RESEARCH PAPER

The Novel Green Magnetic Nanospheres: Synthesis, Characterization, and Photocatalytic Activity Against Organic pollutant

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ABSTRACT

Using green chemistry is an attractive proposed method for making nano photocatalysts for the photodegradation of organic pollutants. This work introduces the novel magnetic green nickel ferrite for the removal of dyes from wastewater. In this regard, green nickel ferrite nanostructures were prepared through a wet chemical route. The peppermint extract was utilized for the engineering of shape and size. The energy-dispersive X-ray spectroscopy (EDS) and X-ray powder diffraction (XRD) analyses confirmed the formation of pure nickel ferrite with a desirable crystalline structure. A scanning electron microscope (SEM) approved that the peppermint extract leads to the formation of regular and uniform nickel ferrite. The obtained hysteresis loop from the vibrating-sample magnetometer (VSM) showed the superparamagnetic behavior of prepared nickel ferrite. The optical property is a key factor for photocatalytic activity. So UV-Vis spectroscopy was applied for characterizing the optical properties of the sample. The optical band gap of prepared nickel ferrite was calculated 2.88 eV. Finally, the prepared green nickel ferrite was applied to remove rhodamine B and methylene blue from the water solution. The results showed that prepared nickel ferrite can be introduced as a promising candidate for the removal of organic pollutants. The prepared nano photocatalyst could photodegrade 71.6% and 84.2% of rhodamine B and methylene blue under visible light.

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INTRODUCTION

Water is known as one of the main factors in the formation of life on earth. However, in recent years, this source of life has been exposed to serious dangers due to destructive human activities. This danger directly threatens human life on earth [1]. In recent decades, with the increasing expansion of the paint, textile and paper industries, the introduction of organic pollutants into the environment has also increased significantly. In this regard, the introduction of organic pollutants into the environment and their penetration into the underground water has brought many concerns [2–4]. In addition, since this problem is directly related to human health, finding a suitable and quick solution is inevitable.

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Several methods have been introduced and used so far, including filtration [5], electro-oxidation[6], photocatalytic process[7, 8], and ozonation [9]. The photocatalytic process is considered as the acceleration of a photoreaction in the presence of a photocatalyst. Photocatalyst is an agent that photodegrades organic pollutants under the sun lights containing UV rays[10], [11]. Since the emergence of photocatalysts as a viable option for environmental pollution control, efforts have been made to improve their reaction rate or photocatalytic activity. Metal oxide semiconductor photocatalysts have been increasingly focused on in recent years due to their potential applications in solar energy conversion and environmental purification[12–14]. Nanophotocatalysts are an important group of advanced materials that have the ability to destroy a wide range of organic pollutants and in this field can help solve environmental problems related to the paint, paper, and textile industries [15, 16]. The most important issue in the field of nano photocatalysts is the selection of the appropriate nanostructure. The nanostructure should be selected in such a way that it is a semiconductor and its optical properties allow the degradation of pollutants under visible light. In this regard, researchers have proposed a wide range of photocatalytic nanomaterials, the most important of which are metal oxide nanomaterials[14]metal sulfide [17], carbon nanostructures [18], and composites related to these nanostructures [19]. Over time, the limitations of using nanostructures in the field of photocatalysts became the focus of researchers. These limitations include high cost, low degradation efficiency, and environmental problems created by the nanostructures themselves[20]. So far, many efforts have been made to overcome these challenges. Various synthesis methods with multiple precursors have been proposed so that nanomaterials can be synthesized with the highest efficiency and lowest cost [21, 22]. In this regard, researchers have used simple chemical methods such as co-precipitation, sol-gel, hydrothermal and ultrasonic for the synthesis of nano photocatalysts, and by changing the effective parameters in these methods, they have been able to synthesize nanostructures with attractive morphological and optical properties[23, 24].

