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Green synthesis of nano size $CoFe_2O_4$ using Chenopodium album leaf extract for photo degradation of organic pollutants

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Abstract

Green synthesis of nanoparticles makes use of environmental friendly, non-toxic and safe reagents. In this study, we synthesised $CoFe_2O_4$ in a green approach, using leaf extract of Chenopodium album. The structure of the synthesised sample was analyzed by X-ray diffraction methods. The synthesised Photocatalyst was applied for photo degradation of methy orange as a reliable model pollutant. The results indicated that $CoFe_2O_4$ exhibited good efficiency for the degradation of MO under UV light irradiation; the degradation ratio reached to 100% after 3 h irradiation. In addition, easy separation of the catalysts from the treated wastewater by magnetic separation makes it available for flow-bed technologies.

Keywords: Photo degradation; Chenopodium album; magnetic nanoparticles; spinel.

Introduction

Water pollution is one of the important challenges of the world. One of the main causes of disease and mortality in the world is water pollution. Both groundwater and surface water are exposed to various pollutants. Due to different sources of pollutants, natural or man-made, the different classifications for contaminants have been considered. Many contaminants, including a wide variety of organic compounds and metals, are toxic to humans and other organisms. Some of these organic contaminants may be biologically decomposable, but many of them are toxic and not be biologically decomposable. Thus, these compounds can persist in the environment for a long time and will cause harmful effects on humans and ecosystems [1-3].

Therefore, it is necessary to develop the methods in order to be able to degrade the organic contaminants present in the industrial wastewater by an effective, safe and efficient manner.

Among these, the pothocatalytic oxidation using semiconductors can be considered as the most effective technique to remove these contaminants. In recent years, heterogeneous photocatalytic reactions have been actively investigated because of easy separation of the catalysts from the treated wastewater. Among these, spinel ferrite nanoparticles have received much attention in the heterogeneous photo degradation of organic contaminants owing to their unique advantages of complete mineralization of organic pollutant [4-8]. Among spinel ferrites, $CoFe_2O_4$ is especially interesting due to its strong

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anisotropy, excellent chemical stability, high coercivity, high corrosion resistivity, moderate saturation magnetization, high mechanical hardness and high Curie temperature [9-11]. $CoFe_2O_4$, have the inversed spinel structure with general formula $B[A_{0.5}B_{0.5}]_2O_4$ [12]. The oxygen atoms are cubic close-packed and the A and B ions occupy both tetrahedral and octahedral positions. All A cations and half of the B cations occupy octahedral sites, while the other half of the B cations occupy tetrahedral sites.

Many preparation methods for $CoFe_2O_4$ nanoparticles have been reported, such as the ball milling, co-precipitation, hydrothermal synthesis, sol-gel, and reaction in a micro-emulsion [13-17].

In recent years, the biosynthesis of nanoparticles by natural sources including plants, fungi, yeast, bacteria, actinomycetes, and etc. have been actively investigated.

Biosynthesis of nanoparticles makes use of eco-friendly, non-toxic and safe reagents [18].

The green method for synthesis of nano particles is simple, efficient, cost effective and eco-friendly in comparison to chemical-mediated synthesis [19-23].

Biosynthesis of nanoparticles especially by plants is the most effective process of synthesis at a very affordable cost [24-27].

In this research, we have utilized the leaf extract of Chenopodium album for synthesizing $CoFe_2O_4$ nano particels. Chenopodium album is a fast-growing weedy annual plant (Figure 1). It is one of the most widely distributed plants in the world [28], tolerant of poor soils, high altitudes, and minimal rainfall. Global warming is just fine with Chenopodium album. In higher concentrations of carbon dioxide, it grows almost double in size. A wide variety of chemical constituent's such as aldehyde, alkaloids, proteins, flavonoids, were reported in phytochemical studies from this plant [29,30].

Figure 1. Picture of Chenopodium album

Experimental

Materials

All chemicals used in the experiment were analytical grade and were obtained from Merck (Germany). Cobalt (II) nitrate hexa hydrate $Co(NO_3)_2.6H_2O$, 99.0%, and ferric (III) nitrate hexa hydrate $FeCl_3.6H_2O$, 98.5%, were used as precursors. X-ray diffraction (XRD) patterns in the 2θ

angular range from 20◦ to 70◦ were obtained by a Bruker make Diffractometer using Cu Kα X-rays of wavelength (λ=1.5406 Å). The radiation source was a low pressure mercury UV lamp emitting at 254 nm (30 W, UV-C) which was placed above a batch photoreactor for degradation experiments. The solutions were analyzed by a UV-visible spectrophotometer (PG Instruments-T 70) at λ=477nm. All glasswares were washed in dilute HNO_3 acid and rinsed thoroughly with distilled water prior to use. pH was adjusted to the required value with 0.1M HCl. The freshly leaves of Chenopodium album (Figure 1) were collected from different agriculture farms at Abadeh, Iran. It was thoroughly washed with distilled water to remove all dust and any dirt, cut into small pieces and dried at room temperature.

