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Short communication

Photodegradation of methylene blue with sphere-like ZnO particles prepared via aqueous solution

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Abstract

Photocatalysis is based on generation of electron-hole pairs under UV light whose energy exceeds the band-gap energy of the semiconductor material itself. The photocatalytic degradation of methylene blue dye was carried out under UV light in the presence of zinc oxide (ZnO). ZnO particles were synthesized by a simple chemical precipitation method in which carboxymethyl inulin was used as an additive. The experiments show that synthesized sphere-like ZnO particles exhibit a remarkable photocatalytic activity.

Keywords: Photodegradation; Methylene blue; Zinc oxide; Carboxymethyl inulin

1. Introduction

The textile industry releases a variety of highly colored effluents including thiazine colorants, such as methylene blue and methylene green. Thiazines are heterocyclic compounds containing a ring of four carbons, one nitrogen and sulfur atoms [1]. Water resources are contaminated by pollution from these compounds due to inadequate and expensive wastewater treatment methods. It is important to develop advance wastewater treatment methods which are more efficient and cheaper than the traditional ones, since high doses of dyes in water are harmful to all living beings. Various wastewater treatment methods have been used to remove the organic pollutants; such as coagulation, adsorption on activated carbon, reverse osmosis, etc [2]. However, these methods are generally based on separation of the pollutants from the water, and those require the expensive post-treatment methods to regenerate the adsorbent materials [3]. In this case, advanced oxidation process (AOP) has a remarkable potential to be used as a renewable energy source [4]. In the various advanced oxidation processes, the most important one is that uses semiconductive oxides as photocatalyst to degrade the organic pollutants [5–9].

2. Experimental

Zinc nitrate hexahydrate (0.03 M) and hexamethylenetetramine (0.03 M) solutions were separately prepared using deionized water. First 3 g/L carboxymethyl inulin (CMI) biopolymer and then zinc nitrate hexahydrate solution were added into hexamethylenetetramine (HMT) solution, and the solution magnetically stirred in a 1 L glass reactor. The obtained solution was heated to 95 °C and kept at temperature for 1.5 h. When the reaction was completed, a white colored precipitate was obtained and dried at 50 °C in vacuum. For the calcination process, the powder was calcined at 700 °C for 3 h. The detailed synthesis method for ZnO powder was reported in a previous study [10].

The methylene blue ($C_{16}H_{18}N_3SCl \cdot 3\ H_2O$, MB) solution with a concentration of 5 mg/L was prepared and 300 mL of this solution was used in the experiments.

The photocatalytic activity of ZnO particles was carried out by measuring the degradation of MB dye. All photocatalytic activity experiments were done in a beaker under the UV illumination. The distance between the solution surface and the UV light source (Philips, TUV T8 1SL, 30 W lamp) was 15 cm. TUV T8 1SL emitted the light of 253.7 nm (UVC region). These type of light sources are used in professional water and air disinfection units. The concentration measurements were performed with a Specord 50 UV–vis spectrometer (Analytic Jena AG).

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Scanning Electron Microscopy (SEM) analysis was done using a SEM (JEOL JSM 6335 F). Phase identification was carried out by X-ray powder diffraction (XRD) analysis on a Phillips PANalytical X'Pert Pro PW 3040/60 powder diffractometer with Cu-Kα radiation. The specific surface area (SSA) of the synthesized samples was determined by nitrogen sorption/desorption isotherms according to multiple point BET method (COSTECH Kelvin 1042).

3. Results and discussion

In order to determine the crystalline structure and phase purity of the ZnO particles, XRD patterns were obtained for both calcinated and non-calcinated ZnO particles. Fig. 1a shows the XRD pattern of the non-calcinated particles, which compares to the ZnO phase (JCPDS no.: 00-21-1486). The pattern of the calcinated particles is identical as to peak positions of another ZnO phase (JCPDS no.: 01-79-0206).

The morphology of the ZnO particles was investigated by SEM analysis. Fig. 1b,c shows ZnO particles have a spherical shape structure containing flake-like forms. Fig. 1d,e demonstrates that flake-like forms became round shape forms by calcination at 700 °C.

The average particle diameters (D_{ave}) for each sample were calculated by measuring the particle sizes in SEM images. The particles obtained at 95 °C were in sphere form with a D_{ave} value of 4109 ± 1498 nm (Fig. 1c). The D_{ave} value of particles decreased by calcination and was found as 3506 ± 2088 nm (Fig. 1e).