Magnetic nanomaterials can be effectively used in the field of photocatalysts due to their unique properties. The magnetic properties of these materials help them to be recovered and used again. For these reasons, the use of magnetic nanomaterials has expanded a lot in recent years, and various magnetic nanomaterials have been used both in pure form and in hybrid form with other nanomaterials [25, 26]. Spinel ferrites (MFe_2O_4) are an important class of magnetic nanomaterials that have been noticed in the field of photocatalysts due to their attractive properties. Research shows that the metal used and the applied method for synthesis determine the photocatalytic performance of ferrite nanomaterials. For this reason, various types of ferrites have been synthesized by different methods and used as nano photocatalysts in the removal of organic pollutants [27, 28]. Various nickel ferrite nanostructures have been used as photocatalysts in the removal of various pollutants, but these nanostructures suffer from limitations such as inappropriate optical properties [29–31].

In this work, nickel ferrite nanostructures were synthesized by a new chemical method. The synthesized nanostructures were identified by XRD, SEM, FTIR, and VSM techniques, and then the synthesized nanostructures were used to remove the ciprofloxacin pollutant and the possible mechanism was investigated.

MATERIALS AND METHODS

Materials

All the materials such as Iron (III) chloride hexahydrate ($Fe(NO_3)_3.6H_2O$) and Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), ammonia, were purchased from Merck Company and applied with any purification.

Green preparation of nickel ferrite nanostructure

The nickel ferrite nanostructure was synthesized via dissolving 2:1 molar ratio of $Fe(NO_3)_3.6H_2O$ and Nickel (II) nitrate hexahydrate in distilled water separately. Then, 5 ml fresh peppermint extract as a capping agent was added to the iron (+3) containing solution and the stirring continued at room temperature, and then the nickel (2+) containing solution was added to the iron (+3) containing solution. Then the ammonia solution was added drop by drop to the solution and stirred for a further 20 min. Finally, the solution was transferred to a 20 mL Teflon-lined stainless-steel autoclave and was then heated at 140 °C for 7 h. Then, the solid was cooled to room temperature and separated by centrifugation at 12000 rpm for

10 min.

Photocatalytic test

The prepared nickel ferrite nanostructure was examined for the removal of rhodamine B and methylene blue under visible light at ambient conditions. 0.003 g/ml concentration of prepared nickel ferrite nanostructure were added to 100 ml of 30 ppm of provided organic pollutants. Before applying light, the mixture of nickel ferrite nanostructure and provided dyes were stirred for 30 min in a dark to make adsorption–desorption equilibrium between the nickel ferrite nanostructure and dyes solution. Then, the mixture was subjected to the provided visible light and at every given time interval, 5 ml pollutants solution was separated for examination with UV-Vis spectrophotometer. The photocatalytic activity of nickel ferrite nanostructure was determined via the following equation (1):

$$Photocatalytic\ efficiency\ \% = \frac{C_0 - C_t}{C_0} \times 100$$

Where C_0 is the initial concentration of dyes C_t is the concentration after the time interval.

RESULTS AND DISCUSSION

The XRD pattern was applied for the investigation of structural and crystalline properties of prepared green nickel ferrite nanostructures. Fig. 1 represents the XRD pattern of prepared nickel ferrite nanostructures. The position of peaks is in good agreement with JCPDS card no. 00-010-0325 with Fd3m space group [32]. Also, no impurity peaks were observed in the XRD pattern. The crystallite size was calculated from (FWHM) (β) of the preferred orientation diffraction peak by using the Debye-Sherrer’ s equation (2)[33]:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (2)$$

Where: λ: is the X-ray wavelength (Å), β: FWHM, θ: Bragg diffraction angle of the XRD peak, and (D) is a mean crystallite size or average grain size. The average grain size of as-obtained nickel ferrite nanostructures was calculated 24 nm. In terms of appearance, the width of the peaks indicates the small size of grains.

