Journal of Geomine (2023), 1(1), 7-12
DOI: 10.22077/jgm.2023.6342.1003

Sunlight-Assisted Degradation of Bromocresol Green Using Co_3O_4 Nanoparticles as a High-Performance Photocatalyst

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Recived: 2023 May 06, Revised: 2023 Jun. 04, Online Published: 2023 Jun. 06

ABSTRACT

Excessive use and discharge of organic pollutants inevitably lead to their accumulation in the environment and bring considerable environmental risks. Innovative methods based on nanotechnology for wastewater treatment processes have been increasing in recent years. In this work, cobalt oxide (Co_3O_4) nanoparticles have been synthesized via a green and simple route and used as the effective photocatalyst for the degradation of bromocresol green. Approximately 88% of bromocresol green was degraded in the presence Co_3O_4 nanoparticles after 5 hours under sunlight. The kinetic studies showed that photocatalytic degradation process followed the pseudo-first-order kinetic model. The photocatalytic performance of Co_3O_4 nanoparticles was evaluated for the treatment of natural wastewater, and the obtained results showed that this system could remove 78% of organic dye within 5 hours. The promising points for this study were the easy operation, simple equipment, good catalytic performance, cleaner reaction profile and environmentally friendly reaction conditions. The obtained results showed that Co_3O_4 nanoparticles were an efficient catalyst that could be employed for the photodegradation of different types of organic pollutants.

KEYWORDS

Cobalt oxide, Nanotechnology, Organic dye, Photodegradation

I. INTRODUCTION

Organic dye is widely employed in leather, ceramics, drug, cosmetic, textile, printing, paper, and food processing industries. The organic dyes are potentially toxic to aquatic organisms, humans, plants and animals. The release of organic dyes as highly toxic, hazardous, carcinogenic, chemical and biologically stable contaminants in wastewater has become one of the essential sources of water pollution in the environment (Nasrollahzadeh et al., 2020). Conventional wastewater treatment techniques such as adsorption (Xiao et al., 2021), coagulation/flocculation (Golob et al., 2005) and reverse osmosis (Yang et al., 2019) have been used to remove organic dyes. Most of these methods cannot be adequate and sufficient in degradation of organic dyes due to shortcomings such as high cost, intensive energy requirements, poor efficiency and the production of hazardous by-products. Therefore, it is essential to develop an environmentally friendly and highly efficient process to remove organic dyes from wastewater. The organic pollutants could be removed from aqueous media with high efficiency using advanced oxidation processes (AOPs). AOP is one of the most cost-effective, easy and reliable methods to remove organic dyes from water (Phan et al., 2019). Semiconductors could be utilized as photocatalysts in AOPs for the efficient degradation of organic contaminants due to low cost, low energy consumption, tunable bandgap, variable oxidation states and low toxicity (Ahmadi et al., 2022). Recently, the semiconductors such as SnO_2 (Honarmand et al., 2019), ZnO (Golmohammadi et al., 2020), CuO (Ighalo et al., 2021), CdO (Somasundaram et al., 2019) and Co_3O_4 nanoparticles (Yang et al., 2019) have been introduced as effective photocatalysts for removal and mineralization of organic dyes. Among them, cobalt oxide (Co_3O_4) nanoparticles as p-type promising semiconductors have attracted increasing attention due to their good photocatalytic performance and high capability of sunlight harvesting. Various techniques have been used for the synthesis of Co_3O_4 nanoparticles such as microwave (Yahyazadehfar et al., 2019), sol-gel (Priyadharsini et al., 2020), solvothermal (Yuanchun et al., 2008), and hydrothermal (Lester et al., 2012) methods. These methods are energy intensive and costly and use toxic chemicals and hazardous solvents in the synthesis process. A suitable alternative to these traditional methods is the green synthesis of nanoparticles, which is considered safe and cost-effective. Calotropis gigantea (Sharma et al., 2015),

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Curcuma longa (Chelliah et al., 2023), Aspalathus linearis (Diallo et al., 2015) plants and walnut green skin (Mohammadi et al., 2021) were introduced for synthesis of Co_3O_4 nanoparticles.

In this study, for the first time, Co_3O_4 nanoparticles were synthesized using Salvia rosmarinus. The photocatalytic degradation of bromocresol green as an organic pollutant model was investigated using the biosynthesized Co_3O_4 nanoparticles under direct sunlight without any auxiliary agent. Also, the removal of bromocresol green from natural wastewater was performed to evaluate the industrial performance of the Co_3O_4 nanoparticles.

