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Research Article

Sol-Gel Synthesis of TiO_2/SiO_2 and ZnO/SiO_2 Composite Films and Evaluation of Their Photocatalytic Activity towards Methyl Green

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The TiO_2/SiO_2 and ZnO/SiO_2 composite films were prepared by sol-gel dip coating method. The surface morphology and crystal structure of thin films were characterized by means of scanning electron microscopy (SEM) with elementary dispersive X-ray analysis (EDX) and X-ray diffractometer (XRD). Optical properties of films have been investigated using ultraviolet and visible spectroscopy (UV-visible spectroscopy). The photocatalytic activity was established by testing the degradation and decolorization of methyl green (MG) from aqueous solution with artificial UV-light.

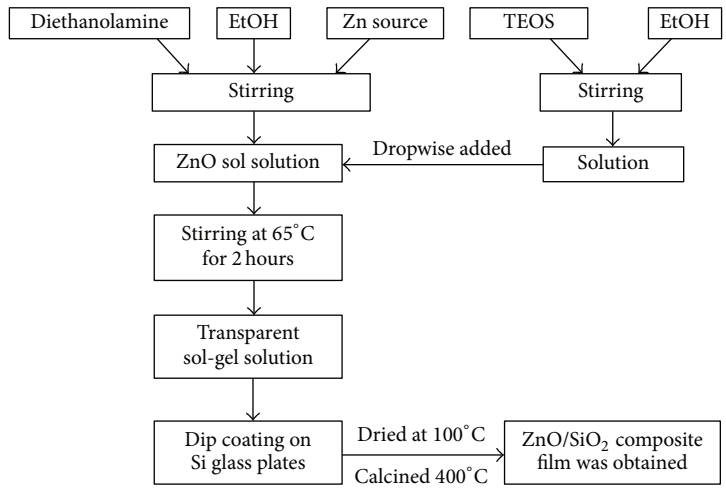
1. Introduction

Nanomaterials may provide solutions to scientific and ecological challenges in the areas of catalysis, medicine, solar energy conversion, and water treatment [1, 2]. This increasing demand must be accompanied by "green" synthesis methods. In the global efforts to decrease generated hazardous waste, "green" chemistry and chemical processes are progressively integrating with contemporary developments in science and industry. Implementation of these sustainable processes should adopt the 12 fundamental principles of green chemistry [3]. These principles are gear to guide in minimizing the use of dangerous products and maximizing the efficiency of chemical processes. Hence, any synthetic route or chemical process should address these principles by using environmentally benign solvents and nontoxic chemicals [4].

From a biological and physiological point of view, the removal of poisonous chemicals from waste water is currently one of the most important subjects in pollution control. MG is a basic triphenylmethane-type dicationic dye, usually used for staining solutions in medicine and biology [5] and as a photochromophore to sensitize gelatinous films [6]. Triphenylmethane dyes are used widely in the textile industry for dyeing of nylon, wool, cotton, and silk as well as for coloring of waxes, varnish, oil, plastics, and fats.

The application of illuminated semiconductors has been effectively working for the decomposition of variety of organic contaminants in water [7]. The major organic compounds that constitute the industrial wastewater include dyes, phenols, chlorophenols, aliphatic alcohols, aromatics, polymers, and carboxylic acids. Among these, toluene, salicylic acid, and 4-chlorophenol have been identified as a water pollutant arising from numerous sources including paper milling, textile, and cosmetic industries [8], causing bad odor to the water. Hence, the destruction of organic compounds is of considerable interest. Over the years, a large number of semiconductors have been utilized as photocatalysts. The most commonly studied photocatalysts are TiO_2 and ZnO [9, 10].

