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Discoloration and degradation of textile dye aqueous solutions with titanium oxide catalysts obtained by the sol–gel method

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Abstract

In this work, we report the preparation of TiO_2 catalysts by the sol–gel method from two different alkoxide precursors: titanium (IV) tetrabutoxy and titanium (IV) isopropoxide, called TiO_2-TBOTC and TiO_2-IPOTC, respectively. The catalysts were used in the photocatalytic discoloration and degradation of textile dye C.I. reactive orange-122 aqueous solutions. TiO_2-TBOTC discolored dye solutions 100% in 40 min with maximum TOC reduction of 65.8%, in contrast to TiO_2-IPOTC, which required 20 min of reaction and yielded maximum TOC reduction of 27.7%. Photocatalyst TiO_2-TBOTC is more efficient than TiO_2-IPOTC.

Keywords: Sol–gel; Titania; Reactive orange-122; Photocatalysis; Discoloration; Degradation

1. Introduction

Recently, environmental contamination has been pointed as one of the greatest problems of modern society, mainly due to the population explosion and the increased industrial activity [1–5].

In this scenario, the textile industry stands out as it produces a large amount of effluents which can cause serious environmental problems as they contain colored compounds resulting from dyes unfixed to fibers during the dyeing process [6–12]. Dyes make up an abundant class of organic compounds characterized by the presence of unsaturated groups (chromophores) such as $-C{=}C-$,$-N{=}N-$ and $-C{\equiv}N-$, which are responsible for the dye colors, and of functional groups responsible for their fixation to fibers as for example, $-NH_2$, $-OH$, $-COOH$ and $-SO_3H$ [13].

The chromophores more often used in dye synthesis belong to the azo dyes class ($-N{=}N-$) [8,9]. Among them, reactive dyes are extensively used, fundamentally due to the capacity of their reactive groups to bind to textile fibers by covalent bonding. This favorable characteristic facilitates their interaction with fibers, enhances fixation rate, and reduces energy consumption [14,15].

Due to the environmental impact of dye-containing effluents, new technologies have been researched for either their degradation or immobilization such as heterogeneous photocatalysis, which belongs to advanced oxidation processes (AOP) [2,16]. This emerging destructive technology ends up leading to the total mineralization of organic pollutants to CO_2 and H_2O [9–11,17,18] with the use of semiconductor catalysts such as titanium dioxide [7,19]. TiO_2 is the most studied semiconductor mainly due to its high photochemical stability in a broad pH range, its low cost, and its nontoxicity [9,17,20].

Commercial titania P25 of Degussa (surface area = $50\ m^2\ g^{-1}$) has been widely used as a catalyst in the photodegradation of dyes [19,20–23]; however, until the moment, no work has reported the production of titania by sol–gel method

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in similar studies. With this purpose two TiO_2 catalysts were synthesized by the sol–gel method and applied to the photodegradation of the textile dye C.I. reactive orange-122. Information on the chemical structure of this dye is not available in current literature, presumably because of commercial confidentiality. It is known that this bi-functional dye has monochlorotriazine and vinylsulphone groups [24]. In the only study found in literature involving the photodegradation of C.I. reactive orange-122, the authors used laccase immobilized on silica chemically modified with imidazol groups as a catalyst [15].

2. Experimental

2.1. Catalysts preparation

In all experiments, chemicals of analytical grade and double quartz distilled water (resistivity ∼18 MΩ cm) were used.

TiO_2 catalysts were prepared by sol–gel method using two different precursors according to the procedure described below.

2.1.1. Synthesis of TiO_2 from titanium (IV) tetrabutoxy (TBOT)

TiO_2 was prepared using the molar ratio $n_{\mathrm{water}}:n_{\mathrm{alkoxide}}:n_{\mathrm{acid}} = 4:1:0.08$. Two solutions were prepared: first, titanium (IV) tetrabutoxy (TBOT) was dissolved in methanol under nitrogen atmosphere; second, HNO_3 (65%), was dissolved in doubly distilled water and methanol. The two solutions were homogenized separately and stirred vigorously for 10 min. After homogenization of both solutions, under nitrogen atmosphere and stirring (1000 rpm), the second solution was added to the TBOT solution via a dropping funnel. The as-prepared, translucent gel (gelation time 3 min) was aged 15 h at ambient temperature [25]. Finally, the product was dried between 40 and 70 °C in rotating evaporator for 2 h and later under high vacuum ($\sim 10^{-3}$ atm.) at 80 °C for 8 h. The titanium oxide thus obtained will hence be referred to as TiO_2-TBOTC. Letter C indicates that the material was calcined in a muffle at 400 °C for 5 h.

