The application of ZnO/SiO$_2$ nanocomposite for the photocatalytic degradation of a textile dye in aqueous solutions in comparison with pure ZnO nanoparticles

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ABSTRACT

One of the major disadvantages of the application of ZnO nanoparticles as photocatalyst in photocatalytic systems is photoinstability due to the photocorrosion under UV light irradiation resulting in the significant reduction in their photocatalytic activity. Therefore, in the present study, SiO$_2$ nanopowders were incorporated into the ZnO nanoparticles to enhance their photocatalytic activity for the decolorization of methylene blue (MB) dye in comparison with pure ZnO/UV process. The efficiency of UV/ZnO/SiO$_2$ process was compared with UV/ZnO process for the decolorization of MB dye and the removal of chemical oxygen demand (COD). The effect of various amounts of SiO$_2$ (5, 10, and 15%) incorporated into ZnO nanoparticles was studied. At optimal SiO$_2$ loading of 10%, the decolorization efficiency of MB and the removal of COD were obtained to be 100 and 81%, respectively. However, using UV/ZnO process at the same operational conditions, the decolorization efficiency of MB and the removal of COD were 66 and 44%, respectively. An initial pH of 7 and initial dye concentration of 25 mg/L were chosen as optimal experimental conditions. It can be stated that the incorporation of SiO$_2$ nanopowders into the ZnO nanoparticles would be beneficial for enhancing their photocatalytic activity.

*Keywords:* Photocatalysis; ZnO nanoparticle; Nanocomposite; Decolorization; COD

1. Introduction

The presence of organic dyes in aqueous environments such as rivers and lakes can cause harmful effect on aquatic life and human health [1–3]. The number of organic dyes used in various textile industries is about 10,000, causing strong color and high chemical oxygen demand (COD) in textile industries. Therefore, in recent years, the purification of colored wastewater has become a major concern [4–6]. Methylene blue (MB) is one of the most widely used organic dyes in textile industries, which its presence in

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aqueous environments can lead to adverse effects on human health including shock, cyanosis, vomiting, diarrhea, increased heart rate, jaundice, and so on [7–9]. An effective wastewater treatment technique for decolorization of colored wastewaters is to mineralize all the toxic contaminants into H_2O, CO_2, and other nontoxic inorganic compounds [10,11]. Recently, the application of advanced oxidation processes (AOPs) has been proposed as an efficient method for the oxidation of organic pollutants such as organic dyes [12,13]. Among various AOPs, photocatalytic processes have been widely used as promising methods due to their low cost and high efficiency for the degradation of low biodegradable organic compounds without the need to add toxic chemicals [4,5,13]. Zinc oxide (ZnO) nanoparticles are considered as promising photocatalyst for the photocatalysis of organic compounds in comparison with TiO_2 nanoparticles [14–16]. The formation of hydroxyl radicals ($OH^•$) as one of the most powerful oxidants during a photocatalytic process using ZnO nanoparticles is exhibited through Eqs. (1)–(3) [17,18]:

$$ZnO + hv \rightarrow ZnO(e^- + h^+) \tag{1}$$

$$h^+ + H_2O \rightarrow H^+ + OH^• \tag{2}$$

$$h^+ + OH^- \rightarrow OH^• \tag{3}$$
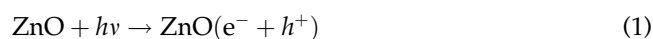
However, the application of pure ZnO nanoparticles has two major disadvantages, including the photoinstability in aqueous solution and high recombination rate of the photogenerated electron–hole pairs, which significantly decrease the photocatalytic activity of pure photocatalyst [15,19]. The incorporation of several semiconductors is a promising method to enhance photocatalytic response to the UV light irradiation and decrease electron–hole recombination [19]. Silica (SiO_2) is a widely used material due to relative ease of preparation, good environmental stability, and compatibility with other materials. This fact encouraged us to prepare a composite of ZnO and SiO_2 to achieve better photocatalytic activity and stability [20]. Zhai and co-workers, in their study, found that the incorporation of SiO_2 into ZnO nanoparticles possess improved stability and relatively better photocatalytic activity for the degradation of Rhodamine B in aqueous solutions [20]. Kuo et al. in their investigation reported that the combination of ZnO nanostructures with silicon substrates can improve their photocatalytic activity toward the photocatalysis of rhodamine B and 4-chlorophenol [21]. Photocatalysts are often applied in the form of