TiO_2 films have been broadly studied in photocatalytic degradation of the dyes, because of their low solubility in wastewater, high oxidation efficiency, ecofriendly properties, and avoiding the need for posttreatment separation in a system. Moreover, the coatings propose a benefit of a strong particle-substrate coupling that allows long-term performance. A variety of methods are obtainable for the preparation of nanostructured TiO_2-based photocatalytic films,



Scheme 1: Preparation route of ZnO/SiO_2 composite film.

such as vacuum arc plasma evaporation [11], electrochemical method [12–14], classical and modified sol-gel methods [15–18], and chemical vapor deposition (CVD) [19, 20].

ZnO has a competitive photocatalytic activity (PA) greater in some cases than TiO_2, for example, in the discoloration of Reactive Blue19, a textile anthraquinone dye, in aqueous suspension [21], and in the oxidation of protocatechuic acid [22]. Furthermore, ZnO thin films have been found to decompose aqueous solutions of reactive dyes [23, 24], as well as phenol and chlorophenol [25], and other environmental pollutants [26, 27].

ZnO is available at low cost, which gives it an important advantage. However, the solar UV-light reaching the surface of the earth and available to excited TiO_2 is relatively small (around 4%), and artificial UV-light sources are somewhat expensive. The biggest advantage of ZnO is that it absorbs over a larger fraction of the solar spectrum than TiO_2 [28, 29]. The biggest advantage of ZnO in comparison with TiO_2 is that it absorbs over a larger fraction of UV spectrum and the corresponding threshold of ZnO is 425 nm [30]. For this reason, ZnO is the most suitable photocatalyt for photocatalytic degradation of dyes under UV-light irradiation.

Recently, some researchers synthesized TiO_2, ZnO thin films, and composite materials for photocatalytic activity of some industrial pollutants and dyes [31–34]. In this context our research group has successfully prepared TiO_2/SiO_2 and ZnO/SiO_2 composite films by sol-gel method. Then, the photocatalytic activity of these composites towards is studied.

2. Materials and Methods

2.1. Materials. Zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$], titanium tetraisopropoxide [$Ti(iso\text{-}OC_3H_7)_4$], tetraethyl orthosilicate [TEOS], methyl green, diethanolamine, and ethanol were purchased and used as such. The aqueous solutions were prepared by using double distilled water. All glassware was cleaned with chromic acid followed by thorough washing with distilled water. Chemical structure of MG is shown in Figure 1.

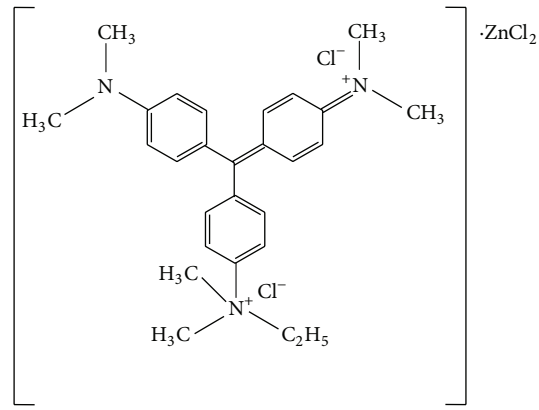
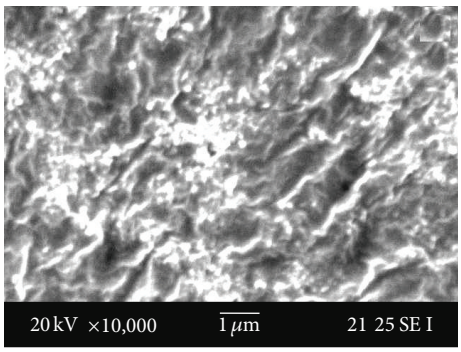


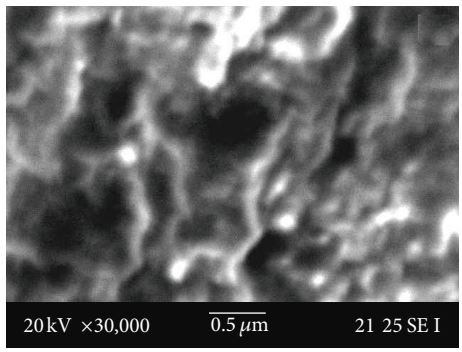
Figure 1: Chemical structure of methyl green.

