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Research Article

Synthesis of Metal/Silica/Titania Composites for the Photocatalytic Removal of Methylene Blue Dye

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The present work deals with the synthesis of the metal-doped titanium dioxide/silica composite by using the sol-gel method. The structure, morphology, and composition of the prepared samples were characterized by using Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The prepared composites were used for the photodegradation of methylene blue dye in sunlight. Different parameters like pH, time, and catalytic concentration were varied to optimize the reaction conditions. Maximum 99.8% degradation was observed with the Ni-doped composite. The results indicate extraordinary efficiency of all metal-doped composites for the removal of the harmful organic pollutant like methylene blue.

1. Introduction

Titanium dioxide is an oxide of titanium which occurs in nature. It has three crystalline forms on the basis of the arrangement of titanium dioxide molecules, named as anatase, rutile, and brookite. Among these three crystalline forms, brookite and anatase are metastable, while the rutile phase is the most thermodynamically stable form. Anatase and brookile are converted to rutile on heating [1].

TiO_2 has gained significant attention of scientists in various fields because of its exceptional properties. It is widely used in numerous applications like in tooth pastes, tints, cosmetics, water splitting, photoconductors, sensors, and carbon-based toxins elimination [2–4].

TiO_2 nanopowders contain interesting catalytic, magnetic, optical, dielectrical, sensing, and recognition properties that are unlike from their bulk counterparts. In the field of wastewater and water treatment, the basic attention has been on the usage of titanium dioxide as a photocatalyst. It is photoactive, it has the ability to utilize visible or near UV light, it is chemically and biologically inactive, and it is also inexpensive. However, these applications, particularly photocatalysis by TiO_2, thoroughly rely on properties such as its crystalline structure, surface area, structural composition, size of the particles, and crystalline nature, with anatase being the maximum energetic photocatalytic form [5]. Regardless of such outstanding properties of TiO_2, there are definite complications which make its applications costly and difficult. Such difficulties comprise nanoparticles agglomeration, phase transformation, decrease in the surface area upon thermal treatment, and high filtration expenses to recover the nanoparticles. To resolve these difficulties, the photocatalyst can be supported on some physical support. Numerous materials are used as a support such as clay, glass, carbon nanotubes, zeolites, polymer substrate, and silica. There are some extra benefits of using a support, e.g., it can adsorb the organic pollutants [6]. Silica can be used as support for the photocatalyst because it has many properties like it is transparent to UV radiation, it provides an extraordinary specific surface area, it has extraordinary adsorption ability for the harmful organic compounds to be degraded, and last but not least, it is chemically inactive and also inexpensive [7].

Thus, the silica-titania composites can be used with enhanced photocatalytic effectiveness as compared to pure titanium dioxide. This composite has advanced stability and a greater specific surface area, particularly when the titania particles are in very low quantity. Besides, owing to the thermal stability of these composites, they can be used for preparations that involve high temperatures [8, 9].

The main kinds of interaction between SiO_2 and TiO_2 are Van der Waals forces and chemical bonds between them, i.e., Si-O-Ti bonds. The point of interaction mainly depends on preparation conditions. Doping of any metal, nonmetal, or semiconductor onto the surface of the silica/titania nanocomposite may be used to increase the catalytic action of the nanocomposite and make it more effective than the simple nanocomposite. The doped nanocomposites may work more efficiently and could be used to remove the harmful organic pollutants from the environment [10–13].

The present work involves the synthesis of the silica/titania composite and metal-doped silica/titania composite via the sol-gel method. The photocatalytic activity of these composites is used for the degradation of methylene blue dye.

Dyes are the major component of most of the textile industries. In developing countries like Pakistan, these dyes are directly drained into different water bodies like rivers and canals and ultimately water contamination takes place. These have been proved to be very harmful for both human and aquatic animals which are present in water bodies. The degradation of these harmful dyes is very essential before they are discharged into the water reservoirs directly [14, 15]. In the present work, degradation of methylene blue is studied under different reaction parameters. Methylene blue is chosen as a model compound for the degradation because its degradation can be studied easily.

2. Experimental Methodology

All analytical grade chemicals were used in the present study. Titanium butoxide was purchased from Sigma-Aldrich, while chromium nitrate, copper sulfate, cobalt nitrate, nickel chloride, and zinc chloride were purchased from BDH. Silica gel was provided by Merck.

