

MANGANESE-DOPED ZINC OXIDE NANOPOWDERS
FOR PHOTOCATALYTIC DECOLORATION
OF REACTIVE BLACK 5 TEXTILE DYE

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Abstract

Zinc oxide photocatalysts doped with manganese (0.04–1 at.%) were synthesized via precipitation technique. Their characteristics were studied by X-ray diffraction (XRD) and BET analysis. The calculated mean size of the crystallites was in the range of 31–45 nm. Manganese doping of ZnO samples results in slight decrease in crystalline size. Increasing the Mn content in ZnO powders results in a lower photocatalytic activity. The pure ZnO nanopowders decolorate Reactive Black 5 dye under ultraviolet light to almost 92% for 2 h.

Key words: Mn-doped ZnO, nanopowders, ultraviolet light, photocatalysis, azo dye

Introduction. ZnO is a low-cost photocatalyst which has been a subject of increasing interest in the recent years for photodegradation of organics in aqueous solutions [1]. Zinc oxide (pure and Mn-doped) was irradiated under visible light [1–3] and ultraviolet light [2,4–6] for degradation of organic compounds. The literature data about the photocatalytic activities of ZnO powders for the degradation of organic textile dyes are very limited [2,4].

During textile manufacturing, a large quantity of toxic azo dyes with intensive colour is introduced in waste waters and respectively into the aquatic systems. It has been reported that some of the dyes are toxic [7], mutagenic [8,9] and carcinogenic [10]. Reactive Black 5 (RB5) azo dye is commonly used in the textile industry and may cause serious environmental problems. We focused this

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investigation on the photocatalytic decoloration of RB5 with ZnO powders doped with manganese, obtained by precipitation.

The doping of ZnO with manganese is often used to modify its electronic and surface properties. The manganese ions can decrease the particle size down to the nanometric scale size [6], increase the density of the oxygen vacancies and surface defects [1,2,4] as well as could change the electron structure of the semiconductor (valence band) [2]. The literature review about the effect of Mn-doping on the photocatalytic properties of ZnO powders is still confusing. The introduction of Mn decreases the photocatalytic activity of ZnO according to [2,4,5], but in some papers the effect of the Mn is quite different [6]. Because of contradictory data, we decided to investigate the photocatalytic properties of Mn-doped and undoped ZnO photocatalyst, synthesized by precipitation, for the decoloration of real textile diazo dye – Reactive Black (RB5) under ultraviolet light.

Experimental. Synthesis of the samples. Zinc oxide samples undoped and doped with Mn were prepared by precipitation method. The analytical grade zinc sulfate (heptahydrate) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, sodium carbonate Na_2CO_3 and manganese sulphate $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were used as raw materials. In a typical experiment, we dissolved 90 g Na_2CO_3 in 850 ml H_2O under heating and stirring (solution 1). 20 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were also dissolved in 140 ml H_2O under heating and stirring (solution 2). Different estimated quantities of manganese sulphate were added to solution 2 to obtain mixture of ZnO doped with 0.04, 0.20, 0.36 and 1 at.% Mn. These mixture solutions of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were added drop by drop in solution 1. After adjusting the pH value to 11, the final mixture solution was stirred under heating for 10 min. The precipitate was separated by filtration, washed several times with distilled water to pH value 7 and dried in air. For preparation of the catalysts, the corresponding precursors were heated for 3 h at 500°C in air.

The final samples doped with 0.04, 0.20, 0.36 and 1 at.% Mn were named with codes ZM1, ZM2, ZM3 and ZM4 respectively.

Analysis of the samples. Chemical composition of the samples was determined using Atomic Absorption Analysis on FAAS – SOLAAR M5 spectrometer. For preparation of standard solutions, standards produced by Titrisol, Merck, Germany were used. The concentration of reference metal content was 1000 ppm. The XRD patterns were recorded by TUR M62 diffractometer with Co K_α radiation. The observed patterns were compared with those in the JCPDS database. The particle size was determined by Scherrer's formula. The determination of the specific surface area of the samples was carried out by nitrogen adsorption at the boiling temperature of liquid nitrogen (77.4 K), using a conventional volume measuring apparatus. Before measuring the surface area, the samples were degassed at 423 K until the residual pressure became lower than 1.333×10^{-2} Pa. The nitrogen (N_2) adsorption-desorption isotherms were used to calculate the specific surface area (A_{BET}) according to BET equation.

