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Kaolinite-titanium oxide nanocomposites prepared via sol-gel as heterogeneous photocatalysts for dyes degradation

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ABSTRACT

A purified natural kaolinite was functionalized with titanium(IV) isopropoxide via the hydrolytic sol-gel route and thermally treated at several temperatures, between 100 and 1000 °C, for 24 h. The resulting solids were used for photodegradation (λ=365 nm, 30 W) of Methylene Blue (MB) and Methyl Orange II (MOII) dyes. All the solids efficiently degraded the dyes and almost total bleaching of the aqueous solutions was observed after 1 h. The best results were found for the solid heated at 400 °C, which degraded 93% of MOII and 99% of MB. Comparative studies with titanium oxide P25 from Degussa were tested and the results reveal lower yields than our systems (45% MB and 15% MOII, 1 h). Kaolinite could promote the dispersion of TiO_2 on the clay surface allowing a fast degradation of dyes. This effect was confirmed by comparison of the results from isolated components (titanium oxide and kaolinite) and titanium oxide-kaolinite nanocomposites.

1. Introduction

One of the greatest current concerns of humankind is to control and prevent environmental contamination; advanced techniques that can diminish or eliminate pollution, including photodegradation, are mandatory. In this sense, disposal of colored effluents produced by textile, paper pulp, plastic, food and other industries represent a technological problem that affects several countries. It is not easy to estimate the annual amount of waste produced by these industries but some studies indicates that there are over 100,000 types of synthetic dyes available in the market with an output of $7{\cdot}10^5$ tons per year, and approximately 5-10% is discharged during their production and utilization [1–3].

Azo dyes such as Methyl Orange II (MOII) represent the largest type of textile dyes in industrial use. These reactive azo dyes are not easily amenable by conventional treatment methods due to their stability and non-biodegradable nature. The colored wastewaters released by textile industry effluents pose a potential environmental hazard to ecosystem and must be treated before being discharged into the natural water bodies [4].

Methylene Blue (MB) is a thiazine cationic dye used for dying silk, leather, plastics, paper and cotton, as well as for the production of ink and copying paper in the office supplies industry. MB has long been used for staining in medicine, bacteriology and microscopy. Although it is not considered to be a very toxic dye, it can cause some harmful effects such as vomiting, increased heart rate, diarrhea, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis on human beings. In this context, MB containing wastewater should be treated by various methods, as the so called Advanced Oxidation Processes [5].

The Advanced Oxidation Processes (AOP) can induce the oxidation of various complex organic compounds such as pesticides, herbicides, drugs and dyes, turning them into products more easily degradable by biological methods. The biological processes associated to AOP can thus become efficient for wastewater treatments. The advantage of these processes is that there is a true destruction of the pollutants and not a transfer of them from one phase to the other, as in other treatments such as adsorption processes. Among the various AOP, heterogeneous photocatalysis involves the use of UV radiation that induces the surface of the semiconductor, such as titanium oxide, zinc oxide, etc., to generate hydroxyl radicals able to oxidize organic compounds considered as contaminants [1–3].

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The degradation of dyes from effluents is environmentally significant because even small amounts of dyes can sometimes be considered extremely toxic, even if they are not visible. Thus, removal of dyes is not only an environmental challenge, but a public health matter, and the government legislation on water from textile and food industries requires efficient and economically viable processes to remove these pollutants [6–8]. Much confusion exists in the literature about the correct designation of bleaching or mineralization. It is recognized that bleaching is only the simple removal of color from wastewater, not considering the complete oxidation of the organic molecules. Mineralization is considered the complete oxidation of the dye into harmless gaseous CO_2 and of nitrogen and sulfur heteroatoms into inorganic ions, such as nitrate or ammonium, and sulfate ions, respectively [9]. Thus, information about real mineralization of the dye or decreases in toxicity is scarce and therefore much attention has been also focused on the reaction types and mechanisms, based on the identification of the transformation products [10]. The effect of common dye bath constituents on the photocatalytic treatment efficiency has been also discussed in order to examine the application of the photocatalytic degradation on real wastewater effluents.

Heterogeneous photocatalysis with TiO_2 particles is seen as a cutting edge technology, much studied in the last decades in environmental remediation. Some features of this process that make it interesting in wastewater treatment is that it takes place at room temperature, the oxidation is often complete to CO_2, the oxygen required in the reaction is obtained from the atmosphere, the low cost of the photocatalysts and their easy reuse; besides, the process is not selective, which allows to treat complex mixtures of contaminants [1].

There are two major drawbacks for the successful use of the TiO_2-based photocatalysts. First, a high specific surface area is crucial to achieve high activity, as well as a good dispersion of TiO_2 on the matrix surface [2,3]. Some TiO_2-based nanocomposite photocatalysts have shown higher photocatalytic performance than commercial TiO_2 Degussa P25 [11]. It has been remarked that heterogeneous photocatalytic reactions occur on the surface of the catalysts and adsorption of the substrate molecules on the TiO_2 particles is a critical point for their degradation [11–15]. Thus, most studies dealing with photocatalysts based on TiO_2 particles have chosen to disperse them throughout matrices such as silica, alumina, clays or zeolites, in order to increase the number of surface active sites available to generate OH radicals and to improve the interaction with the pollutant [14,15]. Recently, clays are receiving increasing attention as supports of TiO_2-based photocatalysts, as they are able to adsorb organic substances on their external surfaces as well as within their interlamellar spaces [16–24].

