J Nanostruct 10(1): 83-91, Winter 2020

RESEARCH PAPER

Auto Combustion Synthesis using Grapefruit Extract: Photocatalyst and Magnetic $MgFe_2O_4$-PbS Nanocomposites

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ARTICLE INFO

Article History:
Received 03 November 2019
Accepted 16 December 2019
Published 01 January 2020

Keywords:
Green Synthesis
Magnetic
Nanocomposites
Photocatalyst

ABSTRACT

Magnesium ferrite ($MgFe_2O_4$) as a core magnetic nanostructure was synthesized via auto combustion method by using grapefruit extract as a biocompatible and cost-effective material. Then flower and star-like PbS were synthesized using thioglycolic acid as a sulfur source without using any chemical template. After that for preparation of magnetic and photocatalyst $MgFe_2O_4$-PbS nanocomposites, lead sulfide were coated on the magnetic core by hydrothermal procedure. Morphology of the prepared products was estimated by transmission electron microscopy (TEM), scanning electron microscopy (SEM), also X-ray diffraction (XRD) pattern show purity and phase of the product. Fourier transforms infrared (FT-IR) spectroscopy show vibration modes of the bonds. Vibrating sample magnetometer (VSM) illustrated that magnesium ferrite nanoparticles have a soft magnetic behaviour with 18 emu/g magnetization and coercivity about 90Oe. The photocatalytic behaviour of $MgFe_2O_4$-PbS nanocomposites were examined using the degradation of two various azo dyes acid brown and acid violet under visible light irradiation. This magnetic photocatalyst can easily separate from water with an external magnetic field and can be used under solar irradiation.

How to cite this article
Hedayati K, Joulaei M, Ghanbari D. Auto Combustion Synthesis using Grapefruit Extract: Photocatalyst and Magnetic $MgFe_2O_4$-PbS Nanocomposites . J Nanostruct, 2020; 10(1): 83-91. DOI: 10.22052/JNS.2020.01.010

INTRODUCTION

Nanotechnology is an interdisciplinary area of research and future industry which has grown rapidly in recent years because their new properties. Semiconductor nanocrystals have drawn attention due to their extreme quantum confinement effect [1, 2].

Ferrites have emerged as novel materials with vast technological and scientific interest considering their physical properties such as large magneto-crystalline anisotropy, chemical and thermal stability and cost-effective preparation. Some of the application are magnetic recording, data storage, radar absorbing materials and magnetoelectric. They have three classes: spinel, garnet and hexagonal. $MgFe_2O_4$ has a cubic structure of spinel is a partially normal spinel and is a magnetic n-type semiconducting material [3-8]. Plant-mediated synthesis of nanoparticles is a cost-effective and environmentally friendly approach which plant extracts seem to be the simplest method and scalable. Plant extracts may act both as reducing agents and stabilizing agents in the synthesis of nanoparticles [9-10].

Lead sulfide is an IV–VI semiconductor and has large excitonic Bhor radius (18 nm), the optical absorption and emission can be easily adjusted from near infrared to ultra violet region (size-dependent optical properties and adjust its band gap from 0.4 eV to higher) by reducing the dimension of nanocrystals. Because of that quantum confinement effect is observed even for

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PbS with relatively large particle size [11-14].

In this work $MgFe_2O_4$-PbS nanocomposites were synthesized by both green auto-combustion and hydrothermal method. The photo catalytic behavior of $MgFe_2O_4$-PbS nanocomposites was estimated using the degradation of two azo dyes under ultraviolet light irradiation and nanocomposites depict magnetic and photo-catalyst performance.

