

PHOTOCATALYTIC DEGRADATION OF SAFRANIN O DYE UNDER VISIBLE LIGHT USING NiO-MgO CATALYSTS

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In this study, NiO-MgO catalysts were used as photocatalysts for the degradation of Safranin O (SO) dye as a textile pollutant model from water. NiO-MgO was prepared by the self-combustion method. Characterization was performed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The photocatalytic activity of the prepared NiO-MgO catalyst was evaluated by experiments involving irradiating the Safranin O (SO) dye aqueous solution containing the prepared material with visible light. The percent photodegradation was determined spectrophotometrically by monitoring the maximum wavelength (λ_{\max}) of Safranin O (SO) at 518 nm at different irradiation times. The dye decolorization rate of the NiO-MgO material under visible light was 98.42%. The effective reusability and stability of the prepared catalysts were also evaluated. This efficiency remained almost unchanged after three cycles of use, demonstrating the reusability and applicability of the material's catalytic activity in the removal of Safranin O from water.

Keywords: NiO-MgO catalyst, Safranin O dye, degradation, advanced oxidation processes

INTRODUCTION

Various processing industries continuously release synthetic dyes, such as the cosmetic industry, pharmaceutical industry, food dye industry, paper making, plastics, leather and textile industry.¹⁻⁹ Due to the persistence of the generated colored wastewater, it causes many long-term detrimental effects. These wastewaters can persist in the environment for long periods, posing serious threats to human health and the fragile balance of aquatic ecosystems. This is largely due to the complex and harmful properties of these dyes, including carcinogenicity, toxicity, and persistence. The textile wastewater is a major source of such pollutants, therefore, the treatment of wastewater containing synthetic dyes is imperative before its release into water resources. However, the complexity of some dyes makes these objectives increasingly challenging and

poses a significant obstacle for researchers and industrialists to effectively address and mitigate the problem of these harmful substances.

Safranin O (SO) is a basic dye that was selected as a pollutant model for the present work. The dye Safranin O (SO) (C.I. name Basic Red 2) is a quinone imine phenazine dye that is considered a stubborn contaminant. It is widely used in textiles and foods, as well as for histology, cytology, biological laboratory purposes, and visible light photopolymerization. Since the dye Safranin O (SO) is known to be carcinogenic in the ecosystem, the presence of any such SO dye in wastewater can have harmful effects on water life, as well as on humans at the bottom of the food chain.¹⁰⁻¹¹

Recently, many different techniques have been suggested in the literature to tackle the situation

by causing the complete degradation of dyes in industrial effluents prior to entering the water bodies. There are several ways to do this: chemical oxidation, coagulation, membrane processes, adsorption, biodegradation, distillation, ultraviolet (UV) disinfection, reverse osmosis, physical processes, photosensitization, solar energy wastewater treatment (SOWAT) and advanced oxidation processes (AOP), developed specifically for the treatment of liquids contaminated with dye-polluted wastewater.¹²⁻³⁰ Among them, photocatalysis is considered one of the “green” treatment methods for degrading non-biodegradable organic compounds in water, especially those with complex and inert properties. This technology utilizes highly reactive hydroxyl radicals (OH•) to effectively attack and oxidize refractory pollutants, thereby degrading stubborn organic matter, with large and complex structures.

The objective of this study was to investigate the potential of photocatalysis as a treatment process for the degradation of Safranin O using a novel material: NiO catalyst supported on MgO (NiO/MgO).

EXPERIMENTAL

Materials and methods

Nickel nitrate (Ni (NO₃)₂·6H₂O, 97%) and magnesium nitrate (Mg (NO₃)₂·6H₂O, 98%) were purchased from Merck. Citric acid (C₂H₅NO₂, 99%) and Tween 80 (C₆₄H₁₂₄O₂₆, 99%) surfactant were purchased from Sigma-Aldrich. For pH adjustment, sulfuric acid (H₂SO₄, 95%) and sodium hydroxide (NaOH, 98%) were purchased from Biochem Chemopharma. Safranin O (SO) (C.I. name Basic Red 2, F. wt = 350.85) was obtained from Fluka. The

chemical structure, formula and properties of Safranin are shown in Table 1. All solutions were prepared with ultrapure Milli-Q water (resistivity of 18.2 M Ω cm).

