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Photocatalytic decolorization of methylene blue using immobilized ZnO nanoparticles prepared by solution combustion method

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ABSTRACT

Photocatalytic decolorization of methylene blue (MB) in aqueous solution was investigated using ZnO nanoparticles immobilized on glass plate. The ZnO nanoparticles were prepared by solution combustion method (SCM) using zinc nitrate as oxidant and glycine as fuel. In the slurry ZnO system the separation and recycling of the photocatalyst is practically difficult. Thus, the ZnO nanoparticles were immobilized on glass supports to solve this problem. The effects of process parameters like, catalyst loading, initial dye concentration, and UV-radiation intensity have been investigated. The best results of MB removal were reported in the 1800 μW cm^{-2} UVC using two layers immobilized ZnO nanoparticles. In addition to removing the color from the wastewater, the photocatalytic reaction simultaneously reduced 62% COD. These results suggest that the photocatalytic decolorization of MB using immobilized ZnO nanoparticles prepared by SCM can be proposed and developed as a method for the treatment of colored wastewaters.

Keywords: ZnO nanoparticles; Methylene blue; Photocatalysis; Solution combustion method

1. Introduction

Rapid progress in industrial activities during recent years has led to the discharge of large amount of wastewater, which pollutes the environment and consequently causes harm to human and other living organisms. The textile industry is one of the highest water consuming with 25 and 250 m^3 per ton of product depending on the dyeing, printing and finishing processes [1]. Dye effluents generated from textile industries create serious environmental problems as they result in undesirable lasting color along with excessive COD loading to the water [2]. In response to the continuous increase in effluent discharge from textile factories, it is necessary to develop effective wastewater treatment methods. Various chemical, physical and processes have been utilized, including coagulation/flocculation, membrane filtration and adsorption. The physicochemical treatment methods only provide separation of the dyes without any dye degradation, creating a waste disposal problem with the large quantities of sludge produced [3]. However, the recent developments of chemical treatment of

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wastewaters gave birth to an improvement of the oxidative degradation of the organic compounds dissolved or dispersed in aqueous media. Among the various chemical and physical processes, heterogeneous photocatalysis has appeared as an emerging destructive technology leading to the degradation of organic compounds into simple mineral acids, carbon dioxide and water [4,5]. Semiconductor photocatalysis is a developed advanced oxidation processes, which can be conveniently applied to dye pollutants for their degradation. Among the various semiconductors employed, TiO_2 and ZnO are known good photocatalysts for the degradation of several environmental contaminants, due to their high photosensitivity, a faster electron transfer to molecular oxygen, stability and large band gap [6]. Recent advances in the field of nanotechnology, particularly the ability to prepare highly ordered nanoparticles of any size and shape, have led to the development of new semiconductor agents. Nano-sized particles possess different physical and chemical properties compared to bulk materials. High catalyst activity may be expected because of their large surface area and different surface properties such as surface defects [7]. However, the smaller particle size is required to obtain high photocatalyst activity because of their large surface area. There are several methods for preparing nanosized ZnO powders such as thermal decomposition [1] chemical vapor deposition [8], sol–gel [9], spray pyrolysis [10] and precipitation [11]. Different methods yield different nanoparticles of ZnO depending on the type of precursor, the solvent, the pH, and the temperature of the reacting solution [12]. The choice of method depends on the final application. Few studies to date have quantitatively evaluated the activity of ZnO nanoparticles prepared by SCM. On the other hand, the use of suspended catalyst powder is efficient due to the large surface area of catalyst available for reaction. However, in large-scale applications, the use of suspended powder requires the separation and recycling of the ultrafine catalyst from the treated wastewater prior to the discharge, which is a time-consuming and expensive process. In addition, the depth of penetration of UV light is limited because of strong absorption by both catalyst particles and dissolved dyes [9]. The above problems can be avoided by immobilization of a photocatalyst over a suitable support [13]. The use of immobilized semiconducting compound such as ZnO, TiO_2, SnO_2, SiO_2, ZrO_2 is gaining importance in the elimination of pollutants from wastewaters. The aim of the present work is to investigate the potential of immobilized ZnO nanoparticles prepare by SCM as a photocatalyst under UV radiation for the oxidation of MB as a model of textile dyes in aqueous solutions. Effects of parameters like catalyst-loading, initial dye concentration, pH, COD removal and UV radiation intensity on the rate of decolorization were investigated.