II. EXPERIMENTAL SECTION

A. MATERIALS AND CHARACTERIZATIONS

Cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$] and bromocresol green were purchased from Merck company. The double distilled water was used throughout the synthesis of Co_3O_4 nanoparticles and degradation experiments. The pH of the prepared solutions was measured by the Metrohm pH meter (Switzerland).The crystalline phase of Co_3O_4 nanoparticles was analyzed by X-ray Diffraction (Philips X'pert diffractometer type PW 1800 goniometer, Cu K_α = 1.5406 A°). Field-emission scanning electron microscopy (FE-SEM) using a TESCAN microscope (FE-SEM, Mira 3-XMU) was utilized to study morphology and surface structure of Co_3O_4 nanoparticles. Using a Shimadzu spectrophotometer (UV-2550 model), the UV-Vis diffuse reflectance spectroscopy (DRS) of Co_3O_4 nanoparticles was measured. FT-NIR spectroscope (RAYLEIGH, WQF-510) was used to record the Fourier-transform infrared (FTIR) spectra of the Co_3O_4 nanoparticles. The concentration of the bromocresol green solutions was analyzed by using UV/Vis spectrophotometer (GENWAY, UK).

B. SYNTHESIS OF Co_3O_4 NANOPARTICLES

The *Salvia rosmarinus* aqueous extract was prepared according to the procedure described in our previous study (Khoshdel et al., 2022). Fig. 1 displayes the procedure of preparing *Salvia rosmarinus* aqueous extract. For the synthesis of Co_3O_4 nanoparticles, initially, *Salvia rosmarinus* extract (10 mL) was added drop by drop under stirring to solution containing $Co(NO_3)_2{\cdot}6H_2O$ (25 mL, 0.1 M) at pH=12 for 0.5 hours at 25 °C. The stirring was continued for another 2 hours at 80 °C. Then, the precipitates were collected by centrifugation and washed with double distilled water, dried and calcinated (2 hours at 600 °C) and grinded finely.

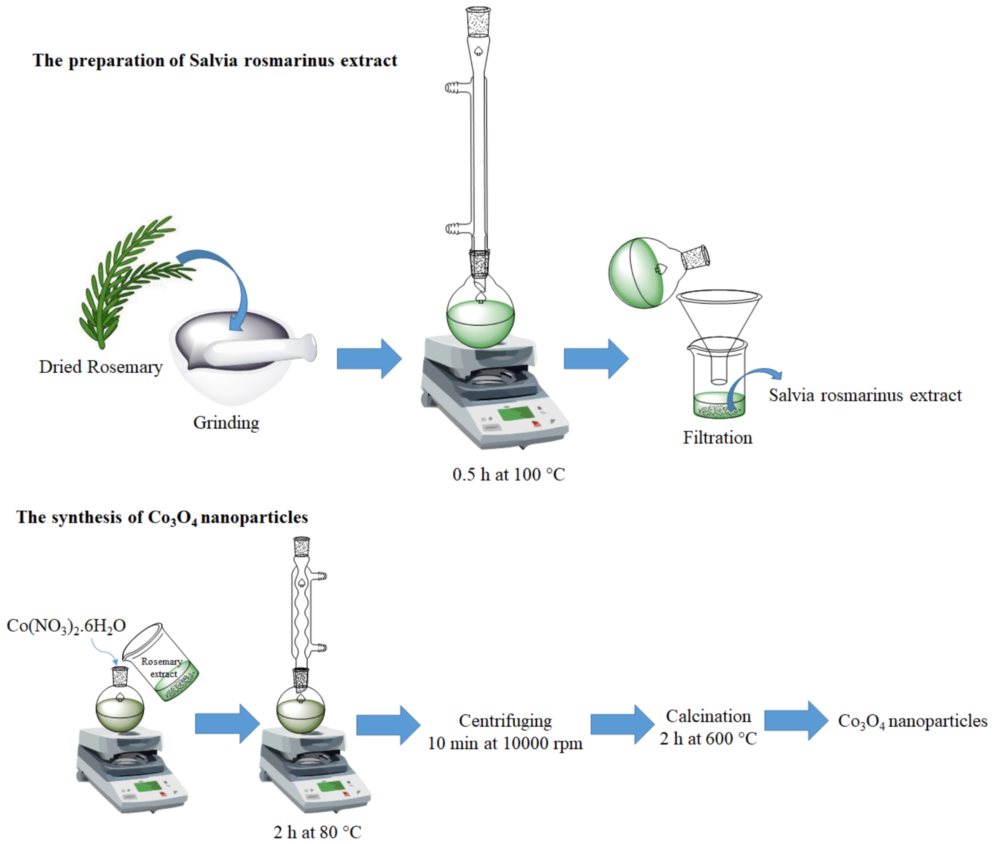

Fig. 1. Preparation procedure diagram of Co_3O_4 nanoparticles.