2.1.2. Synthesis of TiO_2 from titanium (IV) isopropoxide (IPOT)

In this case, TiO_2 oxide was prepared with molar ratio $n_{\mathrm{water}}:n_{\mathrm{alkoxide}}:n_{\mathrm{acid}} = 2.4:1:0.08$. Two solutions were prepared: first, titanium (IV) isopropoxide (IPOT) was dissolved in ethanol under nitrogen atmosphere; second, HNO_3 (65%) was dissolved in doubly distilled water and ethanol. The two solutions were homogenized separately and stirred vigorously for 10 min. After homogenization of both solutions, under nitrogen atmosphere, the second solution was added to the IPOT solution via a dropping funnel. A firm, clear gel formed instantly (∼15 s). The gel was covered and aged overnight, after which the gel pieces were further rinsed 12 times with an acetone:water mixture (1:1) (about three rinses per day) to remove byproducts and residual reagents [26]. Finally, the product was dried and calcined similar to TiO_2-TBOTC. The titanium oxide thus obtained will hence be referred to as TiO_2-IPOTC.

The reagent amounts and the preparation conditions of the titanium oxides are summarized in Table 1.

2.2. Materials' characterization

2.2.1. Specific surface area (S_o), average pore volume (V_p) and average pore diameter (d_p)

Specific surface area (S_o), average pore volume (V_p), and average pore diameter (d_p) of all the obtained materials were determined in equipment Quantachrome Corporation, model Nova 1200. S_o was determined by the Brunauer, Emmett, and Teller (B.E.T) method after sample activation at 150 °C under vacuum for 2 h.

2.2.2. Scanning electron microscopy (SEM)

Micrographs of the materials were obtained in a Scanning Electron Microscope Shimadzu, model-SS 550. The samples were fixed to the surface of a double-face adhesive tape and coated with a gold layer. Acceleration tension was 15 kV.

2.2.3. Photocatalytic tests

The dye C.I. reactive orange-122 (monochlorotriazine and vinylsulphone) was purchased from Chemical Texpal Ltda, located in Valinhos (São Paulo, Brazil). Fig. 1 illustrates the reactor used in the dye photodegradation study. The system contains a 300-mL glass cylindrical photochemical reactor.

In the dye discoloration test reactions with each catalyst, TiO_2-TBOTC and TiO_2-IPOTC, suspensions consisting of 150 mL of 10 mg L^{-1} aqueous solution of reactive orange-122 (pH 6.0) and 50 mg of catalysts were irradiated with a commercial 300-W tungsten halogen lamp (Osram R7S) placed in a jacket immersed in the reaction suspension. The mixtures were magnetically stirred and maintained at 20 ± 1 °C with water refrigeration. Reaction time ranged from 5 to 60 min. After each experiment, the samples were filtered through a Millipore disk with 47 mm diameter and 0.45 μm porosity. The percentage discoloration of the solutions as a function of time was determined with UV/vis spectrophotometer Varian, model Cary-50 at 486 nm. The dye color intensity in the solutions remained unchanged and was measured as absorbance; concentrations were established by calibration curve method. The discoloration percentages were calculated by using the equation given below:

$$\mathrm{Discoloration}\,(\%) = \frac{C_0 - C}{C_0} \times 100$$

where C_0 and C are the initial and the after-treatment dye concentrations in mg L^{-1}, respectively.

