

ORIGINAL RESEARCH PAPER

Photo-Catalytic degradation of Methylene blue by ZnO/SnO₂ nanocomposite

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Abstract

In this study, considering the importance of protecting the environment and preventing the pollution caused by industrial plants, a nanocomposite each component thereof is capable of removing the desired combination to solve this problem has been produced. To achieve this goal, ZnO/SnO₂ nanocomposite was synthesized using the co-precipitation method. The characterization of this nanocomposite was conducted by DLS, XRD, FTIR and SEM. The nanocomposite size was about 15nm. Several parameters such as the initial concentration of the wastewater, as well as the amount of catalyst and time were investigated. The reduction of the particle size due to an increase in the surface area of the nanocomposite increased the amount of decolorization. For all the performed experiments, the dye removal rate was 100% and the difference was to do with the time of the complete removal of methylene blue. A decrease in the concentration of methylene blue in the range of the tested concentrations reduced the decolorization, and by increasing the amount of nanocomposite in the range of the tested values, a decline in decolorization was observed.

Keywords: Co-precipitation; Decolorization; Nanocomposite; Wastewater; ZnO/SnO₂

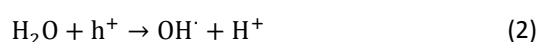
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INTRODUCTION

For almost two decades now, the wastewater problem has become a controversially crucial issue [1]. There are various methods for treating the industrial wastewater. However, each method has its shortcomings [2]. The advanced oxidation processes (AOPs) are one of the treatment technologies developed economically and technically in recent years [1]. Photocatalytic processes are one of the advanced oxidation processes [3]. In the past two decades, zinc oxide has been proposed as an important photocatalyst

for the decomposition of organic compounds in the aqueous system [4]. In an aqueous environment, the photogenerated electrons (e⁻) and holes (h⁺) can react with the dissolved molecular oxygen, surface hydroxyl groups and adsorbed water molecules to form hydroxyl (OH[·]) and superoxide (O⁻) radicals as shown by Eqs (1) and (2) [5]:



The generated hydroxyl radicals react with organic pollutants and change most of them in

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combinations such as water, carbon dioxide and inorganic acids [6]. Numerous studies have to do with improving the photocatalytic efficiency of the semiconductor photocatalysis by reducing the combination rate of the photogenerated electron-hole (e⁻/h⁺) pairs and increasing the charge separation [7]. Fortunately, connecting two semiconductors with different band gap widths can increase the charge separation and extend the energy range of the photoexcitation. Hence, the photocatalysis of the coupled semiconductors, such as ZnO/WO₃ [8, 9], SnO₂/TiO₂ [10, 11], TiO₂/PbS [12] ZnO/TiO₂/SnO₂ [13] and so forth has shown higher photocatalytic activity for the reaction of both liquid and gas phases than that of the single semiconductors. The earlier researches on the photocatalytic activity of the ZnO/SnO₂ systems under UV light (at the Zn/Sn molar ratios; 1:1 and 1:0.5) prepared by the co-precipitation methods were reported by Shen *et al.* [2]. However, it is known that the photocatalytic activity of SnO₂ is much lower than that of the pure ZnO and the coupled ZnO/SnO₂ [14]. In addition, the screening of the photocatalysts under solar light is also a crucial factor which the present work has carried out with this aim. In this study, the nanocomposites ZnO/SnO₂ photocatalysts were prepared by the co-precipitation method [2]. The characterization of the nanocomposites ZnO/SnO₂ photocatalysts was done by DLS, XRD, FTIR, and SEM. The photocatalytic activity of the sample was evaluated by the degradation of methylene blue under natural solar light. Methylene blue is a chemical aromatic and important dye commonly used in textile industry. Because of its aromatic property, this dye tends to be toxic, resistant to biodegradation, cancer-causing and mutagenic [15-17].