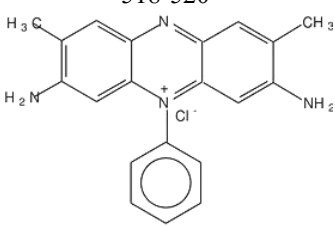
Synthesis of NiO-MgO catalyst

The NiO-MgO catalyst was synthesized by a self-combustion method. Briefly, the precursor nickel and magnesium nitrates were dispersed, respectively, in 20 mL of distilled water. After stirring at ambient temperature with gentle magnetic agitation (200 tr/min), 10 mL of a saturated citric acid solution and 10 mL of the surfactant (Tween 80) were gradually added to the mixture. Later, this solution was maintained for 5 hours with constant agitation (200 tr/min). The gel formed was heated suddenly to 280 °C in order to initiate the auto-ignition of the surfactant. The gel reached boiling, then spontaneously ignited and formed a black powder, as shown in Figure 1. The Ni-MgO powder material obtained was calcined at 500 °C for 2 hours.

Characterization

Different methods were used to characterize the prepared NiO-MgO catalyst. The crystal structure of NiO-MgO was evaluated by X-ray diffraction (XRD) using a Bruker D8 Discover diffractometer (Billerica, MA, USA), with incident CuK α (40 kV and 30 mA). Scanning electron microscopy (SEM) was performed to obtain an insight into the morphology of the catalyst using a Thermo Fisher Quanta 650 SEM (Thermo Fisher, Waltham, MA, U.S.A.) apparatus, with an accelerating voltage of 10 kV. Fourier transform infrared spectroscopy (FTIR) was employed using an FTIR Alpha instrument (Bruker Corporation, Billerica, MA, U.S.A.) to determine the chemical stability of the catalyst. Analyses were conducted in the spectral range between 4000 and 500 cm⁻¹, after 32 scans with a resolution of 4 cm⁻¹.

Table 1
Physico-chemical properties of Safranin O (SO)

Name	Safranin
Formula	C ₂₀ H ₁₉ N ₄ Cl
IUPAC nomenclature	3,7 diamino-2,8-dimethyl-5 phenylphenazinium chloride
Molar mass (g/mol)	350.85
Water solubility (g/L)	50
λ_{max} (nm)	518-520
Structure	
pKa	5.8

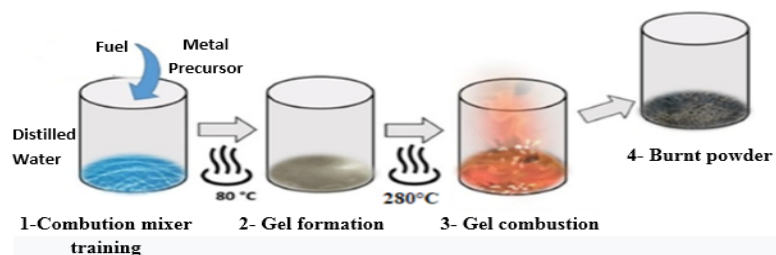


Figure 1: NiO-MgO catalyst synthesized by the self-combustion method



Figure 2: Degradation assembly used for photocatalysis

Photocatalytic degradation of Safranin O

The degradation of Safranin O was carried out in a thermostatically controlled glass beaker of 500 mL volume, cylindrical with double walls for circulation of cooling water. Using a magnetic bar, the solution was kept under continuous stirring to achieve homogeneity. To isolate it from natural light, the solution was covered with aluminum foil. The light used in the experiment was visible light from a 200 watt heat-resistant lamp. The distance between the lamp and the solution to be bleached must not be less than 5 centimeters, and it must not touch the solution because of the risk of explosion. The socket used was resistant to an intensity of 200 watts. All the withdrawn samples were analyzed with a UV-visible spectrophotometer (Pharmacia Biotech model), and the peak at 518 nm was used to monitor Safranin O absorbance over the irradiation time. The percentage of degradation was estimated using the following equation:^{3,4,9}

$$\text{Degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 is the initial dye concentration and C_t is the concentration of Safranin O after a certain reaction time t (min).