Table 1
Reagent amounts and preparation conditions of titanium oxides

Catalysts	Reagents					
	TBOT (mol)	IPOT (mol)	HNO_3 (mmol)	H_2O (mol)	MeOH (mL)	EtOH (mL)
TiO_2-TBOTC	0.0880	–	7.04	0.352	141	–
TiO_2-IPOTC	–	0.0712	5.70	0.171	–	64.3

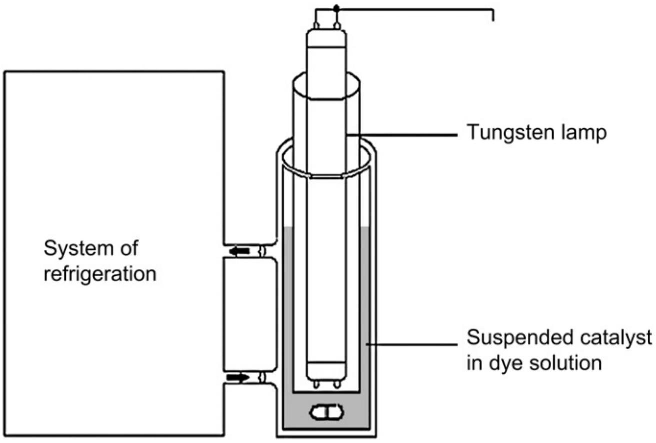

Fig. 1. Schematic diagram of the photocatalytic reactor.

Fig. 2 shows the dye absorption spectrum. The maximum absorption for reactive orange-122, 486 nm, was used in quantitative analysis, as already mentioned.

Photodegradation was evaluated by monitoring the reduction of total organic carbon (TOC) with a TOC-5000 Shimadzu Total Organic Carbon Analyzer. To prevent contamination of the solutions with microorganism, which could mask TOC results, all materials used in the photodegradation experiments were submitted to autoclave. The solutions obtained after each catalysis reaction were kept in freezer for 24 h at most before TOC measurements.

3. Results and discussion

3.1. Materials' characterization

3.1.1. Specific surface area (S_o), average pore volume (V_p) and average pore diameter (d_p)

The results of specific surface area (S_o), average pore volume (V_p) and average pore diameter (d_p) of the synthesized catalysts are presented in Table 2. These values indicate porous structures. The S_o values were high if compared with literature data. For example, the superficial area of Merck's TiO_2 is $10\ m^2\ g^{-1}$ [27]. Catalysts TiO_2-TBOTC and TiO_2-IPOTC (Fig. 3) showed a type IV isotherm with a type H2 desorption hysteresis according to IUPAC classification, which is characteristic of mesoporous materials (20–500 Å) [25,28].

Table 2
S_o, V_p and d_p values of the synthesized catalysts

Catalysts	S_o ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	d_p (nm)
TiO_2-TBOTC	55.5	7.33×10^{-2}	5.29
TiO_2-IPOTC	81.6	7.90×10^{-2}	3.87

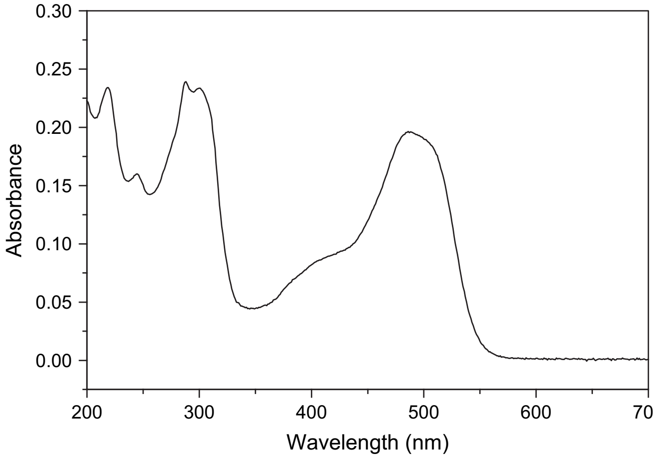

Fig. 2. UV/vis spectrum of $10\ mg\ L^{-1}$ aqueous solution of reactive orange-122.

3.1.2. Scanning electron microscopy (SEM)

Fig. 4 shows scanning electron micrographs of the materials calcined at 400 °C. It can be observed that the materials present a porous structure, which confirms specific surface area results. This morphology is desirable for catalytic applications.

3.1.3. Photocatalytic tests

3.1.3.1. Photodegradation of reactive orange-122 dye. Reactive orange-122 dye was degraded in the presence of TiO_2-TBOTC and TiO_2-IPOTC catalysts using a 300-W tungsten lamp. Neither the experiment without irradiation nor the one without catalysts showed significant degradation.