SiO_2/TiO_2 composite was prepared by the sol-gel technique. Solution A was prepared by dissolving 1.37 g of titanium butoxide and 2.5 g of silica gel in a mixture of 25 mL methanol, 1 mL water, and 0.5 mL HNO_3 under continuous stirring for 1 hour. Solution B was prepared that consists of 5 mL of methanol and 1 mL of water, and its pH was adjusted to 4. Solution B was slowly added to solution A and stirred for 60 min at room temperature. The reaction mixture was aged for 24 hours that resulted in the formation of a gel. The obtained gel was dried at 80°C and calcined at 550°C for 2 hours.

To prepare the metal-doped composite, the same procedure was repeated by the addition of an appropriate quantity of metal salt in the solution A to achieve 1% metal doping. Different metals have been selected for the deposition purpose, i.e., cobalt (Co), chromium (Cr), nickel (Ni), copper (Cu), and zinc (Zn) and hence their corresponding salts (cobalt nitrate, chromium nitrate, nickel chloride, copper sulfate, and zinc chloride) were used.

2.1. Photodegradation Experiments. 100 mL of 20 ppm dye solution was taken in seven different flasks. In six flasks, 0.1 g of the prepared composites was added, while the seventh flask was labelled as blank. All samples were stirred for 30 minutes in dark to achieve adsorption equilibrium. Then, all the samples were exposed to sunlight for a certain period of time, and the absorbance of the solutions was checked by UV/Vis spectrophotometer.

In an effort to study the pH impact, pH of the dye solutions was adjusted to 2, 4, 6, 8, 10, and 12, respectively. Then, 15 mL of the dye solution was taken in twelve test tubes. 0.01 g of the composite was introduced in six tubes, while other six were kept blank. These two units of tubes were exposed to sunlight for two hours. The absorbance of all solutions was noted by the UV/Vis spectrophotometer.

The effect of concentration of the catalyst on the degradation of the MB dye was studied by using various amounts of catalyst from 0.02–0.1 g. The pH of solutions was adjusted at 10. 50 mL of 20 ppm dye solutions were taken in 4 different flasks, and 0.02 g, 0.05 g, 0.07 g, and 0.1 g of the composites were introduced in the beakers, respectively. Then, these flasks were shaken for 30 minutes in dark and then exposed to sunlight for two hours. After 2 hours, the absorbance of the dye solutions was measured with the UV/Vis spectrophotometer.

3. Results and Discussion

The prepared composites were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, and thermogravimetric analysis.

3.1. FT-IR Spectrum of SiO_2/TiO_2. The FT-IR spectrum of the SiO_2/TiO_2 composite is represented in Figure 1. A prominent peak at 1052 cm^{-1} fits to the Si-O-Si asymmetric stretching vibration. A small peak at 795.8 cm^{-1} shows the symmetric vibration of Si-O-Si linkage. A small peak at 941 cm^{-1} corresponds to the Si-O-Ti bond. Two minor peaks corresponding to the stretching and bending vibrations of the OH group were observed at 3400 cm^{-1} and 1600 cm^{-1}.

The spectrum indicates that the prepared composite is free from contaminations and no unburnt carbon is present in it. Typical peaks conforming to TiO_2 and SiO_2 were attained as expected [16].

3.2. FT-IR of Metal-Doped SiO_2/TiO_2 Composite. The FT-IR spectrum of the Cu-doped SiO_2/TiO_2 composite is shown in Figure 2.

No major change is observed in the spectrum of SiO_2/TiO_2 and Cu-doped SiO_2/TiO_2 composite. Approximately similar peaks were obtained in the Cu-doped composite. The peak at 1052 cm^{-1} is slightly broad as compared to the undoped composite and can indicate the occurrence of the metal. Peaks at 1052 cm^{-1} and 941 cm^{-1} correspond to asymmetric Si-O-Si stretching and Si-O-Ti stretching, respectively. Two minor peaks corresponding to O-H stretching and bending vibrations appeared at 3400 and 1600 cm^{-1}. No additional peak conforming to some contamination was noticed that approves the purity of the prepared sample.