2.2. Preparation of TiO_2/SiO_2 and ZnO/SiO_2 Composite Films. Initially diethanolamine in ethanol was stirred well and then zinc acetate dihydrate was added to the previous solution (solution I). Tetraethyl orthosilicate dissolved in ethanol is taken as another (solution II). The solution II is added to the solution I and stirred (600 rpm) at 65°C for 2 hour. The dip coating was achieved when cleaned glass plates were gradually immersed into the solution. The films were dried at 100°C for 4 hours to evaporate the solvent and to remove the organic residuals. Finally the films were calcinated at 400°C to get uniform ZnO/SiO_2 composite film (Scheme 1). The above procedure was also carried out for TiO_2-doped SiO_2 film.

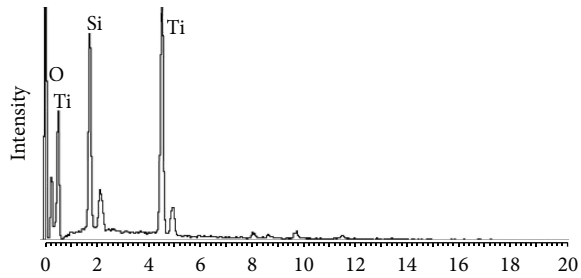
2.3. Analytical Methods. Scanning electron microscopy (SEM) with elementary dispersive X-ray analysis (EDX) experiments was carried out on an FEI Quanta FEG 200 instrument with EDX analyzer facility at 25°C. X-ray diffraction (XRD) spectra were recorded on the X'PERT PRO model X-ray diffractometer from Pan Analytical instruments operated at a voltage of 40 kV and a current of 30 mA with Cu Kα radiation. UV-visible absorbance spectra were measured over a range of 200–800 nm with a Shimadzu



(a)



(b)



Element	App. conc.	Intensity corrn.	Weight%
O K	05.50	0.4412	12.48
Si K	02.22	0.8276	02.69
Ti K	05.68	0.8590	06.61
Total			21.78

(c)

Figure 2: SEM images of TiO_2/SiO_2 composite film with scale bars of (a) 1 μm, (b) 0.5 μm, and (c) EDX spectrum of TiO_2/SiO_2 composite film.

UV-1650PC recording spectrometer using a quartz cell with 10 mm of optical path length.

2.4. Photocatalytic Activity. Photocatalytic studies were carried out in a multilamp photoreactor (HML MP88, supplied by Heber Scientific, India) fitted with eight 8 W mercury UV lamps of wavelength 365 nm. The volume of the reaction solution was maintained as 30 mL. Air was bubbled through the reaction solution for effective stirring. The degradation of MG was followed spectrophotometrically. The solution was diluted to keep the absorbance within the Beer-Lambert law limit.