C. Photocatalytic experiments

The photocatalytic performance of Co_3O_4 nanoparticles was investigated by photodegradation of bromocresol green as a model of organic pollutant sunder direct sunlight. At first, Co_3O_4 nanoparticles (0.1 g) were uniformly dispersed in the bromocresol green solution (20 mg/L), and then the reaction mixture was stirred in darkness until achieving an adsorption-desorption equilibrium. Then, the experiment container was transferred to the open space and exposed to direct sunlight (the intensity of sunlight ~ 250 Klux). To identify the organic pollutants concentration, 3 mL supernatant was separated and centrifuged to measure the UV–Vis absorption spectrum. The kinetic and efficiency of bromocresol green removal were calculated according to the following equations:

$$-\ln\left(\frac{C}{C_0}\right) = kt$$

$$\text{Removal efficeincy } \% = \frac{C_0 - C}{C_0} \times 100$$

Where k was the pseudo-first-order rate constant (min^{-1}), and C_0 and C were the initial and final concentrations of bromocresol green concentration (mg/L) at the reaction time t (min), respectively.

III. Results and discussions

A. Characterization of the synthesized catalysts

The crystallographic information of Co_3O_4 nanoparticles was displayed in Fig. 2 In the XRD pattern of Co_3O_4 nanoparticles, five sharp peaks belonged to the cubic spinel cobalt oxide (JCPDS .No. 01-078-1969) located at 2θ = 31.27°, 36.88°, 44.66°, 59.27° and 65.22° indexed to (2 2 0), (3 1 1), (4 0 0), (5 1 1), and (4 4 0), respectively(Harish et al., 2016). The crystallite size of Co_3O_4 nanoparticles was calculated using the Debye-Scherrer equation(Kombaiah et al., 2018):

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where *D, k, λ, β* and *θ* were the particle size, shape factor (0.9), the wavelength of X-ray, the total maximum at half width (FWHM), and the diffraction angle, respectively. Using the above equation, the size of Co_3O_4 nanoparticles was calculated 16 nm corresponding to (3 1 1) plane.