MATERIALS AND METHODS

$Fe(NO_3)_3.9H_2O$, $Mg(NO_3)_2.6H_2O$, NH_3, $Pb(NO_3)_2$, TGA and NaOH, distilled grapefruit extract and water were supplied from Merck Company. XRD patterns were recorded by Philips (CuK_α radiation). Morphological investigations of the nanoparticles and nanocomposites were obtained using SEM from MIRA3-TESCAN instrument. Fourier transforms infrared (FT-IR) spectroscopy with the range of 400–4000 cm^{-1} and Ultraviolet-visible (UV-vis) was obtained by Bruker. Room temperature magnetic properties were investigated using by vibrating sample magnetometer (VSM) device by Meghnatis Kavir Kashan Company (Iran).

Green Synthesis of $MgFe_2O_4$ Nanoparticles

1.57 g of $Fe(NO_3)_3.9H_2O$ and 0.5 g of $Mg(NO_3)_2.6H_2O$ were dissolved in 10 mL of natural grapefruit extract, and it was stirred for 15 min. Then 5 mL of NH_3 (32%) was slowly added as precipitator the pH of solution and was fixed to 10. Next, all the solution was slowly heated for 1h at 150°C. After drying the product was suddenly ignited and release fire and smoke. The obtained brown precipitate was washed twice with distilled water. Then it was dried in oven for 10h.

Synthesis of $MgFe_2O_4$-PbS Nanoparticles

0.1 g of synthesized magnesium ferrite was dispersed in 100 mL of distilled water and then 0.2 g of $Pb(NO_3)_2$ was dissolved in the solution. After that, 0.5 mL of TGA dissolved in 100 mL of distilled water, then the solutions were mixed and stirring for 2h. After that 10 mL of NaOH (1M) was slowly added to the solution until reaching pH to the 10 and the solution was stirred for 1h. The solution was transferred into stainless steel autoclave (500 mL) and the reaction was remained at 160°C for 5h.

Fig. 1. Preparation mechanism of the magnetic product and star like PbS.

The product was washed by distilled water and centrifuged for 3 times. The procedure is shown in Fig. 1.

Photo degradation of azo-dyes

30 mL of the acid brown and acid violet (20 ppm) were used as a model pollutant to determine the photocatalytic activity. 0.3 g of catalyst was applied for degradation of 30 mL solution. The solution was mixed by a magnet stirrer for 1h in darkness to determine the adsorption of the dye by catalyst and better availability of the surface. The solution was placed under solar irradiation which was placed in a quartz pipe in the middle of reactor. It was turned on after 1h stirring the solution and sampling (1 mL) was done every 10 min. The samples were filtered, centrifuged and their concentration was determined by UV-vis spectrometry.

RESULTS AND DISCUSSION

XRD analysis

Fig. 2(a) shows the XRD pattern of $MgFe_2O_4$ product. Pure cubic phase of normal spinel (space group: Fd-3m, JCPDS No. 88-1935) can be observed in this pattern. The narrow sharp peaks indicate that the magnesium ferrites were well crystallized [15-17].

Fig. 2(b) illustrates XRD pattern of PbS product.

