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# The effect of magnetic field on the magnetic property of Agar/Fe₃O₄ nanocomposite

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## Abstract

Agar/Fe₃O₄nanocomposites were synthesized in the presence of an external magnetic field (~ 0.4 Tesla) and their characteristics were compared to the samples synthesized without considering the external magnetic field. In this study, we used $Fe^{2+}$ and $Fe^{3+}$ for synthesizing $Fe_3O_4$ magnetic nanoparticles in the presence of agar as a polymeric additive, by co-precipitation technique. Vibrating sample magnetometer (VSM) analysis of the samples revealed the saturation magnetism as 33.92 emu/g and 38.92 emu/g for the synthesized samples in the absence and presence of external magnetic field, respectively. The results of scanning electron microscopy (SEM) images showed that the aggregation of magnetic nanoparticles is related to the magnetic property. Magnetic dipole alignment was increased by the sample synthesized in the external magnetic field. The Fourier transforms infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) pattern were also applied to characterize the magnetic nanocomposites.

**Keywords:** Magnetic field; magnetic property; agar; Fe₃O₄ magnetic nanoparticles.

## Introduction

Magnetic nanoparticles as a special class of nanoparticles have attracted great attention and interest in new fields of science and technology [1-6]. This attention comes from their physical and chemical properties which depend on the size and shape of magnetic nanoparticles, fine particle structure, and chemical phase of the particles [7]. Among all magnetic nanoparticles, the ferrite nanoparticles have received more and particular attention due to their properties and applications. This consideration is because of their low cost of production, biocompatibility, high magnetic bipolarity torque, low toxicity, and high degradation efficiency [8-14].

One of the most interesting and perhaps practical features of iron oxide and spinally ferrite is its superparamagnetic behavior [15]. This property brings variety of applications for them, such as magnetic resonance imaging (MRI), high-density magnetic recording media, targeted drug delivery, separation cells, nanocatalysis, cancer treatment, biological sensors, optical applications,

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storing data and chemical applications [16-20]. One of the obstacles on the way of magnetic and especially ferrite nanoparticles improvement is their aggregation due to the attractive force between magnetic nanoparticles [21]. The composites are considered as a one type of solution to dissolve this barrier.

Composite is a material made from at least two different components, whose new properties cannot be individually achieved by each of the components [22]. If one of the components has nano structure (nano particle, nano wire and etc.), then, it would be the multi-phasic materials or nanocomposite. Magnetic nanocomposites have attracted many researchers for their wide applications in many fields such as energy storage devices, electrochromic devices, electronics and sensors, and microwave absorbers [23]. Recently, diverse composite nanomaterials; including polymeric materials as well as reinforced nanoparticles such magnetic, hybrid and multimetallic, have been reported [24-28]. In this regard, they have been applied in various areas like cosmetics [29], catalysis [30-33], drug delivery [34] and also in the synthesis of organic heterocyclic compounds [35-37]. By considering the unique properties of polymers such as flexibility, lightweight, low cost, excellent chemical stability and transparency, it was revealed that they were suitable to be replaced with inorganic materials [38, 39]. Nanocomposites with green matrix and natural polymer such as agar are more preferred, nowadays [40]. Flexibility, low weight and cost, transparency and excellent chemical and thermal stability can also be added to the other advantages of utilizing agar [41].

Agar as a gelatinous, nontoxic and biodegradable substance is a carbohydrate obtainedfrom red marine algae of the class *Rhodophyceae* andis composed of β-1,3-linked-D-galactose and α-1,4-linked 3,6-anhydro-L-galactose units [42]. Agar can be formed like a hard gel at low concentration, and therefore can mostly be used in processed foods, pharmaceutical products and in biotechnology and medicine [41].

Jegan and co-workers [43] have reported agar/$Fe_3O_4$ nanocomposites prepared by co-precipitation method. Although agar-based nanocomposites and $Fe_3O_4$ magnetic nanocomposites have been individually developed in much literature, the combination of them as green nanocomposites needs more research and study.

