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Removal of 2-Mercaptobenzoxazole from Water as Model of Odorous Mercaptan Compounds by a Heterogenous Photocatalytic Process Using Ag-ZnO Nanocomposite Coated Thin Film on Glass Plate

Mohammad Hossein Habibi · Reza Sheibani

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Abstract A photocatalytic process was evaluated for the removal of 2-Mercaptobenzoxazole (MBO) in wastewater. More than 90% of the MBO was removed by photocatalytic oxidation at about 3 h of irradiation time using Ag-ZnO nanocomposite thin film catalysts coated on glass by dip-coating. Ag-ZnO nanocomposite thin film was characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM). The initial concentration of MBO was 20 ppm with optimum pH value of about 8.0. This investigation will give a new insight to understanding the mercaptan photodegradation in aquatic environment.

Keywords Photodegradation · Mercaptan · Nanocomposite thin film

The pollution of the environment by sulphur compounds is always of great concern for aquatic organisms and human. MBO is widely used in industries as rubber vulcanization accelerator or corrosion inhibitor (Allaouia et al. 2010; Yang et al. 2008). Environmental Protection Agency of United States (EPA) estimates that over 450 tons of mercaptobenzothazol may be lost annually into the environment (Vogt 1988; Reddy and Quinn 1997). Other studies have proved that mercaptans are strong pollutant of aquatic compartments with great impact on human health (Yoshioka and Ose 1993; Gold et al. 1993). Biodegradation of such wastewater is considered to be problematic, probably due to the toxic effects ascribed to mercaptobenzothiazol. A few mercaptan-degrading organisms are reported and information on mercaptan degrading pathways is scare (Engels et al. 1993; Dillon et al. 1978; Gundlach et al. 1983; Ensley 1984). Advanced oxidation processes (AOPs) are used for pollutant abatement owing to the high oxidative power of the •OH radical. One of the most important AOPs used to generate •OH radicals employs the metal oxide system. It has been reported that ZnO shows better activity than TiO2 in the photodegradation of some pollutants in aqueous solutions since it can absorb more light quanta (Sakthivel et al. 2003). Recent studies have focussed on the deposition of photoactive TiO2 thin films on glass substrates (Tsoukleris et al. 2007; Choi et al. 2006; Evans and Sheel 2007; Chen and Dionysiou 2006). To the best of our knowledge, there has been no report on the photocatalytic degradation of 2-Mercaptobenzoxazole from water using Ag-ZnO thin films and nanostructures deposited by sol–gel dip-coating.

In this work, we study the treatment of wastewater and removal of odorous MBO by a heterogenous photocatalytic process using Ag-ZnO nanocomposite coated thin film on glass plate. It is concluded that nanostructure Ag-ZnO thin films show remarkable photocatalytic activity for degradation of mercaptan.

Materials and Methods

Nanocomposite Ag-ZnO thin films were deposited on square 1 mm-thick borosilicate glass substrates (75 mm × 25 mm) by sol–gel dip-coating. Nanostructure Ag-ZnO were grown on *g* glass substrates from aqueous solution according to the approach of Habibi and Sheibani (2010). Glass substrates used were pre-coated with six Ag-ZnO thin layers deposited by the sol–gel dip-coating technique. The sol was prepared using zinc acetate dehydrate (Aldrich,

M. H. Habibi (✉) · R. Sheibani
Nanotechnology Laboratory, Department of Chemistry, University of Isfahan, 81746-73441 Isfahan, I.R. Iran
e-mail: habibi@chem.ui.ac.ir

99.99%), 2-propanol and monoethanolamine (Sigma–Aldrich, ≥99.0%) as sol stabilizer. ZnO sol and heated to 60°C continuously stirred for 1 h to achieve a transparent ZnO sol then aged for 1 day. Silver nitrate was used as silver precursor, dissolved in ethanol and acetonitrile as complexing agent. The silver-zinc oxide sol was quite stable and no precipitate was observed. To prepare the film from this Ag-ZnO sol, glass plates of 15 cm^2 area and 1 mm thickness were dipped in the sol slowly then taken out with the same speed and dried in air. The dipping process was repeated for 6 times. The dried films were finally calcined at 450°C for 2 h. The phase structure of Ag-ZnO films were identified by a Brucker D8-advance X-ray diffractometer with Cu Ka radiation. The surface morphology and chemical composition of Ag-ZnO films were studied using a scanning electron microscopy (Philips XL-30 operated at 10 kV of acceleration voltage).

Glass slide coated with ZnO-Ag thin film that placed in 25 mL sample of wastewater containing 20 ppm of MBO was subjected to UV irradiation using two 8 W lamps (Philips; $\lambda = 365$ nm) placed 5 cm above the solutions. All photodegradation experiments were conducted in a batch reactor. The UV lamp was placed in a cooling silica jacket and placed in a jar containing the polluted water. The degradation process was monitored by UV–vis absorbance. All photocatalytic tests were performed at a constant stirring rate (500 rpm) at room temperature (25°C). Control experiments without UV light were also performed (the reaction system was kept in the dark).

