

RESEARCH PAPER

Biosynthesis of MgFe_2O_4 magnetic nanoparticles and their application in photodegradation of malachite green dye and kinetic study

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ABSTRACT

In this study, we have reported the green synthesis of magnesium ferrite using tragacanth gel by the sol-gel method without using any organic chemicals. The sample was characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), vibrating sample magnetometer (VSM), and scanning electron microscopy (SEM). The X-ray powder diffraction (XRD) analysis revealed the formation of cubic phase ferrite MNPs. Magnetic analysis showed that the MgFe_2O_4 had a superparamagnetic behavior with a saturation magnetization of 14 emu/g at room temperature. The present catalyst displays high photocatalytic activity for the removal of malachite green dye under irradiation with visible light. The effects of MgFe_2O_4 dosage, initial dye concentration and visible light irradiation on dye degradation were evaluated. The results demonstrated that the catalyst can degrade ca. 98% of the malachite green dye. The catalyst can be easily recovered by a simple magnetic separation and can be recycled six times with no significant loss of photocatalytic activity.

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INTRODUCTION

Spinel ferrites have achieved huge attention in recent years because of their useful electrical and magnetic properties. Spinel ferrites have different applications in information storage systems, permanent magnets, sensors, magnetic drug delivery, recording heads, antenna rods, catalysis, loading coils, magnetic liquids, telecommunication devices, magnetic refrigeration, and as a microwave absorber [1-7]. So much interest has been paid on the synthesis and characterization of nanoparticles of spinel ferrites. Molecular formula of magnetic spinel ferrites is MFe_2O_4 in which M can be any divalent metal cation. In spinel ferrite, M^{2+} and Fe^{3+} occupy the tetrahedral (A) and octahedral (B) interstitial sites of the fcc lattice formed by O^{2-} ions, respectively [8-12]. The unit cell of a spinel ferrite

consists of 32 oxygen atoms, 16 trivalent irons and 8 divalent metal ions [13, 14].

Magnesium ferrite (MgFe_2O_4) is one of the important spinels with a cubic structure of the normal spinel-type. These nanoparticles have a band gap of 2.18 eV, so their magnetic NPs could be potential photocatalytic to remove the pollution [15, 16]. There are various chemical and physical methods for the synthesis of nanoparticles such as sol-gel methods [2,17-18], sonochemical technique [19], hydrothermal methods [20, 21], microwave processing approaches [22], coprecipitation [23, 24], etc. The use of natural gels in the synthesis of nanoparticles has attracted the attention of researchers, due to the lack of toxicity, cost-effectiveness and environmental compatibility [25-27].

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Lately, various methods, such as coagulation, advanced oxidation processes (AOP), electrochemical, ozonation, sonolysis, and photocatalysis, have been applied in the removal of organic dyes and industrial pollutants [28-31]. Among all the methods, advanced oxidation processes by heterogeneous photocatalysis have been considered for removal of contaminants [32-34]. Malachite green (MG) (Fig. 1) is a cationic triphenylmethane dye which is usually used in the laboratory, coloring agents in leather, food, textile, tannery, plastic, wool, etc. Malachite green is not easily degradable, it is mutagenic and carcinogenic [35, 36]. In this study, we have reported, the synthesis of superparamagnetic magnesium ferrite nanoparticles using TG by the sol-gel method as a cheap, facile and friendly approach to the nature. The photocatalytic activity of magnesium ferrite nanoparticles has been assessed for the removal of MG dye. The magnesium ferrite nanoparticles demonstrated the highest catalytic properties for the degradation of MG in short time.

EXPERIMENTS

Materials

The Tragacanth gum (TG) was obtained from a local health food store. All the chemicals were purchased from Merck and daijung (Darmstadt, Korea), and used without further purification. Phase identification of MgFe₂O₄ MNPs was characterized by X-ray powder diffraction (XRD) with a X'Pert PRO advanced diffractometer using Cu (K α) radiation (wavelength: 1.5406 Å) in the range of 2 θ from 10 to 80. The morphological properties of the sample were studied by using scanning electron microscope (Zeiss EVO 18, Germany). Optical properties was assessed by a double beam UV-Vis absorption spectrophotometer (Analytical Jena-Specord 205, Germany). The infrared spectra

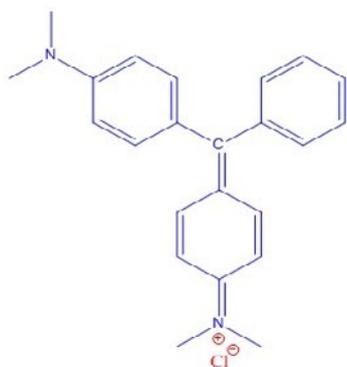


Fig. 1. Chemical structure of malachite green

(FTIR, Mattson, Unicam Ltd., Cambridge, UK) and vibrating sample magnetometer (VSM, Meghnatis Kavir Kashan Co., Kashan, Iran) were used to detect functional groups and investigate magnetic properties of the sample, respectively.