EXPERIMENTS

The synthesis of ZnO/SnO₂ photocatalysts

Nanocomposites ZnO/SnO₂ photocatalysts were synthesized using the co-precipitation method. Zinc sulfate heptahydrate (ZnSO₄·7H₂O, Merck) and tin chloride pentahydrate (SnCl₄·5H₂O, Sigma-Aldrich) were used as the starting materials, and ammonium hydroxide solution (NH₄OH, 25%, Merck) was used as a co-precipitant without further purification. ZnSO₄·7H₂O and SnCl₄·5H₂O at a certain molar ratio were dissolved in 1 liter

of deionized water and magnetically stirred in a dropwise and slow manner at a rate of up to 30 seconds in the NH₄OH (25%) solution to maintain the pH of the solution at 7. During the reaction, the color of solution was milky white and the white amorphous precipitate was slowly formed. The resultant solution was stirred constantly for 30 minutes. The obtained precipitates were centrifuged and washed three times with deionized water until no and were found in the filtrates. The removal of and ions was confirmed by comparing the conductivity of the filtrates to that of the fresh ultrapure water used for the washing [2]. Then the wet precipitate was dried at in air for 12 h to form the precursors of the coupled ZnO/SnO₂ photocatalysts. At last the precursors were calcined at for 2 h at a rate of in air to prepare the nanosized photocatalysts. The nanosized ZnO (Z) and SnO₂ (S) were also prepared by the same procedure as mentioned above.

Characterization of photocatalysts

The Horiba LB-550 particle size analyzer (PSA) uses dynamic light scattering (DLS) measurements to measure the particle size over the range of 0.001–6 μm.

To determine the crystal phase composition of the coupled ZnO/SnO₂ photocatalyst powders, the X-ray diffraction (XRD) analysis was carried out at room temperature using a Bruker D8-Advance instrument with the Cu Kα radiation (40 kV, 40 mA) at the scattering angles between 10° and 70° in the increments of 0.05°. The mean grain size of the photocatalyst was estimated using the Debye–Scherrer equation:

$$\tau = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

where τ is the mean grain size (nm), λ is the wavelength of the X-ray radiation (1.5406 Å), β is the corrected full-width at half maximum (FWHM in radian) and θ is the diffraction angle (degree).

The UV-Vis diffuse reflectance spectra (UV-Vis DRS) were carried out in air at room temperature using the SHIMADZU UV-1800 UV-V spectrophotometer to achieve a resolution of 1 nm.

The infrared spectra (IR) were obtained using a Perkin Elmer RX I Fourier transform infrared (FTIR) spectrometer.

The scanning electron microscopy observation (SEM) was performed using Perkin Elmer EM 3200 SEM.

Photocatalytic activity of the photocatalysts

The photodegradation of methylene blue in the aqueous solution was performed in the presence of the 0.33, 0.50, 0.66 and 0.83 g amounts of ZnO/SnO₂ photocatalysts. In this study, the synthetic wastewater with the distilled water contaminated by methylene blue at the concentrations of 10, 15, 20 and 30 mg/L was used. All the photocatalytic experiments were performed in a batch photocatalytic reactor and in each experiment, 500 ml of wastewater was poured inside the reactor at first and then the ZnO/SnO₂ photocatalysts were weighed precisely and added to the solution and at the next step were ultrasonically sonicated for 15 min. The suspensions were magnetically stirred in the dark for 90 min to ensure an adsorption/desorption equilibrium [2]. The reaction was started by putting the reactor under solar light and turning on the magnetic stirrer. The dispersion was sampled after various reaction times and the analytical samples were centrifuged at 9000 rpm for 10 min, and then filtered through a 0.2 millipore filter to remove the particles [18]. The MB concentrations of the filtrates were analyzed by UV-Vis spectroscopy.

RESULTS AND DISCUSSION

The characterization of the coupled ZnO/SnO₂ photocatalysts

The particle size distribution by the DLS measurement of the ZnO/SnO₂ photocatalysts nanoparticles has been shown in Fig. 1. The average size of the coupled ZnO/SnO₂ photocatalysts is about 15 nm.

Fig. 2 shows the XRD pattern of the coupled ZnO/SnO₂ photocatalysts. This diagram is similar to the XRD spectrum of the synthesized ZnO/SnO₂ nanocomposite by Hamrouni *et al.* [2]. The structure of ZnO and SnO₂ in the sample has been identified as the typical hexagonal wurtzite [JCPDS No. 89-11397] and tetragonal structure [JCPDS No. 41-1445], respectively. The crystal planes are (1 0 1) and (1 1 0) for ZnO and SnO₂, respectively. The mean grain size of ZnO is always found larger than that of SnO₂, but the addition of SnO₂ and ZnO to each other reduces remarkably their mean grain size and the SnO₂ and ZnO particles prevent each other's growth [2].