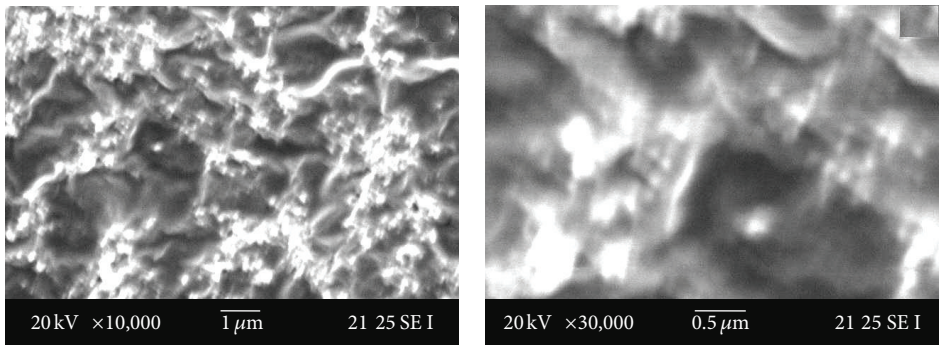
3. Results and Discussion

3.1. Characterization of TiO_2/SiO_2 and ZnO/SiO_2 Composite Films

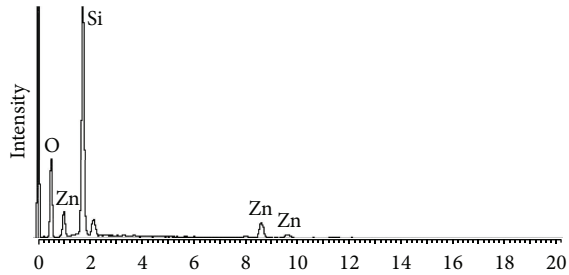
3.1.1. SEM with EDX Analysis. The morphology of the TiO_2/SiO_2 and ZnO/SiO_2 composite films was determined by scanning electron microscopy. Figure 2 shows SEM micrograph of TiO_2/SiO_2 film annealed at 400°C (scale bars of 1 and 0.5 μm) (Figures 2(a) and 2(b)). EDX analysis confirmed the presence of Ti, Si, and O (Figure 2(c)). Figure 3 shows SEM micrograph of ZnO/SiO_2 film annealed at 400°C (scale bars of 1 and 0.5 μm) (Figures 3(a) and 3(b)). EDX analysis confirmed the presence of Zn, Si, and O (Figure 3(c)). Uniform morphology of the prepared composite materials has been confirmed from the previous observation.

3.1.2. XRD Analysis. Figure 4(a) shows XRD of TiO_2-doped SiO_2 composite film. The peaks at 23.5°, 27.0°, 38.0°, 42.4°, and 48.8° are the diffractions of the TiO_2 (1 0 1), SiO_2 (1 0 1), TiO_2 (1 1 2), SiO_2 (2 0 0), and TiO_2 (2 0 0). The diffractogram consists of broad diffraction peaks of TiO_2 anatase phase (JCPDS file no. 84-1286). Figure 4(b) shows XRD of ZnO-doped SiO_2 composite film. The peaks at 26.5°, 31.7°, 33.3°, 36.0°, 49.4°, and 68.9° are the diffractions of the SiO_2 (1 0 1), ZnO (1 0 0), ZnO (0 0 2), ZnO (1 0 1), SiO_2 (1 1 2), and ZnO (2 0 1). The diffractogram consists of broad diffraction peaks of ZnO (JCPDS file no. 36-1451).

3.1.3. Optical Transmittance Analysis. Optical transmittance spectra of TiO_2/SiO_2 and ZnO/SiO_2 composite films



(a) (b)

