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The photodegradation of Methylene Blue and Methyl Orange dyes and their mixture by ZnO obtained by hydrothermally activated precipitates

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Dedicated to Acad. Bogdan Kurtev on the occasion of his 100th birth anniversary

Zinc oxide sample was obtained by precipitation followed by hydrothermal treatment. The sample was characterized by PXRD, BET method and TG-DTA methods. Thermal treatment at 170°C results in formation of well crystallized wurtzite phase. The BET analysis revealed prevailing quantity of mesopores (15 - 50 nm). The hysteresis loop of the adsorption–desorption isotherms implies the presence of cylindrical pores. The photocatalytic degradation of two types of dyes, namely hetero- polyaromatic (Methylene Blue, MB) and azoic (Methyl Orange, MO) dye and the simultaneous photodegradation of the mixture of MO and MB dyes in aqueous solution under UV irradiation have been studied. The rate of degradation of MB and the mixture MO+MB is higher than those of MO dye.

Key words: ZnO, photocatalysis; Methyl Orange; Methylene Blue

INTRODUCTION

The environmental problems associated with toxic water pollutants have attracted much attention. Wastewater from textile, paper, and some other industrial processes contain residual dyes, which are nonbiodegradable, toxic and carcinogenic. Various chemical, physical and biological processes (coagulation/flocculation, reverse osmosis, etc.) have been developed in order to remove the color from textile effluents. [1]. However, these techniques are nondestructive, since they only transfer the nonbiodegradable matter into sludge. Among advanced oxidation processes (AOPs), heterogeneous photocatalysis has appeared as an emerging destructive technology leading to the total mineralization of most organic pollutants [2].

Several semiconductors such as TiO_2, WO_3, $SrTiO_3$, Fe_2O_3 and ZnO have energies of their band gap sufficient for catalysing a wide range of redox reactions. ZnO is the most extensively studied semiconductor found from the literature [3] because it is be inexpensive, non-toxic, highly photoactive It has been found to be the most promising for photocatalytic destruction of organic pollutants.

Methyl orange is one of the representative azo dyes, which are the most important class of synthetic organic dyes used in the textile industry. The absorption spectrum shows two absorption peaks at ~ 270 and 463 nm. Methylene blue is a heterocyclic aromatic chemical compound with maximum absorption of light around 670 nm. P. Wongkalasin *et al.* have studied the photocatalytic degradation of mixtures of two azo dyes – Acid Yellow (AY) monoazo dye and Acid Black (AB) diazo dye by using a mesoporous-assembled TiO_2 nanocrystal photocatalyst [4]. According to the best of our knowledge, the photocatalytic degradation of dye mixtures by ZnO particles has been not studied yet. Therefore, in the present work we have investigated the photocatalytic degradation of single dyes MO and MB and their mixture over ZnO powders, prepared by precipitation followed by hydrothermal activation.

EXPERIMENTAL

Preparation and Characterization

Zinc acetate was dissolved in deionized water in order to obtain 0.2 M solution (sol A). Urea aqueous solution (0.6 M) was added dropwise to sol A under vigorous stirring. The pH of solution was adjusted to 7. The resultant mixture was transferred into an autoclave and subjected to hydrothermal at

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90 °C for 12 h, then the autoclave was left to cool to room temperature. The final product was washed several times and dried in oven at 100 °C Finally, the sample were thermally treated in programmable oven at 170 °C for 3 hours.

The X-ray diffraction (XRD) patterns were carried out on a Bruker D2 Phaser diffractometer using Cu Kα radiation (λ = 0.154056 nm). The specific surface area measurement and the pore size distribution were accomplished on an automated apparatus NOVA Win – CFR Quantachrom – Gas Sorption System. The calculation of the surface area was done using the BET equation, whereupon the pore size distribution, as well as the average pore diameter were evaluated by DFT method assuming a cylindrical model of the pores. The total pore volume was estimated in accordance with the rule of Gurvich at relative pressure of 0.96. The differential thermal analysis has been accomplished on a combined DTA/TG apparatus LABSYSEVO 1600 (SETARAM Company; France). Synthetic air was used as carrier gas, with flow rate of 20 ml/min, heating rate 10K/min up to 350 °C.