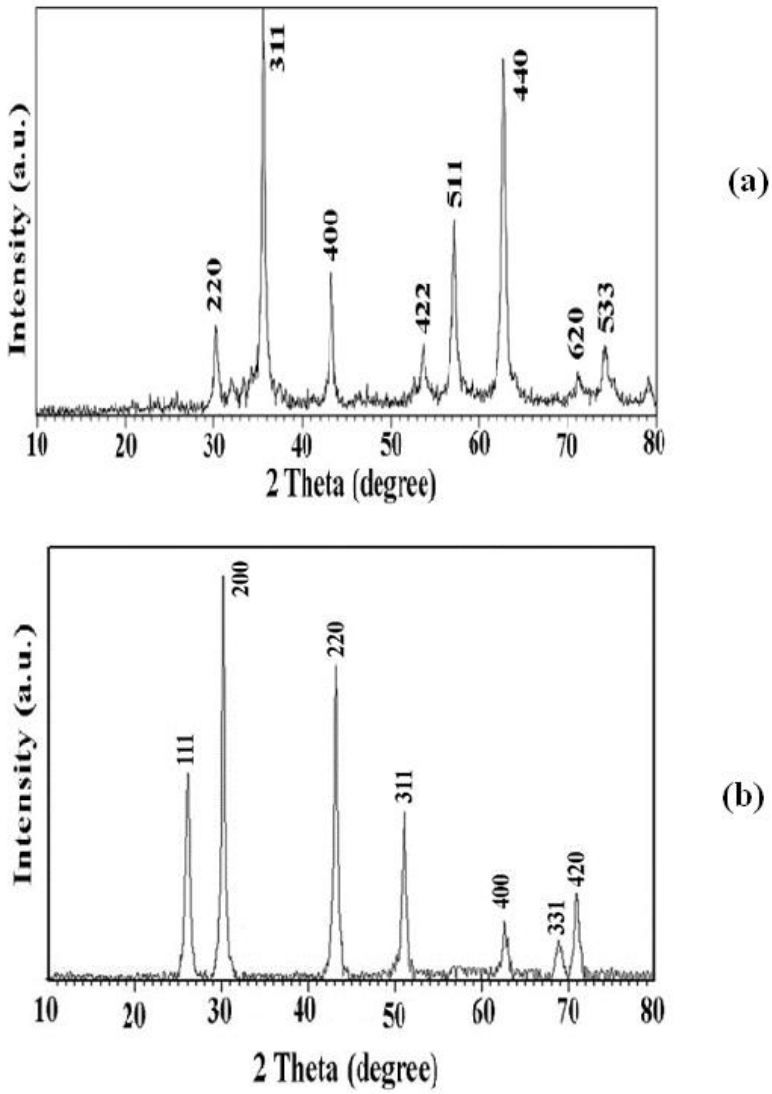

Fig. 2. XRD pattern of the (a) magnesium ferriteand (b) PbS nanoparticles.

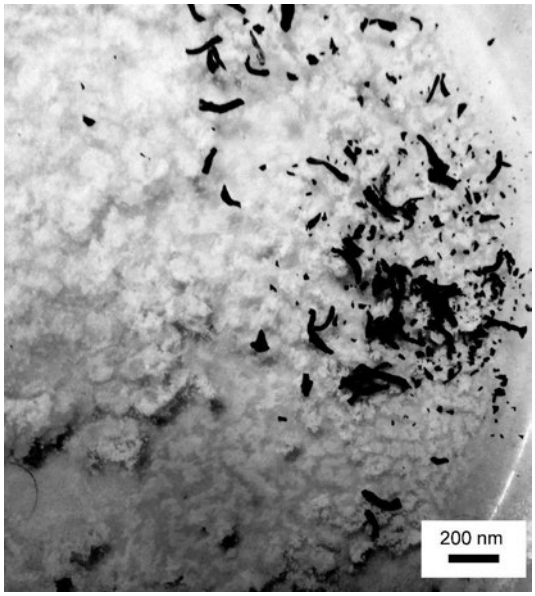

Fig. 3. TEM image of the product prepared in the presence of Grapefruit extract.

It can be observed that cubic phase (JCPDS No.77-0244) with Fd-3m space group which is consistent with pure lead sulfide was prepared.

The calculated crystalline sizes from Scherrer equation, $D = 0.9\lambda/\beta Cos\theta$, where β is the width of the observed diffraction peak at its half maximum intensity, and λ is the X-ray wavelength (CuKa radiation: 0.154 nm). The average crystalline size forfor $MgFe_2O_4$ and PbS nanoparticles were found to be about 40 and 45 nm respectively.

Morphological analysis

Fig. 3 illustrates TEM image of $MgFe_2O_4$ nanoparticles prepared in the presence of grapefruit extract that confirm synthesis of nanoparticles and shows the mediocre size of nanoparticles is about 50 nm. Because of magnetic interaction nanoparticles were agglomerated to each other [18-20].