RESULTS AND DISCUSSION

SEM analysis

Scanning electron microscopy (SEM) observation was carried out on the synthesized

catalysts in order to better understand the development of the morphology and size of the crystallites. The results are shown in Figure 3. The analysis shows that the shape of the crystallites of the NiO-MgO catalysts is quasi-spherical, with an irregular structure.

FTIR analysis

The infrared transmission spectrum of the NiO-MgO catalyst was obtained after calcination of the material at 500 °C for 2 hours. The wavelengths studied are between 400 and 4000 cm^{-1} . The FTIR spectrum of the prepared catalyst is shown in Figure 4.

Different absorption bands of the NiO/MgO material were observed around 3600-3400, 2200-2400, 1500-1800 and around 444.41 cm^{-1} . The strong absorption peak in the range of 3200-3600 cm^{-1} and centered at 3400 cm^{-1} corresponds to the stretching vibration of the intermolecular hydrogen bond (O-H) existing between the adsorbed water molecules, and indicates a lower amount of hydroxyl groups. The weak peak recorded at 2350 cm^{-1} is ascribed to the asymmetric stretching vibration of CO_2 , which is due to the aerial CO_2 . The peaks observed at 444.41 cm^{-1} are assigned to the metal-oxygen

bending vibration, confirming Ni–O/Mg–O stretching vibration.

X-ray diffraction

The analysis by X-ray diffraction was carried out on the NiO-MgO catalyst prepared by the self-combustion method after being calcined at a temperature of 500 °C for 2 hours. The results of the XRD analysis are displayed in Figure 5. Sharp, well-defined peaks are observed at (2 theta) values of approximately 36, 42 and 62°, corresponding to the reticular plane (111), (200) and (202), respectively, the one at the 2 theta of

42° being the most intense peak. All these peaks could be indexed to a face-centered cubic structure, while the formation of the NiO-MgO solid phase was confirmed by the determination of the lattice parameter of MgO (JCPDS card n° 96-101-1174), which is close to that of NiO (JCPDS card n° 96-101-0096). The size of the crystallites of the synthesized catalyst was determined by XRD (Debye-Scherrer relationship); the value of crystallite size (nm) being 8 nm. These results are in harmony with those from similar work reported by Mohammad Jafarbegloo *et al.*³¹