suspension [4], resulting in UV light scattering and difficult recycling of the applied photocatalyst for later use [22]. Therefore, in recent years, the applications of suitable supports such as sand, polymer films, activated carbon, and glass plates have been considered for the immobilization of photocatalyst [4,5,18,23,24]. To the best of our knowledge, there is no report on the use of ZnO/SiO_2 nanocomposite for the photocatalytic degradation of MB in aqueous solutions. According to the afore-mentioned statements, in the present study, SiO_2 nanoparticles were incorporated into pure ZnO nanoparticles and its potential for the photocatalytic oxidation of MB as a model organic pollutant was evaluated.
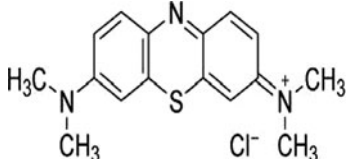
2. Materials and methods

2.1. Materials

MB dye (>99% purity) was purchased from Merck, Germany. The chemical composition and general characteristics of the dye are shown in Table 1. Zinc oxide and silica nanoparticles were provided by US Research Nanomaterials, USA and PlasmaChem GmbH, Germany, respectively. The pH of solutions was adjusted using 0.1 M HCl or 0.1 M NaOH. All other analytical grade reagents were purchased from Merck, Germany.

2.2. Preparation and immobilization of ZnO/SiO_2 nanocomposite

A 3% suspension of ZnO and SiO_2 nanoparticles was prepared with variable weight ratio of SiO_2 (5, 10, and 15%). The resulting suspensions were mixed with a magnetic stirrer at 500 rpm for 2 h. In order to improve the dispersion of nanoparticles in solution, each suspension was sonicated in an ultrasonic bath (Starsonic 18–35, Italy) under 30 kHz frequencies for 90 min. The homogeneous suspension was then coated on the surface of glass plates (3 cm × 30 cm) using a pipet. Before coating, the glass plates were thoroughly cleaned, conditioned by sonication for 1 h in acetone, and dried prior to use. Additionally, they were dipped in NaOH solution (50%) for 24 h for surficial functionalization of the plates with hydroxyl groups to avoid detachment of the immobilized nanocomposite. After coating, the glass plates containing immobilized nanocomposite were dried in an oven at 40°C for 12 h. After drying, the glass plates were calcined at 450°C for 1 h [18,23]. Finally, they were washed with distilled water for removing loosely attached ZnO/SiO_2 nanocomposite.

Table 1
Characteristics of MB dye

CI name	Chemical structure	Molecular formula	M_w (g/mol)	λ_{max} (nm)
Methylene blue (MB)		$C_{16}H_{18}N_3CLS$	373.90	663

2.3. Experimental system

A 1,000 mL batch recirculation flow mode rectangular experimental reactor made of plexiglass was used to conduct the photocatalytic degradation of MB in aqueous phase (Fig. 1). Three glass plates were placed in reactor and five 6-W low-pressure UVC lamps (Philips, Holland) were placed 1 cm from the surface of the three glass plates containing immobilized nanocomposite. This configuration reduces the distance between the catalyst surface and the source of irradiation enhancing the production of the hydroxyl radicals. In addition, this configuration would be beneficial to avoid the detachment of immobilized nanocomposite from the surface of glass plates. Recirculation of the solution containing MB was carried out through a precise peristaltic pump. The solution was kept at a temperature of 25°C by placing the pipes within cooled water. In a typical manner, an initial MB concentration of 20 mg/L, initial pH of 7, and reaction time of 120 min were applied using five UV lamps.