Fig. 4 shows SEM images of PbS nanoparticles with thioglycolic acid as a sulfur source and stability agents, which was previously used as the stability agent to prevent the chalcogenide nanocrystals from aggregating and makes important roles in anisotropic growth of PbS crystals to flower-shaped dendrite during the hydrothermal process.

Results show flower like nanostructure were obtained. Sizes of each separate denderitic nano particle are less than 50 nm. Shape and particle size can be controlled by the super saturation during the

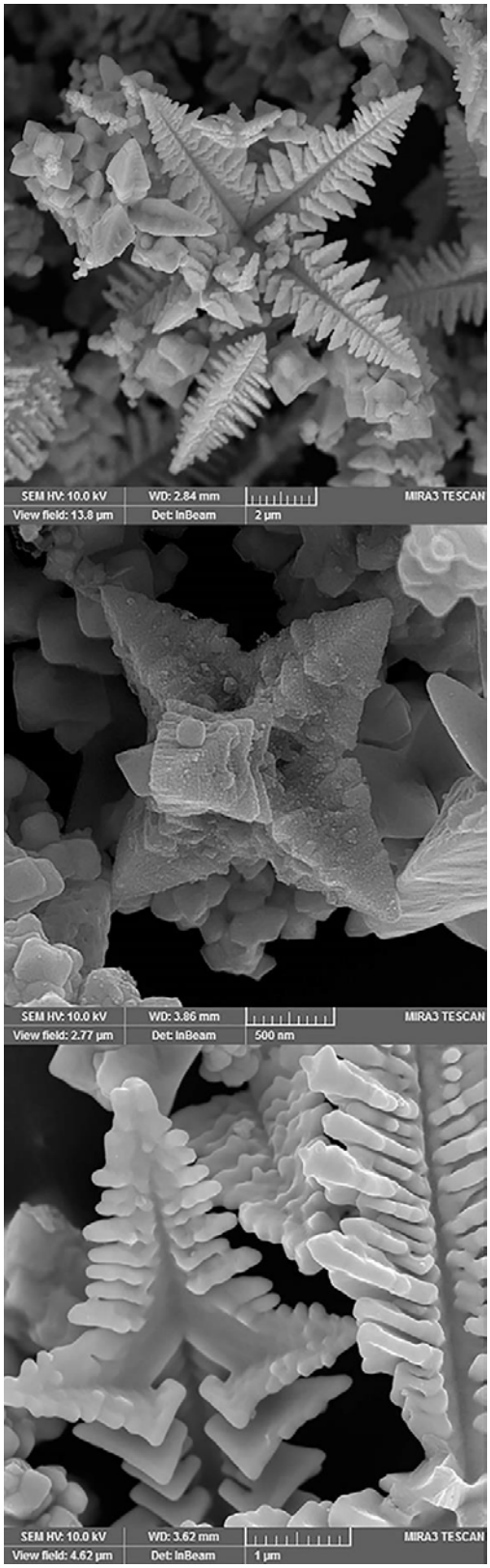

Fig. 4. SEM images of the product PbS.

