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Influence of activated carbon upon titania on aqueous photocatalytic consecutive runs of phenol photodegradation

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Abstract

The photocatalytic degradation of phenol was performed at room temperature in aqueous suspended mixtures of TiO_2 and activated carbon (AC). The main objective of the present work was to verify the potential of TiO_2/AC system in the photocatalytic degradation of phenol and the principal intermediate products after performing three consecutive runs. The phenol disappearance follows a first-order kinetics. Therefore, the apparent first-order rate constant of phenol and total organic carbon photodegradations were selected to evaluate the photoefficiency of the system. From the present results it can be concluded that there is a synergistic effect between both solids which is determined by the numbers of photocatalytic runs. From a practical point of view, TiO_2/AC is able to photomineralize phenol and total organic carbon for three and two, respectively, consecutive runs more efficiently than TiO_2 alone.

Keywords: Phenol; Total organic carbon; Photodegradation; Titania; Activated carbon; Kinetics; Synergy

1. Introduction

One of the most important challenges for science is to develop efficient methods to control environmental pollution. Heterogeneous photocatalysis has recently emerged as an efficient method for purifying water and air [1–5]. Up to now, in more than 1700 references that have been recently collected on this discipline [6], titania under the shape of anatase has always been found as the best photocatalyst.

Several attempts has been performed to increase the photoefficiency of titania either by noble metal deposition or by ion doping. In photocatalytic degradations of organic pollutant, which are essentially total oxidation reactions, such modifications did not enhance the photocatalytic activity of titania and were rather detrimental. For ion doping, either of the p-type obtained by dissolving in the lattice of titania hetero-cations of valence lower than that of Ti^{4+} (Al^{3+}, Cr^{3+} and Ga^{3+}) or of the n-type obtained by dissolving hetero-cations of valence higher than +4 (Nb^{5+}, Ta^{5+} and Sb^{5+}), the inhibiting effect was ascribed to an increase in the electron–hole recombination rate [7]. Actually, p-type doping agents create acceptor centers which trap photoelectrons and then, once negatively charged, attract holes, thus behaving as recombination centers [8]. On the opposite, n-type doping agents create donor centers. By increasing the concentration of conduction electrons in the solid, they also favor the electron–hole recombination, which is detrimental for the photoefficiency [7]. Noble metal deposits help the electron–hole pair separation by attracting the photoelectrons because of a favorable difference between the Fermi level and that of titania. However, once negatively charged, metal particles, especially for highly loaded samples ($\%M > 5$), attract holes and subsequently recombine them with electrons [7]. A third way to possibly increase the photocatalytic efficiency of titania consists in adding an inorganic co-adsorbent to the photocatalyst, such as silica, alumina, zeolites or clays [9–11]. In fact, no improvement of photoefficiency was observed for the systems containing silica or alumina [10] and it was concluded that photogenerated oxidizing species cannot migrate from the original site to the co-adsorbent to react there with adsorbed

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pollutant molecules. Moreover, Takeda et al. [11] concluded that an optimum adsorption strength of the propionaldehyde on the co-adsorbent is needed to improve titania's photoactivity.

Another type of inert co-adsorbent is activated carbon (AC). It has been already used in gas phase [11–13] or in aqueous phase [9–10,14–18] reactions. Gas phase reactions concerned NO_x removal from the air [12,13] and the oxidation of gaseous propionaldehyde [11]. Aqueous phase photocatalytic degradation concerned organic pollutants such as dichloromethane [9] or propyzamide [14,15]. Except in the case of NO_x removal [12,13] where AC was merely mixed to titania, carbon was generally used as a support for titania. Adding activated carbon to titania is expected not only to induce some beneficial effect because of the high adsorption capacity of AC with respect to organic molecules but also resolve the problem of achieving an optimum adsorption strength of the adsorbed molecules on the co-adsorbent to improve titania's photoactivity. In fact, a synergy effect was reported by some of us using titania and activated carbon [16–18] in the photocatalytic degradation of phenol, 4-chlorophenol, and a common acid herbicide 2,4-dichlorophenoxyacetic acid (2,4-D). More recently, Araña et al. [19–21] have been studied the surface interaction [19] between TiO_2 and activated carbon as a support for the photocatalytic degradation of organic compounds in aqueous [20] or gas phase [21].