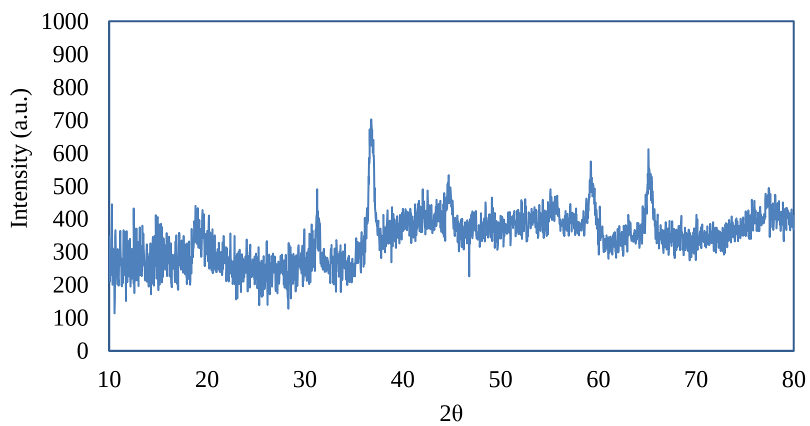

Fig. 2. XRD pattern of Co_3O_4 nanoparticles

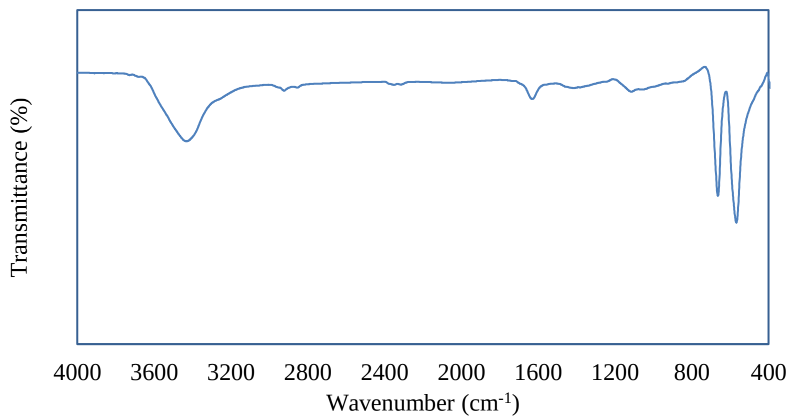

Fig. 3. FTIR spectrum of Co_3O_4 nanoparticles

FT-IR was employed to characterize the chemical bonding, impurity, defects, and elemental structure of Co_3O_4 nanoparticles. A broad band at 3100–3600 cm^{-1} and a short band at 1623 cm^{-1} were related to stretching and bending vibrations of the hydroxyl group (O–H), respectively (Ebrahimi et al., 2021). The peaks at 663 cm^{-1} and 566 cm^{-1} were assigned to the stretching vibration mode of Co-O bonds (X. Yang et al., 2023). FT-IR results indicated the successful synthesis of high purity Co_3O_4 nanoparticles (Fig. 3).

The FE-SEM image of Co_3O_4 nanoparticles was displayed in Fig. 4. As shown in Fig. 4, the morphology of Co_3O_4 nanoparticles was spherical with the negligible agglomerates. According to FE-SEM image, the size of Co_3O_4 nanoparticles was about 21 nm.

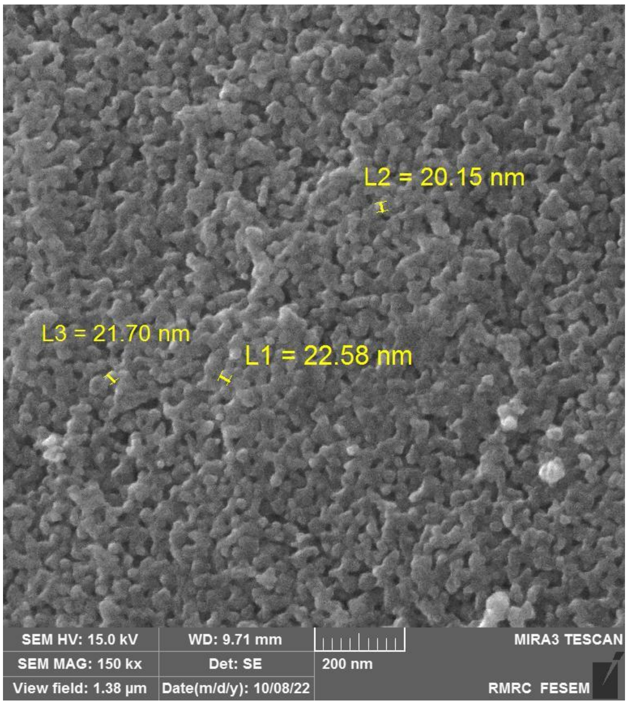

Fig. 4. FE-SEM image of Co_3O_4 nanoparticles

To identify the optical response of Co_3O_4 nanoparticles, DRS analysis was employed to determine the reflectance spectrum. Co_3O_4 nanoparticles showed a broad absorption in both ultraviolet and visible light regions (Fig. 5a). The Tauc's plot of the biosynthesized Co_3O_4 nanoparticles was revealed in Fig. 5b. According to Kubelka-Munk formula, the bandgap energy (E_g) of 2.02 eV was estimated. This result was similar to the findings in the literature (Y. Yang et al., 2022). Based on this analysis, it was found that Co_3O_4 nanoparticles could be activated in the range of visible light.