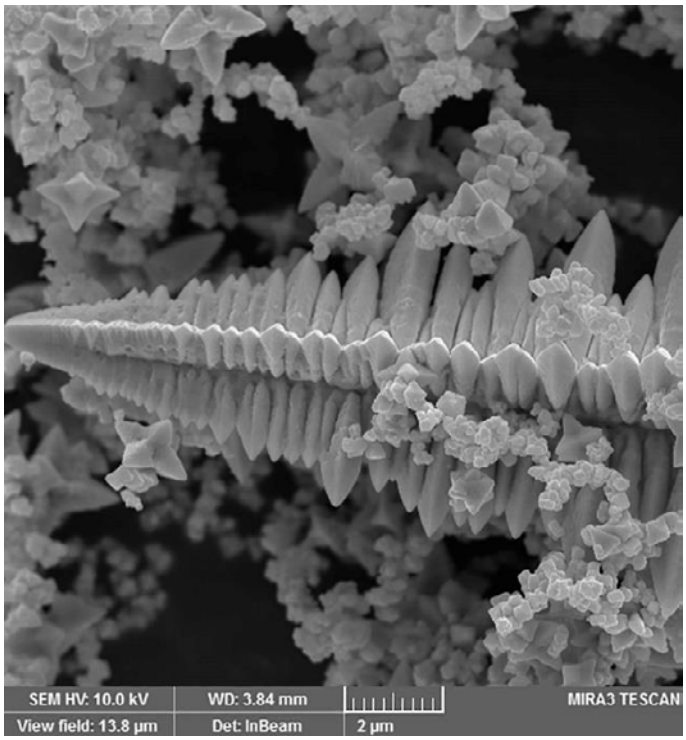

Fig. 5. SEM images of $MgFe_2O_4$-PbS nanocomposite.

nucleation and crystal growth processes, which it can strongly be affected by precipitation conditions.

The shape of nanoparticles strongly influences the properties. Hydrothermal is one of the best methods for preferential growth that depends on the solubility of minerals in hot water under high pressure. A temperature gradient is maintained between the opposite ends of the growth reactor. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal.

Fig. 5 illustrates SEM images of the $MgFe_2O_4$-PbS nanocomposite. Images approve presence of magnetic nanoparticles with average diameter size less than 100 nm beside dendrite lead sulfide micro/nano structure.

EDS analysis

Fig. 6(a) shows the EDX pattern of the $MgFe_2O_4$ nanoparticles that confirmed the presence of iron, magnesium and oxygen and there were no other peaks for impurities.

Fig. 6(b) shows the EDX pattern of the PbS nanoparticles that confirmed the presence of lead and sulfur and there were no other peaks for impurities.

FT-IR analysis

Fig. 7 shows the FT-IR spectrum of the prepared $MgFe_2O_4$ nanoparticles, peaks at 430 and 567 cm^{-1} are related to the Mg–O and Fe–O bonds in $MgFe_2O_4$. The absorption peak at 3413 cm^{-1} is because of O–H groups that are adsorbed on the surface of nanoparticles.

Magnetic properties

Room temperature magnetic properties of samples were studied by using vibrating sample magnetometer instrument. A hysteresis loop of magnetic MgFe2O4 nanoparticles is shown in Fig. 8(a). Magnetic property of $MgFe_2O_4$ nanoparticles show ferromagnetic behavior with saturation magnetization of 17 emu/g and the coercivity is about 90 Oe.

Hysteresis loop of magnetic $MgFe_2O_4$-PbS nanocomposites prepared by hydrothermal method at 160^0C for 5 h illustrates in Fig. 8(b). It shows ferromagnetic behaviour and has a saturation magnetization of 6emu/g and coercivity about 130 Oe.

This magnetization indicates that $MgFe_2O_4$-PbS nanocomposites inherit the magnetic property from the $MgFe_2O_4$; however, the magnetization is