2. Materials and methods

2.1. Materials

The MB was purchased from Baker and May, England, and used without further purification. Chemical structure of MB is shown in Fig. 1 and its characteristics are listed in Table 1. Solutions were prepared with the dye using distilled deionized water. The pH of solutions was adjusted with NaOH and HNO_3. All other reagents were analytical grade.

2.2. Preparation and characterization of ZnO nanoparticles

In a typical combustion synthesis, the catalyst precursor is smoldered with a fuel in solution. The ZnO nanoparticles were prepared by the SCM using zinc nitrate (Junsei, Japan) as oxidant and glycine as fuel (H_2N-CH_2-COOH) (Carlo Erba, Italy). The zinc nitrate, formed after zinc hydroxide and nitric acid reacts, acts as oxidant. The oxidant solution was then diluted with distilled water in a beaker and glycine was added to the starting solution in the beaker. The solution mixture in the beaker was heated on a hot plate with stirring at a temperature of about 80–100°C. As the distilled water evaporated, the solution became viscous with air bubbles. The nitrate ions reacted with the fuel and intense heat was generated (about 1500–1800°C), resulting in high pressure and ultimately, an explosion. This method involves the liberation of a large volume of gases, nearly seven times the moles of the catalyst that leads to the high porosity and high surface area of the material [14]. The entire experiment was performed inside a stainless steel chamber for safety reasons.

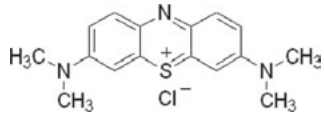

Fig. 1. Chemical structure of the methylene blue dye.

Table 1
Properties of the MB dye

Properties	Description
Molecular formula	$C_{16}H_{18}N_3SCl$
Molecular mass	319.85 (g mol–1)
λ_{max}	662 (nm)
Color index name	C.I. Basic Blue 9
Synonyms	Calcozine blue ZF, External blue 1, methylthionine chloride
Chemical class	Cationic

2.3. Immobilization of ZnO nanoparticles on glass plates

To prepare the immobilized ZnO on glass plates (3 cm × 30 cm) modified heat attachment method was used [15]. In this procedure, a suspension containing 5 g l^{-1} ZnO nanoparticles in distilled water was prepared. Prepared suspension was sonicated in an ultrasonic bath (Starsonic 18–35, Liarre, Italy) under 30 kHz frequency for 90 min in order to improve the dispersion of ZnO nanoparticles in water. The glass plates were first cleaned thoroughly, conditioned by sonication for 1 h in acetone and dried prior to use. Glass plates treated with a dilute NaOH (0.01 M) in order to increase the number of OH groups and better contact of ZnO nanoparticles on glass plates. The sonicated suspension was poured on the glass plates (2.8 mg cm^{-2} per layer) and then placed in an oven (Dena Medi & Lab Works, Iran) at 30–40°C. After drying, the glass plates were fired at 450°C for 1 h. The glass plates were washed with distilled water for removing loosely attached ZnO nanoparticles.

2.4. Evaluation of photocatalytic property

Photocatalytic activity of the ZnO nanoparticles was evaluated by measuring the decolorization of MB under the illumination of UV light. The photoreaction was conducted in a semi-circulation batch reactor. The reactor was a glass vessel and it was wrapped around by an aluminium foil for reflection of UV light back into the reactor. The 8 W UVA and UVC low pressure mercury vapor lamps were used to supply irradiation.

3. Analytical methods

Samples were collected at different times and immediately analyzed for color intensity and COD. The dye concentrations in a sample were determined, using a spectrophotometer device UV-Visible (Unico Model, America) against standard calibration curves. Percent decolorization was calculated relative to the initial absorbance of the untreated textile effluent. The COD was measured by the open reflux method according to the Standard Methods [16]. The percentage of decolorization and COD removal were calculated as follows:

$$\text{Decolorization or COD removal (\%)} = \left(1 - \frac{C}{C_0}\right) \times 100 \quad (1)$$