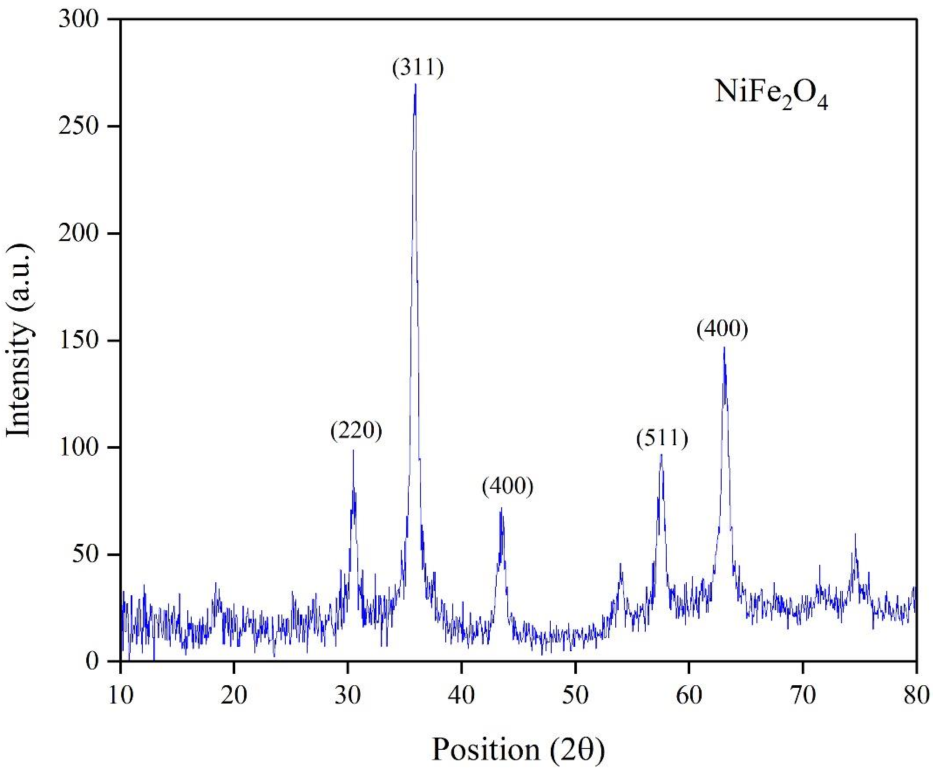

Fig. 1. XRD patterns of prepared $NiFe_2O_4$ nanoparticles.