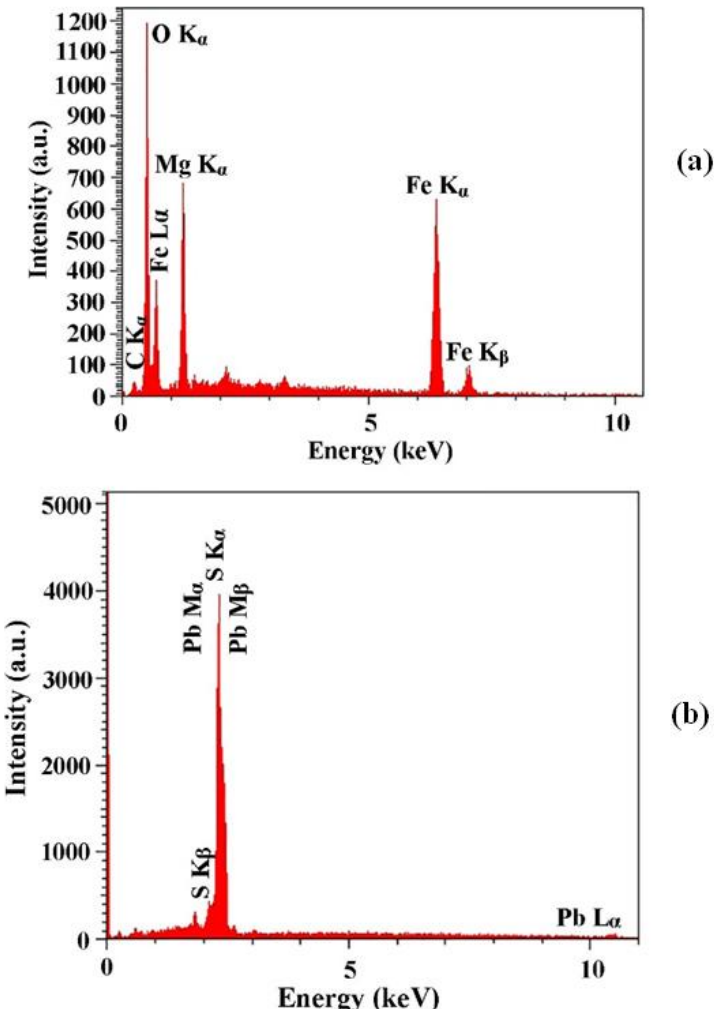

Fig. 6. EDX analysis of the obtained (a) $MgFe_2O_4$ nanoparticles and (b) PbS nanoparticles.

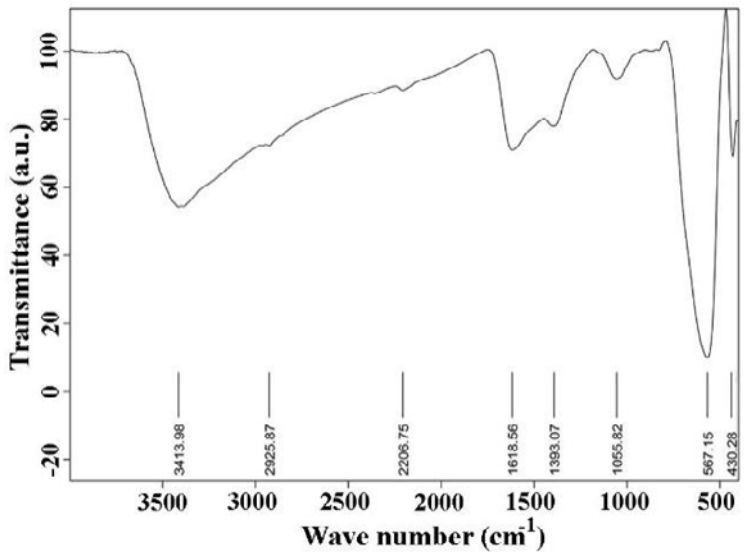

Fig. 7. FT-IR spectrum of $MgFe_2O_4$ nanoparticles.