where C_0 is initial dye concentration or COD (mg l^{-1}), C is final dye concentration or COD (mg l^{-1}) after UV irradiation. Irradiation intensity of UV lamps was measured by UV3 meter (Sibata Scientific Technology. LTD. Co.Japan). The crystalline phase of synthesized ZnO and solid structures was analyzed using a Siemens XRD D5000 (Philips, the Netherlands). The accelerating voltage of 40 kV and emission current of 30 mA was used with Cu Kα irradiation. The average crystalline size of the samples was calculated according to Debye–Scherrer formula [17]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

where D is the average crystallite size (Å), λ is the wavelength of the X-ray irradiation (Cu Kα = 1.54178 Å), β is the full width at half maximum intensity of the peak and θ is the diffraction angle. The morphology of the formed ZnO nanoparticle was characterized by scanning electron microscopy (Philips XL30). The specific surface area of the ZnO nanoparticle was determined using the Brunauer-Emmett-Teller (BET) method (Micromeritics, Gemini).

4. Results and discussion

4.1. Preparation and characteristics of the ZnO nanoparticle

Different methods of ZnO nanoparticles synthesis have been reported to have higher activities in degrading pollutants [8,9,18]. However, the smaller particle size is required to obtain high activity because of their large surface area. In this study, we employed a SCM to prepare ZnO nanoparticles, which is a simple method for producing single-phase ZnO nanoparticle. Using SCM method, the synthesized ZnO powder showed the best characteristics. The XRD pattern of ZnO powder is shown in Fig. 2.

The spectra show well-defined peaks typical of ZnO in the crystal structure of zincite, according to the Joint Committee on Powder Diffraction Standard (JCPDS) card number 36–1,451. The peaks are quite sharp indicating the crystalline nature of the nanoparticles. No peaks from other phases of ZnO or from impurities are observed, suggesting that high-purity ZnO nanoparticle has been obtained. The ZnO nanoparticle diameter D was calculated using the Debye–Sherrer formula $D = K\lambda/(\beta \cos\theta)$, where K is Sherrer constant, λ is the X-ray

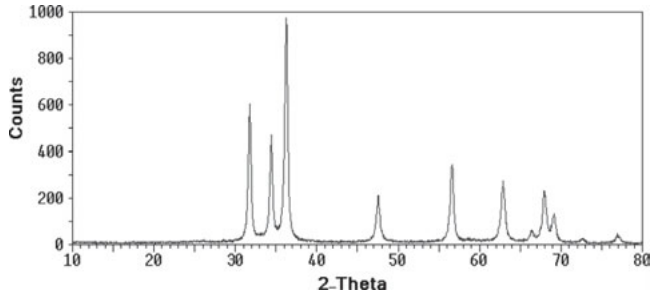

Fig. 2. X-ray diffraction (XRD) patterns of the ZnO nanoparticles.

wavelength, β is the peak width of half-maximum, and θ is the Bragg diffraction angle [17]. The average particles size of ZnO nanoparticles is about 20 nm. SEM analyses were carried out to characterize the surface of ZnO nanoparticles. The SEM micrograph shows that ZnO nanoparticles have a good porosity and the dimensions are less than 20 nm and were spherical ZnO nanoparticles, with uniform size (Fig. 3). This is highly important to achieve the large active catalyst surface needed for adsorption. We used the BET method to determine the specific surface area of the prepared ZnO nanoparticle. Results indicate the specific surface area of combustion synthesized ZnO is 135 $m^2 g^{-1}$. These results agree with previous findings showing that ZnO nanoparticles prepared by SCM are of the same quality [14].

4.2. Photocatalytic decolorization experiment of MB

The photocatalytic activity of the immobilized ZnO nanoparticles was estimated by using MB and the UVA lamps as the model pollutant and lamp source, respectively. A preliminary photocatalytic study were carried out under three different conditions, that is, by keeping the ZnO nanoparticles containing solution in the dark, in presence of UV light but in absence of the catalyst and in presence of both ZnO nanoparticles and UV irradiation was investigated. It was observed that presence of ZnO nanoparticles only does not catalyze the MB. Only a minor loss of the MB on to the ZnO nanoparticles surface could be observed due to the initial adsorption of MB on ZnO nanoparticles surface. When solutions were irradiated by UV light no significant change in the absorbance was recorded. This finding is in agreement with the behaviour of other textile dyes [19]. However, better results were observed when immobilized ZnO nanoparticles are added to the solution in the presence UV light.