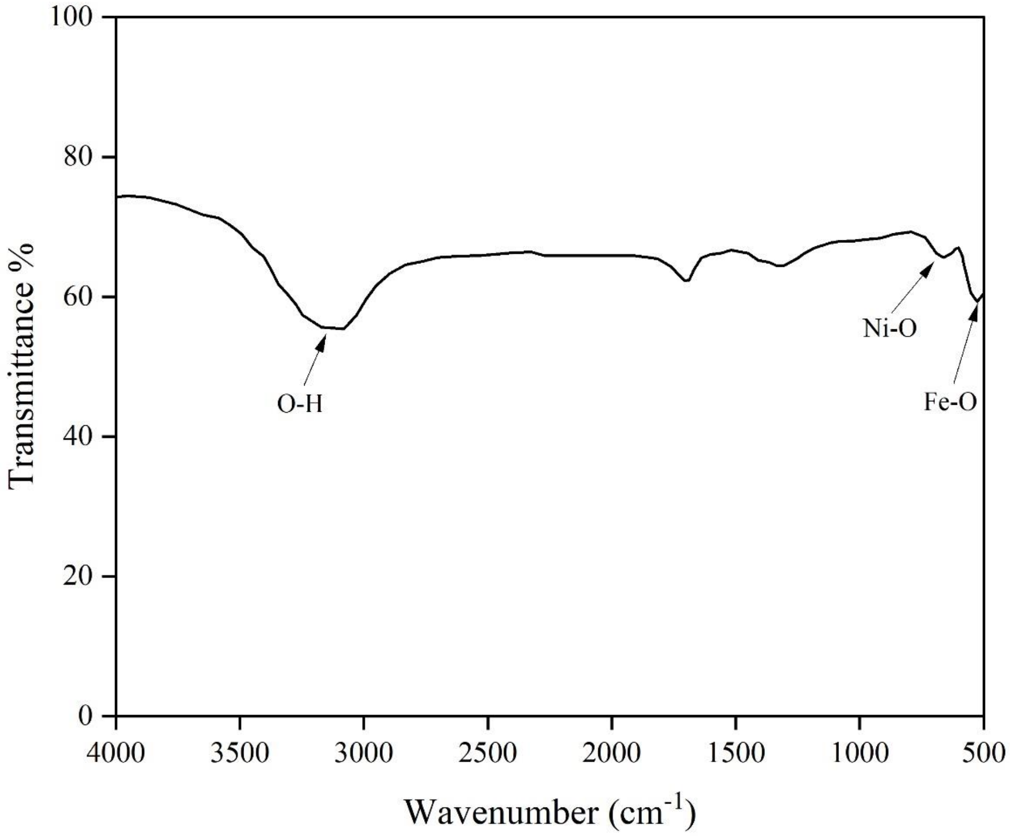

Fig. 2. FTIR spectrum of prepared $NiFe_2O_4$ nanoparticles.

Fig. 2 shows the FTIR spectrum of prepared green nickel oxide nanostructures. The presence of peaks at 647 and 532 cm^{-1} are attributed to the Ni-O and Fe-O bonds, respectively [34]. The presence of different peaks at 1000-1600 cm^{-1} can be assigned to the linked peppermint extract on the surface of nickel ferrite. The FTIR spectrum shows broad peaks at 3435 cm^{-1}, corresponding to the stretching mode of the hydroxyl group, and a weak band at about 1640 cm^{-1} that is related to H–O–H bending vibration mode due to the adsorption of water molecules on the nickel ferrite surface.

The scanning electron microscope images were applied for the investigation of morphological properties of prepared green nickel nanostructures. As can be seen from Fig. 3, the regular morphology of spherical nanoparticles has been synthesized. The higher magnification of SEM image confirm the narrow size distribution of the prepared sample. It should be noted that no common chemical capping agent was used in this work and therefore the small size and regular shape of prepared nickel ferrite are attributed to the peppermint extract. The SEM images suggest the peppermint extract as an excellent capping agent for the preparation of nickel ferrite nanostructures.

EDS analysis was applied for the chemical analysis of the as-obtained sample. Fig. 4 shows the EDS analysis of the prepared sample. It can be concluded that the synthesized sample formed with any impurity. As well as seen, the Fe, Ni, and O elements are presented in the EDS analysis.

The magnetic properties of prepared green nickel ferrite was investigated via the VSM hysteresis loop (Fig. 5). At the ambient condition, the coercivity (H_c) was determined 0 emu/g, and magnetization at saturation (Ms) was measured 34 emu/g. As a result, the prepared green nickel ferrite nanoparticles exhibit superparamagnetic properties. This excellent magnetic feature is a key factor in the reusability of prepared nickel ferrite in the photocatalytic process.