The SEM micrographs of the ZnO/SnO₂ photocatalysts have been shown in Fig. 3. The coupled ZnO/SnO₂ photocatalyst is almost in the

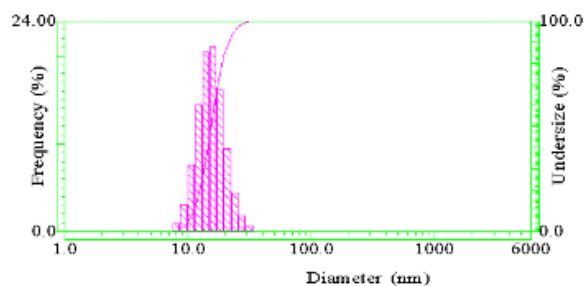


Fig. 1. The particle size distribution of the ZnO/SnO₂ photocatalysts nanoparticles.

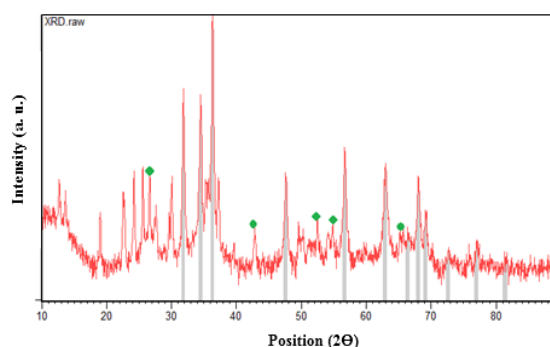


Fig. 2. The XRD patterns of the coupled ZnO/SnO₂ photocatalysts (the lines and dots show ZnO and SnO₂, respectively).

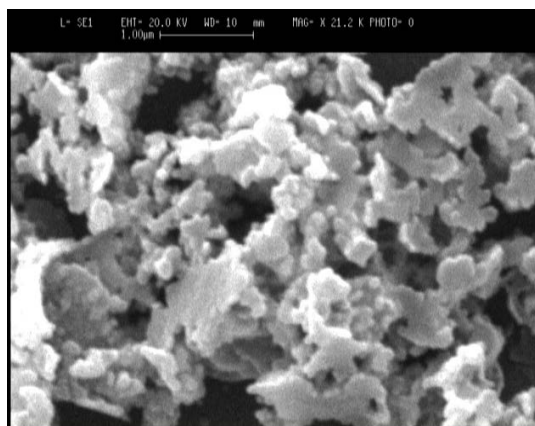


Fig. 3. The SEM image of the coupled ZnO/SnO₂ photocatalysts.

plate-like form.

Fig. 4 illustrates the FTIR spectra of the coupled ZnO/SnO₂ photocatalysts. As indicated in Fig. 4, the ZnO/SnO₂ spectrum absorption peak at 625 is to do with the Sn-O stretching vibration and the one at 464 belongs to the ZnO [19]. The peaks at 1173, 1221 and 3443 cm⁻¹ correspond to O-H bending and stretching vibrations [20].

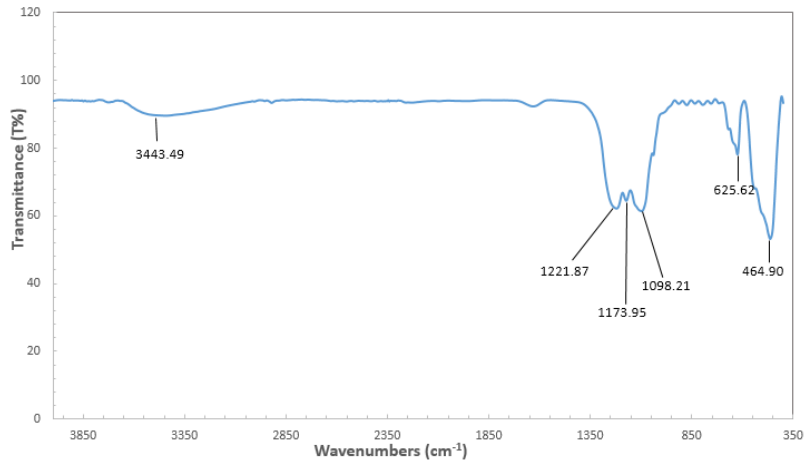


Fig. 4. The FTIR spectra of the ZnO/SnO₂ nanocomposites.