The photocatalytic decoloration of RB5 was determined using 150 ml dye water solution with initial concentration of 20 ppm. Photocatalytic experiments were conducted with UV-lamp (Sylvania BLB, 18 W), with maximum emission at 365 nm. The process of decoloration was monitored by UV-Vis absorbance spectrophotometer BOECO S26 in the wavelength range from 200 to 800 nm. All photo catalytic tests were carried out at a constant stirring rate (400 rpm) at ambient conditions. The samples were equilibrated in dark about 30 min before irradiation. To test the photocatalytic activity of ZnO powders, sample aliquots of the suspension were taken away from the reaction vessel at regular time intervals. The powder was then separated from the aliquot by centrifugation before the UV-Vis spectrophotometric measurement of dye concentration. After that, the aliquot, together with the photocatalyst powder, was returned back to the reaction vessel. The degradation of the dye was evaluated using the following equation:

$$(1) \quad \text{Decoloration} = 100 \times \left[\frac{C_0 - C}{C_0} \right] [\%],$$

where C_0 is the initial absorbance of the dye, C is the absorbance of the dye after 120 min.

Results and discussion. The chemical composition, specific surface area (A_{BET}) and crystallite size of the pure and Mn-doped oxide samples are represented on Table 1. It illustrates that the specific surface areas of all oxides is not changed significantly for the samples ZM1–ZM4. Compared with the pure ZnO, Mn doping in ZnO samples results in a slight decrease in the crystallite size. YANG et al. [11] and STAUMAL et al. [12] have also reported that increase of Mn content in ZnO leads to a smaller particle size.

The X-ray diffraction analysis of the oxide samples (Fig. 1) illustrates the formation of wurtzite ZnO phase (JCPDS 36-1451). It can be seen from the figure that the increase of manganese concentration results in lower crystallinity of the ZnO samples.

Figure 2 presents the changes of the intensity of the absorption peak of the dye, corresponding to azo bond with time in the presence of 0.3 g ZnO. It took

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Specific surface area, manganese concentration and crystallite size of the prepared samples

Samples	Mn concentration [at.%]	A_{BET} [m^2/g]	Crystallite size [nm]
ZnO	–	22	45
ZM1	0.04	23	43
ZM2	0.20	23	31
ZM3	0.36	23	34
ZM4	1	23	34

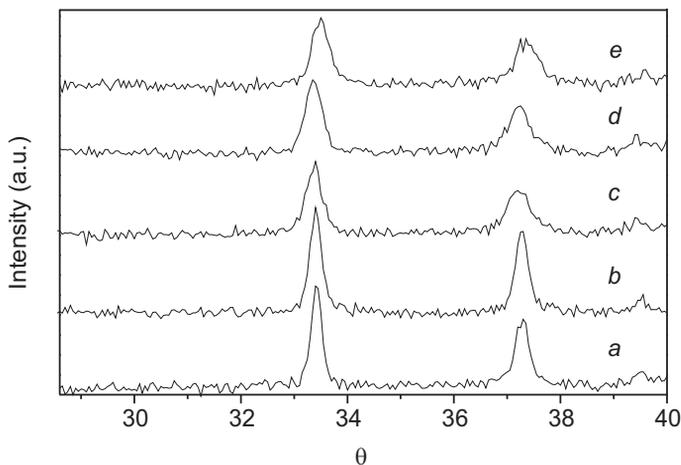


Fig. 1. XRD spectra of samples: (a) ZnO; (b) ZM1; (c) ZM2; (d) ZM3; (e) ZM4

less than 15 min for ZnO to decolorize 50% of the dye irradiated with ultraviolet light (Fig. 2). Similar activity of ZnO powders for degradation of methylene blue was observed [2].

