



## Research paper

# Photodegradation of aniline in water in the presence of chemically activated halloysite

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## ABSTRACT

Photocatalytic degradation of aniline was investigated in aqueous solutions containing halloysite (Hal) nanotubes, chemically activated halloysite (AHal), and photocatalysts: TiO<sub>2</sub> (anatase) and commercial titania P25, under UV illumination. Powder X-ray diffraction (XRD), UV–Vis/DR spectra and nitrogen adsorption isotherms were carried out to characterize the activated halloysite. The effects of the AHal and titania photocatalyst amount as well as aniline concentration were examined. It is observed that the photodegradation of aniline has a similar course in the presence of AHal and in the presence of P25 and TiO<sub>2</sub>, both with respect to the decomposition of aniline and in decreasing the amounts of photoproducts being formed during the irradiation of aniline. The photodegradation of aniline is clearly slower in presence of Hal nanotubes than for AHal and P25. The disappearance of aniline follows approximately according to the Langmuir–Hinshelwood kinetics. The values of rate photodegradation constant are decreasing in the following order: P25 > TiO<sub>2</sub> > AHal > Hal nanotubes. These results have indicated that halloysite containing titanium dioxide could be employed during photocatalytic removal of aniline from the aqueous solution, similarly to commercial titania photocatalysts.

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## 1. Introduction

Aniline and its derivatives are important chemicals used in the production of antioxidants, rubbers, dyes, pharmaceuticals, pesticides and herbicides (Jen et al., 2001). These compounds are frequently found in industrial effluents and surface water due to their use in industrial manufacture (and as a result of the biodegradation of xenobiotic compounds including azo dyes and herbicides) (Emtiazzi et al., 2001). They have been identified as potential carcinogens (Chu et al., 2007) and found to possess the ability of preventing oxygen uptake in blood and damaging the spleen (Karunakaran et al., 2005). A large number of methods, including chemical (Sarasa et al., 2002; Gomes et al., 2005; Han et al., 2006; Jagtap and Ramaswamy, 2006), and photochemical ones (Sauleda and Brillas, 2001; Kamble et al., 2003; Kumar and Mathur, 2004; Canle et al., 2005; Wang et al., 2007; Tang et al., 2010a, 2010b), have been used to remove aniline and its derivatives from water. The decomposition of environmental pollutants using semiconductors as photocatalysts is a rapidly growing area of research. Among various semiconductors, TiO<sub>2</sub> is one of the most widely investigated as a photosensitizer because of its high effectiveness, stability and nontoxicity (Fujishima et al., 2000; Styliadi et al., 2004; An et al., 2010; Muneer et al., 2010; Zhang et al., 2011). Sanchez et al., Kumar and Mathur, Canle et al., and Tang et al. studied the TiO<sub>2</sub>-photocatalyzed degradation

of aniline in an aqueous solution (Sanchez et al., 1997; Kumar and Mathur, 2004; Canle et al., 2005; Tang et al., 2010a, 2010b). TiO<sub>2</sub> in pillared clays improved the photocatalytic activity (Ooka et al., 2004; Sun et al., 2006; Nikolopoulou et al., 2009). In aqueous dispersions, clays have been used in a combination with TiO<sub>2</sub> to enhance the removal of organic pollutants by photocatalytic degradation (Mogyorósi et al., 2002; Kibanova et al., 2009). Papoulis et al. (2010, 2013) prepared palygorskite-TiO<sub>2</sub> and halloysite-TiO<sub>2</sub> nanocomposites by deposition of the anatase form of TiO<sub>2</sub> on the clay mineral surfaces using a sol–gel method with titanium isopropoxide as a precursor. Clay mineral-titania samples showed a significantly higher activity in decomposing NO<sub>x</sub> gas and toluene under UV and visible-light irradiation compared to that of standard commercial titania, P25.