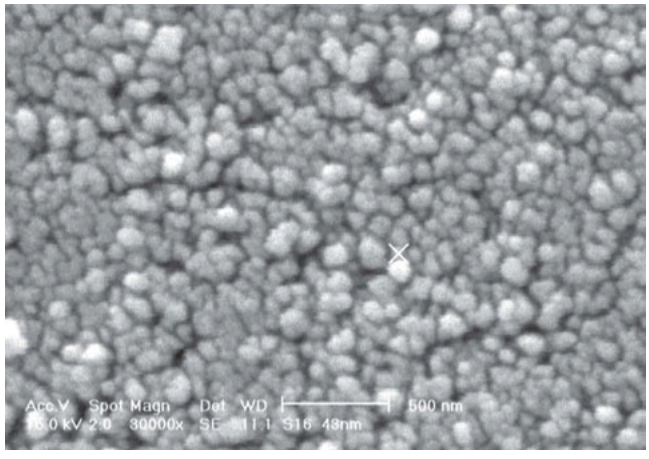

Fig. 3. SEM images of the ZnO nanoparticles.

About 98% of the 5 mg l^{-1} dye was photodegraded within 40 min of experiment. Different researches have shown that the photocatalytic decolorization system is greatly influenced by the operational parameters. The concentration of the semiconductor, initial dye concentration, nature and intensity of the light source of the reaction medium must be optimized to produce the maximum rate of dye removal.

4.3. Effect of initial MB concentration

Initial concentration of the dye is one of the most important parameter, which has to be analyzed as it may affect the efficiency of the photocatalytic process. Therefore, the experiment was carried out by varying the initial concentration of MB from 1 to 4 mg l^{-1}. The effect of initial MB concentration on dye removal efficiency is shown in Fig. 4. The decrease of decolorization as the dye concentration is as a result that the generation of hydroxyl radicals on the catalyst surface is reduced since the active sites are covered by dye [17]. When the dye concentration increased, the amount of the dye adsorbed onto the surface of the catalyst also increased. During that process, the amount of the light intensity, radiation time and thus the active site of the catalyst remained constant, resulting in the number of the hydroxyl radicals attacking the dye molecules became limited. As a result, the photocatalytic treatment efficiency decreased.

4.4. Effect of the immobilized ZnO nanoparticles

The effect of catalyst on dye removal efficiency is shown in Fig. 5. Two layers of ZnO nanoparticles demonstrated to be sufficient in obtaining a favourable photocatalytic activity. The increase in the amount of catalyst increased the number of active sites on the photocatalyst surface, which in turn, increased the number of hydroxyl, and superoxide radicals. MB molecules are then adsorbed on the active sites for the degradation process to occur. Subsequent the catalyst layers incur higher detachment apparently, due to the cohesive

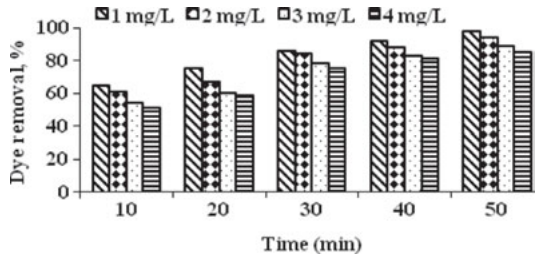

Fig. 4. Effect of the initial MB concentration on the removal percentage of the MB: C_0 = (1–4 mg l^{-1}), T = 25°C, L_{UVC} = 8W.

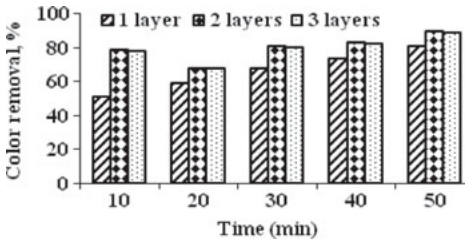

Fig. 5. Effect of the number of catalyst layers on the removal percentage of the MB: C_0 = 4 mg l^{-1}, T = 25°C, L_{UVC} = 8W.

forces between the coating layers are greater than the adhering force to the substrate [19]. Excessive catalyst layers also imply more wastage of catalyst. The immobilization temperature determined in this study is consistent with the findings by literature review that the optimum calcination temperature of hybrid coating is 450°C in order to obtain both good mechanical stability and enhanced photocatalytic activity of the film [15]. Therefore, two catalyst layers calcined at 450°C is sufficient, based on decolorization efficiency, production cost, time and energy consumption required by calcination process [20]. Without the catalyst, the degradation of dye occurs directly by penetration of UV light directly onto the dye molecule. This process is shown to be ineffective by the low percent degradation of MB. Thus, it could be observed that, a catalyst layer plays an important role in the degradation process.