Decoloration of the dye for Mn-doped ZnO and undoped zinc oxide catalysts after 120 min of irradiation is shown in Fig. 3. As it can be seen in Fig. 3a, for catalyst concentration of 0.08 g the decreasing of Mn content leads to en-

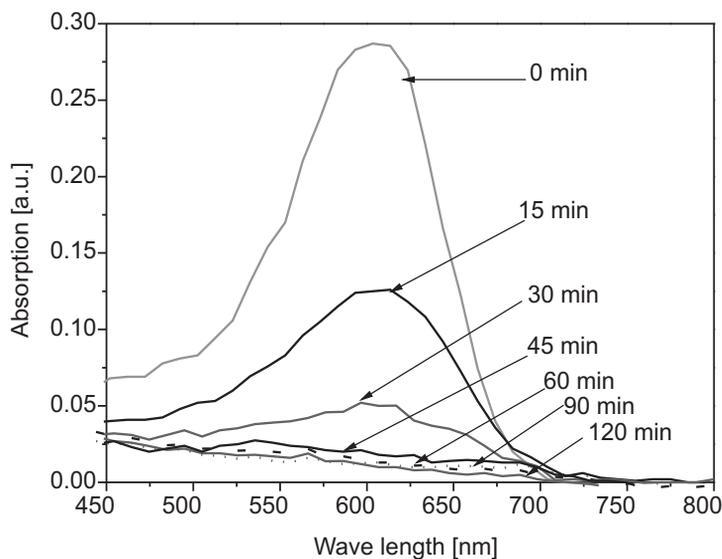


Fig. 2. Decolouration of the RB5 dye vs time (concentration of 20 ppm), proved by changes of the intensity of the peak, corresponding to azo bond (-N=N-); ZnO catalyst content is 0.3 g

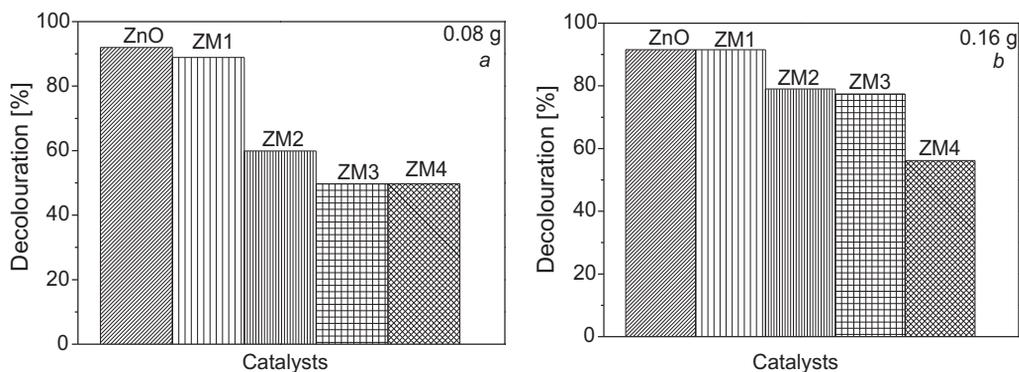


Fig. 3. Decolouration of the dye after 120 min under UV irradiation using ZnO, ZM1; ZM2; ZM3; ZM4 catalysts; content (a) 0.08 g and (b) 0.16 g

hancement of the photocatalytic activity. Similar behaviour is also registered for catalyst concentration of 0.16 g (Fig. 3b). The samples with 0.16 g ZnO exhibited higher activities than the samples containing 0.08 g catalyst. Pure ZnO samples showed the highest photocatalytic activity. According to BARICK et al. [5] manganese ions can substitute Zn ions in ZnO lattice and act as recombination centres for electrons and holes that lead to decrease of the photodegradation efficiency of Mn-doped ZnO samples. The optical transparency of $Mn_xZn_{1-x}O$ powders decreases with the increase of dopant concentration [4] and this could also be a reason for the lower activity of Mn-doped ZnO than the pure ZnO. Zinc oxide powders doped with Mn, Co and Ni decolorize to about 20% Methylene Blue dye for 90 min [5], while our doped samples are more active photocatalysts (approx. 90% decoloration for 120 min).

Conclusions. Manganese-doped ZnO nanopowders (0.04, 0.20, 0.36 and 1 at.%) were prepared by the precipitation method. The average size of the crystallites of undoped ZnO was 45 nm. The introduction of Mn in ZnO resulted in a decrease of crystallite size up to 34 nm. The experiments showed that Mn-doped ZnO powders possessed lower photocatalytic activities for Reactive Black 5 dye decolouration than the pure ZnO. The pure ZnO decolourated the azo dye to almost 92% for 2 h.

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