Preparation of the leaf extract

The fresh leaf extract used for the synthesis prepared from 20 g of dried leaves were cut to small pieces in a 500 mL Erlenmeyer flask containing 50 mL double distilled water and boiled for 5 min and allowed to cool to room temperature. The aqueous extract was filtered with Whatman 1 filter paper.

Synthesis of magnetite nanoparticles

$CoFe_2O_4$ were prepared by coprecipitation method. In a typical reaction, $Co(NO_3)_2.\ 6H_2O$ and $FeCl_3.6H_2O$ with the molar ratios 1:2 were dissolved in 100 mL of double distilled water under mild stirring at room temprature. The mixture was then treated through a drop-by-drop addition of 5 mL of the aqueous solution of Chenopodium album leaf extract undervigorous stirring. Final pH of the reaction mixture was adjusted to pH=8 and stirring was continued for 1 h at 60 °C. The mixture was allowed to cool down to room temperature. The precipitate was washed several times with double distilled water and filtered. The resulting powder was then dried and calcined at 450 °C for 3 h. The structure of the synthesised sample was analyzed by X-ray diffraction methods.

Photocatalytic activity test

The photocatalytic activity of the catalyst was examined under irradiation of two 30 w high-power mercury lamps at 254 nm (30 W, UV-C) which were placed above a batch photoreactor. 0.05 g of photocatalyst was added to 100 mL methylorange solution (30 ppm) and the mixture was stirred for 30 min to obtain better dispersion and adsorption performance prior to the degradation. The initial solution pH was adjusted to pH=3 by the diluted HCl solution. The starting point of the reaction was defined as the time when the UV light was turned on and H_2O_2 (1 mL) was added to the reaction mixture. After degradation time lasted 3 h, the remaining MO in the sample solution was determined using a UV-visible spectrophotometer at 477 nm, which is the maximum absorbance wavelength of the MO solution.

Results and discussion

The magnetite nanoparticles $CoFe_2O_4$ were successfully synthesized by this green method using Chenopodium album leaf extract. The Chenopodium album leaf extract has the ability to act as reducing agent and stabilizer for magnetite nanoparticles. The magnetite nanoparticles were capped by the C=O of carboxylic group in Chenopodium album leaf extract. In this process, initially, metallic salts hydrolyzes to form metalic hydroxide and releases H^+ ions, thereafter, the hydroxide is partially reduced by the leaf extract to

form $CoFe_2O_4$ –NPs. At the end of the reaction, $CoFe_2O_4$ nanoparticles were capped and stabilized by protein chain of leaf extract.

X-Ray diffraction studies

X-ray diffraction pattern of synthesized $CoFe_2O_4$ is presented in Figure 2. Peak details of synthesized $CoFe_2O_4$ nanoparticles are summarized in Table 1.

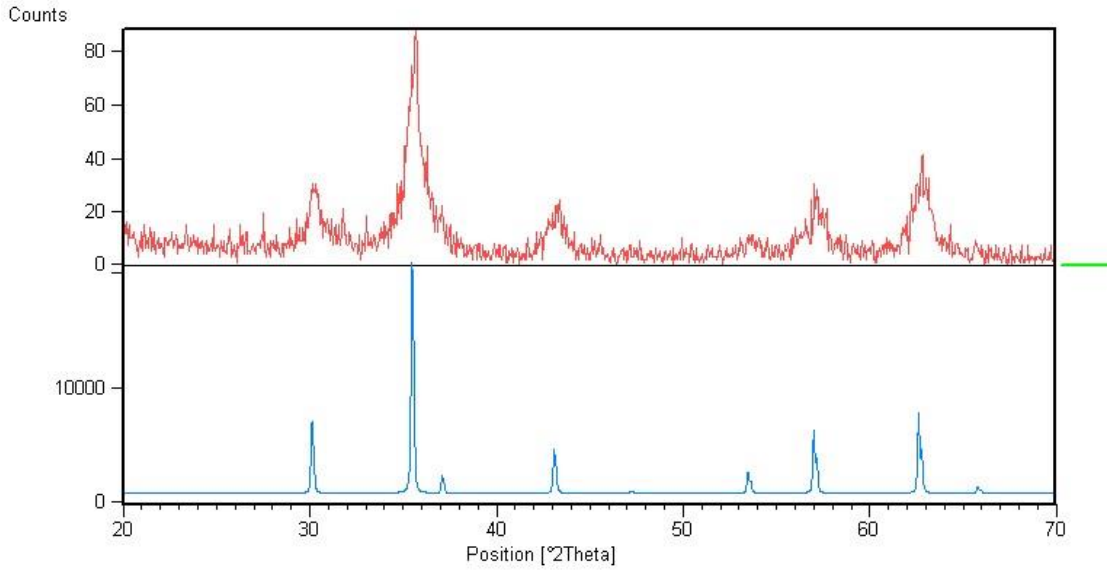

Figure 2. XRD pattern of synthesized $CoFe_2O_4$

Table 1. Peak analysis of XRD pattern of synthesized $CoFe_2O_4$

2θ (deg)	**FWHM**	**Miller indices (hkl)**
30.22	0.3936	220
35.57	0.5904	311
43.14	0.9840	400
53.69	0.7872	422
57.22	0.7872	511
62.85	0.4920	440
74.32	0.7200	533

The sharp and broad peaks in this XRD pattern, confirming the single phase formation of pure $CoFe_2O_4$ with the expected cubic inverse spinel structure with Fd3m space group and without any impurity phase. The lattice constant, calculated from (311) reflections were 8.3578.