In this work, a natural purified São Simão's (Brazil) kaolinite was used to synthesize a new composite with titanium(IV) isopropoxide via the hydrolytic sol-gel route; the materials obtained by thermal treatment at various temperatures were evaluated for the degradation of the two dyes, Methylene Blue (MB) and Methyl Orange II (MOII).

2. Experimental

2.1. Purification of kaolin

The kaolin employed in this work came from the municipality of São Simão, State of São Paulo, Brazil, and was kindly supplied by the mining company Darcy R.O. Silva & Cia. It was purified according to the dispersion–decantation method [25], which yielded very pure kaolinite (see Figure 1), used for further intercalation experiments. In the formulation of the intercalated and grafted compounds, purified kaolinite is abbreviated as *Ka*. All other chemicals were from Sigma-Aldrich, Acros Organics and TiO_2 Degussa P25 and were used as received, without further purification.

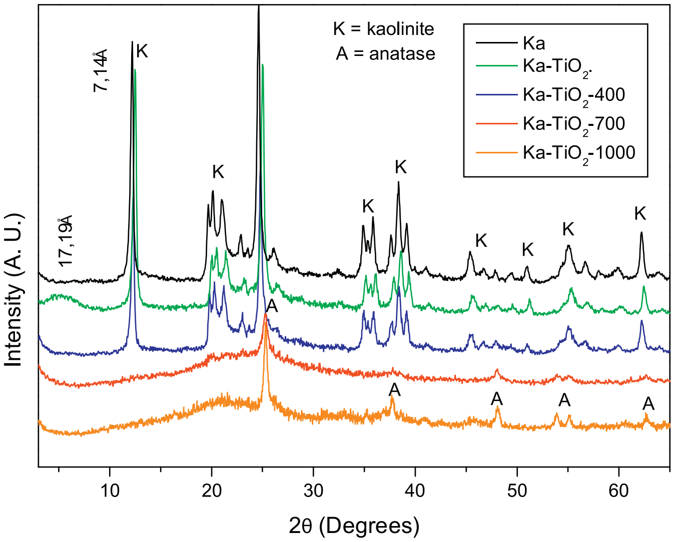

Figure 1. Powder X-ray diffraction patterns of purified kaolinite, and the solids obtained after reaction with Ti(IV) isoproxide and calcination.

2.2. Synthesis of photocatalysts

Kaolinite (10.0 g), ethanol (200 cm^3), acetic acid (1 cm^3), and Ti(IV) isopropoxide (2.0 cm^3) were mixed in a beaker, and kept under stirring for 24 h at room temperature. The mixture was washed with distilled water and centrifuged several times, to remove the un-anchored alkoxide from the surface of the clay. The solid was dried at 100 °C for 24 h and split into four fractions, one was used as dried, and the other three were heated in static air at 400, 700, and 1000 °C for 24 h. These temperatures were chosen based on the results from thermal analysis (see Section 3.1.). The sol-gel steps are presented in Figure 2. The expected kaolinite/TiO_2 mass ratio was 1.58, that is very close to the final formula of the nanocomposites, assuming that total hydrolysis and condensation of the alkoxide occurred.

2.3. Characterization techniques

The powder X-ray diffraction (PXRD) diagrams of the solids were acquired in a Siemens D-500 diffractometer operating at 40 kV and 30 mA, using filtered Cu Kα radiation and varying 2θ angle from 2° to 65°. All the analyses were processed at a scan speed of 2° 2θ/min.

The thermal analyses (TG/DSC) were carried out in a TA Instruments SDT Q600 simultaneous DSC-TGA thermal analyzer, from 25 to 1100 °C, at a heating rate of 10 °C/min and under an air flow of 100 cm^3/min.

The Fourier transform infrared absorption spectra were obtained in a Perkin-Elmer Spectrum-One spectrophotometer, using the KBr pellet technique.

Nitrogen adsorption-desorption was carried out at -196 °C using a static volumetric apparatus (Micromeritics ASAP 2020 adsorption analyzer). Prior to the adsorption measurements, the sample (ca. 0.2 g) was outgassed at 120 °C for 24 h under a vacuum better than 0.1 Pa.

Scanning electron microscopy (SEM) was performed using a JEOL microscope (model JSM5610LV). A drop of powder suspension was deposited on a copper grid and the selected area recorded.

The point of zero charge (pH_{ZPC}) was determined by using 5 flasks with 25 mg of each sample, adding aliquots of 1.25, 2.5, 5, 7.5 and 10 cm^3 of 0.1 mol/dm^3 HCl and other 5 with equal volumes