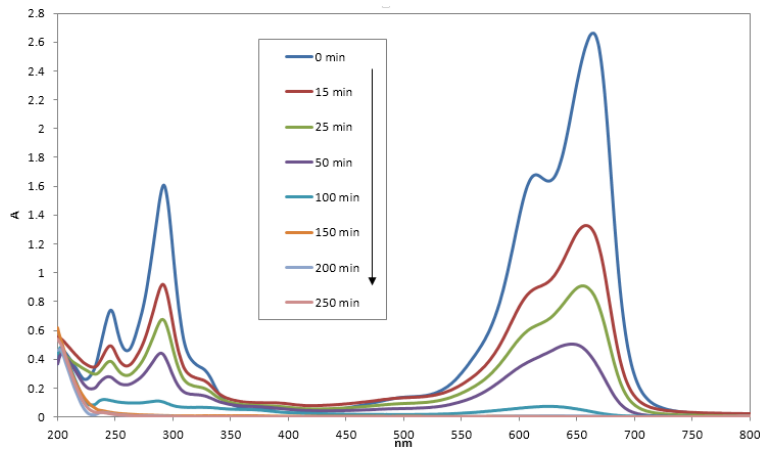


Fig. 5. The absorbance spectra changes of the 20 mg/L MB solution in the presence of 0.5 g ZnO/SnO₂ and irradiation.

Photocatalytic activity

The photocatalytic activity of ZnO/SnO₂ photocatalysts was tested under solar light on a sunny day from 11 a.m. for 250 min. The decolorization efficiency of methylene blue (E) has been shown by the equation (4):

$$E(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (4)$$

where C_0 is the initial dye concentration and C is the dye concentration at time t . According to the previous studies [21], the photocatalytic decolorization of methylene blue follows the pseudo-first-order kinetic model.

Fig. 5 shows the time-dependent UV-Vis spectra of 20 mg/L of methylene blue and 0.5 g of ZnO/SnO₂ nanocomposite during the irradiation. As

can be seen, the absorption peak at 663 nm, corresponding to the dye, diminished and finally disappeared during reaction, which indicated that the dyes had been degraded.

The effect of the initial dye

The 10, 15, 20 and 30 mg/L concentrations of methylene blue tested by certain amounts of ZnO/SnO₂ photocatalysts have been illustrated in Figs. 6 to 9.

Experimental results show that the dye removal ratio is 100% at all methylene blue concentrations. However, by reducing the methylene blue concentration, the dye is removed in less time. The reason for the reduced dye in the photocatalytic process is the chemical reactions 5 to 13, showing the mechanism of the photocatalytic

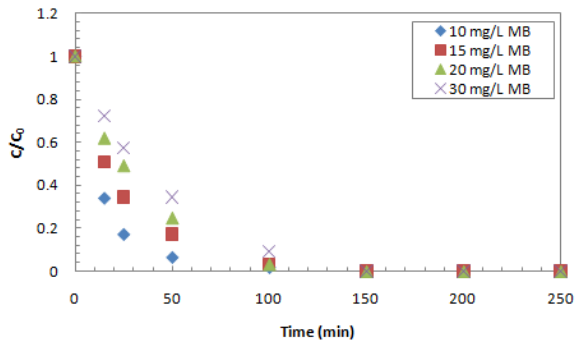


Fig. 6. The effect of 10, 15, 20 and 30 mg/L concentrations of methylene blue in the presence of 0.33 g ZnO/SnO₂ nanopcomposite.

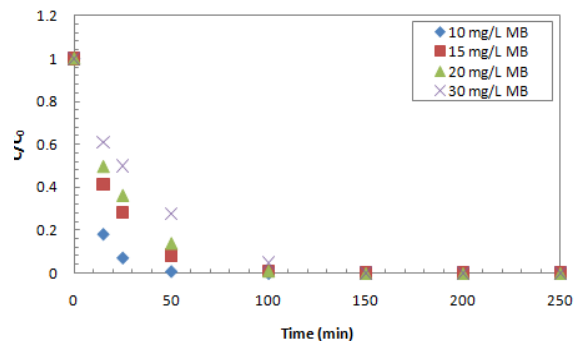


Fig. 8. The effect of 10, 15, 20 and 30 mg/L concentrations of methylene blue in the presence of 0.66 g ZnO/SnO₂ nanopcomposite.