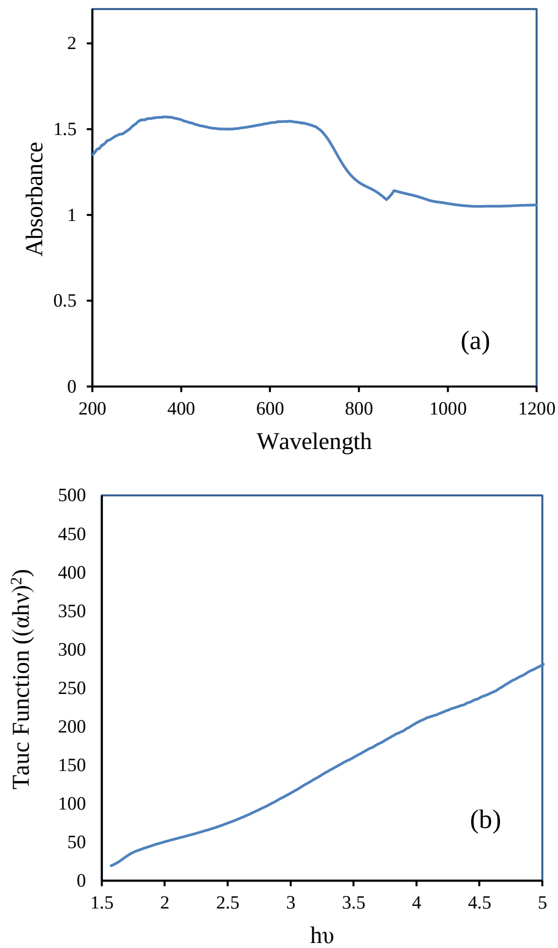

Fig. 5. a) UV–vis DRS and b) Tauc's plot of Co_3O_4 nanoparticles

B. DEGRADATION OF BROMOCRESOL GREEN

In this study, the bromocresol green was utilized as target pollutant to investigate the photocatalytic performance of Co_3O_4 nanoparticles. Fig. 6 displayes the bromocresol green removal efficiency. Approximately 88% of bromocresol green was degraded in the presence of Co_3O_4 nanoparticles after 5 hours of solar irradiation (Fig. 6a). The kinetic rate constant (k) of the bromocresol green degradation reaction could be considered based on the pseudo-first-order model equation (Fig. 6b). The obtained results showed that bromocresol green was well degraded using Co_3O_4 nanoparticles during the photocatalytic reaction.

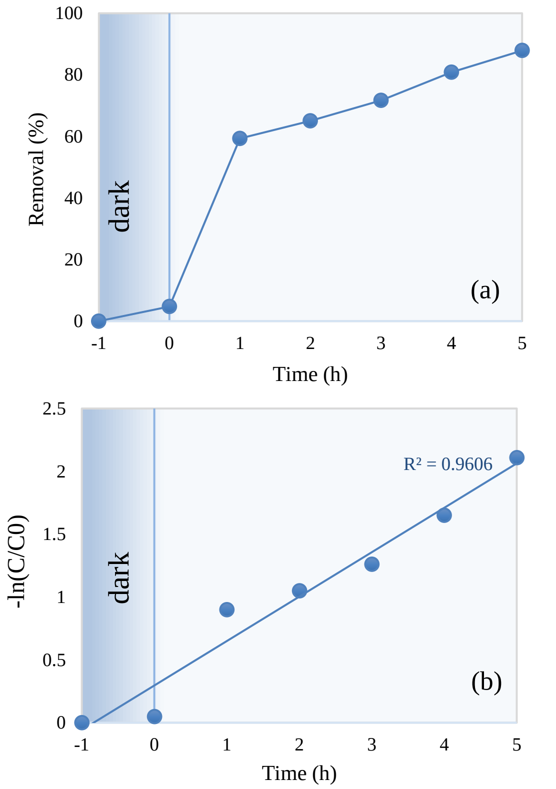

Fig. 6. a) Photocatalytic and b) kinetic degradation of bromocresol green

C. Application in Real Media

To evaluate the feasibility of Co_3O_4 photocatalyst, the degradation of bromocresol green was carried out on natural wastewater. The photodegradation performance of 78% was obtained for actual wastewater samples after 5 h of reaction under direct sunlight. The result for bromocresol green removal in actual wastewater revealed that this photocatalytic system was a suitable technique for removing organic dyes from wastewater solution.

IV. Conclusions

For the first time, Co_3O_4 nanoparticles were fabricated *via* a simple and green route using the extract of *Salvia rosmarinus*. The biosynthesized Co_3O_4 nanoparticles were characterized, indicating the spherically shaped nanoparticles with an average diameter of 21 nm and E_g = 2.02 eV. The photocatalytic activity of Co_3O_4 nanoparticles was studied for the degradation of bromocresol green under sunlight. The obtained results indicated the degradation of 88% of bromocresol green within 5 hours.

Acknowledgment

We highly appreciate the Birjand University of Technology and the University of Birjand for financially supporting this study.

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