

Investigations on solar degradation of acid orange 7 (C.I. 15510) in textile wastewater with micro- and nanosized titanium dioxide*

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Received 08.05.2010

Abstract

Catalytic activation is necessary for solar photodegradation of dyes in textile industry wastewater treatment, and TiO₂ could be used for this purpose. Changing the size of titanium oxide and doping it with metals like Sn(IV) can also improve its catalytic behavior. The results of this study showed that solar degradation of acid orange 7 in the presence of nanosized particles as a catalyst is possible within 1 h of radiation.

Key Words: Azo dyes, nanosized particulates, Sn-doped TiO₂, solar irradiation, textile wastewater

Introduction

Textile wastewater treatment is still a great environmental problem today. Azo dyes represent the largest class of textile dyes in industrial use, accounting for 50% of all commercial dyes (Rafols and Barcelo, 1997). Due to the large number of aromatic groups present in these molecules and their stabilities, most azo dyes are nonbiodegradable, and conventional treatment methods are found to be ineffective for the decolorization and degradation processes (Liakou et al., 1997).

Chemical processes such as chlorination and ozonation are the most frequently used methods for removal of the textile dyes from wastewater. Others are flocculation, reverse osmosis, and adsorption onto activated carbon. However, these processes only transfer the contaminants from one phase to another, and further treatments are required. Namely, the advanced oxidation processes have been extensively investigated (Guillard et al., 2003). Among these processes, heterogeneous photocatalysis is an emerging destructive technology leading to total mineralization of most of organic pollutants. In most cases, the degradation is conducted for dissolved compounds in water with ultraviolet-illuminated TiO₂. Among various semiconducting materials, most attention has been given to TiO₂ because of its high photocatalytic activity, resistance to photocorrosion, low cost, nontoxicity, and favorable band gap energy. That is why TiO₂ has a real advantage in photocatalytic

*Paper presented at the 6th Nanoscience and Nanotechnology Conference (NanoTRVI), İzmir, Turkey, June 15-18, 2010.

activity (Nagaveni et al., 2004). Another important advantage is the fact that the process can be powered by natural sunlight (Augugliaro et al., 2002), thus significantly reducing the electrical power requirements and operating costs. It should be noted that with visible light, the photodegradation processes proceed by different routes, involving, for example, electron transfer from the excited state of the dye molecules adsorbed on the TiO_2 surface into the conduction band.

The aim of the present study was to investigate the photocatalytic activity of TiO_2 for degradation of acid orange 7 dye (AO7), which is frequently used in the textile industry. The rate constant of the photocatalytic reactions was determined by simulation of solar light. For this purpose, TiO_2 and metal-doped TiO_2 were used as catalysts.

Materials and Methods

Commercial azo dye AO7 ($\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_4\text{SNa}$) was obtained from the local textile industry. TiO_2 was obtained from Merck (99%). Nanosized Sn-doped TiO_2 ($(\text{Ti}, \text{Sn})\text{O}_2$) was synthesized by sol-gel technique and used without any purification. Double distilled water was supplied by Millipore Corporation's Milli-Q distillation unit. Model textile wastewater was prepared using AO7 and some auxiliary textile chemicals (Rocogal PAA and Rocoacid GBK).

Dye concentration was measured by a Cary 5000 UV-VIS spectrophotometer (Varian). An ATAC lab-dye HT10 machine was used to prepare model textile wastewater. Photodegradation studies were performed with a SUNTEST XLS+ (Atlas) apparatus equipped with a 2.2 kW xenon lamp with an effect of 346 Wm^{-2} . FTIR spectra were examined using a Nicolet 6700 spectrometer with 0.09 cm^{-1} optical resolution and 15 scan velocities. The scanning electron microscopy (SEM) was performed on an EVO 40 (Carl Zeiss) with a secondary electron contrast mode. To avoid charging effects, the deposited samples were subsequently coated with a 20-nm gold layer (Bal-Tec SDC 005).

Color removal in the samples was determined using absorbance value $\lambda_{\text{max}} = 485 \text{ nm}$ for AO7. Degradation was quantified by detecting final dye concentration in the samples before, during, and after the visible irradiation. Samples were filtered before analysis using a $0.45\text{-}\mu\text{m}$ Millipore PVDF filter. All sample preparation details for FTIR spectrometry and SEM analysis were described by Aksu (2008).