3.3. Scanning Electron Microscopy (SEM). SEM images show that the composites were successfully synthesized. In Figure 3(a), particles of titania are seen deposited on the surface of the silica. Figure 3(b) shows the dispersion of both metal and titania on the surface of silica. These images

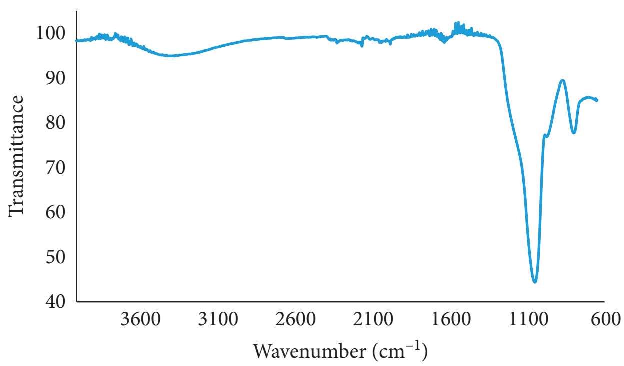

Figure 1: FT-IR of the TiO_2/SiO_2 composite.

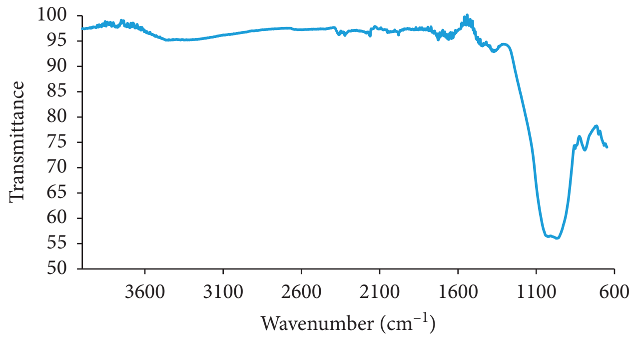

Figure 2: FT-IR spectrum of Cu-doped SiO_2/TiO_2 composite.

reveal that the titania and metal particles are successfully deposited onto the surface of silica as desired [17].

3.4. Thermogravimetric Analysis of the SiO_2/TiO_2 Composite. TGA was used for the quantitative approximation of the thermal losses of the synthesized composites. TGA graph of the SiO_2/TiO_2 composite and Cu-doped SiO_2/TiO_2 composite is shown in Figure 4.

The graph demonstrates that about 5% mass loss was observed up to 100°C which corresponds to the loss of solvent molecules. Above this temperature only a small mass loss (2%) was observed up to 1000°C that may be due to the condensation of-Si-OH and -Ti-OH groups and subsequent removal of water molecules. Besides all these, it was established that the prepared composite is thermally stable up to 1000°C. The TGA graph obtained from the Cu-doped SiO_2/TiO_2 composite was similar as the SiO_2/TiO_2 composite [18].

4. Applications of Prepared Metal-Doped SiO_2/TiO_2 Composites

The prepared SiO_2/TiO_2 composite and metal/SiO_2/TiO_2 composites were used for the photocatalytic degradation of methylene blue dye in sunlight.

4.1. Effect of Time. Percentage degradation of methylene blue dye after different time intervals by using SiO_2/TiO_2 and metal/SiO_2/TiO_2 composites is shown in Figure 5.

Simple SiO_2/TiO_2 composite showed good photocatalytic activity, i.e., 83.6% degradation of methylene blue was observed. However, metal doping enhanced the photocatalytic efficiency of the composite for the degradation of dye. In these 1st row transition metals, Ni-doped composites showed extraordinary photocatalytic efficiency, and 99.9% degradation of the dye was observed. Both Cr/SiO_2/TiO_2 and Zn/SiO_2/TiO_2 composites exhibited 99.1% degradation. Cu and Co metal-doped composite also show good catalytic activity. Hence, it can be concluded that metal doping increases the photocatalytic efficiency of the prepared SiO_2/TiO_2 composite.

4.2. Effect of pH. pH values also affect the degradation of dye. In an effort to study the pH impact, pH of the dye solutions was adjusted to 2, 4, 6, 8, 10, and 12, respectively, and photodegradation experiments were performed with all the composites. Maximum degradation was observed at pH 12 in all the samples.

The graph of the percentage degradation of methylene blue at different pH values in the presence of simple SiO_2/TiO_2 and different metal-doped SiO_2/TiO_2 composite is given below (Figure 6).

