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The synthesis of sulphur and boron-containing titania photocatalysts and the evaluation of their photocatalytic activity

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ABSTRACT

Aqueous photocatalytic oxidation of methyl-*tert*-butyl ether, *p*-toluidine, *tert*-butyl alcohol, *i*-propanol, 2-ethoxy ethanol and phenol, was studied using sulphur and boron-containing titania photocatalysts, active in visible light. The activity of the catalysts, compared to commercial Degussa P25, was tested in PCO of the pollutants dependent on the admixture content. The performance of S- and B–TiO_2 under visible light in PCO of MTBE, TBA and *i*-propanol was surpassing that of P25 under UV. However, in respect of *p*-toluidine and phenol both S- and B-containing titania showed an inferior, although comparable, performance, to that of P25. Experiments were carried out under artificial and solar light.

1. Introduction

Aqueous photocatalytic oxidation (PCO) of organic groundwater pollutants, methyl-*tert*-butyl ether (MTBE, $CH_3–O–C(CH_3)_3$), *tert*-butyl alcohol ($(H_3C)_3C–OH$, TBA), *i*-propanol ($H_3C–CH(OH)–CH_3$), 2-ethoxy ethanol, *p*-toluidine, and phenol, was studied using two series of titania photocatalysts, synthesised by sol–gel method, doped with sulphur and boron active in visible light.

Methyl-*tert*-butyl ether, banned for its use in the USA, is still widely used as an oxygenated component of motor fuels by the rest of the world. Water pollution with MTBE may occur due to traffic accidents, fuel leaks or inappropriate fuel disposal. This substance is of particular concern because of its accumulation in groundwater due to its low biodegradability [1]. Physical removal and chemical oxidation methods, such as air stripping, activated carbon adsorption, ozonation and treatment with Fenton's reagent have been proven to be ineffective against MTBE [2–4].

p-Toluidine is a widely used industrial chemical, with its use ranging from a component of several jet and rocket fuels to applications in paint and pharmaceutical industries [5]. Also, at former munitions sites *p*-toluidine is a degradation intermediate of *p*-nitrotoluene, and occurs in tobacco smoke [6]. Thus, the pollution of soil and groundwater with *p*-toluidine occurs at the military sites; industrial emissions are also possible. Non-biodegradable *p*-toluidine may accumulate in groundwater aquifers in toxic amounts. Conventional water treatment methods have been shown to be inadequate against *p*-toluidine pollution [7].

Phenol, being a substantial environment pollutant of, for example, oil shale industry [8], has a reputation of a standard model contaminant used to test the activity of various oxidation methods and catalysts. *tert*-Butyl alcohol (TBA) can be primarily found in the groundwater as a result of MTBE hydrolysis; it may also enter groundwater as an impurity of MTBE-blended motor fuels [9]. 2-Ethoxy ethanol is used in multiple applications in industry and transport and also may accumulate in subsurface aquifers. The main interest in *i*-propanol, however, was to study the PCO of secondary carbon atom when compared to primary carbon of 2-EE, tertiary carbon atom of MTBE and TBA and aromatic structures of phenol and *p*-toluidine. Thus the choice of model pollutants was serving the systematic study of the catalysts' performance on pollutant substances of different molecular structure found simultaneously in polluted groundwater. Although dyes are often used as test objects for novel photocatalysts, the authors believe that the performance of the latter would better be checked by real and chemically stable pollutants, unlike dyes that can spontaneously decompose under visible irradiation. Also, often the modified catalysts exhibit dramatically different performance with different

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substances [10]. In case when various pollutants can be found simultaneously in, for example, fuel-polluted groundwaters, the knowledge of photocatalytic activity against multiple targets is necessary.

Subjected to electromagnetic irradiation of appropriate energy, the excited semiconductor's valence band electrons are displaced to the conduction band, forming positively charged holes oxidizing the water molecules into hydroxyl radicals reacting with the pollutant. Also, the direct oxidation of organic pollutant adsorbed on the photocatalyst surface by the positively charged holes takes place.

Most commonly used titanium dioxide photocatalysts can be excited only by ultraviolet irradiation, as the band-gap energy of TiO_2 is 3.2 eV. This way, only 4% of the solar radiation reaching the Earth surface can be used. However, the semiconductor band-gap can be reduced by doping, i.e. introducing additive atoms into titanium dioxide structure, thus forming a crystalline structure with a misbalance in charge carriers. These charge carriers, either electrons or holes, have enough energy to create a new energetic level inside the band-gap (named either donor or acceptor level, depending on whether it is formed by electrons or holes respectively), which is occupied at room temperature by electrons. When subjected to electromagnetic irradiation, the electrons of donor or acceptor level can be excited and displaced to the conduction band from an energetic level inside the band-gap with less energy required for electron excitation, i.e. light with greater wavelength may be utilised.

Sulphur- and boron-containing titania visible light-sensitive photocatalysts were synthesised using sol–gel method and tested in PCO of the abovementioned pollutants. An undoped titania sample synthesised by the same pattern was used as a reference. The performance of the modified catalysts, dependent on the admixture content, was compared to one another and to that of Degussa P25 titanium dioxide.