Preparation of MgFe₂O₄ MNPs

In the first step, 40 ml of deionized water was poured into a beaker and then 0.2 g of tragacanth gum (TG) was added to deionized water and stirred for 80 minutes at 70°C to obtain a clear TG solution. After that, 1mmol of Mg (NO₃)₂·6H₂O and 2mmol of Fe (NO₃)₃·9H₂O were added to the TG solution. The beaker was placed in a sand bath at 75°C with continuous stirring until the formation of dry gel. Finally, the dry gel was calcined at 600°C for four hours.

Photocatalytic dye degradation

Experiments were carried out in a batch mode photoreactor. The irradiation source was a fluorescent lamp ($\lambda > 400$ nm, 80 W, Parmis, Iran) placed above the batch photoreactor. The photocatalytic dye degradation experiment was conducted by various amounts of MgFe₂O₄ (0.005, 0.01, 0.015 and 0.02 g) in photoreactor containing 50 mL of a dye solution (20 mg/L) at room temperature. The effect of initial dye concentration on the photodegradation of dyes was investigated. The MgFe₂O₄ (0.015 g) was added to 50 mL of various dye concentrations (5, 10, 15 and 20 mg/L). The effect of visible light irradiation on the removal of dyes was surveyed. The MgFe₂O₄ MNPs were separated from the solution applying a magnet, and the alteration on the absorbance at a λ_{\max} of MG dye (619 nm) was checked by UV-Vis spectrophotometer. The degradation percentage of dye was calculated from the following equation

$$\% \text{ Degradation} = \frac{A_0 - A_t}{A_0} \times 100$$

Where A_0 is the initial absorbance and A_t is the absorbance at the time t .

The removal of MG follows the pseudo-first order kinetics and the rate constant is determined by the following relation:

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

The rate constant k is calculated from the slope of straight line portion of $\ln(C_0/C_t)$ versus t plot.

RESULTS AND DISCUSSION

Characterization of $MgFe_2O_4$ nanoparticles

Fig. 2a shows the IR spectrum of the sample calcined at 600°C for 4 hours. According to Fig. 2a, two strong absorption bands ν_1 and ν_2 are observed at 612 cm^{-1} and 421 cm^{-1} , respectively. The difference between ν_1 and ν_2 is due to the changes in bond length (Fe-O) at the octahedral and tetrahedral sites. The bands at 3400 cm^{-1} and 1630 cm^{-1} are characteristic for hydroxyl group (O-H) [15].

The XRD pattern of the sample is shown in Fig. 2b. XRD analysis displayed a series of diffraction peaks at 2θ of 30.35, 35.78, 37.11, 43.35, 53.71, 57.28, 62.87 and 74.10 which can be assigned to (220), (311), (400), (422), (511), (440) and (533) planes, respectively. All the diffraction peaks were readily indexed to a pure cubic structure ferrite (JSPDS Card no. 73-2211) with $a=b=c= 8.363 \text{ \AA}$. The average crystallite size of sample was calculated from the full width at half maximum (FWHM) of the XRD patterns using the well-known Scherrer formula: $D = 0.9\lambda/\beta \cos\theta$,

Where D is the crystallite size (nm), β is the full width at half maximum of the peak, λ is the X-ray wavelength of Cu $K\alpha = 0.154 \text{ nm}$ and θ is the

Bragg angle [37]. Based on the Scherrer formula, the average crystallite size of $MgFe_2O_4$ MNPs was calculated to be about 11 nm.

The SEM image shows the particle size and external morphology of the ferrite nanoparticles that calcined at 600°C for 4h (Fig. 2c). It can be seen from the SEM image that the ferrite nanoparticles have fairly uniform spherical shape and narrow size distributions.