Again it is evident that the prepared composites have remarkable ability to degrade methylene blue dye at various pH values. Metal doping enhanced the photocatalytic efficiency of the composite. As expected, Ni/SiO_2/TiO_2 exhibited maximum degradation at 12 pH.

4.3. Effect of Catalytic Concentration. The effect of concentration of catalyst on the degradation of MB dye was studied by using various amounts of catalyst from 0.02–0.1 g. The pH of solutions was adjusted at 10. It was observed that the percentage degradation of the dye increased as the amount of the catalyst was increased from 0.02 to 0.1 g as shown in Figure 7. Hence, it can be concluded that the amount of the catalyst has a direct relationship to the photodegradation of the dye.

As expected, metal-doped composites show extraordinary degradation of methylene blue.

4.4. Kinetics. Langmuir–Hinshelwood models are used for the examination of photocatalytic reactions between organic moiety and metal oxides. In this study, the catalytic activities of the M/SiO_2/TiO_2 composite were simulated by using this kinetic model. The model is established on the ensuing expectations:

(i) Catalyst only degrades the adsorbed molecules
(ii) The byproducts of methylene blue are not measured
(iii) The adsorbed molecules control the rate of the reaction

Langmuir model can be expressed as follows:

$$r = -\frac{dC}{dt} = \frac{kKC}{(1 + KC)}, \quad (1)$$

where r is the rate of degradation, C is the concentration of the methylene blue, t is the time (h), k is the rate constant of reaction, and K is the coefficient of adsorption. For the little value of C, the KC can be discounted in the denominator,

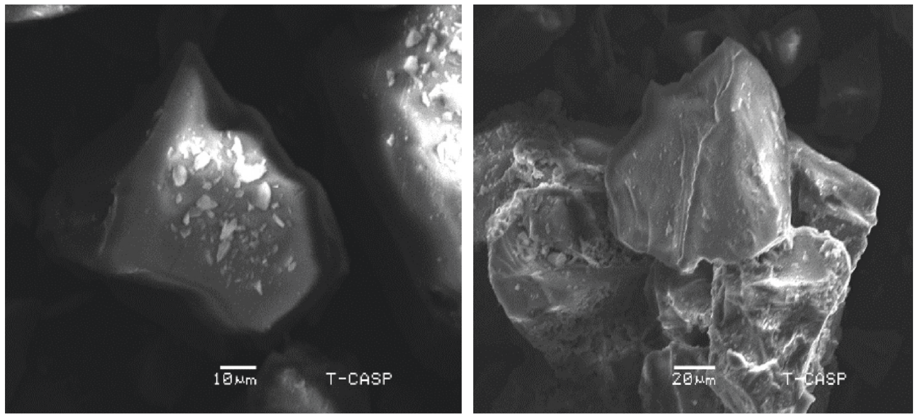

Figure 3: SEM images of (a) SiO_2/TiO_2 composite and (b) $Cu/SiO_2/TiO_2$ composite.

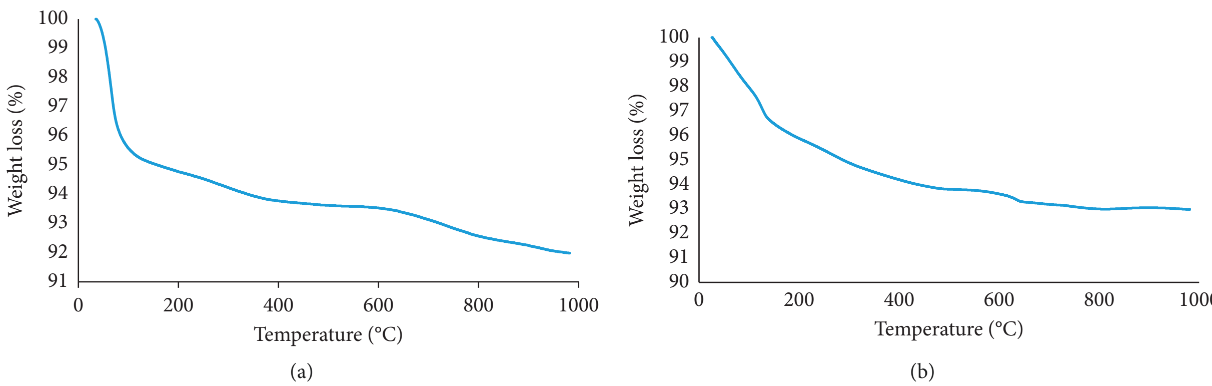

Figure 4: TGA graph of (a) silica/titania composite and (b) Cu-doped silica/titania composite.