The photocatalytic degradation experiments were performed in an glass reactor. Single MO or MB dyes (10 ppm) and mixed bi-component MO and MB dye solutions (1:1) were freshly prepared and used for the photocatalytic activity testing. A desired amount (150 mg) of the synthesized photocatalyst was suspended in 150 ml aqueous solutions of both single and mixed dyes under various reaction conditions by using a magnetic stirrer. Prior to the photocatalytic activity testing, the continuously suspended mixture was left for 30 min in a dark. The photocatalytic reaction was started by exposing the mixture in the reactor to UV light irradiation (maximum emission at wavelength 365 nm 2.6 mW/cm^2). Feed air stream was passing continuously bubbling through the suspension saturating the contaminated water in dissolved oxygen (semi-batch reactor). The suspension was periodically withdrawn for analysis from the reactor, and the sample was then centrifuged to remove the photocatalyst powder. The course of the oxidative discoloration reaction was monitored by UV-Vis absorbance spectrophotometer UV-1600PC within the wavelength range from 200 to 800 nm. The photocatalytic decolorization efficiency D (%) was evaluated by the following equation:

$$D = (Co - C)/Co \times 100 \tag{1}$$

where Co is the initial dye concentration and C is the dye concentration after irradiation at selected time interval. Equation (1) is based on the pseudo-first order kinetics, assuming the dissolved oxygen concentration to be constant (air stream – semi-batch reactor) – in this approximation the conversion degree is function only of the dye concentration.

RESULTS AND DISCUSSION

The XRD pattern of ZnO sample after thermal treatment possesses well crystallized wurtzite phase with predominant peaks, corresponding to (100) and (101) planes (Fig. 1).The average crystallite size about 17 nm. The application of urea precipitant promotes the crystallization of wurtzite phase [5].

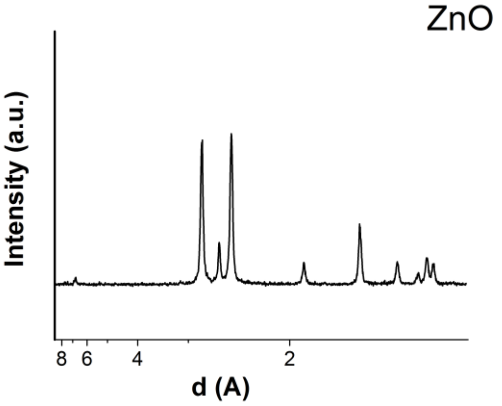

Fig. 1. X-ray diffractogram of ZnO powder.

The adsorption-desorption isotherm is identified as type IV, while the hysteresis loop is type I according to IUPAC nomenclature, revealing the type of mesoporous structure (Fig. 2). The hysteresis loop is in the relative pressure range 0.8–0.9, which is a confirmation of the existence of cylindrical pores [6]. It is also visible that the adsorption-desorption isotherm loop is closed at a relative pressures of about 0.5÷0.6, which is typical of mesoporous structures (as is the case with our ZnO sample) having prevailing cylindrical pores or close to cylindrical shape pores [7]. The inset of Fig.2 represents the pore size distribution. It is seen that the sample consist of mesopores with size within in the range 15 nm - 50 nm. Similar distributions of pores have obtained by another researchers for zinc oxide powders [8]. The specific surface area and average pore volume of ZnO are evaluated to be approximately 42 m^2/g and 0.27 cm^3/g, respectively.

Fig. 3 represents TG and DTA curves of the precipitate, dried at 100 °C. One endothermic peak is observed on the pattern with maximum at 244 °C, which corresponds to the zinc acetate decomposition. The corresponding weight loss is 21.5%. Other research groups have registered that the decomposition of zinc acetate occurred nearly this temperature [8].