2.4. Analytical methods

To measure the residual concentration of MB in the solutions, the samples were collected at regular time intervals and immediately analyzed using UV–vis spectrophotometer (DR-5000, Hach Co) at the λ_{max} of 663 nm. After that, the decolorization efficiency of MB was calculated using a suitable calibration curve. The COD was measured by the open reflux method according to the standard methods [25]. The decolorization efficiency and COD removal were calculated as follows:

$$\text{Decolorization or COD removal}(\%) = \left(1 - \frac{C}{C_0}\right) \times 100 \tag{4}$$

where C_0 is the initial dye or COD concentration (mg/L) and C is the final dye or COD concentration (mg/L) after UV irradiation. In addition, light intensity of the UV lamps was measured using Lutron light meter (Model, 254-UVC, Taiwan).
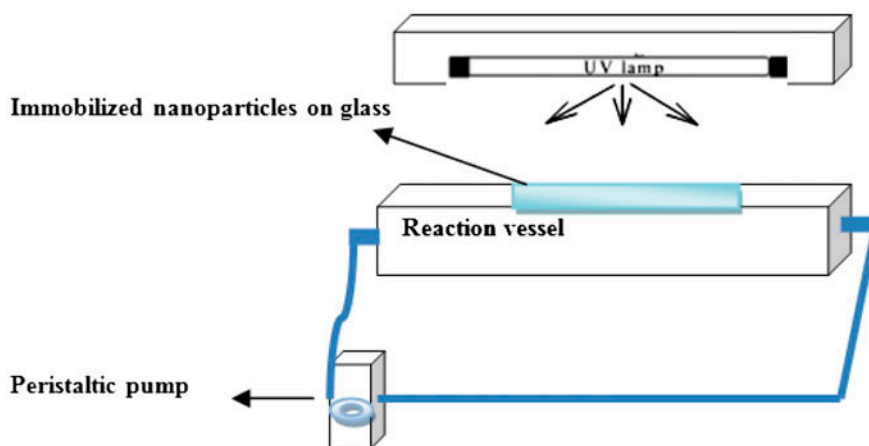

Fig. 1. Schematic flow diagram of the photocatalytic reactor.

3. Results and discussion

3.1. Characterization of the nanocomposite

Scanning electron microscopy (SEM) was carried out and the results showed that the size of applied ZnO nanoparticles was less than 100 nm (Fig. 2(a)). The porosity of pure ZnO nanoparticles remained at a satisfactory level after the immobilization of the nanoparticles onto glass plates. However, the porosity of pure ZnO nanoparticles decreased after combining with SiO_2 nanopowders. The porosity of pure ZnO nanoparticles was filled with SiO_2 nanopowders, creating an even and uniform surface for the photocatalysis of MB in aqueous phase (Fig. 2(b)). This uniform structure can be beneficial to avoid detachment of the immobilized nanostructures. The net weight of immobilized ZnO/SiO_2 nanocomposite onto each glass plate was determined from differences between glass weight before and after coating process. The difference in weight of the plates before and after each experimental run showed that the reduction in weight of the photocatalyst has been negligible. This suggested satisfactory and highly stable fixation of ZnO/SiO_2 nanocomposite onto the glass plates. Therefore, ZnO/SiO_2 nanocomposite immobilized on the glass plates can be applied as a cost-efficient and reliable photocatalyst for the decolorization of MB. To ensure the adequate performance of the nanocomposite, the nanocomposite was reactivated in the furnace at a temperature of 450°C after each experimental run.