Results and Discussion

The hydroxy azo dyes underwent azo-hydrazone tautomerism (Figure 1). The spectrum of AO7 in the visible region exhibited a main band with a maximum at 485 nm and a shoulder at 430 nm. In the aqueous phase, 2

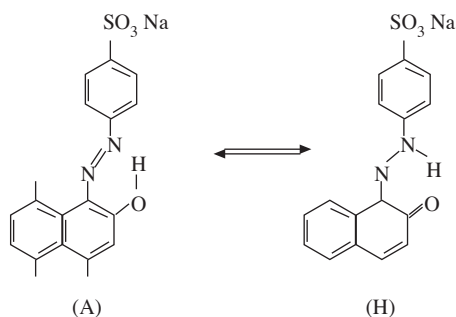


Figure 1. Acid orange 7: A) azo form, H) hydrazone form.

forms of AO7 were in equilibrium; the band at 485 nm revealed the presence of the hydrazone form, whereas the shoulder at 430 nm indicated the presence of the azo form (Liakou et al., 1997).

The second derivative ($d^2A/d\lambda^2$) spectrum of AO7 is shown in Figure 2. The azo form of this dye typically absorbs at 400-440 nm, and hydrazone at 475-510 nm (Oakes and Gratton, 1998).

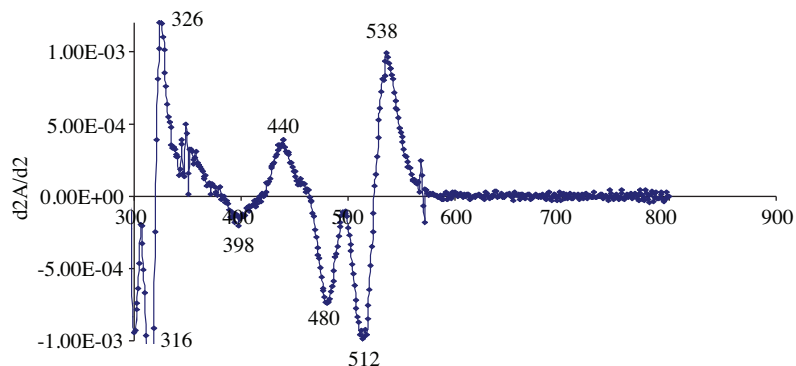


Figure 2. Second derivative ($d^2A/d\lambda^2$) spectra of AO7 at a concentration of 5.71×10^{-5} M.

The effect of light intensity on AO7 degradation is presented in Figure 3. It was observed that an increase in light intensity led to an increase in the degradation rate. There are more photons per unit time and unit area at higher light intensities, and thus the change of photon activation on the dye also increases.

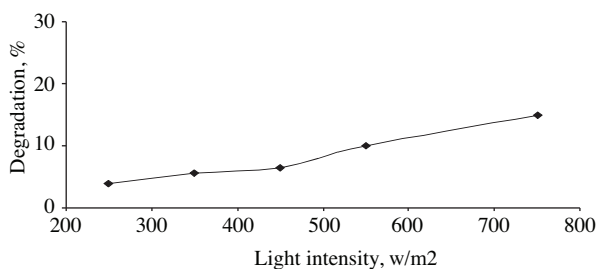


Figure 3. Effect of light intensity and photodegradation of AO7: $[AO7] = 8.57 \times 10^{-5}$ M, irradiation time = 10 min.

Van't Hoff (Equation 1) and half-life time ($t_{1/2}$) method (Equation 2) equations were used for identification of the reaction kinetics order, assuming that k_A and t were the reaction rate constant and irradiation time, respectively. It was found that the degradation reaction of AO7 obeys second order reaction kinetics.

$$N = \ln[-dA/dt]_2 - \ln[-dA/dt]_1 / \ln[A]_2 - \ln[A]_1 \quad (1)$$

$$t_{1/2} = 1/k_A \times a \quad (2)$$

TiO₂ and (Ti, Sn)O₂ catalysts were used for degradation of AO7 and textile wastewater using the solar light source. All results for the degradation percentage of AO7 within 1 h are outlined in the Table.

Using FTIR spectroscopy, it is possible to obtain more information about the type of coordination of a ligand with a metallic ion (Bauer et al., 1999). The FTIR spectra of AO7 and AO7-TiO₂ are presented in Figure 4. A notable difference could be observed in bands at 1193, 1280, and 1305 cm⁻¹ in the AO7-TiO₂

spectra, which were not present in the spectrum of TiO_2 . Bauer et al. (1999) suggested that the 1280 cm^{-1} band corresponds to the interaction that leads to a charge transfer forming the carbonyl group to the Ti(IV) electron acceptor center on the TiO_2 surface. Bourikas et al. (2005) suggested that the 1198 and 1304 cm^{-1} bands provide strong evidence that the AO7 molecule adsorbs on the titania surface via the 2 oxygen atoms of the sulfonate group of the dye (Figure 5). Our results are in very good agreement with the spectroscopic observations, as well as with the results of Bauer and Bourikas proposing the same structure for adsorbed AO7.