The magnetic attributes of $MgFe_2O_4$ -NPs have been investigated by using vibrating sample magnetometer (VSM). Magnetization curve shows superparamagnetic properties which means magnetic remanence (M_r) and coercive force (H_c) are zero. As can be observed in Fig. 2d, the specific saturation magnetization value was measured to be 14 emu/g for $MgFe_2O_4$ -NPs. The prepared $MgFe_2O_4$ MNPs, were studied as a catalyst for removal of the MG dye with visible light irradiation and air at room temperature.

Effect of visible light irradiation and $MgFe_2O_4$ MNPs catalyst

Removal of MG dye was evaluated with visible light irradiation only, and catalyst under both

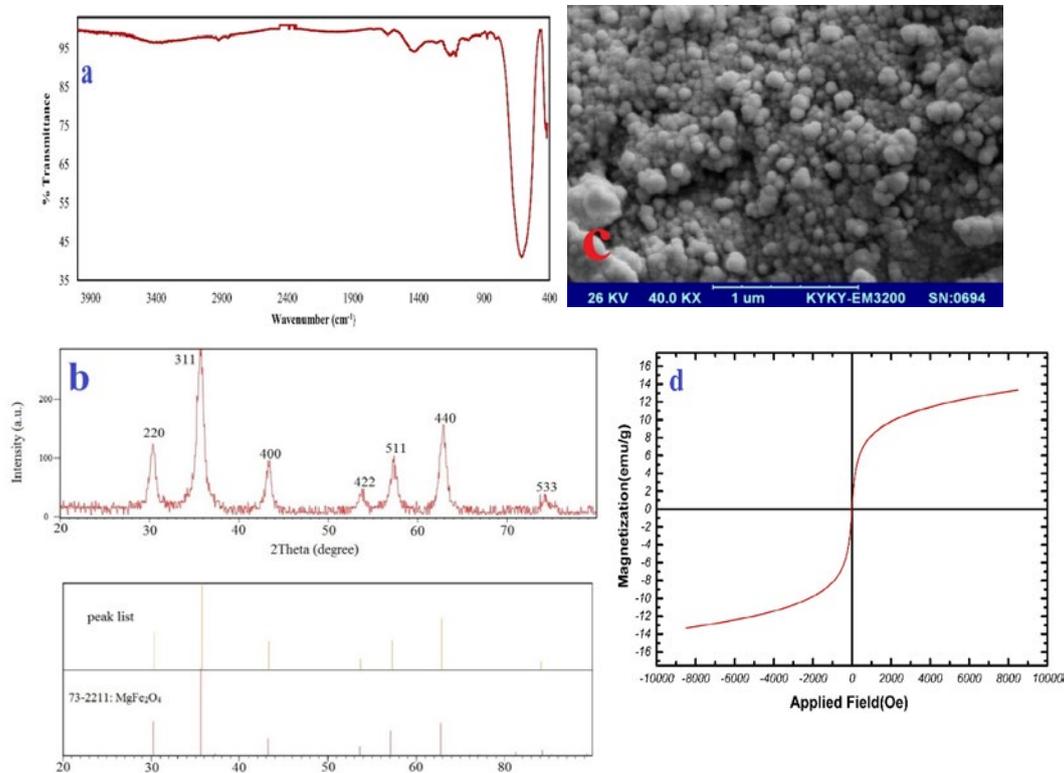


Fig. 2. a) FT-IR spectrum, b) XRD pattern, c) SEM micrograph, and d) Magnetization curve of $MgFe_2O_4$ MNPs.

visible light irradiation and dark. In the first case, without any catalyst, we had maximum degradation of 9%, while using magnetic magnesium ferrite catalyst without visible light irradiation, we had no degradation. As shown in Fig. 3, in the presence of both catalyst and light, 98% of MG dye is degraded at the irradiation time of 60 min.

Effect of photocatalyst dosage

Fig. 4 displays the decolorization efficiency at various concentrations of catalyst (0.005, 0.01, 0.015 and 0.02 gr) at 50 ml of MG dye. The experiments were done by the catalyst at a fixed dye concentration, 20 mg/L of at 60 minutes of irradiation. Experimental results show a trend of reduced removal with increasing magnesium ferrite concentration. Heterogeneous photocatalytic reactions are well known to exhibit an adequate increase in photodegradation with catalyst loading

[38]. Generally, in any given photocatalytic application, the optimum catalyst concentration must be determined, in order to avoid excess catalyst and ensure total absorption of efficient photons [39]. Fig. 4 suggests that the initial rate of decolorization may increase linearly up to about 0.015 g magnesium ferrite.