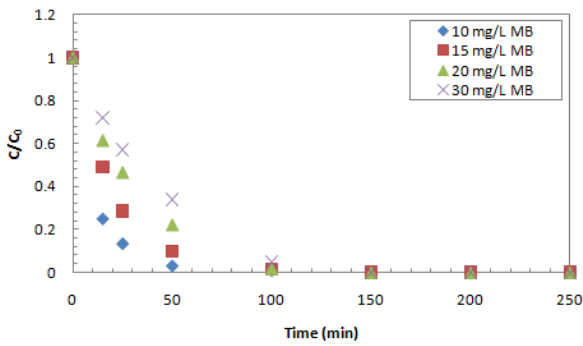


Fig. 7. The effect of 10, 15, 20 and 30 mg/L concentrations of methylene blue in the presence of 0.50 g ZnO/SnO₂ nanopcomposite.

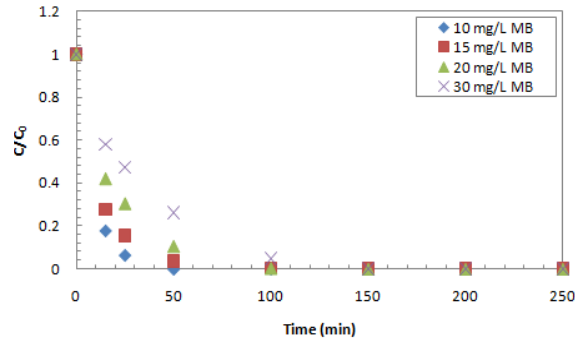
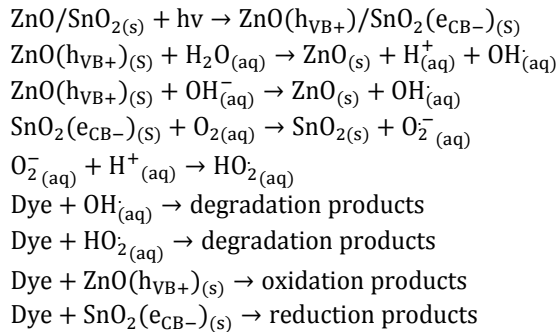


Fig. 9. The effect of 10, 15, 20 and 30 mg/L concentrations of methylene blue in the presence of 0.83 g ZnO/SnO₂ nanopcomposite.

decolorization of methylene blue according to an earlier investigation [7].



It is generally considered that by increasing the dye concentrations to a certain level, the degradation rate increases and by further increasing the dye concentration, the degradation rate of the dye is decreased. The degradation rate relates to the possibility of radicals formation on the catalyst surface and to the possibility of the radicals reacting with the dye molecules. Therefore, by increasing the initial concentrations of the dye,

the probability of the reaction between the dye molecules and the oxidizing species is increased, leading to an enhancement in the decolorization rate. In contrast, by further increasing the dye concentration, the dye degradation efficiency decreases [22]. The probable reason is that at high dye concentrations, the active sites are covered with dye ions and therefore the generation of radicals on the surface is decreased. Another reason is the UV-screening effect of the dye itself [22]. Also, the number of hydroxyl radicals produced remains stable by increasing the dye concentration and by fixing the concentration of the catalyst and irradiation, thereby decreasing the decolorization rate. In addition, the intermediate products formed by the degradation of dye are increased by increasing the initial dye concentration and therefore there is the possibility of the competing of the intermediate products with the dye molecules to degradation [23-25]. As can be seen, that less the dye decolorization time is, the less the concentration will be in 10 mg/L

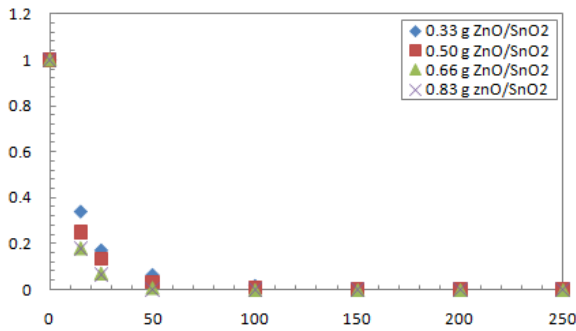


Fig. 10. The effect of 0.33, 0.50, 0.66 and 0.83 g amounts of ZnO/SnO₂ nanocomposite in the presence of 10 mg/L methylene blue.