Fig. 5 shows the discoloration results obtained for the dye solution by using TiO_2-TBOTC and TiO_2-IPOTC. It was observed that TiO_2-IPOTC afforded 100% dye discoloration in 15 min whereas TiO_2-TBOTC afforded only 40% in 15 min and 100% in 40 min.

TOC results of dye solutions degraded with TiO_2-TBOTC and TiO_2-IPOTC are shown in Fig. 6. A reduction of 65.8% in TOC was observed for contact time shorter than 60 min with TiO_2-TBOTC, whereas with TiO_2-IPOTC, the maximum mineralization obtained was 27.7% in 60 min. From these results (Figs. 5 and 6), it can be observed that the solution discolors more quickly with TiO_2-IPOTC than with TiO_2-TBOTC despite the larger amount of organic substance in the dye solution. This can be associated to the material

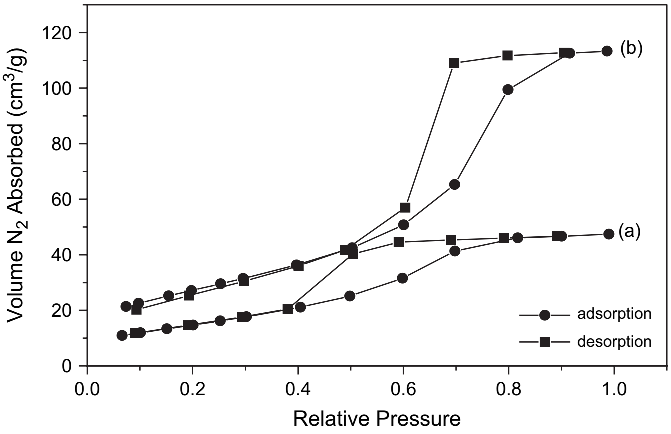

Fig. 3. N_2 adsorption–desorption isotherms for the TiO_2-TBOTC (a) and TiO_2-IPOTC (b) catalysts.

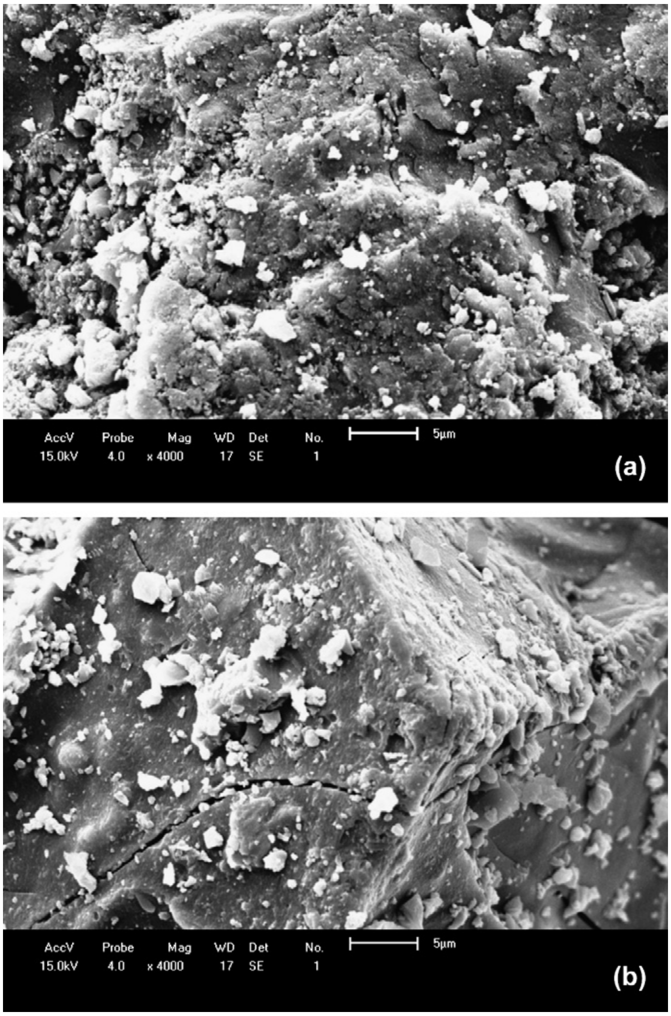

Fig. 4. Scanning electron micrographs of TiO_2-TBOTC (a) (magnification: 4000×) and TiO_2-IPOTC (b) (increase: 4000×).