3.2. Effect of initial pH

The photocatalytic decolorization of organic dyes is affected by the solution pH. Therefore, the effect of initial pH on the photocatalytic decolorization of MB was evaluated by varying the initial pH between 3 and 11, while the initial dye concentration and irradiation time were constant at 20 mg/L and 120 min, respectively. As a result, the decolorization efficiency of MB at initial pH values of 3, 5, 7, 8, 9, and 11 was obtained to be 86.5, 93.5, 99.5, 98.0, 98.5, and 100%, respectively (Fig. 3). Based on this, the decolorization efficiency was the highest at pH of 11 and the lowest decolorization efficiency was observed at pH of 3. At alkaline pH values, the production of hydroxyl radicals is maximized, resulting in higher photocatalytic degradation of MB in aqueous solution [12]. Anyway, decreasing initial pH from 11 to 7 resulted in a negligible decrease in the decolorization efficiency of MB. Since the pH of textile wastewaters is nearly 8 which is near the neutral pH [26], a solution pH of 7 was considered as optimal and economical value for conducting the rest of the experiments. In accordance with our study, Leng et al. [27] reported that increasing initial pH from 6.5 to 11 led to a considerable increase in decolorization efficiency [27]. In another study, Lachheb et al. [28] reported that the alkaline pH favored the decolorization efficiency of MB. At pH values of 3, 7, 9, and 12, the time needed for 50% decolorization efficiency were obtained to be 15.2, 13.2, 11, and 8.8 min, respectively. The reason for the difference between the irradiation time of Lachheb et al.'s study and the present study is due to the type of the lamp, the intensity of the irradiation, the properties of the wastewater, and the concentration of the MB [28].

3.3. Effect of initial dye concentration

Fig. 4 exhibits the effect of initial MB concentration on its photocatalytic decolorization efficiency. The effect of initial dye concentration was assessed by varying the concentration between 10 and 50 mg/L, while the reaction time, initial pH were constant at 120 min and 7, respectively. At initial dye
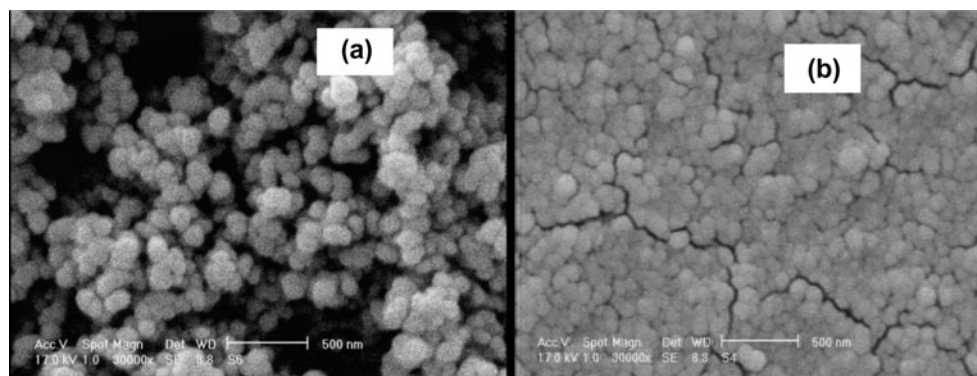

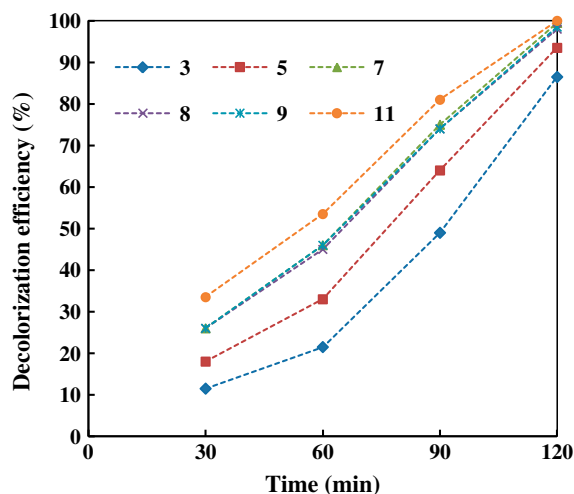Fig. 2. SEM images of pure ZnO nanoparticles (a) and ZnO/SiO_2 nanocomposite (b).