Results and Discussion

The X-ray diffraction patterns of thin films deposited by sol–gel shows peaks for ZnO were detected with Miller indices (110), (002), (111), and (200) corresponding to Bragg angles 31.8, 34.5, 36.48 and 44.34 respectively. The diffraction peaks were indexed to the hexagonal wurtzite structure (space group P63mc) and the *d*-values calculated are in good agreement with JCPDS no. 75-1526 (Fig. 1). Thin films of Ag-ZnO were deposited on glass slides by sol–gel onto glass slides and calcined in air at 550°C. The scanning electron micrographs of films depicting the topography are shown in Fig. 2. For the pure ZnO films (Fig. 2a), it can be seen that the oxide consists of very thin and light long nano-fibers exhibiting all possible orientations, together with small grains. In contrast to the pure ZnO films, the Ag-ZnO films revealed the presence of nanometer size clusters (Fig. 2b). The film surface is well-covered without any pinholes and cracks. Such surface morphology with nanosized grains may offer increased surface area.

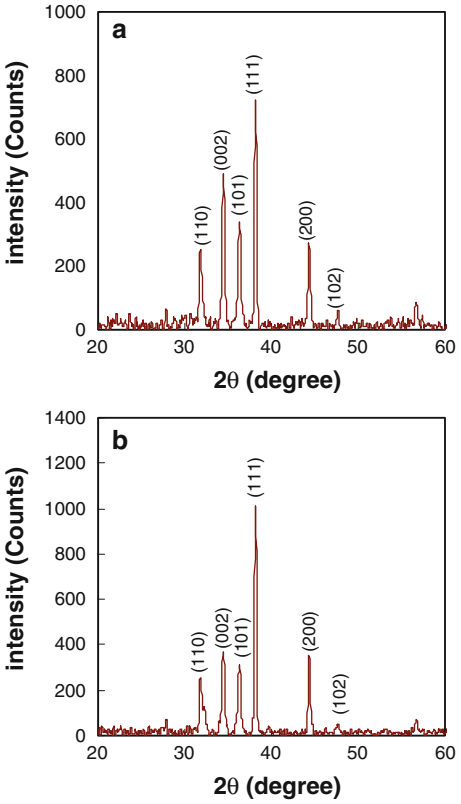

Fig. 1 XRD pattern of five layer of Ag-ZnO thin film coated on glass slides, prepared by 5 cm/min dip coating preheated in 275°C and annealed in different temp. (**a** 550°C, **b** 450°C)

Ag-ZnO thin films deposited by dip-coating technique were applied for the photodegradation of MBO in wastewater. Figure 3 represents the decay of 2-mercaptobenzoxazole with the irradiation time. Using the dip-coating catalyst, mercaptan considerably degrades with time and the concentration is reduced to more than 90% within 3 h. This indicates that the Ag-ZnO thin film photocatalyst is efficient in MBO removal. This catalytic activity difference can be explained on basis of grain size measurements. In order to observe the effect of oxygen on the photocatalytic degradation of MBO, some experiments were carried out by varying the flux of air. The temperature of experiments was maintained at 25°C by water circulation. The obtained results were shown in the Fig. 4. It can be seen that the photocatalytic degradation of MBO in the absence of air is relatively low but by increasing air flux the photocatalytic degradation of MBO was increased. In otherwords, the oxygen is necessary for photocatalytic degradation of MBO. The effect of solution pH was studied in the range of 4–10 at optimized air flux. Figure 5 demonstrates the photocatalytic degradation of MBO at different pH. The best result for photocatalytic degradation of MBO was obtained in pH range from 8 to 9. The effect of layer number of Ag-ZnO thin film on the photocatalytic

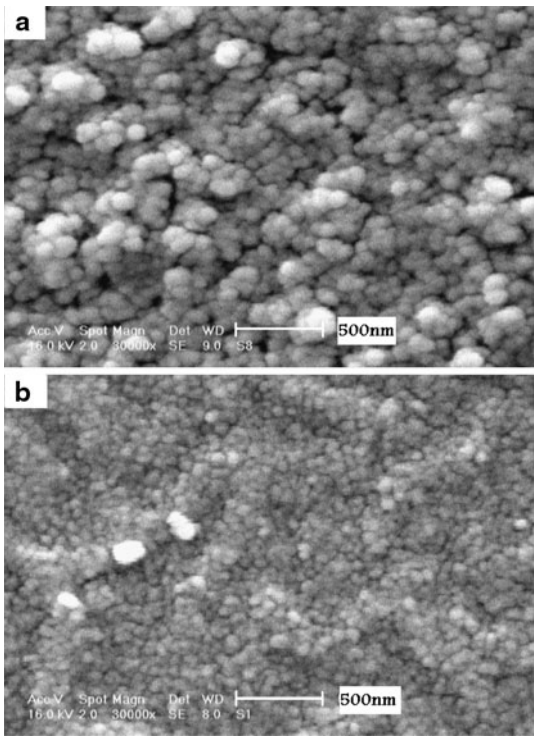

Fig. 2 SEM images of ZnO (**a**) and Ag-ZnO thin film (**b**) prepared by 5 cm/min dip coating rate, preheated in 275°C and then annealed in 550°C

