PAPER

Green synthesis, characterization, and photocatalytic activity of cobalt chromite spinel nanoparticles

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Abstract

Eriochrome Black T, an azo dye, was degraded under visible light irradiation using CoCr2O4 nanoparticles as a photocatalyst. In this study, CoCr2O4 cubic-spinel nanoparticles were synthesized via a novel and green sol-gel method. The synthesized sample was characterized by EDX, XRD, TEM, FESEM, DRS, and FTIR. The CoCr2O4 NPs have good photocatalytic activity for degradation of Eriochrome Black T (EBT) dye at room conditions so that 90% of EBT was degraded in 90 min under the visible light. The CoCr2O4 NPs reusability was scanned and confirmed that the nano-photocatalyst shows a few declines in its activity after the three runs.

1. Introduction

Providing healthy and clean water to meet human utilization is a prominent challenge of the 21st century. Also, global climate change, population growth, reduce water reserves, enhance industrial and agricultural activity are the biggest concern globally [1, 2]. Furthermore, the frequently addition of inorganic and organics pollutants from diverse sources such as chemical spills, industrial evacuation, and agricultural wastewater poses significant threats to the available natural water source and is main hazardous to the ecosystem [3, 4]. The crisis conditions about industrial pollutants are that they are consist of various dyes with high chemically stable and difficult decomposition so the elimination of synthetic dyes from wastewaters is a serious environmental task that has to be deal with scientifically. Between various chemical and physical methods, degradation techniques are one of the beneficial processes that have been favorably applied for dye removal from wastewater [5–10].

Nanotechnology has excellent potential in advancing wastewater and water treatment to improve treatment performance as well as to increase water supply by secure use of uncommon water sources. Nanotechnology is an interdisciplinary science containing medical, toxicology, physics, biology, engineering, chemistry, mechanics, and newly environment [11–15]. Diverse methods have been presented for the preparation of nanomaterials [16–18]. Researchers are interested in green synthesis by expending natural polymers because they are non-toxic, cost-effective, easily achievable and eco-friendly [19, 20]. Gum is naturally situated polysaccharide component in plants that are often easily available, economical, and green [21–23].

Herein, CoCr2O4 spinel NPs were synthesized via the sol-gel method and their photocatalytic activity for degradation of EBT dye was investigated in aqueous solution under visible irradiation. CoCr2O4 NPs were characterized by FTIR, XRD, FE-SEM, EDX, TEM, and DRS technique. The molecular structure of EBT dye is given in figure 1.

2. Experimental

2.1. General information

The tragacanth gum (TG) was acquired from a native health food shop. The CoCl2.6H2O and CrCl3.6H2O were purchased from Merck. The structural attributes of CoCr2O4 nanoparticles were certified by x-ray powder
diffraction (XRD) analysis on with a X’Pert PRO advanced diffractometer using Cu (Kα) radiation in wavelength: 1.5406 Å, operated at 40 kV and 40 mA (2θ = 10–80). The FT-IR spectroscopy was recorded by Jasco 6300. Morphology of the sample surfaces was perused by scanning electron microscope (Tescan Mira3) equipped with an energy dispersive x-ray spectrometer (EDX). The TEM analysis of the catalyst was conducted using an EM 208S. Diffuse reflectance UV–Vis spectroscopy (DRS, Shimadzu, UV-2550) was used to evaluate the band gap energy of the samples. UV–Vis absorption spectra were collected on a Metrohm (Analytical Jena-Specord 205) double-beam instrument.

2.2. Photocatalysts preparation
Firstly, 0.2 g of the TG was added and blended in deionized water (40 ml) and stirred (70 °C for 80 min). In next step, 2 mmol CrCl3.6H2O and 1 mmol CoCl2.6H2O were dissolved in 10 ml of deionized water and added to the gel solution. Afterwards, the container moved to a sand bath with continuous stirring (75 °C for 12 h). In final, the obtained black color resin was calcined for 4 h at 600 °C to acquire green color CoCr2O4 NPs.

