and also for determining their catalytic efficiency for industrial applicability.

## 2. Experimental

### 2.1. Materials

Almond Shell Activated Carbon (ASAC) was prepared from the physical activation of almond shell, which was obtained from the local company in Sfax (Tunisia). Ammoxidation process was used to modify the activated carbon surface using a method described in a previous work [36]. The textural properties of the material are listed in Table 1.

Titanium isopropoxide, (Ti (OPr<sup>i</sup>)<sub>4</sub>, TTIP, Sigma–Aldrich, purity: 97%) tetrabutyl titanate (Aldrich, 99.9%), isopropyl alcohol (99.5%, Riedel deHäen), absolute ethanol, acetic acid and sodium hydroxide were used as reagents for the preparation of photocatalysts. Commercial TiO<sub>2</sub> (Degussa P25, Degussa Chemical) was used in photocatalytic degradation experiments for the comparison. Industrial phosphoric acid solution (54% P<sub>2</sub>O<sub>5</sub>) produced by the SIAPE society was used to evaluate the photocatalytic efficiency of synthesized photocatalysts. This phosphoric acid contains 578 ± 5 ppm of TOC. The details of this industrial product are found in a previous study [36].

### 2.2. Preparation of TiO<sub>2</sub>/ASAC photocatalysts

#### 2.2.1. Hydrothermal method

The ASAC was pre-treated with 1 mol/L acetic acid, deionized water and 1 mol/L sodium hydroxide in turn. Then, 5 mL of tetrabutyl titanate was dissolved in 20 mL of absolute ethanol into which 20 mL of 1 mol/L acetic acid had been added; the mixture was continuously stirred for 2 h. The obtained transparent TiO<sub>2</sub> sol and pre-treated ASAC were transferred into a sealed reactor and heated at 150 °C for 8 h. Afterwards, the prepared were separated and dried at room temperature. Finally, the prepared composite was washed with deionized water and anhydrous ethanol successively and finally dried in a vacuum oven at 60 °C for 4 h. The photocatalysts prepared by this method, were named TiO<sub>2</sub>/ASAC (H), with the letter (H) indicates the hydrothermal treatment.

#### 2.2.2. Sol–gel method

Catalyst samples were prepared from alkoxide precursor in the following way: 5 g of ASAC was homogenized and settled in 30 mL

titanium isopropoxide solution at 30% in isopropyl alcohol during 12 h. After that time, it was observed a polymerized gel, which was dried at 96 °C for 5 h. This process was repeated four times, trying to get more impregnation of TiO<sub>2</sub> on activated carbon. After the impregnation process has finished, the material is calcined under nitrogen at 500 °C for 5 h. The synthesized photocatalysts are named TiO<sub>2</sub>/ASAC (S), where the letter (S) indicates the sol–gel process.

### 2.3. Characterization of photocatalysts

Several techniques were employed for the characterization of the samples. In order to determine the crystal phase composition and the TiO<sub>2</sub> crystallite size in the photocatalysts, X-ray diffraction measurements were carried out at room temperature using a X-ray diffractometer (Philips® PW 1710 diffractometer, Cu Kα, 40 kV/40 mA, scanning rate of 2 θ per min). The crystallite size was calculated by X-ray line broadening analysis using Scherrer equation ( $D = K\lambda/\beta \cos \theta$ ) [37].

The micrographs of TiO<sub>2</sub>/ASAC and original ASAC samples were examined by a scanning electron microscope (SEM, Hitachi SU-70). The structural feature of these samples was observed at the accelerated voltage of 1.0 kV. Before observation, the samples were coated with gold in E-1010 Ion sputter. Energy dispersive X-ray analysis (EDX) was employed for the quantitative determination of TiO<sub>2</sub> contained in the carbon matrix. This was determined using Hitachi SU-70, SEM equipped with a microanalysis system EDX (Oxford X- Max 50 mm<sup>2</sup>).

Nitrogen adsorption–desorption isotherms were measured at –196 °C on a Fisons Sorptomatic 1990 after outgassing (10<sup>–5</sup> Pa) for 24 h at ambient temperature. The specific surface area, S<sub>BET</sub>, was determined according to the Brunauer–Emmet–Teller (BET) equation, Dubinin's theory, the comparison plot, and the DFT method [38]. The total surface area was estimated from the average values obtained using the Dubinin–Radushkevich theory, comparison plot and DFT methods.

The thermochemical properties (thermogravimetric/thermo-differential analyses) of the photocatalysts were examined on a thermoanalyzer (SETERAM Labsys) in the 50–600 °C temperature range.

Differential scanning calorimetry was performed under nitrogen (N<sub>2</sub>) atmosphere. The calorimeter measured the heat flux from the sample with a unit of mJ/s mg. The rate of heating was 10 °C/s.

### 2.4. Photocatalytic degradation experiments

Photodegradation of TOC from industrial phosphoric acid was conducted in a laboratory-scale photoreactor (Fig. 1). It is a cylindrical photoreactor (diameter = 8 cm, height = 12 cm), operating in a closed recirculating circuit driven by a centrifugal pump and with a stirred reservoir tank equipped with a device for withdrawal of samples. Illumination was carried out using a lamp (11 W low-pressure mercury lamp, Philips, Holland) with wavelengths ≤254 nm. The photocatalyst (1.2 g) was mixed in 200 mL of an industrial phosphoric acid solution at different temperatures (25–45 °C). Before irradiation, the suspensions were stirred under dark conditions for 30 min. During the photocatalytic tests, the shaking of the suspensions was controlled to ensure that the suspension was homogeneous. At given time intervals, about 4 mL of aliquots were sampled, and separated by filtration to determine TOC<sub>r</sub>. The degradation percentage of TOC by TiO<sub>2</sub>/ASAC samples was calculated as follows:

$$\text{Degradation percentage of TOC (\%)} = \frac{\text{TOC}_0 - \text{TOC}_r}{\text{TOC}_0} \times 100 \quad (1)$$

where TOC<sub>0</sub> and TOC<sub>r</sub> are the concentrations of initial and residual Total Organic Carbon.

**Table 1**  
Textural and structural properties of the samples.

	Sample		
	ASAC	TiO <sub>2</sub> /ASAC (H)	TiO <sub>2</sub> /ASAC (S)
S <sub>BET</sub> (m <sup>2</sup> /g)	1398	661	815
Total pore volume (cm <sup>3</sup> /g)	0.80	0.39	0.45
Pore diameter (nm)	2.4	5.3	3.9
Crystallite size, D (nm)	–	18	24
Anatase Content, A (%)	–	94	79
TiO <sub>2</sub> (wt.%)	–	24.7	21.5

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