Effect of Initial Dye Concentration

Removal of MG dye by visible irradiation/ $MgFe_2O_4$ process was studied by varying the initial concentration of MG (5, 10, 15, 20 mg/L) at a constant $MgFe_2O_4$ dosage (0.015 g) (Fig. 5). The photocatalytic degradation of MG dye was not much decrease with increasing the initial dye concentration from 5 to 20 mg/L after 60 min.

Photodegradation of MG dye at different times

The photocatalytic activities of the as-synthesized magnetic $MgFe_2O_4$ photocatalyst

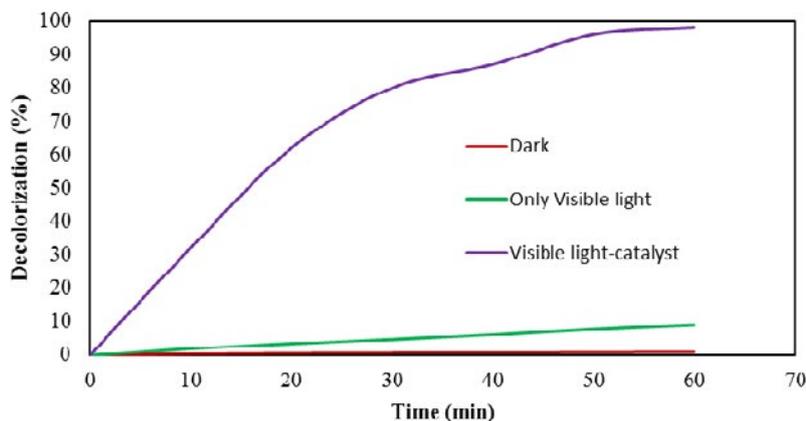


Fig. 3. Effect of visible light irradiation on the decolorization efficiency (%). Reaction conditions: MG=20 mg/L, catalyst=0.015g, pH=natural and room temperature.

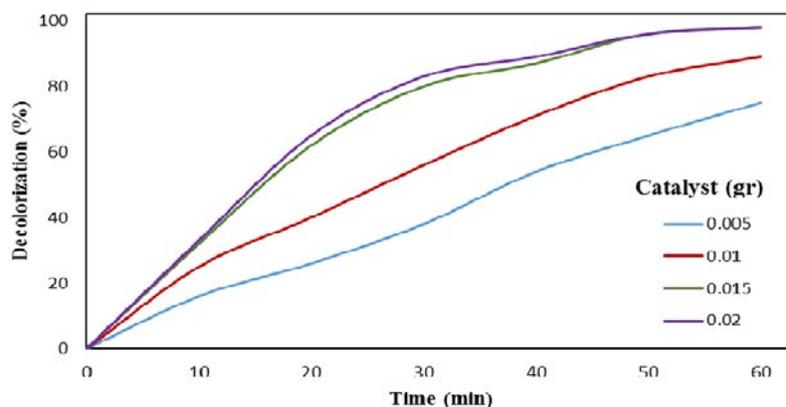


Fig. 4. The effect of photocatalyst dosage on the photocatalytic degradation of MG dye (pH = natural, MG =20 mg/L).

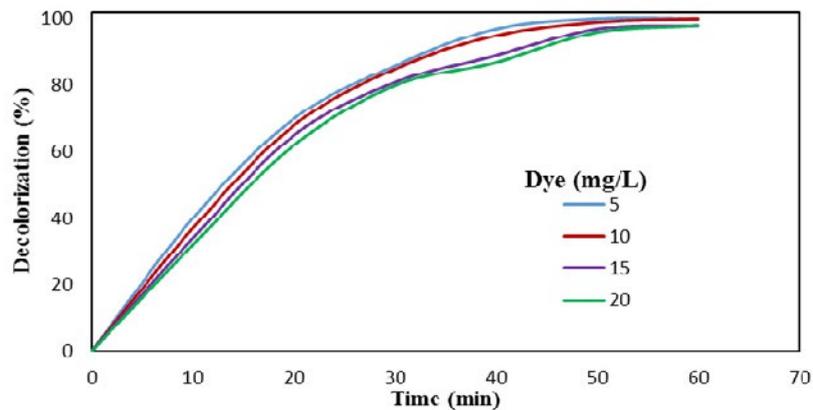


Fig. 5. Effect of initial concentration of MG dye on the decolorization efficiency (%).