preparation process. In the synthesis processes, TiO_2-IPOTC gel is formed within 15 s and the TiO_2-TBOTC gel within 180 s. The literature reports on the regimes in which sols, precipitates, or monolithic gels are formed based on systematic studies of the effects of hydrolysis level, alkoxide concentration, and alkoxide type. The addition of acid during synthesis accelerates hydrolysis and decelerates condensation, resulting in increased gelation time. Upon modification of the alkoxide precursors, the hydrolysis rate decreases in the order: ethoxide > butoxide > isopropoxide. Hydrolysis rate decreases with increasing steric hindrance of the alkoxide precursors, which is a common property of many other alkoxide systems. This behavior implies that small, linear, easily hydrolysable alkoxide precursors together with an acidic sol–gel medium, seems to fulfill the requirements for forced hydrolysis. Consequently, nucleation dominates over particle growth, which leads to high dispersion [25,29]. As already mentioned, an increase in gelation time favors the formation of highly particled materials, which increases their catalytic properties. This is in accordance with the more efficient degradation of the dye by TiO_2-TBOTC than by TiO_2-IPOTC.

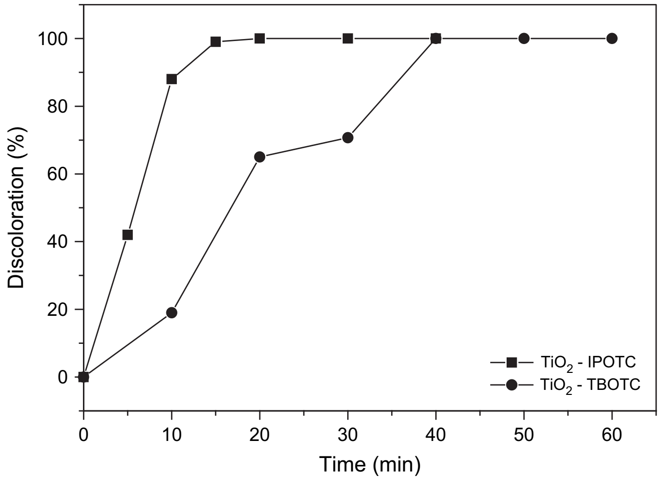

Fig. 5. Discoloration (%) of 150 mL of 10 mg L^{-1} aqueous solution of reactive orange-122 with TiO_2-TBOTC and TiO_2-IPOTC (300-W lamp).

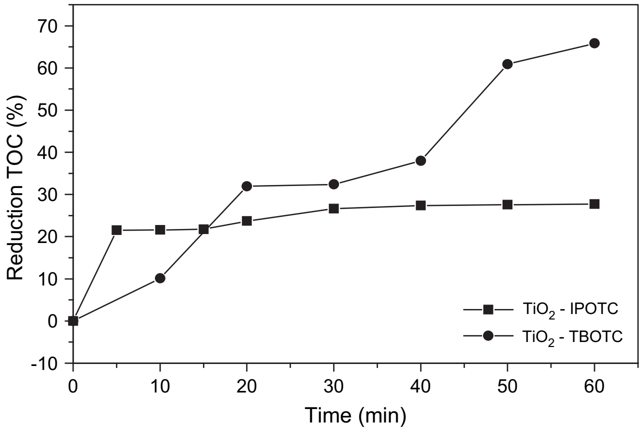

Fig. 6. Reduction of TOC of 150 mL of 10 mg L^{-1} aqueous solution of reactive orange-122 with TiO_2-TBOTC and TiO_2-IPOTC (300-W lamp).

4. Conclusions

This work demonstrated that catalysts TiO_2-TBOTC and TiO_2-IPOTC were successfully prepared by the sol–gel process. Specific surface area and SEM micrograph analysis showed that porous and particled materials were obtained, supporting the use of the sol–gel method to produce materials with enhanced catalytic properties.

The photocatalytic tests accomplished showed the high efficiency of TiO_2-TBOTC in the discoloration and mineralization of textile dye reactive orange-122.

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