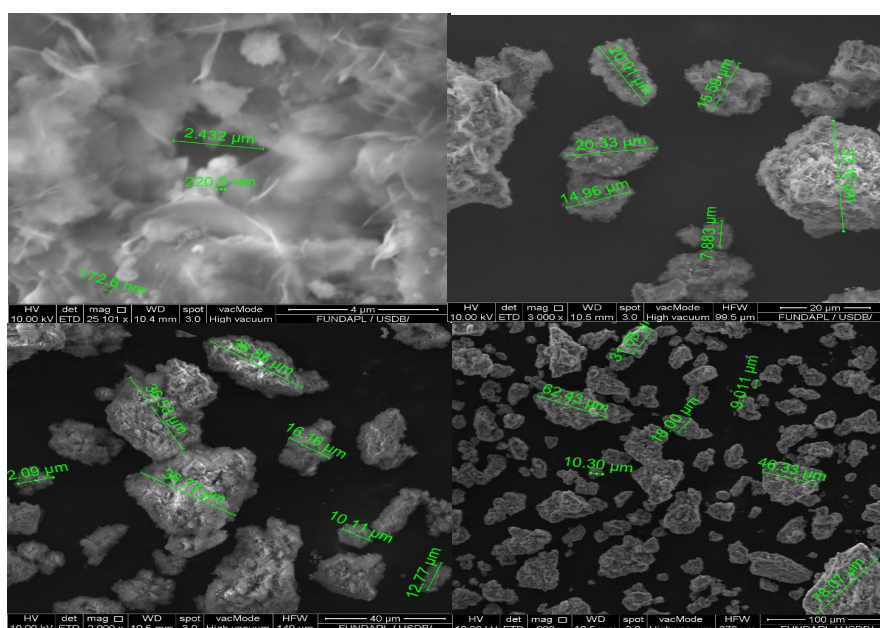


Figure 3: Scanning electron microscopy images of NiO-MgO catalyst

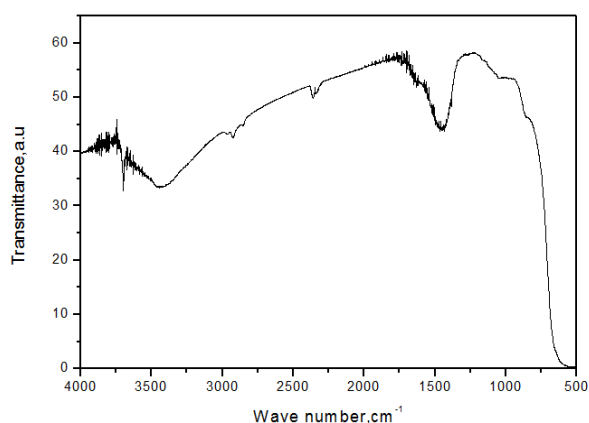


Figure 4: FT-IR spectrum of NiO-MgO catalyst

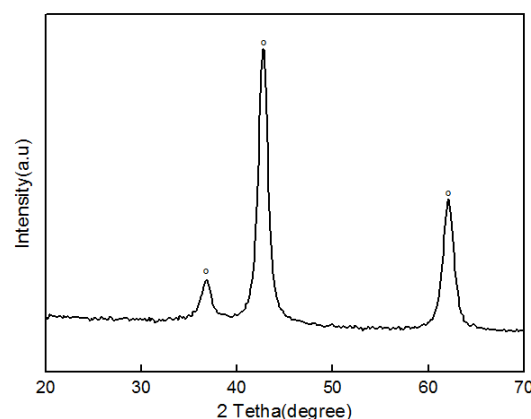


Figure 5: XRD pattern of NiO-MgO catalyst

Photocatalytic activity: experimental results

Adsorption, direct photolysis, and photocatalysis

Preliminary tests were performed to evaluate the photocatalytic performance of the prepared

material. To investigate the degradation process of Safranin O in wastewater, three successive experiments were undertaken: the first one was carried in the presence of the NiO-MgO catalyst,

without radiation (to reveal adsorption phenomena); the second – under light radiation without NiO-MgO catalyst (*i.e.*, photolysis); and the third one was performed under light radiation and in the presence of suspended NiO-MgO catalyst (*i.e.*, photocatalysis).

Figure 6 shows the progression of Safranin O degradation under these three regimens. It can be seen that photocatalysis has a significant effect on the photodegradation of Safranin O (up to 98% of Safranin O is degraded), while the effects of adsorption and photolysis are negligible (18.27% and 4.32%). These results are consistent with those reported by previous studies,^{6,7,9,24,25} where the researchers identified heterogeneous photocatalysis as a method that can oxidize most organic pollutants.

Effect of initial Safranin concentration

To study the effect of initial pollutant concentration on the photocatalytic degradation efficiency of Safranin O, we varied its concentration in the range from 10 to 30 mg/L at a free pH of 6.5 and a 0.04 g dose of NiO-MgO catalyst. The curve in Figure 7 represents the development of the degradation rate of Safranin O

within 150 minutes for different initial concentrations of the pollutant. The results show that the lower the initial concentration, the more obvious the degradation of Safranin O. At low substrate concentrations (10 mg/L) and irradiation times of 150 min, the degradation rate was as high as approximately 98.42%, while at initial concentrations of 20 and 30 mg/L, the degradation rate dropped to 92.53%. In other words, as the concentration of the pollutant increases, the degradation efficiency decreases. Our results are consistent with those reported previously in other works.^{3,6,7,8,9,24,30,32}

The degradation of Safranin O under visible light (intensity = 200 W) increased with increasing illumination time, as shown in Figure 8 (98.42% at the end of the reaction). An important change in the color of the solution during the reaction time is observed; the reduction of this color indicating the destruction of the chromosphere group responsible for the dye color (chromophoric groups of Safranin O are broken down and opened by the attack of OH radicals). The Safranin O dye was degraded into H₂O, CO₂ and mineral acids. These results are in agreement with those of similar works.^{5,6,9,11,32}