Fig. 3. The effect of initial pH on the decolorization efficiency (%) of MB (Initial dye concentration = 20 mg/L and light intensity = 3,950 μW/cm²).
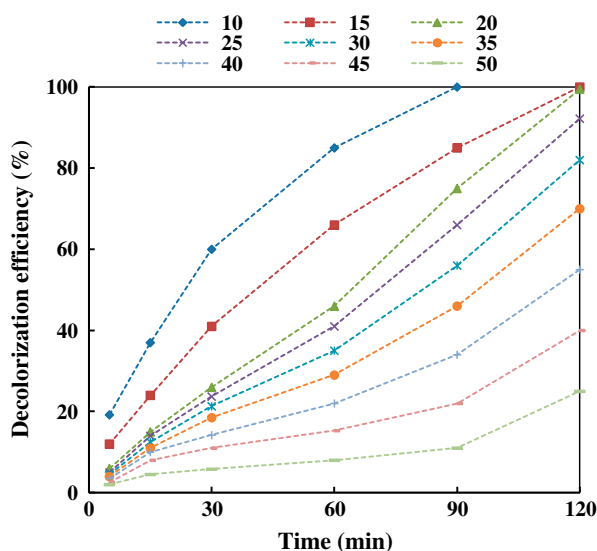

Fig. 4. The effect of initial dye concentration on the decolorization efficiency (%) of MB (initial pH 7.0 and light intensity = 3,950 μW/cm²).

concentrations of 10, 15, 20, 25, 30, 35, 40, 45, and 50 mg/L, the decolorization efficiency were 100, 100, 99.5, 92.2, 82.0, 70.0, 55.0, 40.0, and 25.0%, respectively, indicating that the decolorization efficiency decreased with increasing initial dye concentration. It can be explained by the fact that increasing initial dye concentration reduces the transparency of the solution, which causes the decrease in the adsorption of UV light irradiation by the photocatalyst. This leads to the lower production of hydroxyl radical during photocatalysis and lower photocatalytic decolorization of MB.

Moreover, decreasing the decolorization efficiency with increasing the initial dye concentration will be predictable as the number of generated hydroxyl radicals remains constant during the photocatalysis [29]. Additionally, increasing initial MB concentration produces leads to the production of higher amount of intermediates, causing the competition between these intermediate substances and the dye molecules to be degraded [26,30]. Chakrabarti and Dutta [13], in their study, showed that the photocatalytic decolorization of MB dye over ZnO catalyst decreased with increasing initial dye concentration [13]. According to the results, an initial dye concentration of 25 mg/L was chosen as selective value for conducting the rest of the experiments.

3.4. Effect of light intensity

Fig. 5 shows the effect of light intensity on the photocatalytic decolorization of MB. In this set of experiments, the initial dye concentration, initial pH, and irradiation time were set to 25 mg/L, 7, and 120 min, respectively. As the light intensity increased from 2,030 to 3,950 μW/cm², the decolorization efficiency increased from 32.0 to 92.2%, respectively (Fig. 5). Increasing the decolorization efficiency with increasing UV light intensity can be explained by the enhanced stimulation of nanophotocatalyst immobilized on the glass plates. The increase in the number of stimulated electrons leads to a significant increase in the number of generated hydroxyl radicals, causing an increase in the photocatalytic degradation of the target pollutant [31]. Akyol and Bayramoglu [12] investigated the photocatalytic degradation of
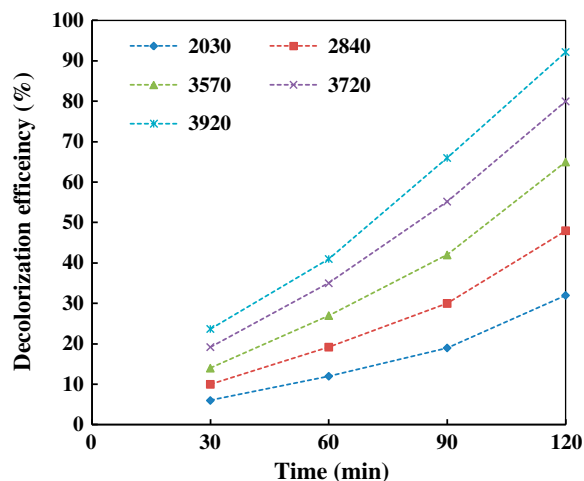

Fig. 5. The effect of light intensity on the decolorization efficiency (%) of MB (Initial dye concentration = 25 mg/L and initial pH 7.0).