In continuation of previous works on the introduction of new recoverable magnetic nanocomposite and due to the importance of biopolymer, herein, the features of the Agar/$Fe_3O_4$ magnetic nanocomposite in the presence and absence of external magnetic field have been studied for the first time.

**Experimental**
*Materials and apparatus*
The solvents, $FeCl_2.4H_2O$, $FeCl_3.4H_2O$, $NH_3$, and agar were purchased from Merck, Fluka and Aldrich. IR spectra was recorded on a Shimadzu IR-470 spectrometer by the method of KBr pellets. Scanning electron microscopy (SEM) images were taken with VEGA-TESCAN instrument. X-ray diffraction (XRD) patterns of the solid powders were recorded with an X' Pert Pro X-ray diffractometer operating at 40 mA, 40 kV. Magnetic susceptibility measurements were performed using a Lake Shore VSM 7410. The thermal properties of the nanocomposites were measured through a STA 504 type thermogravimeteric (TG) analyzer. Samples were heated from 50 °C to 800 °C.

## Syntheses of Fe₃O₄ nanocomposites

At first, agar (1 g) was added to deionized water (20 mL) and stirred by a mechanical stirrer for 15 minutes at 70℃ to 80℃.Then, a mixture of $FeCl_2.4H_2O$ (0.65 g) and $FeCl_3.6H_2O$ (1.75 g), in 1:2 molar ratio, in deionized water (2 mL) was added to the previously mentioned solution and stirred for about 45 min. Afterwards, ammonia (10 mL) was added dropwise to the solution mixtureand stirred for about 2 hours. Finally, the synthesized nanocomposite was washed twice with distilled water. The final composites were dried for 3 h at 80 °C. The black material was collected with an external magnet and turned to powder with a pounder. In the second stage, the nanocomposite was synthesized in the presence of an external magnetite field with the same above-mentioned conditions. The synthesizing process in the external magnetic field (~ 0.4T) was carried out during the ammonia-adding stage and it took about 2 h. The synthetic method in the absence and presence of magnetic field is illustrated in Scheme 1.
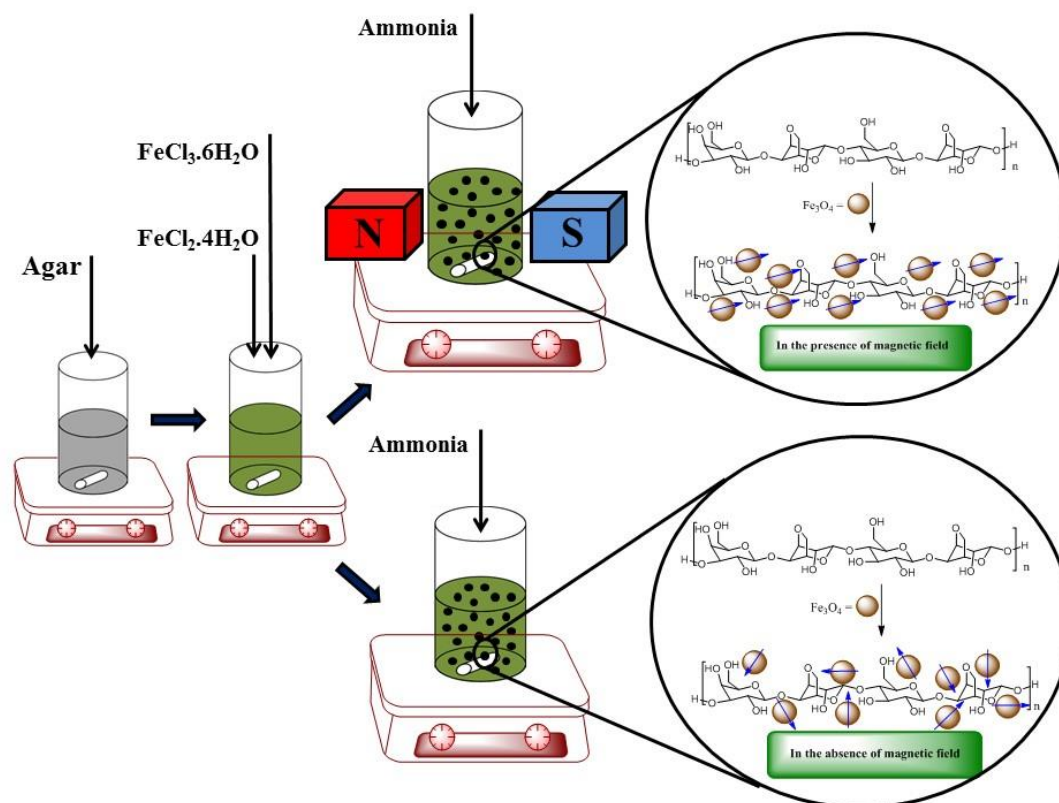