2. Experimental

Two thermostatted at 20 ± 1 °C 200-mL simple batch reactors with inner diameter 100 mm (evaporation dishes), aperture $40\ m^2\ m^{-3}$, mechanically agitated with magnetic stirrers, were used in PCO experiments: the one used for the PCO was called "active" and the other containing no photocatalyst was called "reference". Both reactors were exposed to identical experimental conditions. The samples from the active reactor were compared to the reference samples to avoid complications caused by water evaporation. A UV-light source, Philips 365-nm low pressure luminescent mercury UV-lamp (Sylvania Blacklight F 15 W 350 BL-T8), was positioned horizontally over the reactors, providing the irradiance of about $0.7\ mW\ cm^{-2}$ measured at a distance of 25 cm, corresponding to the level of the free surface of the reactor by the optical radiometer Micropulse MP100 (Micropulse Technology, UK). With daylight fluorescent lamp (Philips TLD 15 W/33–640), the irradiance was measured indirectly, being calculated from the illuminance, measured by TES luxmeter (TES Inc., Taiwan), using lumen to watt ratio of 684, as the response of human eye to light with the illuminance of 684 lumens (lm) equals to that to the irradiance of 1 W [11]. With Philips TLD lamp, the amount of UV-irradiation was also specifically measured using the abovementioned Micropulse radiometer for 254 and 365 nm and total amount of UV by using Ocean Optics USB2000 + UV–VIS spectrometer. Only negligibly small fraction of UV around 365–400 nm was observed. These measurements are also confirmed by the publicly available data from the lamp manufacturer [12]. Thus, any noticeable action of the photocatalyst when using Philips TLD lamp as the irradiation source may not be attributed to the UV fraction emitted by the lamp but is clearly due to the activity of the catalysts in visible light region. There were also some experiments conducted outdoors, using natural solar irradiation. A schematic representation of the experimental setup can be seen in Fig. 1.

The experiments were carried out using aqueous solutions of the chemicals supplied by Aldrich. With all chemicals except 2-EE, the experiments were conducted with synthetic solutions (i.e. the pollutants dissolved in distilled water) at $100\ mg\ L^{-1}$; with 2-EE the concentration was higher, being $300\ mg\ L^{-1}$. The concentrations were chosen with reference to those that may be found in real contaminated aquifers used in previously conducted experiments [7,13]. The experiments were carried out in acidic (pH 3), natural (pH 6.5) and alkaline (pH 11) media, adjusted either by 4 N sulphuric acid or 15% sodium hydroxide. The treatment time for MTBE was 2 h under artificial light and 30 min under solar radiation. With *i*-propanol, treatment time was also 2 h. For *p*-toluidine and phenol, treatment time was 24 h. TBA solutions were treated for 4 h. Treatment time for 2-EE was chosen to be 24 h under artificial and 5 h under solar light. The treatment time in every case was chosen to reduce the concentration of pollutants below 50% of the residual concentration and was used in calculations of the process efficiency E (see Eq. (1)). All the experiments were carried out for at least three times under identical experimental conditions to derive the average value of the process efficiency. The average deviation of data in parallel experiments did not exceed 5%.

Adsorption experiments with the pollutants on the photocatalyst surface were carried out at respective pH in closed flasks thermostatted at 20 ± 1 °C and equipped with magnetic stirrers. The adsorbed amount of substances was derived from the batch mass balance: the concentration of the dissolved substance was determined before and after adsorption.

Titanium dioxide Degussa P25, eight sulphur-containing and five boron-containing synthetic catalysts were used. Sulphur-containing photocatalysts were prepared by the hydrolysis of titanium tetrabutoxide with addition of a pre-calculated amount of 0.1 N sodium thiosulphate as sulphur source, followed by calcination at 400 °C for 4 h. After this, the catalyst was washed with hot distilled water applied in a sequence of 10–15 rinsing rounds (ca. 1 L per 1 g of catalyst) in order to clean the catalyst surface from water-soluble compounds. In case of boron-containing photocatalysts, sodium tetraborate was used as boron source. An additional catalyst was synthesised using the same pattern, although without the addition of sulphur or boron sources. The experiments were performed in photocatalyst suspensions of $1\ g\ L^{-1}$.

Many authors indicate complete transformation of sulphide to sulphate at calcination temperature in air from 300 to 500 °C [14]. For verification of the catalysts stability, the S-modified catalyst was suspended in distilled water in amount of $1\ g\ L^{-1}$ under the UV light for 24 h. The sulphate determination was carried out with the IC (Dionex DX-120) with no corresponding peaks observed at the sensitivity of 10 ppb. As for carbon, the available

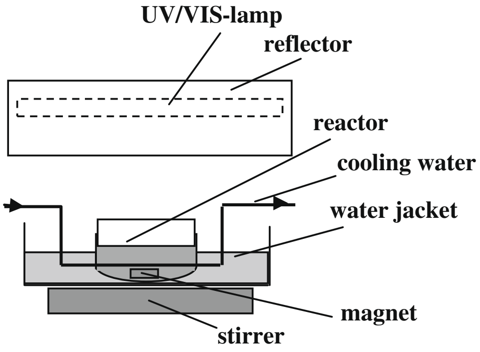

Fig. 1. Experimental setup.