Halloysite (Hal) is a 1:1 layered clay mineral with one silica tetrahedron sheet and one alumina octahedron sheet (Brigatti et al., 2006). Due to its unique tubular structure in nano-scale and many physico-chemical properties (good mechanical properties, excellent chemical stability, high specific surface area and porosity, and large adsorption capacity), Hal is an available natural nanomaterial, which makes it attractive for technological applications (Dong et al., 2012). Several methods have been suggested to improve surface properties of clay minerals (Mellouk et al., 2009; Tang et al., 2010a, 2010b; Cheng et al., 2011; Yuan et al., 2015). Acid treatment is a traditional chemical activation method which causes the disaggregation of clay particles, elimination of mineral impurities, and dissolution of external layers. As a result, surface area, surface activity, and pore volumes of clay mineral increase

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(Lenarda et al., 2007; Panda et al., 2010; Zhang et al., 2012; Banaś et al., 2013). The acid treated Hal with mesopores is competitive in different industrial uses and it was used as adsorbent and catalyst support (Liu et al., 2011; Luo et al., 2011; Zhang et al., 2012; Wang et al., 2013; Szczepanik et al., 2014).

In this work, the way of aniline degradation in an aqueous solution by photocatalytic decomposition in the presence of AHal under the UV illumination is presented. In this study, raw Hal mineral from a Polish strip mine “Dunino” (DHal), located in the vicinity of Legnica, a town in south-western part of Poland, was activated, and their chemical composition, structure, and the specific surface area were studied. This mineral contains much more amount of TiO<sub>2</sub> (anatase) in comparing with different halloysites from Australia, New Zealand, USA and Algeria (Belkassa et al., 2013; Pasbakhsh et al., 2013). If DHal containing TiO<sub>2</sub> is applied as photocatalyst, it is possible to omit the procedures of receiving of halloysite-TiO<sub>2</sub> nanocomposites. The photocatalytic activity of AHal for aniline degradation was investigated, and compared with the photocatalytic activity of Degussa-P25 and TiO<sub>2</sub> (anatase) catalysts in the same conditions. Also aniline photodegradation was examined in the presence of commercial Hal nanotubes (ComHal) (Sigma Aldrich).

## 2. Experimental

### 2.1. Materials

DHal was obtained from the strip mine “Dunino” (Intermark Company, Legnica, Poland). ComHal has a specific surface area of 64 m<sup>2</sup>/g, (Sigma-Aldrich) and was used as received. TiO<sub>2</sub> powder (anatase, 99.8%) (a specific surface area of 11.4 m<sup>2</sup>/g, Zielińska et al., 2003) from Aldrich, Degussa P25 titanium dioxide from Evonik (Degussa) were used as received. P 25 has a specific surface area of 49 m<sup>2</sup>/g and is composed of 80% anatase and 20% of rutile (Ohno et al., 2001). Aniline (Aldrich) was freshly distilled under reduced pressure and stored in a refrigerator prior to use. Deionized water was used throughout the present work.

### 2.2. Preparation of AHal samples

DHal was dried, powdered and screened through a sieve and next washed with deionized water. AHal was obtained in the following manner: DHal was processed by washing, drying and grinding; next, the magnetic fraction was separated using a 2-T magnetic separator. The obtained non-magnetic fraction of the DHal was cleaned with distilled water, dried, and followed by reductive bleaching with sodium hydrosulfite in the solution of sulfuric acid. Particles fraction of 0.32 mm–0.2 mm was used for irradiation and chromatographic experiments in the case of DHal and AHal.

### 2.3. Characterization and analysis

The analysis of DHal and AHal was performed using wavelength dispersive X-ray fluorescence analysis (WDXRF) (the AXIOS spectrometer from PANalytical equipped with the X-ray tube, Rh anode, with a maximum power of 2.4 kW and X-ray exit windows placed at 45° just in the front of the sample holder). X-ray powder diffraction measurements were performed in the Bragg–Brentano geometry using the X'Pert Pro MPD diffractometer (PANalytical) equipped with Cu-anode 1.8 kW X-ray tube with a linear exit window (Banaś et al., 2013).

Infrared spectra, which were recorded using a Perkin-Elmer Spectrum 400 FT-IR/FT-NIR spectrometer with a smart endurance single bounce diamond, attenuated total reflection (ATR) cell. Spectra in the 4000–650 cm<sup>-1</sup> range were obtained by the co-addition of 40 scans with a resolution of 4 cm<sup>-1</sup>. Before the measurements, all samples were dried and powdered in an agate mortar. UV–Vis reflectance spectra were measured on a UV–VIS–NIR UV-3600 Shimadzu spectrophotometer.