2.3. Photocatalytic dye degradation
The photocatalytic activity of CoCr2O4 NPs was perused by a series of experiments for the degradation of EBT dye. Tests were performed in a batch reactor by a 90 W lamp (λ > 400 nm). Variant amount of CoCr2O4 NPs (0.02, 0.03, 0.04 and 0.05) was added to 20 mg l−1 concentration of a dye solution (50 ml) for analysis the photocatalytic dye degradation at room conditions. Also different dye (EBT) concentrations (10, 20, 30 and 40 mg l−1) were prepared and tested with optimized dosage of catalyst in 50 ml volume. Degradation of Eriochrome Black T dye was monitored in the absence and presence of visible light. For this intention, 50 ml of dye solution (20 mg l−1) was prepared and 0.04 g of NPs sample was dispersed in it. The suspensions were stirred by a magnetic stirrer and after determined time, the suspended nanoparticles and solution above catalyst were separated by a centrifuge (universal 320 Hettich) at 4000 rpm for 15 min. The concentration of EBT dye was also estimated by UV–Vis spectrophotometer at a λmax = 538 nm (maximum wavelength of EBT dye).

The following relation was exploited for the estimation of photodegradation efficiency.

\[
\%\text{Degradation} = \frac{A_0 - A_t}{A_0}
\]

Where, A0 is prime absorbance and At is absorbance at definite time t.

3. Results and discussion
3.1. Characterization of cobalt chromite catalyst
FTIR analysis was executed to consider the chemical structure of the as-prepared samples. Figure 2(a) displays FTIR absorption spectra of CoCr2O4 NPs. two peaks at 528 cm−1 and 629 cm−1 can be seen. These peaks refer to the stretching vibration of the metal- oxygen bond [24]. These two bands confirmed that Chromium and Cobalt were placed in oxygen surrounding in the spinel structure. The small peak at 876 cm−1 can be attributed to the stretching vibration of cobalt-oxygen band in the spinel structure [25]. Also, can be said the bands at 1626 and 3424 cm−1 are specific for stretching vibrations of a surface hydroxyl group (O–H).

The phase and structural determination of the spinel CoCr2O4 nanoparticles were characterized by XRD technique. As shown in the XRD pattern (figure 2(b)), for the synthesized CoCr2O4 NPs via a green sol-gel method, all peaks are excellent indexed to CoCr2O4 (PDF card No.: 22-1084). The average crystallite size of synthesized nanoparticles was calculated from the Scherrer formula (2):

![Figure 1. Structure of Eriochrome Black T (EBT) dye.](image-url)
Here $\theta$ is the reflection angle, $\beta$ is the full width at half maximum (FWHM) of the peak, $\lambda$ is the x-ray wavelength of Cu K$\alpha$ = 0.154 nm and $D$ is the crystallite size (nm) [26]. By use of the mentioned equation, the computed amount of average crystallite size was 21 nm for CoCr$_2$O$_4$ NPs.

The morphology of the CoCr$_2$O$_4$ NPs was recorded by SEM and TEM micrographs. SEM micrographs of CoCr$_2$O$_4$ NPs are shown in figure 2(c). It can be observed that nanoparticles have spherical shapes. TEM image (figure 2(d)) shows the morphology and particle size of the CoCr$_2$O$_4$ NPs. the CoCr$_2$O$_4$ NPs morphology is spherical and particle size is roughly 35–40 nm.

EDX analysis was applied to further confirm the compositions of the prepared sample. Figure 2(e) indicates that the CoCr$_2$O$_4$ NPs contain Co, Cr, and O.

Electronic state and optical absorption features of CoCr$_2$O$_4$ photocatalyst were measured using DRS analysis (figure 2(f)). The band gap energy was evaluated by using the Tauc equation (3) [27].

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

That $E_g$, $A$, $h\nu$, and $\alpha$ are the band gap, edge width parameters independent of photon energy, energy of the incident photon, and absorption coefficient, respectively. The result showed that the band gap of CoCr$_2$O$_4$ is roughly 2.4 eV (figure 2(g)). So, it is confirmed that synthesized nanoparticles are the good photocatalyst in a visible-light region.

In order to study photocatalytic activity, photodegradation of Eriochrome Black T dye was performed as a water pollutant using CoCr$_2$O$_4$ NPs in the optimum condition.

### 3.2. Effect of visible light irradiation on CoCr$_2$O$_4$ NPs

In this part, the photocatalytic activity of CoCr$_2$O$_4$ NPs on the degradation of Eriochrome Black T dye was studied in three conditions; visible light irradiation without CoCr$_2$O$_4$ NPs, Nanocatalyst under dark, and CoCr$_2$O$_4$ NPs under visible light irradiation. In visible light alone state, we have only 4% degradation. By using CoCr$_2$O$_4$ NPs catalyst under dark condition, we have dye removal of 42%. Figure 3 displays by applying both catalyst and light, 90% of EBT dye was decomposition at 90 min. These consequences indicate that CoCr$_2$O$_4$ nanoparticles have good photocatalytic activity for degradation of EBT dye.