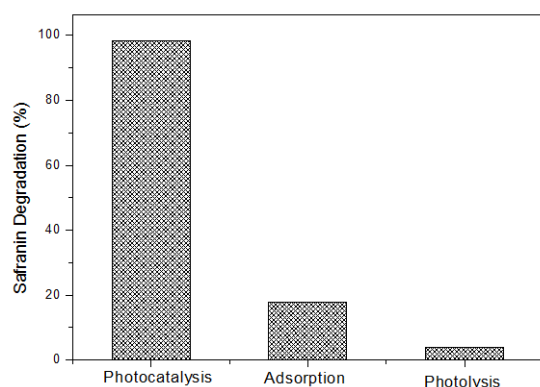


Figure 6: Degradation of Safranin O during different processes ($C = 10$ mg/L, C catalyst = 0.04 g/L, and free pH 6.5)

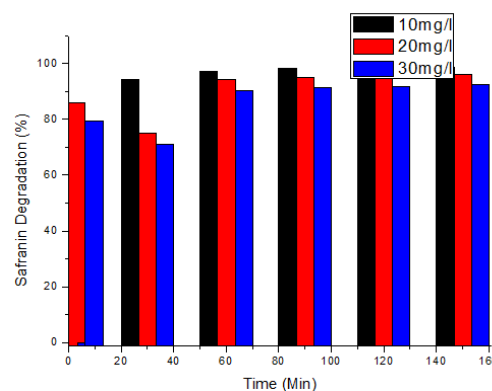


Figure 7: Photodegradation of Safranin O with time at different concentrations with visible light (free pH 6.5 and catalyst concentration = 0.04 g/L)

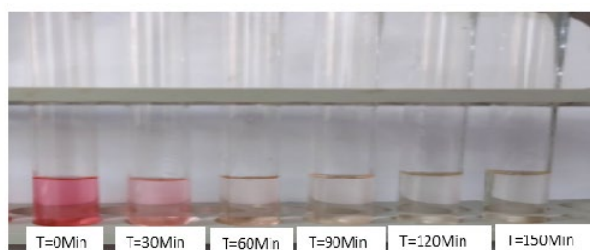


Figure 8: Kinetics of Safranin O photodegradation under visible light ($C = 10$ mg/L, C catalyst = 0.04 g/L, and free pH 6.5)

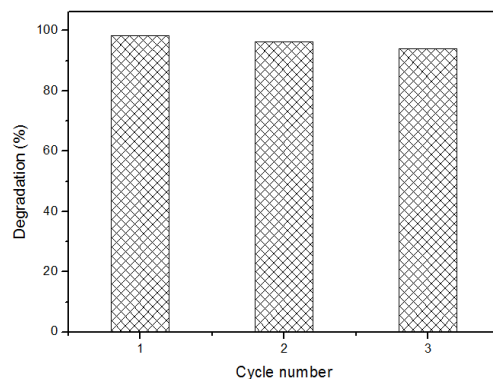


Figure 9: Photodegradation of Safranin O over three catalytic cycles in sunlight ($C = 10$ mg/L, C catalyst = 0.4 g/L, and free pH 6.5)

Reusability of NiO-MgO catalyst

Recyclability is one of the most important variables in catalysis research.³ By recycling, the material's efficiency was tested. Following each 150-min treatment, the catalyst was washed with distilled water and dried in an oven. According to the findings of our study on the photodegradation efficiency of Safranin O under visible light radiation following the reuse of recycled catalysts (Fig. 9), NiO-MgO continues to exhibit the same photocatalytic performance after three consecutive cycles, with a constant yield (94%) for a 150-min visible light irradiation period, with 4% of loss. This loss can be explained by the washing of the catalyst during the first use and cleaning step. These outcomes are consistent with those mentioned in related works.^{2,3}

CONCLUSION

The present work reports on the development of a NiO-MgO catalyst by a self-combustion method and its application in the degradation of Safranin O in water systems using the photocatalysis process. The results showed that NiO-MgO exhibited good photocatalytic activity, and the degradation rate of Safranin O was 98.42% at a free pH of 6.5, within 150 minutes of visible light exposure. Therefore, it can be concluded that NiO-MgO is a stable, robust, efficient, recyclable and separable photocatalyst for Safranin O removal. Therefore, the NiO-MgO photocatalyst can be recommended as a promising material for environmental remediation.

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