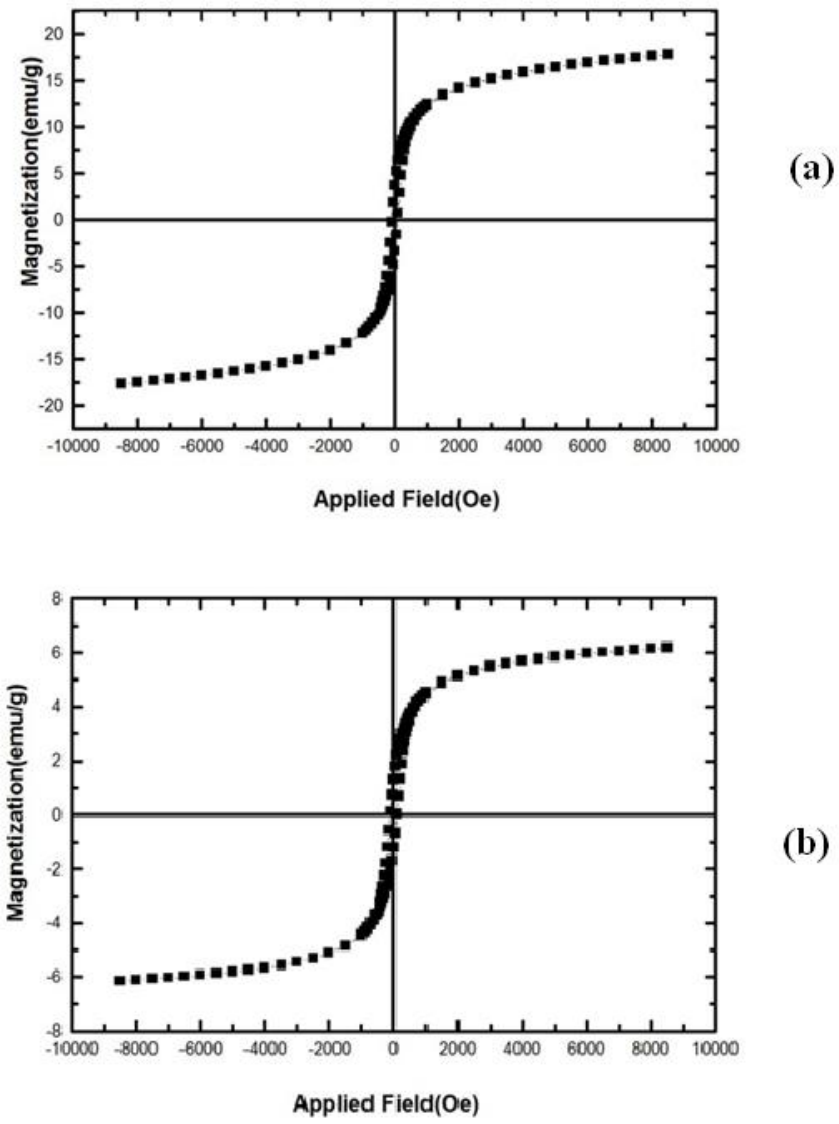

Fig. 8. VSM curve of the (a) $MgFe_2O_4$ nanoparticles and (b) $MgFe_2O_4$–PbS nanocomposite.

lower due to presence of lead sulfide. This reduction in saturation magnetization is due to the interfacial effect of the typical nanocomposite. The magnetic property of the prepared nanocomposites is an essential characteristic of a re-generable and reusable magnetic heterogeneous catalyst.

Photocatalytic properties

The photo-catalytic activity of the $MgFe_2O_4$-PbS nanocomposite was evaluated by monitoring the degradation of acid-violet and acid brown in an aqueous solution under solar irradiation. The UV-vis spectra of changes in the concentration of acid brown in 60 min are illustrated in Fig. 9. Organic dyes decompose to carbon dioxide, water and other less toxic or nontoxic residuals. Fig. 10 shows degradation of the both acid violet and acid brown after 60 min exposure to the $MgFe_2O_4$-PbS nanocomposite.

CONCLUSION

The magnesium ferrite nanoparticles and lead sulfide were synthesized via a green method at presence of grapefruit extract using auto combustion procedure, and then $MgFe_2O_4$-PbS nanocomposites were prepared by hydrothermal method. TEM image shows the size of $MgFe_2O_4$ nanoparticles is about 50 nm.SEM images