Nitrogen adsorption isotherms were measured at –196 °C on ASAP 2020 volumetric analyzer manufactured by Micromeritics, Inc. (Norcross, GA, USA). All samples were outgassed at 350 °C for 6 h prior to adsorption measurements. The BET (Brunauer–Emmett–Teller) specific surface area  $S_{\text{BET}}$  was calculated from nitrogen adsorption isotherms in the range of relative pressures from 0.05 to 0.3 using the cross-sectional area of 0.162 nm<sup>2</sup> per nitrogen molecule. The single-point total pore volume of pores ( $V_t$ ) was estimated from the volume adsorbed at a relative pressure of  $p/p_0 = 0.3$ .

Specific surface area ( $S_{\text{BET}}$ , m<sup>2</sup>/g), calculated from adsorption isotherms was equal, i.e. 43.1 m<sup>2</sup>/g and 48.8 m<sup>2</sup>/g for DHal and AHal, respectively (Szczepanik et al., 2014).

The concentration of aniline was measured with the spectrophotometric method. UV–visible absorption spectra were recorded on a UV–VIS–NIR UV-3600 Shimadzu spectrophotometer.

Inverse liquid chromatography was used for aniline adsorption measurements on DHal, AHal, and ComHal applying the method of the division peak. Thermo Scientific Dionex UltiMate 3000 Series chromatography system (Thermo Fisher Scientific Inc., USA) was used, consisting of a triple pump, an autosampler, and diode array UV detector modules (DAD). The chromatograph measurement was controlled by the computer with Chromeleon software. Additionally, the DAD system was equipped with an additional exit of the analog signal to which the analog-to-digital converter was connected. The signal from this converter was directed to the second computer with the KSPD software which was used to calculate total surface of the chromatographic peak, the height of part of the chromatographic peak, the areas of its individual segments of the chromatographic peak, and the retention time (Lech, 2011).

DHal, AHal, ComHal, TiO<sub>2</sub> and P25 samples used in the experiments were dispersed in deionized water and then packed into a column (length 200 mm, inner diameter 4.0 mm) at atmospheric pressure. The HPLC eluent was water of Millipore quality. Experiments were performed at temperature 25 ± 0.1 °C and 0.1 ml·min<sup>-1</sup> flow. The injection volume was 50 µl and the sample concentration was 200 mg/dm<sup>3</sup>, UV absorbance was measured at 230 nm.

### 2.4. Experimental procedures and techniques

Irradiation experiments were carried out with a 700 cm<sup>3</sup> Heraeus UV reactor system. A UV low-pressure Hg immersion lamp TNN 15/32, cooled by air, served as a light source (the light emitted by the lamp was 254 nm). The temperature of the photoreactor was maintained within 25 ± 0.1 °C.

The photocatalytic degradation of aniline was conducted in the presence of AHal, ComHal, P25 and TiO<sub>2</sub> (0.1–0.4 g/700 cm<sup>3</sup> of aniline solution). Before the irradiation, the solution was magnetically stirred in dark for 30 min to ensure adsorption–desorption equilibrium. The photo-illumination was performed with continuous stirring of solution. At given time intervals, 4 ml of solution was sampled and centrifuged at 5500 rpm (Centrifuge MPW-352, MPW Med. Instruments) for 10 min to remove catalyst particles. After that, the supernatant was filtered through a 0.20 µm filter (Chromafil RC-20/15 MS); the remaining concentrations of aniline were measured by spectrophotometric method. Concentration of aniline solutions in deionized water was in the range 10–40 mg/dm<sup>3</sup>, and pH was about 6 through all experiments.

## 3. Results and discussion

### 3.1. Characterization of AHal

The diffraction patterns of DHal and AHal are presented in Fig. 1. The obtained diffractograms were analyzed with Highscore 3.0e from PANalytical. The analysis is based on, first, the identification of the strongest diffraction peaks in the diffractograms. Then, diffraction patterns were fitted with Pseudo-Voigt peak shapes. In the

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