Fig. 6a shows the optical absorbance spectra

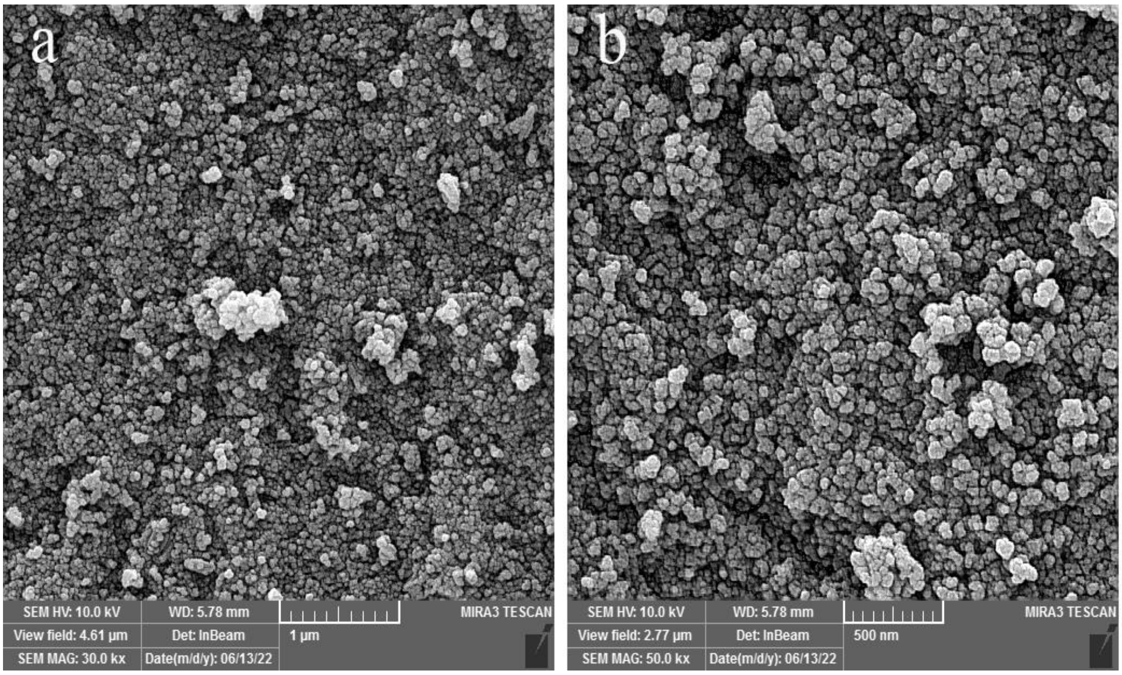

Fig. 3. SEM images of prepared $NiFe_2O_4$ nanoparticles at different magnifications.

of prepared nickel ferrite nanospheres. Fig. 6b shows the calculated band gap for nickel ferrite nanostructures. the optical band gap was determined through Tauc equation and extrapolating the linear section of the drawing of $(\alpha h\nu)^2$ vs $h\nu$. In this regard, the optical band gap of prepared nickel ferrite nanostructures was measured 2.88 eV which matches the band gap that was previously reported. Photocatalytic activity is based on the principle of irradiating a

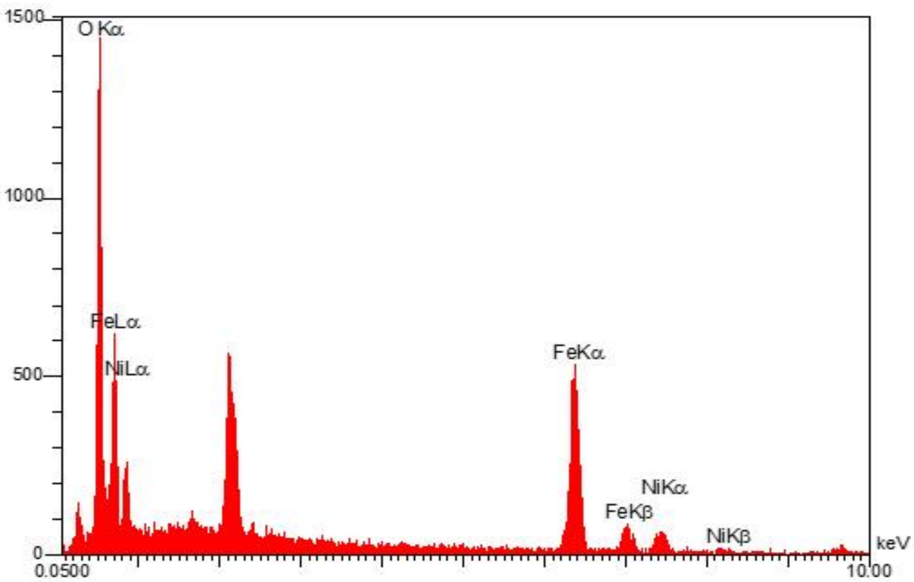

Fig. 4. EDS analysis of as-obtained $NiFe_2O_4$ nanoparticles.