Table. Summary of the reaction rate constants for degradation of the samples.

Sample	K	$t_{1/2}$ (min)	Degradation (%)
5.71×10^{-5} M AO7	0.00012	$1.50\text{E} + 08$	7
Textile wastewater	0.00010	$1.75\text{E} + 08$	15
5.71×10^{-5} M AO7 + 0.02 g TiO_2	0.0147	47	52
Textile wastewater + 0.02 g TiO_2	0.00010	$1.75\text{E} + 08$	15
Textile wastewater + 0.02 g $(\text{Ti}, \text{Sn})\text{O}_2$	0.008	87	35

SEM was employed to characterize the surface morphology of the catalyst $(\text{Ti}, \text{Sn})\text{O}_2$. The nano and micro particle sizes of the catalyst are comparable (Figure 6).

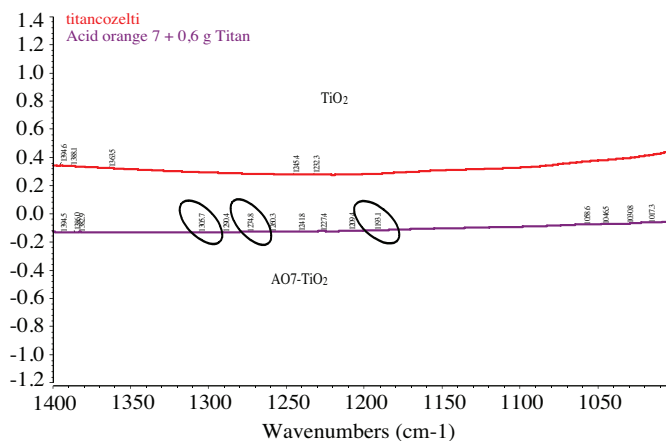


Figure 4. FTIR spectra of AO7 and AO7- TiO_2 .

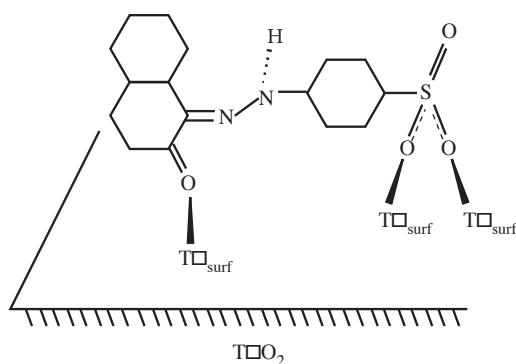


Figure 5. Proposed adsorption model of AO7 on the surface of TiO_2 (Bourikas et al., 2005).

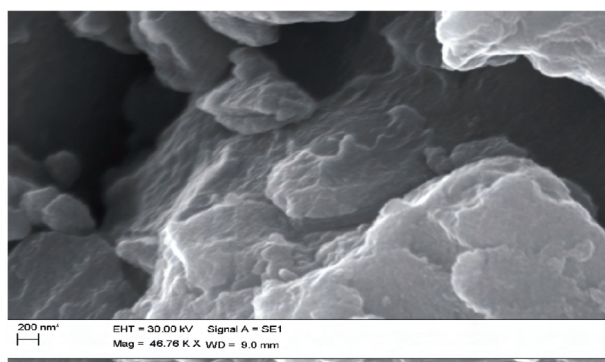


Figure 6. SEM photo image of $(\text{Ti}, \text{Sn})\text{O}_2$.

Conclusions

Photodegradation of AO7 in an aqueous solution and textile wastewater with the catalysis of TiO₂ and (Ti, Sn)O₂ under solar light may be a solution for feasible processing of wastewater treatment. The effects of irradiation time, initial AO7 concentration, and light intensity were found to be important factors for degradation. The derivative spectroscopy in the UV-VIS region provides additional possibilities for the interpretation of absorption spectra and analysis of overlapping bands. It was suggested that the 1280 cm⁻¹ band corresponds to the interaction carbonyl group to the Ti(IV) electron acceptor center on the TiO₂ surface, and that the 1198 and 1304 cm⁻¹ bands provide strong evidence that the AO7 molecule is adsorbed on the TiO₂ surface via 2 oxygen atoms of the sulfonate group of the dye. Solar degradation of model textile wastewater with the catalysis of (Ti, Sn)O₂ may easily cause degradation in 1 h of radiation. As a result, the nanoparticle catalyst will be the future for treatment of textile wastewaters.

Acknowledgements

The authors would like to thank TÜBİTAK (İÇTAG-C, 039) and Uludağ University (AFP 2002/53) for their financial support.

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