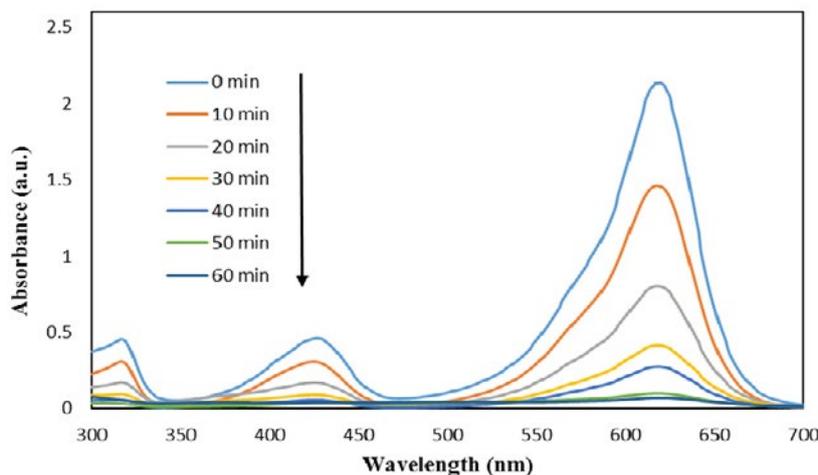


Fig. 6. Absorption spectra of MG aqueous solutions taken at various photocatalytic degradation times using $MgFe_2O_4$ MNPs.

for degradation of the MG were investigated in the presence of visible light irradiation and air at room temperature. The UV-visible spectra of MG aqueous solution in the presence of magnetic photocatalyst and air under visible light irradiation ($\lambda > 400$ nm) at room temperature for various time intervals are shown in Fig. 6. Obviously, the major absorption peak of MG is located at 619 nm which declines quickly with increasing exposure time and fully vanishes after irradiation for about 60 min. Almost 98% of MG can be degraded in 60 min. These results indicate that magnesium ferrite MNPs has a unique visible-light photocatalytic activity for degradation of the organic dyes.

Kinetic studies

Most of the photodegradation reactions of

pollutants obey first order reaction kinetics [40], where the relationship between degradation rate and irradiation time (t) can be described by $\ln(C_0/C_t) = kt$,

where k is the reaction rate constant. A plot of $\ln(C_0/C_t)$ versus time represents a straight line; the slope equals the apparent first-order rate constant k . The kinetics of photodegradation of MG dye by $MgFe_2O_4$ nanoparticles were investigated and the results are revealed in Fig. 7. According to the slope of line (Fig. 7) the rate constant value for removal of MG dye was calculated to be $k = 0.0636 \text{ min}^{-1}$. Furthermore, the fitting correlation coefficient (R^2) is calculated to be 0.989.

Reuse of the photocatalyst

The magnesium ferrite MNPs catalyst can be used repeatedly for the removal of dye solution.

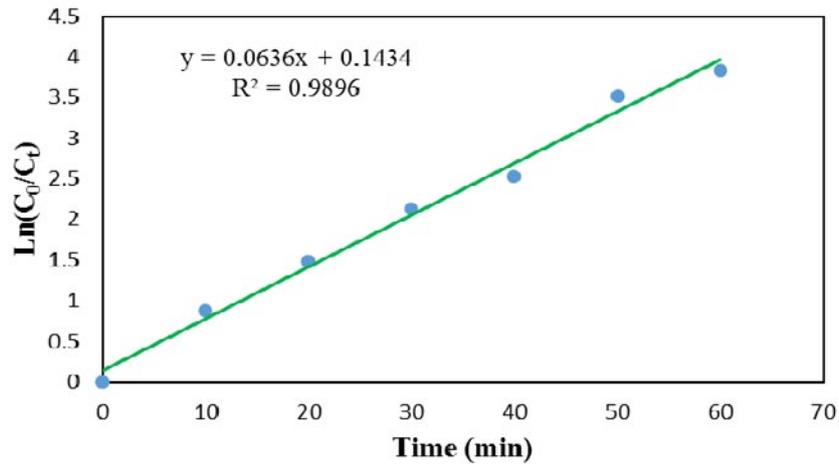


Fig. 7. Relation curve between $\ln(C_0/C_t)$ and time (t).