**Scheme1.**The synthesis of Agar/Fe₃O₄ nanocomposite in the absence and presence of magnetic field

## Results and discussions

The X-ray diffraction (XRD) pattern of the agar/Fe₃O₄ nanocomposites in the presence and absence of the external magnetic field is shown in Figure 1. The crystalline peaks observed at the diffraction angles (2θ) of 31.1, 36.1, 57.1 and 63.1 degrees are related to the (220), (311), (511) and (440) plates, respectively. These results are similar to the characteristic data of cubic Fe₃O₄ (JCPDS card No. 01-075-0449). Furthermore, the average crystallite size of the nanoparticles in the nanocomposites was calculated using Scherrer equation: $D=0.9\lambda/\beta \cos \theta$,

where D is the particle size, $\lambda$ is the X-ray wavelength (nm), $\theta$ is Bragg's angle, and $\beta$ is the excess line broadening(radiant). Full-width-at-half-maximum (FWHM) of (311) diffraction reflection and Scherrer equation revealed the average crystallite size of $Fe_3O_4$nanoparticles about 23 nm while this value in the synthesized samples in the absence of magnetic field was 25nm.This result indicates that the synthesis of nanocomposites in the presence of magnetic field causes more dipole alignment during the magnetic nanoparticles synthesis. In other words, magnetic field aligns more with magnetic dipoles or magnetic nanoparticles to its direction. This means stronger magnetic power and therefore more attraction between the nano magnetic particles.
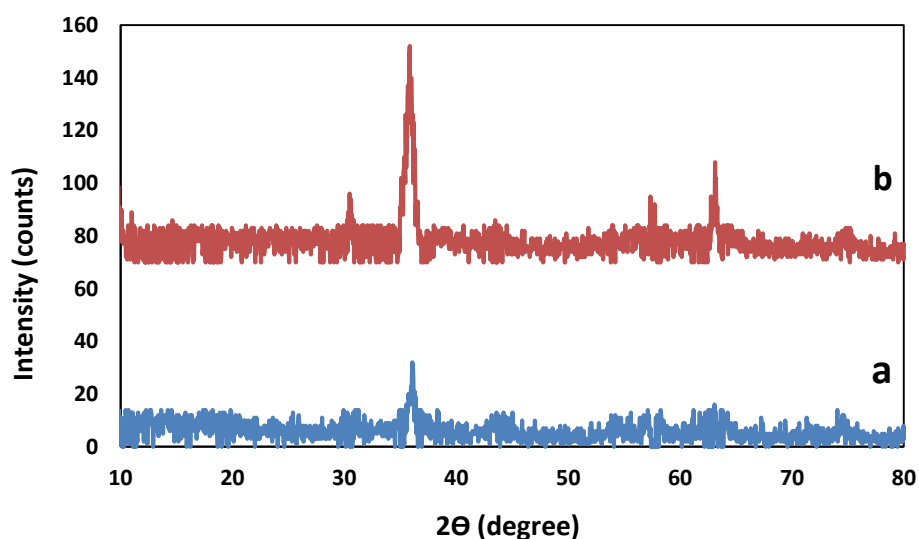