The crystalline size of the particles was calculated using the modified Debye-Scherrer equations [31]. Modified Scherrer equation plots $\ln \beta$ against $\ln \frac{1}{\cos \theta}$ and obtains the intercept

of a least squares line regression. After getting the intercept, then the exponential of the intercept is obtained:

$$e^{\ln\frac{K\lambda}{L}} = \frac{K\lambda}{L} \qquad (1)$$

Having K = 0.9 and λ (λ Cukα = 0.15405 nm), from which a single value of L is obtained through all of the available peaks. The results indicate that nanocrystalline $CoFe_2O_4$ powder with crystallite size of 13 nm have been successfully obtained.

Photocatalytic activity

In this section, we report on the photoactivity of $CoFe_2O_4$. Because of its environmental significance and nonbio-degradation, methyl orange was selected as a reliable model pollutant in photo catalytic activity investigation. The existence of an optimum hydrogen peroxide concentration is typical and well-known in photocatalytic oxidation. This optimum value was previously found to be 10 mM for MO degradation [32].

PH is another main factor influencing the rate of degradation of some organic compounds in the photo catalytic process. The photo degradation of MO at different pH from 3 to 10 have been studied [33,34], and the best results obtained in acidic solution (pH = 3).

The photo degradation of MO is carried out in the presence of $CoFe_2O_4$ photocatalyst and H_2O_2 under UV irradiation at pH=3. The results showed that the intensity of the characteristic peak of MO at λ_{max} = 477 nm decreased gradually and complete dis-coloration of dye was observed after 3 h under optimum conditions. This proves that photocatalytic degradation is a viable means of dye removal from wastewaters.

In the first step, calibration curve was obtained using standard MO solutions with known concentrations (Figure 3).

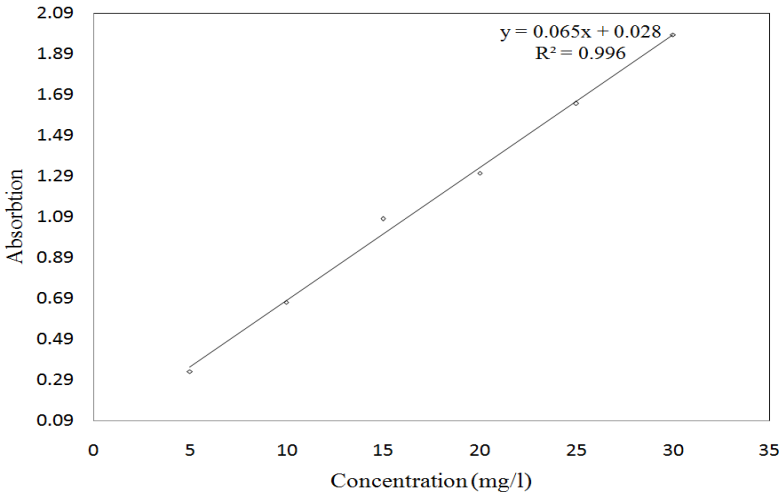

Figure 3. Calibration curve of MO

Consequently, the degradation efficiency of the photo catalytic process was evaluated by the degradation ratio (D) of MO, which was calculated with the following formula:

$$D(\%) = \frac{C_0 - C_t}{C_0} \times 100 \qquad (2)$$

Where D% was the degradation rate of MO, C_0 and C_t denote the initial and the time-dependent concentration respectively. The results indicated that

$CoFe_2O_4$ exhibited the best efficiency for the degradation of MO under UV light irradiation, which the degradation ratio reached up to 100% after 3 h of irradiation. The attractive features of this degradation process were very short reaction time, high efficiency, simple work-up procedure, as well as provision of an ecofriendly and green synthesis making it an excellent alternative to other reported protocols [4-8].

Conclusion

$CoFe_2O_4$ nano magnetic particles were synthesized by a convenient, facile, reliable, cost effective and eco-friendly method in one pot reaction using Chenopodium album leaf extract. The crystalline size of magnetite nanoparticles was 13 nm and can be applied in a variety of existing applications. In this study, $CoFe_2O_4$ as photocatalyst showed a high activity for Methyl Orange degradation under UV irradiation. Magnetic nanoparticles have a good potential for treatment of contaminated water duo to easy separation by applying a magnetic field.

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