Specific surface area of the particles was calculated using the BET equation over the pressure range $P/P_0 = 0.05$–0.20, where a linear relationship was maintained. The particles were degassed at 80 °C prior to analysis and the adsorption of N_2

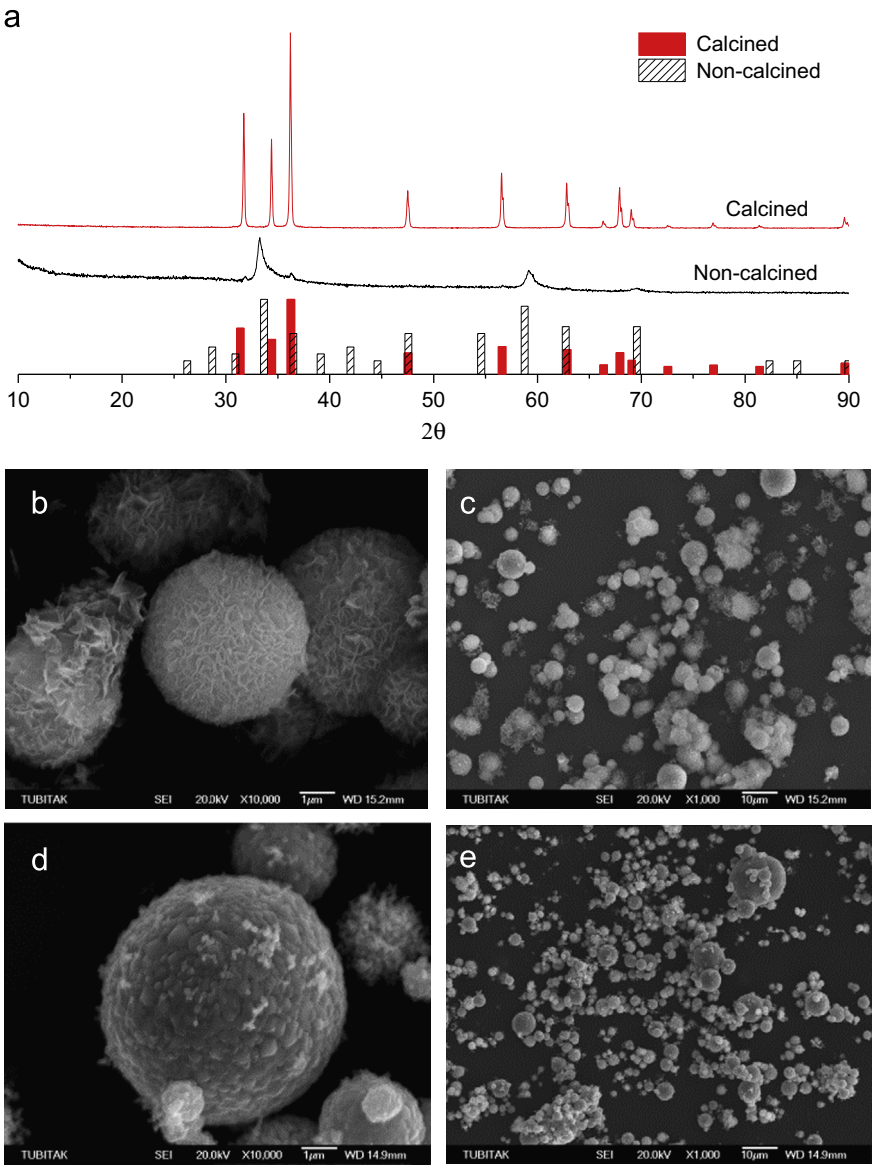

Fig. 1. XRD pattern of ZnO particles (a), SEM images of ZnO particles before (b, c) and after (d, e) calcination at 700 °C.

was measured at −196 °C. The BET surface area of the particles increased from 2.71 m^2/g to 3.14 m^2/g by calcination process. No micropore volume was detected in the measurements.

In the photocatalytic activity experiments, 0.1 g of synthesized ZnO photocatalyst was added into 5 mg/L solution of MB under constant stirring. Prior to UV illumination, the suspension was continuously stirred for half an hour to reach adsorption–desorption equilibrium with MB dye on the photocatalyst surface in the dark. Then, the dye solution was exposed to UV light illumination under constant stirring. The concentration changes of the dye solution were measured using a UV–vis spectrometer. The concentration changes of MB versus irradiation time are shown in Fig. 2.

Extrapolation of Langmuir–Hinshelwood (L–H) kinetic model, which is known to be a good model for the description of solid–gas reactions, can be modified for solid–liquid reactions [11]. According to the L–H model, the rate of a unimolecular surface reaction, R, is proportional to θ. Eqs. (1) and (2) respectively take place when the reactant is more strongly absorbed on the surface than the products.

$$R = -dC/dt = k_\tau\theta = k_\tau KC_0/(1 + KC_0 + K_sC_s) \quad (1)$$

$$R = -dC/dt = k_\tau\theta = k_\tau KC_0/(1 + KC_0) \quad (2)$$

where k_τ, is the reaction rate constant, θ is the fraction of the surface covered by the reactant, K is the adsorption coefficient of the reactant, C_0 is the initial concentration of the reactant, K_s, is the adsorption coefficient of the solvent, and C, is the concentration of the solvent. Eqs. (3) and (4) are obtained from the integration of Eqs. (1) and (2), respectively [11].