4.5. Effect of UVA irradiation

A series of experiments were carried out to examine the influence of irradiation intensity on decolorization rate of MB dye using immobilized ZnO nanoparticles and the result is shown in Fig. 6. It shows that decolorization rate decreases with an increase of initial concentration, at all UV intensity levels. That means MB removal increases with increasing UV light intensity,

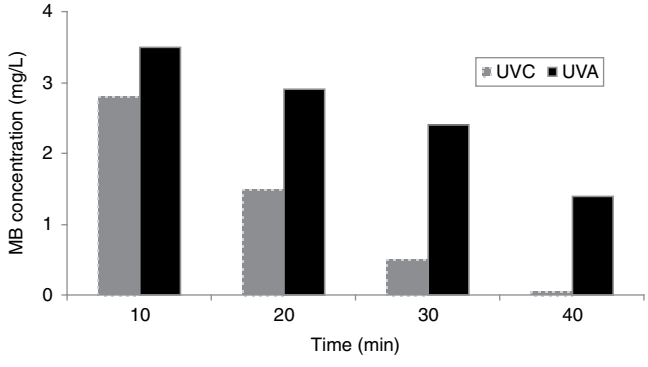

Fig. 6. Effect of the UV irradiation on the MB removal with two layers of the catalyst: C_0 = 4 mg l^{-1}, T = 25°C.

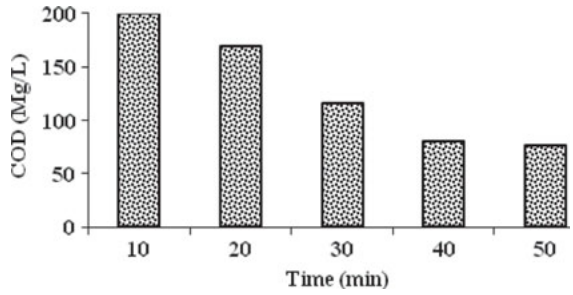

Fig. 7. Effect of the photocatalytic process on the COD removal: COD = 200 mg l^{-1}, T = 25°C, L_{UVC} = 8 W.

which produces more photons to excite more electron hole pairs. A higher MB removal was observed for UVC lamp. This is probably due to a higher UV intensity was applied using UVC lamp. The measured UV intensity of UVC lamp (1800 μW cm^{-2}) was more than that using UVA lamp (120 μW cm^{-2}).

4.6. Chemical oxygen demand

The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of wastewater. In the present work results of chemical oxygen demand were taken as one of the parameter to judge the efficiency of the photochemical process for the degradation of MB dye solution. The open reflux method was applied for COD determination and the treated solution showed a significant decrease in the COD value of the initial colour solution from 200 to 76 mg l^{-1} of the treated solution indicating the high potential of the photocatalytic process for the removal of MB from wastewater. The results of this process shows that COD samples in this study reduced up to 62% respectively (Fig. 7). Results from different research also confirmed the COD reduction after Photocatalytic process tests [21].

5. Conclusions

This study was conducted in order to investigate the decolorization by the photocatalytic process using ZnO nanoparticles prepared by SCM. The experimental results showed that the photocatalytic process can be a suitable pretreatment method for MB decolorization under the optimal operating conditions. Based on the obtained results, it can be stated the particle size of the ZnO powder synthesized by the SCM was less than 20 nm. This small particle size might be a helpful factor for the decolorization. Moreover, the results indicated that decolorization was obviously affected by catalyst layers, time, initial concentration, UV irradiation. The prepared ZnO nanoparticles and UV light had a negligible effect

when they were used on their own. In addition to the removal of colors, the reaction simultaneously reduced the COD. Furthermore, decolorization efficiency of the photocatalytic process increased with the increase in catalyst loading up to two layers. Therefore, the prepared ZnO nanoparticles have the potential to improve the quality of the wastewater from textile and other industries. The economy may be further improved using certain modifications.

Acknowledgements

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