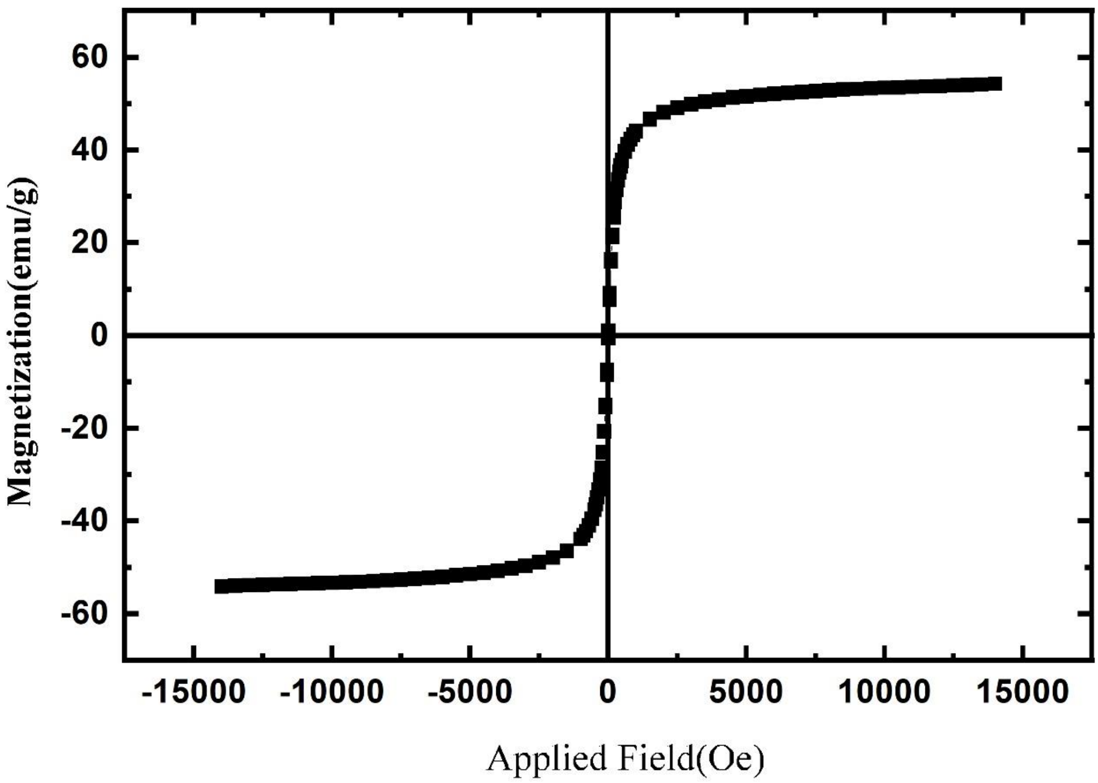

Fig. 5. VSM analysis of synthesized $NiFe_2O_4$ nanoparticles

semiconductor material with light that leads to electro-hole pair formation. Electrons in the valence band of this material absorb enough energy equal to or greater than that of the band gap to shift from the valence band to the conduction band, leaving holes. In this work, photocatalytic performance was investigated via photodegradation of rhodamine B and methylene blue. As well as