$$\ln(C_0/C) + K(C_0-C)/(1 + K_sC_s) = k_\tau Kt/(1 + K_sC_s) \quad (3)$$

$$\ln(C_0/C) + K(C_0-C) = k_\tau Kt \quad (4)$$

When C_0 is very small, Eqs. (3) and (4) reduce to Eq. (5).

$$\ln(C_0/C) = kt \quad (5)$$

The first order rate constant, k, is calculated from the graph between $\ln(C_0/C)$ and irradiation time. The degradation rate, R_D, is calculated by the following equation:

$$R_D = (C_0-C/C_0)100 \quad (6)$$

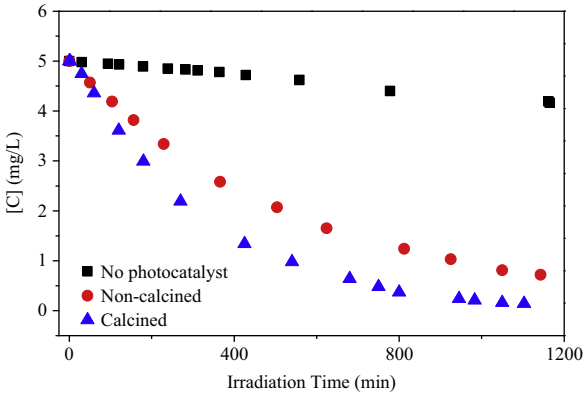

Fig. 2. The concentration changes of MB versus irradiation time.

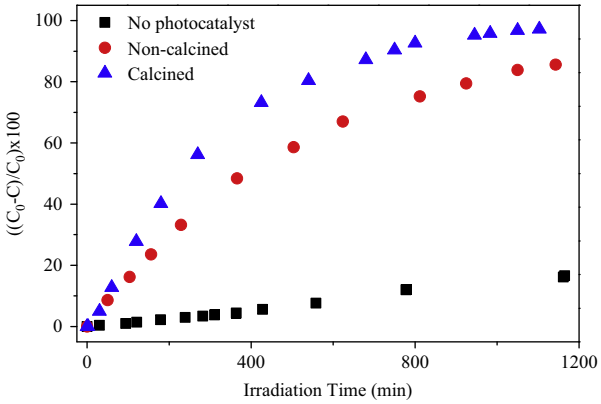

Fig. 3. The degradation efficiencies of MB dye versus irradiation time.

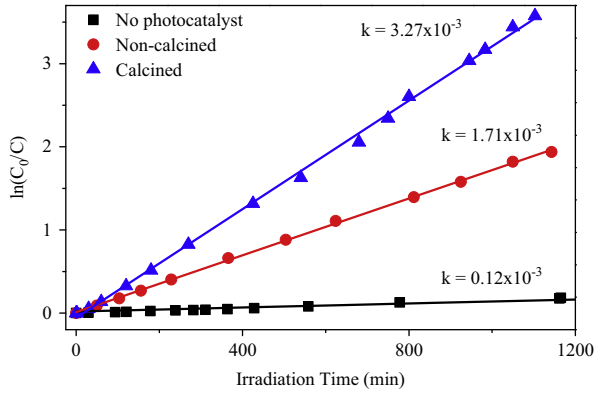

Fig. 4. First order linear transforms of disappearance of MB by photocatalysis under UV-irradiation.

Fig. 3 illustrates the degradation efficiencies of MB dye versus irradiation time.

The decomposition of MB under UV-irradiation was fitted to the first order kinetic model, as expected. Fig. 4 gives first order linear transforms of disappearance of MB by photocatalysis under UV-irradiation. The rate constant values, fitting equations and regression coefficients are reported in Table 1.

The obtained results in the experiments show that the synthesized sphere-like ZnO particles were considerably effective on MB degradation. Photocatalytic activity of ZnO decreased due to the effect of the polymeric additive. Therefore, the polymer was removed from the particle structure through the calcination to increase the photocatalytic activity.

4. Conclusions

In this study, the photocatalytic activity of sphere-like ZnO particles on the degradation of MB was carried out under UV light. The relatively higher degradation rate was obtained with calcined sphere-like ZnO particles. The MB dye content in the 300 mL solution (containing 0.05 g ZnO) decreased to 2.8% of its initial value within 1103 min. While the value of degradation rate constant was 0.12×10^{-3} min^{-1} without photocatalyst, the values of that were respectively obtained as 1.71×10^{-3} min^{-1} and 3.27×10^{-3} min^{-1} with non-calcined

Table 1
The rate constant values, fitting equations and regression coefficients of the degradation reactions.

Experiment	Equation	Rate constant k ($\times 10^{-3}$) min^{-1}	Regression coefficient R^2
No photocatalyst	$y=0.00012x+0.01902$	0.12	0.9988
Non-calcined	$y=0.00171x+0.01082$	1.71	0.9994
Calcined	$y=0.00327x-0.05605$	3.27	0.9987

and calcined photocatalysts. The obtained results show that sphere-like ZnO particles have a potential to be used as a photocatalyst in the degradation of MB dye.

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