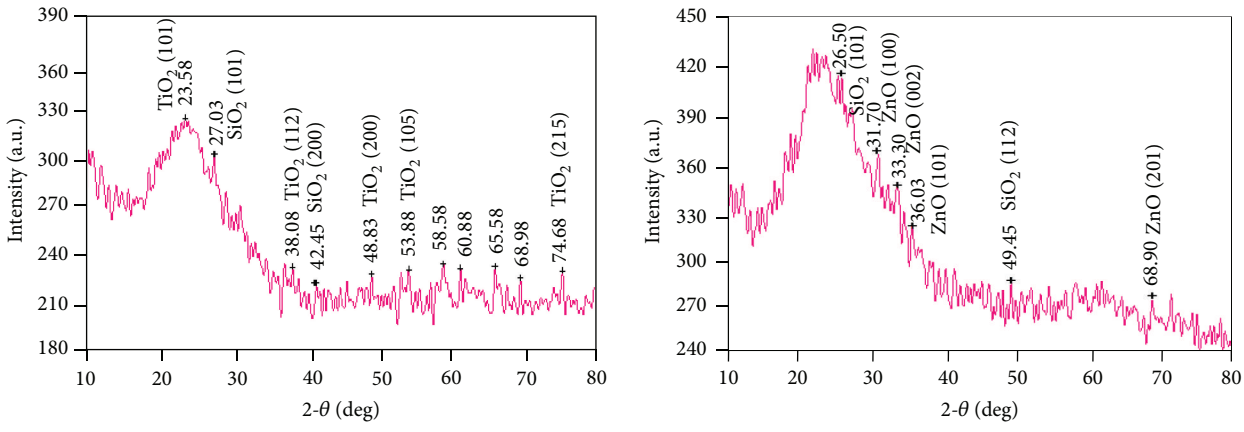


Binding energy

Element	App. conc.	Intensity corrn.	Weight%
O K	10.33	0.8796	11.74
Si K	07.67	0.7576	10.13
Zn K	04.70	0.8259	05.70
Total			27.56

(c)

Figure 3: SEM images of ZnO/SiO_2 composite film with scale bars of (a) 1 μm, (b) 0.5 μm, and (c) EDX spectrum of ZnO/SiO_2 composite film.



(a) (b)

Figure 4: XRD amorphous data of (a) TiO_2/SiO_2 composite film and (b) ZnO/SiO_2 composite film.

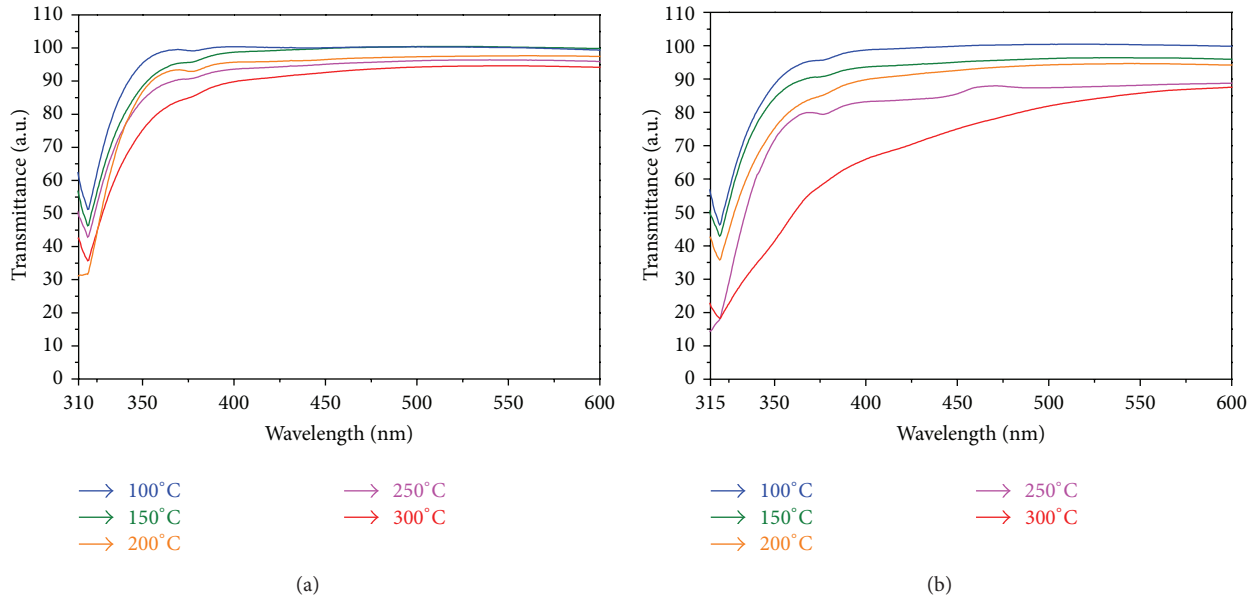


FIGURE 5: Optical transmittance spectra of (a) TiO_2/SiO_2 composite film and (b) ZnO/SiO_2 composite film.