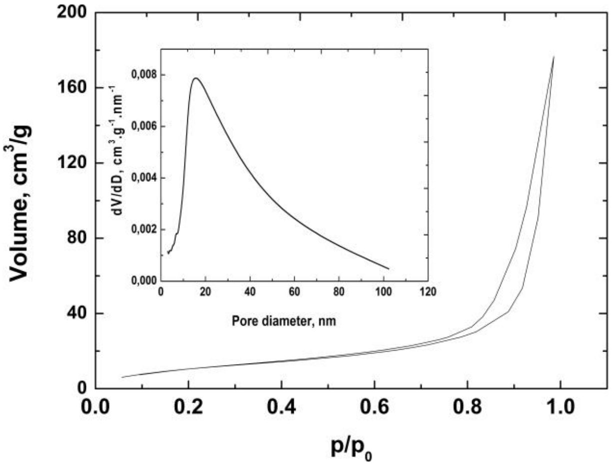

Fig. 2. Adsorption-desorption isotherm of the sample.

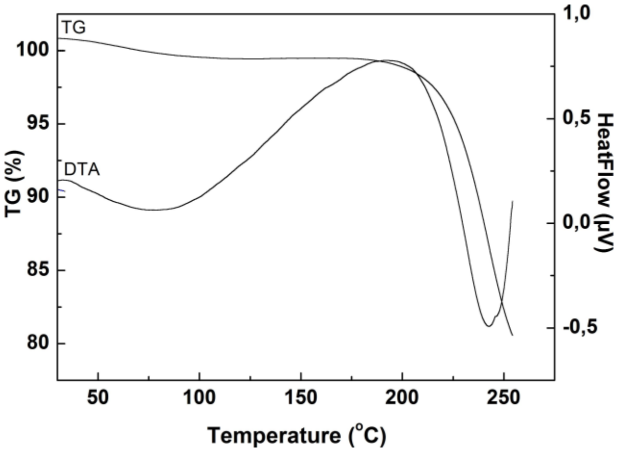

Fig. 3. DTA/TG analysis of the precipitate, dried at 100 °C.

The UV–visible spectra profiles of MO and MB and their mixture are shown comparatively in Fig. 4. From the figure, the absorption maxima of MO and MB dyes are 464 and 664 nm, respectively. It is clear that these values are not changed upon their mixing.

The photocatalytic properties of ZnO nanoparticle on decolorization of Methyl Orange were studied (Fig. 5). Extent of photocatalytic degradation was determined by the reduction in absorbance of the solution. During the first stage of photodecolorization, methylene blue was decayed with fast decolorization rate, followed by the second stage, which was characterized by a rather slow decolorization rate. Similar trend is registered for the mixture MB+MO. The slow kinetics of methylene blue decolorization in the second stage of decolorization might be due to the difficulty in converting the N-atoms of the dye into oxidized nitrogen compounds [9]. In addition the accumulated intermediates in the first stage decrease the rate of oxidative photocatalytic reaction. The experiments show also that the decolorization rate of MB is higher than those of MO (Table 1). This could be explained by the easier loss of π-electrons and disruption of the conjugated double-bond and single-bond, propagating on a larger carbon atom skeleton and better delocalization in comparison to single benzene rings in the MO dye.

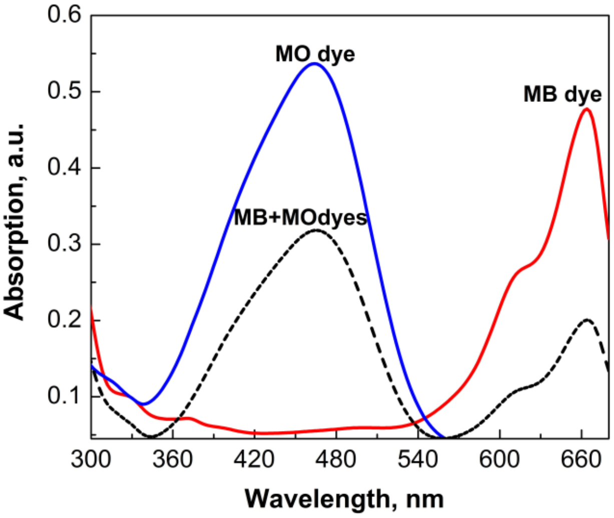

Fig. 4. Absorption spectra of MO dye, MB dye and mixture MO+MB.

