



## Preparation of TiO<sub>2</sub>-pillared montmorillonite as photocatalyst Part II Photocatalytic degradation of a textile azo dye

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### ABSTRACT

Use of a photocatalyst based on TiO<sub>2</sub>-pillared montmorillonite prepared by microwave has been studied with respect to photodegradation of Solophenyl red 3BL, an azo dye produced from textile plants. Experiments were carried out with an aqueous dye concentration of 100 mg L<sup>-1</sup>, at different pH and photocatalyst contents (400–5000 mg L<sup>-1</sup>). The lower the pH, the higher the dye photodegradation rate constants: 0.0966 and 0.0006 min<sup>-1</sup>, obtained at pH = 2.5 and pH = 11 respectively. This is in agreement with a higher adsorption of the dye on the catalyst at acidic rather than at basic pH. At pH = 5.8 and 2.5 g L<sup>-1</sup> of TiO<sub>2</sub>-pillared montmorillonite, initial degradation rate constant of the dye (0.0096 min<sup>-1</sup>) was 1.4 fold lower with the synthesized photocatalyst than with commercial Degussa P25 (1 g L<sup>-1</sup>) for about the same molar amount of TiO<sub>2</sub> in dispersion. According to XRD patterns, rate constants were related to the rate of TiO<sub>2</sub> crystallization within the catalyst. A photosensitized oxidation accounted for about 25 ± 5%, and a direct excitation of the photocatalyst accounted for 80 ± 10% of the global photodegradation process, leading mainly to oxidation of the dye by HO<sup>•</sup>.

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### 1. Introduction

Many dyes are ubiquitous in the environment, since 15–20% of the world dye production is estimated to be released into the environment (Spadaro et al., 1994; Houas et al., 2001). Dyes are not easily biodegradable because of increased complexity of chemical structures and presence of aromatic rings (Brown and Laboureur, 1983; Chang and Lin, 2000). Under aerobic conditions, metabolisation of azo dyes is difficult (Robinson et al., 2001). Conventional treatments (adsorption on activated carbon, ultrafiltration, reverse osmosis and coagulation) often consist in transferring pollution from an aqueous phase towards a new medium, yielding formation of a concentrated sludge, thus creating a significant secondary disposal problem. In addition, overall materials' regeneration is very expensive. Ozonation and chlorination treatments can also be used for the destruction of dyes, but the former is still expensive and the latter does not reduce the amount of carbon in the effluent (Lin and Lin, 1993). A promising way to achieve efficient dye effluent removal is to use titanium dioxide as a photocatalyst.

Very high yields in the photocatalytic degradation of organic compounds have been observed in numerous works, and demonstrate that TiO<sub>2</sub> is a material of great importance (Bahnemann, 1999; Zielinska et al., 2001; Konstantinou and Albanis, 2004). The larger specific surface area and lower particle size increased the photocatalyst efficiency (Calza et al., 2007). Recent work has reported the

use of titanium dioxide nanoparticles as photocatalysts (Cappelletti et al., 2008). Technological development of TiO<sub>2</sub> is still required because TiO<sub>2</sub> powder used as an aqueous dispersion is very difficult to recover. TiO<sub>2</sub> supported on different minerals or TiO<sub>2</sub> thin films therefore appeared to be a promising way to enlarge application fields and overcome TiO<sub>2</sub> recovery problems (Zhiyong et al., 2008). However, with these supported materials, the photoactivity is not as observed with TiO<sub>2</sub> powder dispersion, mainly because of saturation of active sites on TiO<sub>2</sub> particles. Mesoporous materials based on clay minerals, zeolites, silica or activated carbons and incorporating metal oxides have also been synthesized (Yang et al., 1998; Mogyorósi et al., 2001; Vicente et al., 2001; Valverde et al., 2002; Mogyorósi et al., 2003). Photoactivity of such structures has been demonstrated by studying photodegradation of dyes such as acid black 1, orange II, methyl orange, methylene blue, and organic hazardous compounds as endocrine disruptors (Liu et al., 1999; Houas et al., 2001; Grzechulska and Morawski, 2002; Mogyorósi et al., 2002; Ooka et al., 2003; Zhu et al., 2005; Zhiyong et al., 2008). The main advantage of such new materials lies in their easy recovery from treated effluent (Ding et al., 1999).

Many works related to fundamental mechanisms of photocatalytic degradation processes have been published (D'Oliveira et al., 1990; Herrmann et al., 1993; Richard, 1993; Pichat, 1994; Bahnemann et al., 1997; Zhang et al., 1998; Bahnemann, 1999; Houas et al., 2001; Konstantinou and Albanis, 2004; Tariq et al., 2007). The main primary step is the adsorption of the organic substrate on the support during the equilibrium step, followed by an electronic transfer of e<sup>-</sup> from the conduction band of TiO<sub>2</sub> toward the substrate, and/or, from the

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