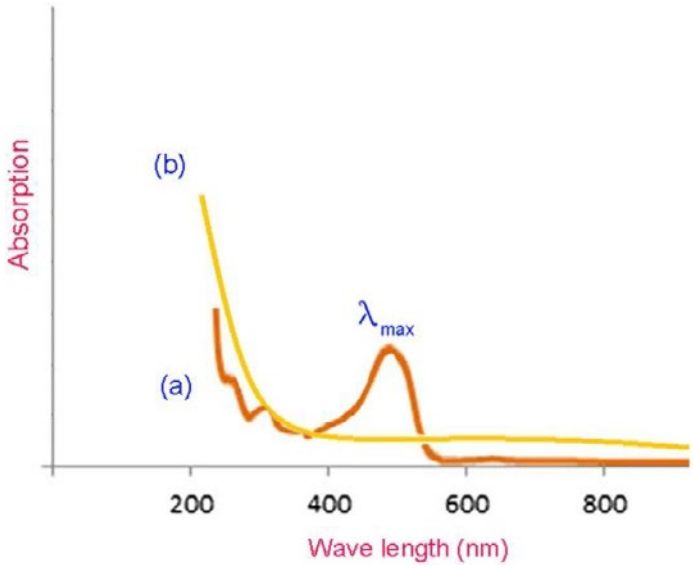

Fig. 9. UV- vis spectra Photo degradation of acid brown under solar irradiation (a) 0 min (b) 60 min.

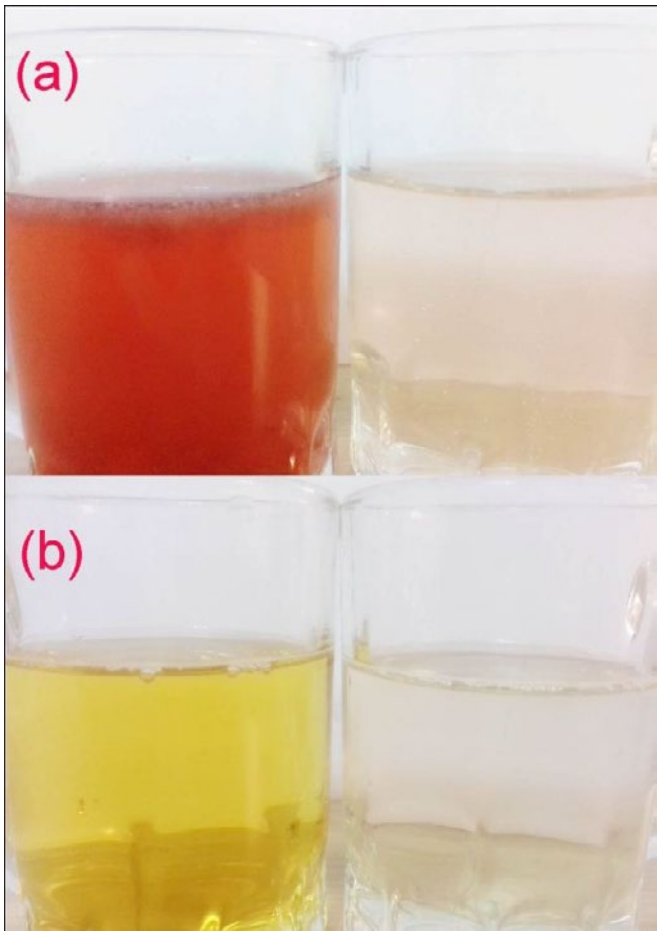

Fig. 10. Photo degradation under solar irradiation (a) acid violet (b) acid brown.

shown flower-shaped dendrite shape of PbS nanoparticles. The EDX pattern of the $MgFe_2O_4$ and PdS nanoparticles confirmed were no other peaks for impurities.VSM estimated that nanocomposites exhibit either ferromagnetic behaviour. The photocatalytic behaviour of $MgFe_2O_4$-PbS nanocomposite was tested by applying the degradation of two azo dyes under solar light irradiation. The results show that both auto combustion and hydrothermal are suitable methods for preparation of cost-effective $MgFe_2O_4$-PbS nanocomposites with preferential growth.

CONFLICT OF INTEREST

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

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