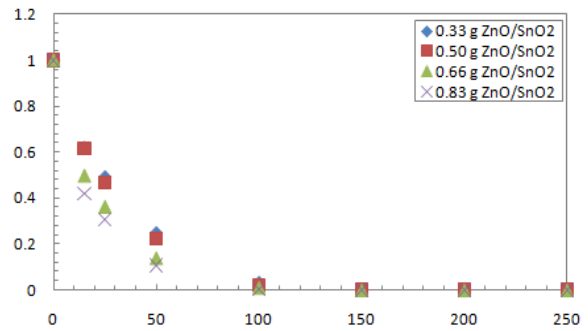


Fig. 12. The effect of 0.33, 0.50, 0.66 and 0.83 g amounts of ZnO/SnO₂ nanocomposite in the presence of 20 mg/L methylene blue.

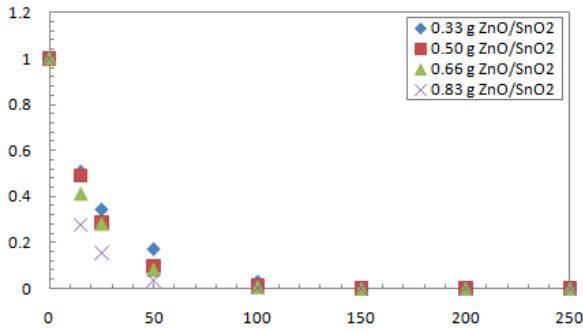


Fig. 11. The effect of 0.33, 0.50, 0.66 and 0.83 g amounts of ZnO/SnO₂ nanocomposite in the presence of 15 mg/L methylene blue.

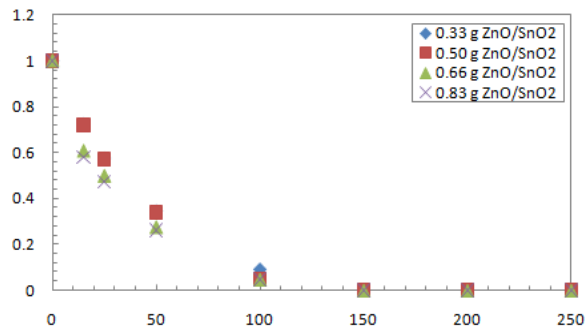


Fig. 13. The effect of 0.33, 0.50, 0.66 and 0.83 g amounts of ZnO/SnO₂ nanocomposite in the presence of 30 mg/L methylene blue.



Fig. 14. From left to right, the color of the sample before being put under solar light, after 15, 25 and 50 min under solar light, respectively.

methylene blue.

Another result is that methylene blue is reduced at 15, 20 and 30 mg/L concentrations by 100 min. In the other words, the percentage of increasing the dye removal from wastewater is low and negligible after 100 min. The reason for a rapid increase in decolorization at the initial times and then the fixing of it for a long time is that at the beginning the amount of dye is high but by the progressing

of reaction the amount of dye becomes low. For these reasons, 100 min is used as the optimum time for the above experiments.

Effect of ZnO/SnO₂ dosage

The 0.33, 0.50, 0.66 and 0.83 g amounts of coupled ZnO/SnO₂ photocatalysts tested at certain concentrations of methylene blue have been shown in Figs. 10 to 13.

As can be seen, the less the dye decolorization time is, the more the amount of nanocomposite, will be in 0.83 g of ZnO/SnO₂. That is, the amounts of decolorization increase by increasing the surface area of the catalyst [26]. According to the experimental results, 0.66 g of the ZnO/SnO₂ nanocomposite due to its following related changes and the resulting affordability was selected as the optimum amount in the presence of 15, 20 and 30 mg/L methylene blue concentrations.

Figs. 14 illustrates the color of the solution in decolorization in 10 mg/L of methylene blue in the presence of 0.83 g of the ZnO/SnO₂ nanocomposite at different times. It can be observed that after different times, the color of the solution began fading away and finally disappeared.

CONCLUSION

In this study, the photocatalytic removal of the dye pollutions from the wastewater by the ZnO/SnO₂ nanocomposite was investigated. The effect of various parameters such as the amount of photocatalyst, reaction time, concentration of the pollutant in the wastewater was tested. The results showed that by increasing the surface area the particle size of the nanocomposite is reduced, leading to an increase in the amount of decolorization. A reduction in the concentration of methylene blue in the range of the tested concentrations reduced the time decolorization. The decolorization time was decreased by increasing the amount of ZnO/SnO₂ nanocomposite in the range of the tested values. 0.66 g was the optimum of the ZnO/SnO₂ nanocomposite in the empirical tests conducted in 15, 20 and 30 mg/L of methylene blue. The optimum time of the tests in 15, 20 and 30 mg/L of methylene blue was 100 min.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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