Remazol Red F3B using ZnO as photocatalyst and reported that increasing light power from 12 to 30 W led to increase in the decolorization efficiency and the TOC removal efficiency [12]. Moreover, in another study carried out by Heredia and Duffy [32], it was demonstrated that an increase in the UV light intensity led to an increase in the removal of *E. coli*, and that in lower irradiation intensities, longer retention times are needed [32]. In another study, Kamat et al. [33] investigated the removal of 4-chlorocatechol (4-CC) and reported that the efficiency of the reactor increases as the intensity and time of the irradiation increased [33].

3.5. Effect of the amount of SiO_2 nanopowders on the photocatalytic decolorization

Fig. 6 shows the effect of the amount of SiO_2 nanopowders incorporated into the pure ZnO nanocatalyst on the photocatalytic decolorization of MB within a reaction time of 120 min. However, the efficiencies were compared at reaction time of 90 min. At 5, 10, and 15% of SiO_2 incorporated into the ZnO nanoparticles, the decolorization efficiency (%) of MB was obtained to be 84, 100, and 91.6%, respectively, while the removal of COD were 57.5, 81.0, and 74.2%, respectively. Accordingly, 10% SiO_2/ZnO nanocomposite can be chosen as optimal combination. Compared with the 10% SiO_2/ZnO nanocomposite and at the same operational conditions, the decolorization efficiency (%) of MB and the removal of COD over

pure ZnO nanoparticles were 66 and 44%, respectively (Fig. 7). Given these results, it can be stated that the incorporation of SiO_2 into the ZnO nanoparticles increases the photocatalytic decolorization of MB in comparison with the pure ZnO nanoparticles. The combination of different semiconductors can lead to the reduction of the empty spaces related to oxygen and as a result increases green luminescence, because oxygen vacancy is responsible for green luminescence. Additional amounts of each semiconductor in the combination make energy loss (as a result of the return of the particles from a stimulated state to a basic resting state), and therefore luminescence will be reduced [34]. As shown in Figs. (6) and (7), the removal of COD was lower than that of the decolorization of MB for both pure ZnO photocatalyst and ZnO/SiO_2 nanocomposite as catalyst. This can be explained by the fact that the photocatalytic decolorization of an organic dye like MB results in the production of some by-products which are not completely mineralized. Therefore, they need more irradiation time to be converted to water and carbon dioxide [35]. In agreement with our results, Kong et al. conducted a study on the photocatalytic degradation of MB using TiO_2/ZnO nanocomposite and their results showed that this method can improve the optical properties of the ZnO nanoparticles for better photocatalysis of the target pollutants [36]. Luo et al. [37] reported that the incorporation of silica into the structure of ZnO nanoparticles can improve their optical and electrical properties of the pure ZnO nanoparticles [37].
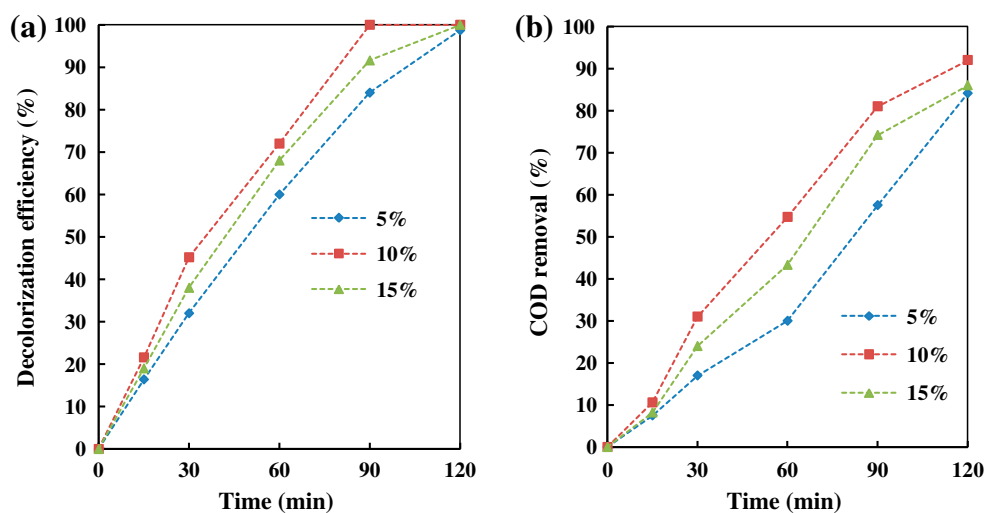