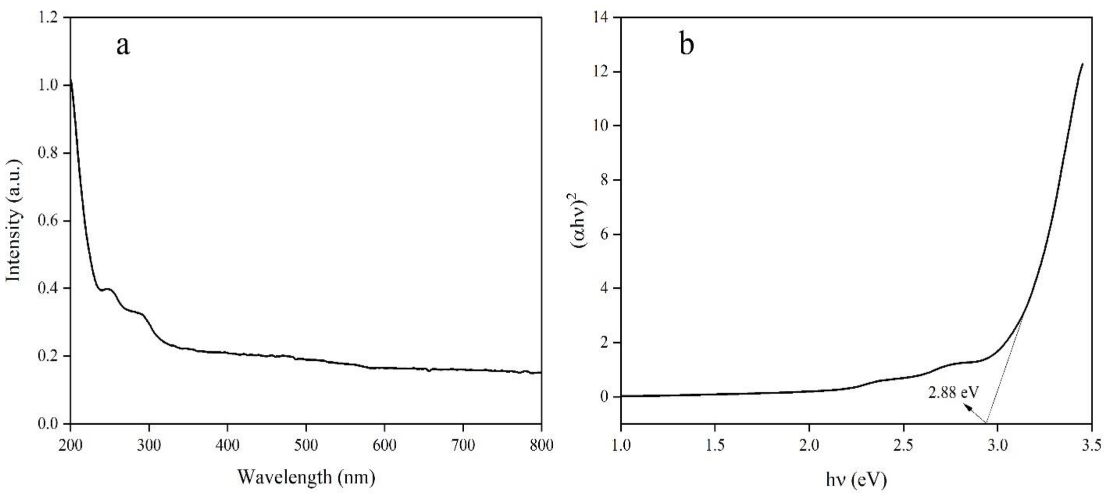

Fig. 6. a) UV-Vis absorption spectra of synthesized $NiFe_2O_4$ nanoparticles b) Optical band gap of prepared $NiFe_2O_4$ nanoparticles

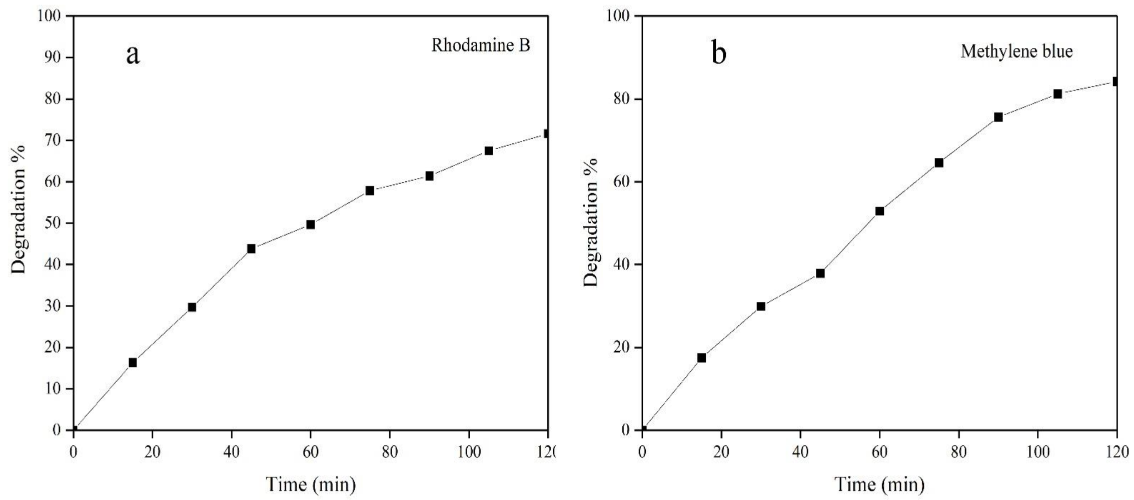

Fig. 7. Photocatalytic activity of prepared $NiFe_2O_4$ nanoparticles against a) Rhodamine B b) Methylene blue under visible light.

seen in Fig. 7, 71.6% and 84.2% of rhodamine B and methylene blue were removed from the solution after 120 min solar light irradiation. The reactive oxygene species (ROS) are the major ones responsible for the photodegradation of organic pollutants. The hydroxyl radicals are one of these active species that are caused by a positive charge hole reaction with water molecules. Superoxide anions are also produced from the reaction of negative charge electron with oxygen molecules. In addition to this, due to the presence of nickel ferrite nanostructures, there may be a chance of the Fenton process intensifies the photocatalytic process [35].

CONCLUSION

The green nickel ferrite nanostructures were synthesized via a hydrothermal route. The peppermint extract was applied as capping agent. The peppermint extract leads to the formation of a regular shape of nickel ferrite with narrow size distribution. The prepared nanostructures were characterized via XRD, FTIR, SEM, EDS, and VSM analysis. Results showed the superparamagnetic behavior of prepared nickel ferrite nanospheres with saturation magnetization of 34 emu/g. The optical properties of the prepared sample was investigated via UV-Vis spectroscopy. The optical band gap of prepared nickel ferrite nanospheres was calculated 2.88 eV. Finally, the prepared sample was applied for photodegradation of rhodamine B and methylene blue under visible light. The prepared green nickel ferrite showed considerable photocatalytic activity and degraded 71.6% and 84.2% of rhodamine B and methylene blue after 120 min irradiation.

CONFLICT OF INTEREST

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

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