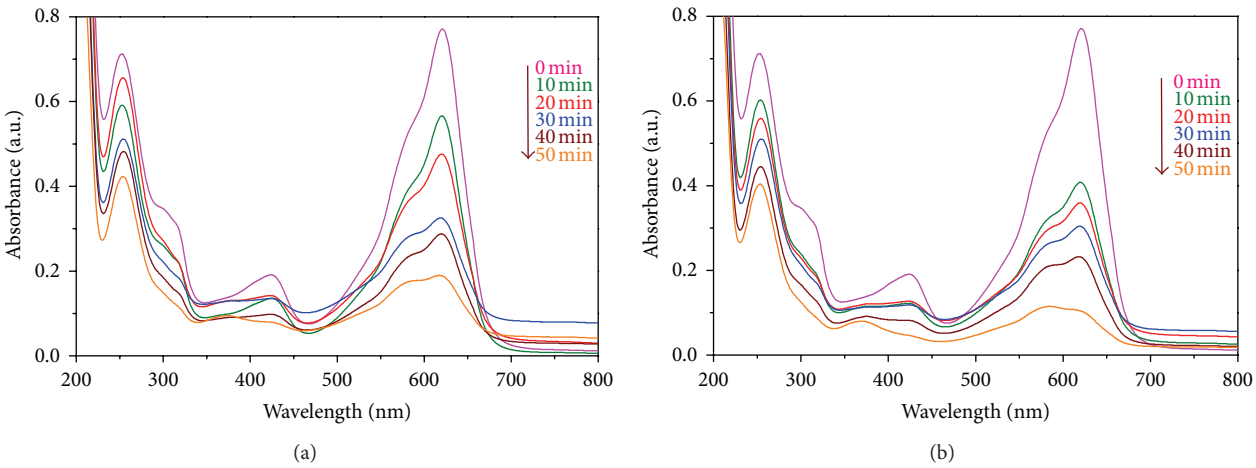


FIGURE 6: UV-visible absorption spectra of methyl green at 10-minute interval: (a) TiO_2/SiO_2 composite film and (b) ZnO/SiO_2 composite film.

annealed at different temperatures (100°C, 150°C, 200°C, 250°C, and 300°C) are shown in Figure 5. When the films were heated at different temperatures, the transmittance of the films becomes lower as the temperature increases. Transmittance of the ZnO/SiO_2 film was slightly lower than the TiO_2/SiO_2 with increasing temperature (Figures 5(a) and 5(b)).

3.2. Photodegradation and Decolorization of MG

3.2.1. Photodegradation of Methyl Green with Artificial UV Light. The photodegradation of MG in aqueous medium in the presence of atmospheric air on TiO_2/SiO_2 and ZnO/SiO_2 composite films was studied using multilamp photoreactor with mercury UV lamps of wavelength 365 nm. The reference wavelength of MG reaction solution is 630 nm. Initially the dye solution is dark green in color; after the photodegradation and decolorization the color of the solution becomes pale green. The reaction time affords the photodegradtation and decolorization of MG.

3.2.2. Photocatalytic Activity of TiO_2/SiO_2 and ZnO/SiO_2 Composite Films. The absorption spectrum of MG in the presence of TiO_2/SiO_2 and ZnO/SiO_2 is shown in Figures 6(a) and 6(b), respectively. The absorption spectrum shows the decrease in intensity with respect to time. The rapid decrease in the intensity of ZnO/SiO_2 is noted in the photocatalysis compared with TiO_2/SiO_2. The enhanced