In addition, Herrmann and co-workers have already observed that depositing titania by different ways (electrophoresis deposition, dip coating and impregnation of a precursor) on different supports (stainless steel, glass and quartz) induced some modifications which were detrimental for titania's photocatalytic activity [22]. This was mainly explained by the contamination of titania by foreign ions penetrating the lattice during the final thermal treatment which is necessary to the stabilization of the material. This produce a doping of supported titania with its correlative detrimental effect explained above. Therefore, to better put in evidence any synergistic effect between both solids, the use of powdered titania and powdered activated carbon maintained in an aqueous suspended mixture enables one to preserve the respective initial surface state of each solid constituent. Having this in mind, the main objective of this work is to extrapolate the above associative or synergistic effect between titania and activated carbon to a single study of photocatalytic consecutive runs of phenol and total organic carbon (TOC) photodegradations, taking into account for the later the principal intermediate products detected during phenol degradation.

2. Experimental

2.1. Materials

Phenol, hydroquinone (HQ) and *para*-benzoquinone (BQ) which corresponded to the initial pollutant and to the main intermediate compounds, respectively, were purchased from Aldrich, with the highest purity grade and used as received. The photocatalyst was TiO_2 Degussa P25, mainly anatase (ca. 70%) under the shape of non-porous polyhedral particles of ca. 30 nm mean size with a surface area of 50 m^2/g. The same high purity activated carbon (Merck, ref. 102186, <1& ash), already used by some of us in previous photocatalytic studies [16–18] was employed. It has a total (B.E.T.) surface area of 775 m^2/g. The mean pore diameter is close to 8 Å (measured by the Horvath–Kawazoe method) and the particle size is around 60 μm.

2.2. Photoreactor and light source

The batch photoreactor was a cylindrical flask made of pyrex of ca. 100 ml with a bottom optical window of ca. 4 cm diameter and was open to air. Irradiation was provided by a high pressure mercury lamp (Phillips HPK 125 W) and was filtered by a circulating-water cell (thickness 2.2 cm) equipped with a 340 nm cut-off filter (Corning 0.52). The water cell was used to remove all the IR beams, thus preventing any heating of the suspension, especially in the presence of black activated carbon. The cut-off filter, although decreasing the overall UV-light power available, enables one to eliminated any photochemical side reaction.

2.3. Analysis

Millipore disks (0.45 μm) were used to remove particulate matter before HPLC analysis. Although non-agglomerate solid particles may pass through these membranes, our experience showed that the performance of the chromatographic column was not impaired for a long period of use. The HPLC system comprised a LDC/Milton Roy Constametric 3200 isocratic pump and a Waters 486 tunable absorbance detector (Millipore) adjusted at 270 nm for the detection of phenol and of the main intermediate products. A reverse-phase column (length, 250 mm; internal diameter, 4.6 mm; particle diameter, 5 μm) ODS2-Spherisorb (Chrompack) was used. The mobile phase was composed of acetonitrile and deionized doubly distilled water. The ratio of CH_3CN/H_2O was 10/90 (v/v) and the flow rate was 1 ml/min.

2.4. Procedure

In an ordinary photocatalytic test performed at room temperature (20 °C), 50 mg TiO_2 and 10 mg AC were added under stirring in 20 ml of a millimolar solution of phenol (94 ppm) and maintained in the dark for 15 min to reach a complete adsorption at equilibrium as we have reported in a previous work [16]. At time $t = 0$, a screen was removed from the window of the water cell located in front on the preheated lamp. The quantity of 50 mg of titania was chosen since in our conditions there is a full absorption of the UV-light entering the photoreactor and because it has shown a optimum of composition in the photodegradation of phenol [16]. The quantity of 10 mg AC was chosen to ensure a good adsorption of phenol related to the high surface area of AC without disturbing the UV-absorption by titania nor phenol adsorption on it [16]. The oxidation involved oxygen from the air dissolved at saturation ($\leq$1.4 mmol/l). Samples of the suspension were removed at regular intervals for analysis. Each aliquot removed from photoreactor was equal to 0.17 ml. Eight aliquots for