### 3.3. Effect of photocatalyst dosage

From an economic viewpoint, the catalyst amount is a significant parameter in the photocatalysis method [28]. For measuring the impact of photocatalyst amount on decolorization, different concentrations (between 0.02–0.05 gr) of the CoCr$_2$O$_4$ NPs were inquired in 50 ml of EBT dye (20 mg l$^{-1}$), at a constant time of 90 min. The results are exposed in figure 4 and confirmed enhancing catalyst dosage resulted in enhancing the degradation of EBT dye. By enhancing the photocatalyst amount, the active reaction sites of nanocatalyst and reactive radicals are raised and as a result enhanced photodegradation efficiency [29, 30]. Degradation percentage improved from 56% to 90% as a
result of changing CoCr$_2$O$_4$ NPs dosage from 0.02 to 0.05 gr. Thus, 0.04 gr catalyst was chosen as the appropriate amount for this experiment.

3.4. Effect of initial dye concentration
The concentration of dye is one of the main parameters that changed the degradation efficiency in photocatalytic degradations [26]. So, photocatalytic degradation of EBT dye was surveyed by varying initial EBT dye concentrations (10–40 mg l$^{-1}$) with constant CoCr$_2$O$_4$ dosage (0.04 g). As shown in figure 5 the degradation percent of EBT decreases from 92% to 61% when the initial dye concentration reaches from 10 to 40 mg l$^{-1}$, respectively.

3.5. Effect the irradiation time on the dye degradation
The UV–vis absorption spectra of the EBT were followed for monitoring the photodegradation in present of CoCr$_2$O$_4$ nano photocatalyst at diverse irradiation time. UV–vis absorbance spectra were investigated for presumed the impact of irradiation time on degradation amount. The decrease in absorbance intensity at 538 nm (maximum wavelength of EBT dye) with increasing irradiation time is certified in figure 6. Approximately 90% of EBT was degraded in 90 min.

3.6. Reuse of the photocatalyst
The reusability and regeneration of as-prepared nanoparticles were appraised for the degradation of EBT dye in the optimized reaction conditions. So, nanoparticles were gathered from the decolorized solution by centrifuge and washed with distilled water under ultrasonic irradiation and used in the next run. As shown in figure 7, the photocatalytic activity of the CoCr$_2$O$_4$ NPs displays a small diminish in its performance after the three runs. Thus can say that CoCr$_2$O$_4$ NPs are stable and preserve high decolorization efficiency.
Figure 5. Effect of the initial concentration of EBT dye on the decolorization efficiency (%).

Figure 6. Absorption spectra of EBT solutions (20 mg l$^{-1}$) in the presence of 0.04 g of CoCr$_2$O$_4$ photocatalyst under visible light radiation.

Figure 7. Recyclability of CoCr$_2$O$_4$ NPs.
3.7. Effect the temperature on dye degradation

Comparison between the yield of photocatalytic degradation and thermal decomposition was considered and obtained result shown in Figure 8. For investigated the impact of temperature on dye degradation efficiency, different temperature was selected and applied. By changing the temperature from room temperature to 40 °C, the photodegradation efficiency was changed from 90% to 93% after 90 min. Also, by increasing the temperature to 50 °C, the degradation efficiency was reduced to 88%. These results confirm the photocatalytic activity of CoCr2O4 nanoparticles for degradation of EBT dye and temperature has little performance on thermal decomposition of selected dye.

4. Conclusions

In summary, spinel CoCr2O4 nanoparticles were prepared by a green sol-gel method and used as advantageous heterogeneous photocatalysts for water purification. This easy method has important benefits such as non-toxic, inexpensive, free from any organic solvents and surfactant, and environmentally friendly. The structure of the as-synthesized sample was characterized by EDX, XRD, FESEM, TEM, DRS, and FTIR. XRD pattern confirmed CoCr2O4 was successfully synthesized with a pure phase cubic spinel structure without diffraction peaks of impurities. The photocatalytic activity of the synthesized catalyst was investigated on the aqueous solution of EBT dye. Results show that 90% of EBT dye was considerably degraded after 90 min under the visible light irradiation, room temperature, and natural pH.

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