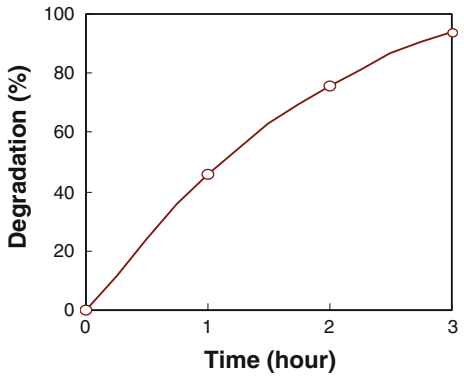

Fig. 3 Degradation profile of 2-Mercaptobenzoxazole under UV irradiation and by using 0.064% Ag-ZnO thin film and 20 mL/min air current

degradation of MBO was studied at optimized oxygen flux and solution pH and obtained results were shown in Fig. 6. The photocatalytic degradation efficiency of the MBO was increased by increasing the layer number of Ag-ZnO thin film up to 5 layer. This can be rationalized in terms of availability of active sites on Ag-ZnO surface. Results also showed that the glass plates coated with Ag-ZnO nanoparticles can be used repeatedly with small loss of efficiency (Fig. 7). This result showed that the nanostructure Ag-ZnO thin films coated on glass is photochemically stable.

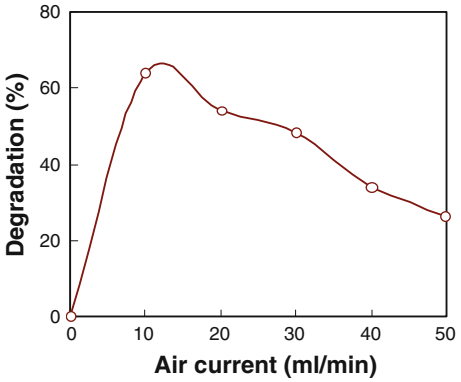

Fig. 4 Degradation profile of 2-Mercaptobenzoxazole in various air flow using 0.064% molar ratio Ag-ZnO thin films and UV irradiation

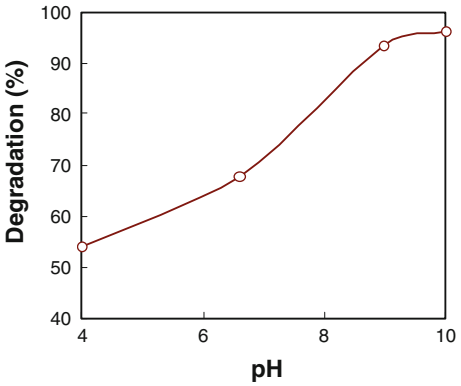

Fig. 5 Degradation profile of 2-Mercaptobenzoxazole in various solution pH using 0.064% molar ratio Ag-ZnO thin films and UV irradiation

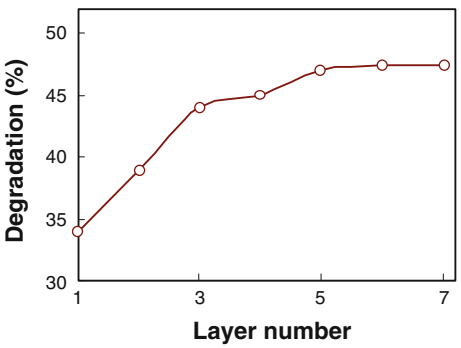

Fig. 6 Optimization layer number of 0.064% Ag-ZnO thin film for degradation of 2-Mercaptobenzoxazole after UV irradiation, and 20 mL/min air flow

Conclusion

Ag-ZnO thin films coated on glass has been observed to be an efficient photocatalyst for the degradation of odorous MBO in wastewater. The experimental results indicated that the extent of MBO degradation in wastewater by Ag-ZnO thin films was about 90%. In this regard, Ag-ZnO

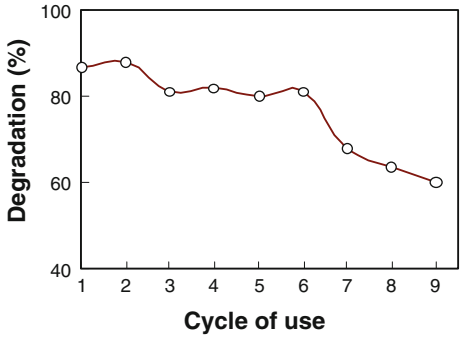

Fig. 7 Degradation reproducibility of 0.064% Ag-ZnO thin film for degradation of 2-Mercaptobenzoxazole after UV irradiation and 20 mL/min air current

thin films offer the perspective of developing a new generation of efficient photocatalysts.

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