Fig. 6. The effect of the amount of silica on the decolorization efficiency (%) of MB (a) and COD removal (%) (b) during photocatalytic process over ZnO/SiO_2 (Initial dye concentration = 25 mg/L, initial pH 7.0, and light intensity = 3,950 μW/cm^2).
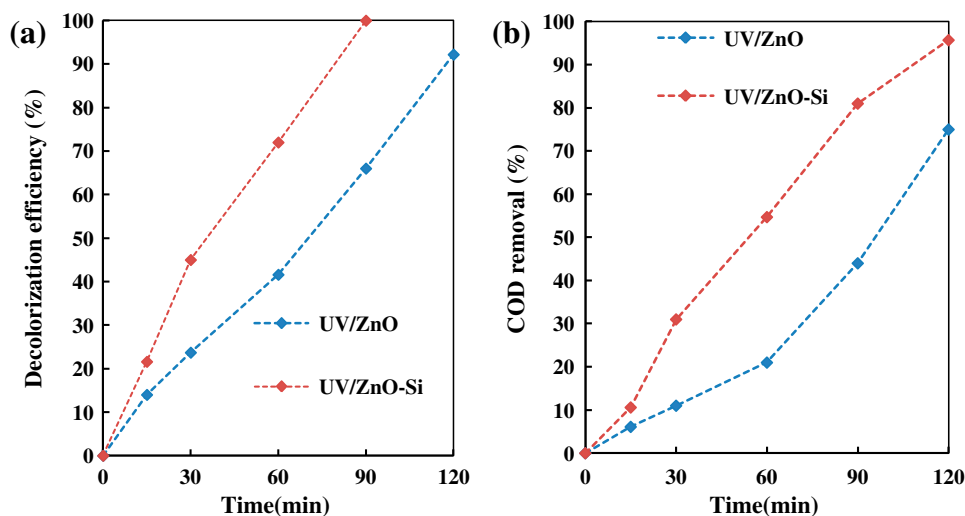
Fig. 7. Comparison of the decolorization efficiency (%) and COD removal (%) in UV/ZnO and UV/ZnO/SiO$_2$ processes (Initial dye concentration = 25 mg/L, initial pH 7.0, light intensity = 3,950 μW/cm^2, and amount of SiO$_2$ = 10%).

4. Conclusions

In the present investigation, photocatalytic decolorization of a textile dye over ZnO/SiO$_2$ nanocomposite was considered. The results suggested that the UV/ZnO/SiO$_2$ process is efficient enough to degrade dye and COD in aqueous solution in comparison with the UV/ZnO process. As a result, increasing initial pH and decreasing initial MB concentration favored the decolorization efficiency. Because of the immobilization of the applied photocatalyst on a suitable support, the photocatalyst can be used in repeated experimental runs without the need to synthesize or purchase new photocatalyst. This characteristic of the applied photocatalyst improves cost-efficiency of the process. Overall, immobilized ZnO/SiO$_2$ can be used as an efficient and promising catalyst with high reusability potential from an application point of view. In the future, the application of ZnO/SiO$_2$ nanocomposite can be used for the photocatalytic degradation of other target pollutant by applying different supports.

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