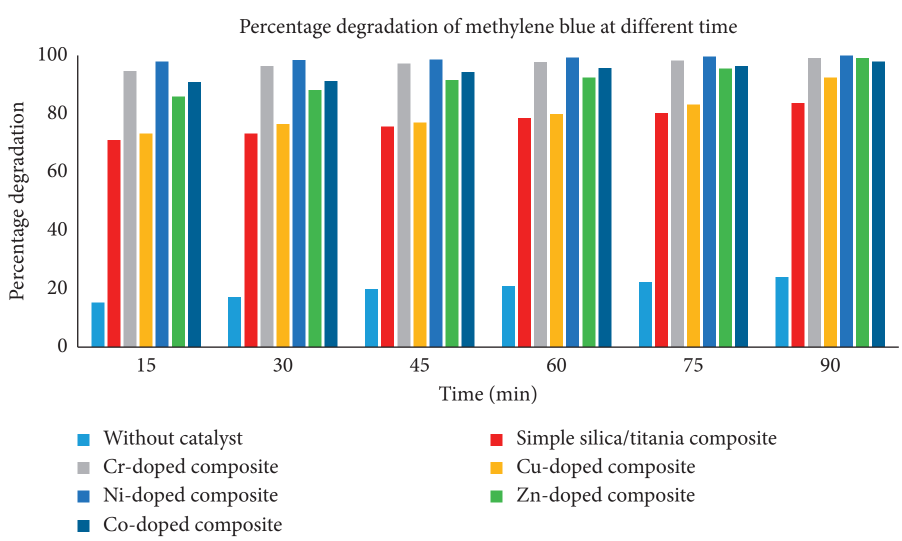

Figure 5: Time effect on percentage degradation of methylene blue in the presence of SiO_2/TiO_2 and metal/SiO_2/TiO_2 composites.

and hence, the rate of photodegradation influences the first-order kinetics.

$$r = -\frac{dC}{dt} = kKC = k'C, \tag{2}$$

where k' is the apparent kinetic constant of a pseudo-first-order reaction.

Integrating equation (2) gives

$$\ln \frac{C}{C_o} = k't, \tag{3}$$

where C_o is the original concentration. By plotting $\ln C/C_o$ versus t, it is possible to determine the apparent kinetic constant (k').

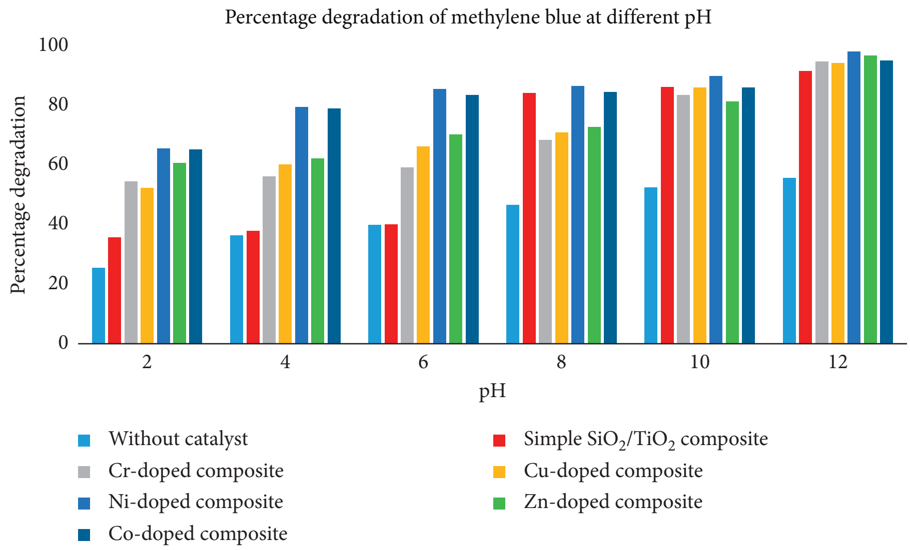

Figure 6: Degradation of methylene blue with various composites at different pH values.