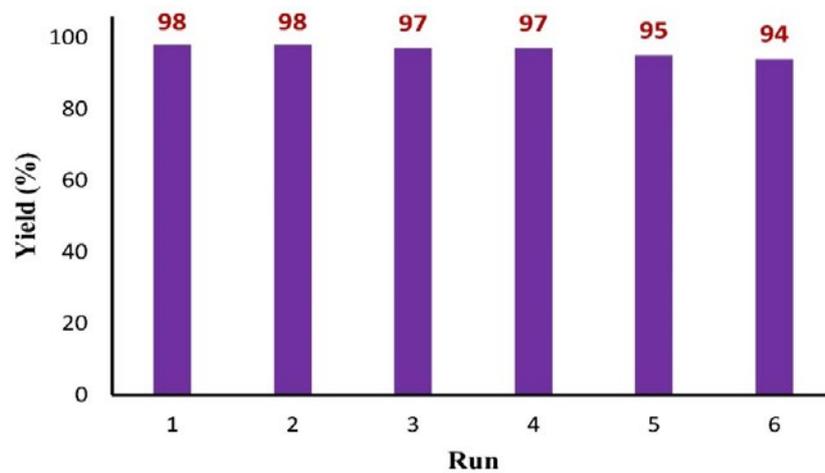


Fig. 8. Recyclability of $MgFe_2O_4$ MNPs ($MgFe_2O_4 = 0.015$ g, $MG = 20$ mg/L).

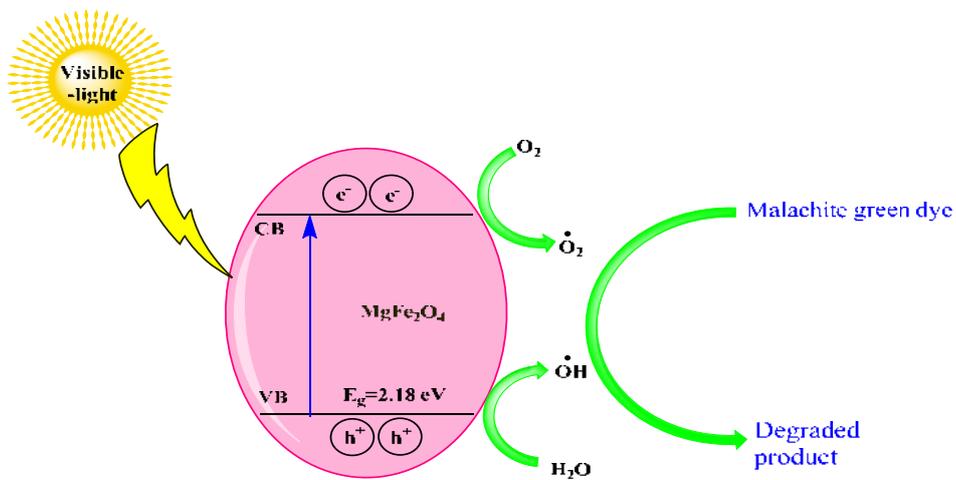


Fig. 9. Proposed mechanism for the photodegradation of malachite green dye

To measure the reusability of the catalyst, the removal of MG under visible light irradiation was investigated after gathering and reusing the same catalyst for subsequent runs. It can be seen from Fig. 8, the photocatalytic activity of the catalyst does not show any clear loss after six recycles for the photodegradation of MG, illustrating that the magnetic photocatalyst has good stability. Moreover, the MgFe₂O₄ MNPs is able to be separated from the reaction solution by a magnet after degradation. So, the magnetic photocatalyst is stable against photocorrosion during the degradation of organic dye.

Proposed mechanism for the photodegradation of dye in the presence of MgFe₂O₄ MNPs

A proposed mechanism for the photodegradation of malachite green dye in the presence of MgFe₂O₄ MNPs under visible light irradiation is demonstrated in Fig. 9. The valence band holes and their electron pair transfer to the surface, where they react with absorbed electron donors and electron acceptors (water, hydroxide ions) generating surface-bound hydroxyl radicals. The surface OH radicals can oxidize malachite green dye [34].

CONCLUSION

The biosynthesis of superparamagnetic magnesium ferrite nanoparticles using tragacanth gel (TG) by the sol-gel method is reported in this paper. A single phase with a cubic spinel structure was formed after heat treatment at 600°C for only 4 h. This method has many advantages such as nontoxic, economic viability, ease to scale up, less time consuming and environmentally friendly approach for the synthesis of MgFe₂O₄ nanoparticles without using any organic chemicals. The photocatalytic activity of magnesium ferrite nanoparticles has been evaluated for the degradation of malachite green dye in water under visible light irradiation. It was demonstrated that the catalyst could remove as high as 98% of the dye. The current photocatalyst could be removed from the reaction mixture with external magnet and its recyclability remains effective and active after six cycles.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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