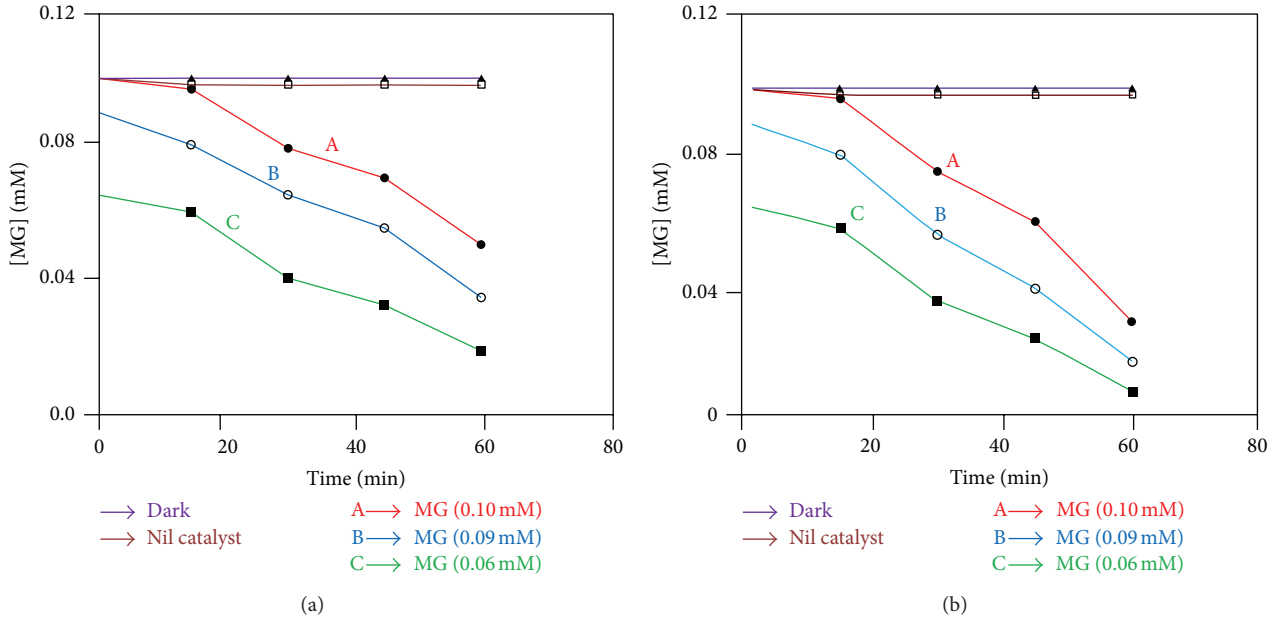


FIGURE 7: Photodegradation at different concentration of methyl green: (a) TiO_2/SiO_2 composite film and (b) ZnO/SiO_2 composite film.

photocatalytic activity shown by ZnO/SiO_2 is compared with TiO_2/SiO_2 composites.

3.2.3. Effect of Dye Concentration. The progress of the photodegradation of MG represents increases with light intensity in the presence of TiO_2/SiO_2 and ZnO/SiO_2 composite films. Different concentrations of MG were prepared and used for the photodegradation process. At lower concentration, the degradation and decolorization of MG are high but at higher concentration, the photocatalytic activity is low (Figure 7). The photodegradation of TiO_2/SiO_2 and ZnO/SiO_2 is shown in Figures 7(a) and 7(b), respectively. From these figures, it is concluded that the degradation efficiency of ZnO/SiO_2 composite film is higher than TiO_2/SiO_2 composites only at lower concentration of MG.

4. Conclusions

TiO_2/SiO_2 and ZnO/SiO_2 composite films were prepared by the sol-gel method. The prepared films were characterized by SEM with EDX, XRD, and optical transmittance studies. TiO_2/SiO_2 and ZnO/SiO_2 films were used for the photodegradation of MG under UV-light irradiation. The photodegradation of MG on TiO_2/SiO_2 and ZnO/SiO_2 composite films in aqueous medium has been studied as a function of dye concentration. ZnO/SiO_2 composite film exhibited reasonable activity under UV-light and had much better activity when compared to that of TiO_2/SiO_2 composite films.

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