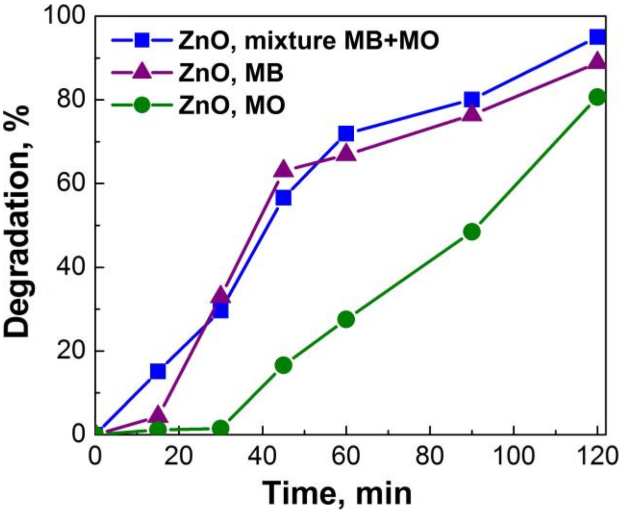

Fig. 5. Decolorization of model dye solutions over ZnO powder.

The adsorption capacity of the sample is presented in Table 1. It is seen in the Table that the photocatalytic activity does not follow the changes of the sorption properties. ZnO surface is positively charged below pH 9 based on their zpc=9.0, whereupon this anionic dye MO has stronger adsorption affinity in comparison to the cationic dye MB under our experimental conditions (pH factor 6.8). Similar results were obtained for photocatalytic degradation of Acid Brown 14 for ZnO powders [3].

Table 1. Adsorption capacity and rate constants of oxidative decolorization process of ZnO sample.

Type of solution	**Adsorption capacity, mg/g**	**k (x10^{-3}, min^{-1})**
MB dye	0.028	17.4
MO dye	0.072	9.7
Mixture MB+MO dyes, evaluated by the strongest absorption peak of MB dye	0.105	21.6

CONCLUSION

Zinc oxide sample was obtained by combination of precipitation and hydrothermal treatment. Mesopores in the range (15 - 50 nm) were registered. The large specific surface area, pore volume, greater share of mesopores and high degree of crystallinity contribute to high photocatalytic efficiency of the ZnO powders. The photocatalytic decolorization rates of Methylene Blue (MB) and the bi-component mixture MB and Methyl orange (MO) are faster than MO dye under UV irradiation. During the first stage of photodecolorization, methylene blue was decayed with fast decolorization rate, which could be explained by the easier disruption of the conjugated double-bond and single-system. Methyl orange decolorizates slower due to the difficult destruction of single benzene rings.

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ФОТОКАТАЛИТИЧНО РАЗГРАЖДАНЕ НА МЕТИЛЕНОВО СИНЬО И МЕТИЛ ОРАНЖЕВО БАГРИЛА И ТЯХНАТА СМЕС ЧРЕЗ ZnO, ПОЛУЧЕН ОТ ХИДРОТЕРМАЛНО АКТИВИРАНА УТАЙКА

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(Резюме)

Образец от цинков оксид беше получен чрез утаяване и последваща хидротермална обработка. Той бе охарактеризиран посредством прахова рентгенова дифракция, БЕТ метод и ТГ – ДТА анализи. Беше регистрирано формирането на добре кристализирала вюрцитна фаза след термичната обработка при 170 °C. С помощта на БЕТ метода беше установено наличието на преобладаващи мезопори (15-50 nm). От вида на хистерезисните примки, наблюдавани в адсорбционно – десорбционните изотерми на образеца, съдим за присъствие на цилиндрични пори. Изследвано беше фотокаталитичното разлагане на два вида багрила – хетерополиароматно (Метиленово Синьо) и азо багрило (Метил Оранжево), както и фотокаталитичното обезцветяване на багрилата при съвместното им присъствие във воден разтвор, под действие на ултравиолетова светлина. Установено беше, че скоростта на разграждане на Метиленовото синьо, както и на сместта от Метиленово синьо и Метил оранжево е по-висока, отколкото скоростта на разлагане на метил оранжевото багрило.