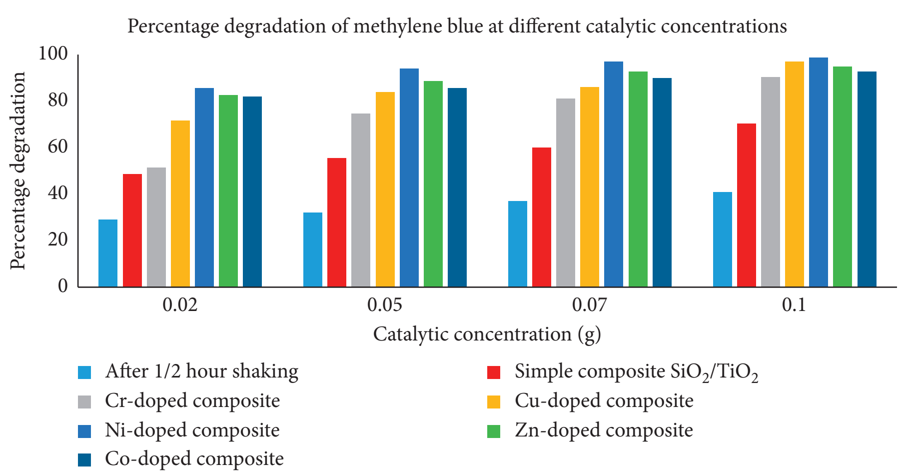

Figure 7: Percentage degradation of methylene blue with various catalyst doses.

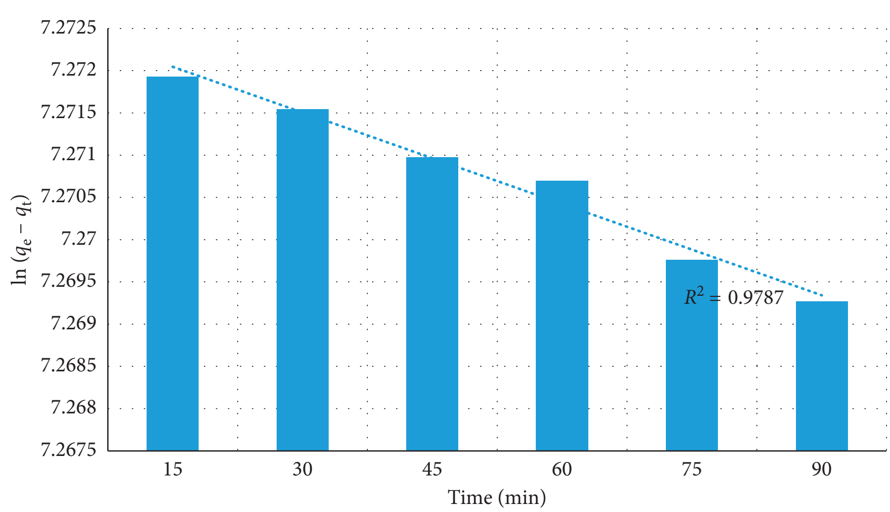

Figure 8: First-order kinetics for the degradation of methylene blue.

For the calculation of the kinetic mechanisms, the degradation data after 90 minutes were taken. A graph was plotted between $\ln(q_e - q_t)$ verses time where q_e and q_t are the adsorption capacities ($mg \cdot g^{-1}$) at equilibrium and at time t, respectively. The correlation coefficient (R) was greater than 0.9. The correlation coefficient greater than 0.9 shows that the reaction follows the first-order kinetics (Figure 8).

5. Conclusion

First row transition metal-doped SiO_2/TiO_2 composites were successfully prepared via the sol-gel method. FT-IR, TGA, and SEM analyses confirmed the formation of thermally stable composites. The prepared composites showed exceptional activity for the degradation of methylene blue dye. Three parameters including pH, time, and concentration of the catalyst were investigated to find out the optimum conditions for degradation. It was observed that an increase in the irradiation time, basic pH, and high concentration of the catalyst favors the degradation process. Metal doping increased the photocatalytic efficiency of the composite. All five metal-doped composites showed excellent results in degradation of dye, and among these five metals, i.e., Cu, Ni, Co, Cr, and Zn, the nickel metal-doped composite resulted in maximum degradation.

Data Availability

The spectroscopic data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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