**Figure 1.**The XRD pattern and the reference $Fe_3O_4$of: (a) agar/$Fe_3O_4$ in the absence of magnetic field, (b) agar/$Fe_3O_4$ in the presence of magnetic field

The FT-IR spectra of the synthesized samples were depicted in Figure 2. The graph 1 is related to agar/$Fe_3O_4$ nanocomposite synthesized in the absence of the external magnetic field and graph 2 is related to agar/$Fe_3O_4$ nanocomposite fabricated in the external magnetite field. The FT-IR spectroscopy confirms the synthesis of the nanocomposite. The comparison of agar and agar/$Fe_3O_4$ spectra can confirm the synthesis of nanocomposite. As it can be seen in the FT-IR spectrum of agar, the absorption band at around 1043 $cm^{-1}$is attributed to the 3,6-anhydro-galactose bridges. The bands at 1656 $cm^{-1}$areassigned to O-H bending vibration and the bands at 2800 and 2900 $cm^{-1}$ are related to C-H stretching vibration. The broad band around 3400 $cm^{-1}$is due to stretching vibrations of hydroxyl groups and of hydrogen-bonded of water on the surface. The above-mentioned peaks which appeared in the agar/$Fe_3O_4$ nanocomposites were synthesized in the presence and the absence of magnetic field. The spectrum of agar/$Fe_3O_4$ shows the absorption at 568 $cm^{-1}$ for Fe-O band and also the broad absorption at 3424 $cm^{-1}$ represents the stretching vibrations of hydroxyl groups from iron oxide. The characteristic Fe-O bending peak at 621 $cm^{-1}$ can be attributed to the high crystallinity of $Fe_3O_4$ nanoparticles [15].
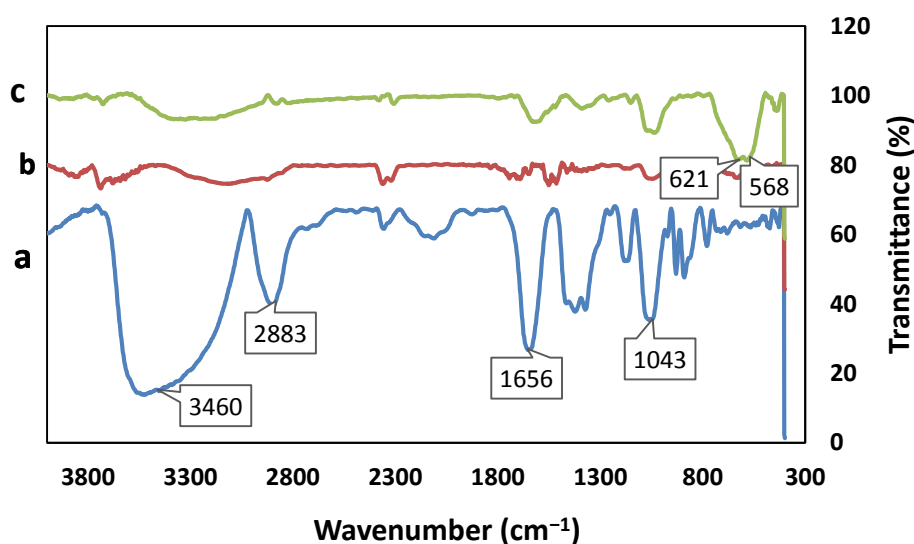
**Figure 2.** FT-IR spectra of: (a) agar, (b) agar/Fe$_3$O$_4$ in the absence of magnetic field, (c) agar/Fe$_3$O$_4$ in the presence of magnetic field

The SEM images of agar/Fe$_3$O$_4$ nanocomposite are shown in Figure 3.The average size of the nanoparticles in the sample synthesized in an external magnetic field is slightly greater than the sample synthesized without any external magnetic field. This is in agreement with XRD result, which comes from the more magnetic dipole alignment by the external magnetic field. In other words, by comparing the particles in the images, one can see that aggregations in image (a) are more accumulated than in image (b) and this is because of the more magnetic strength of image (a) as compared to image (b).
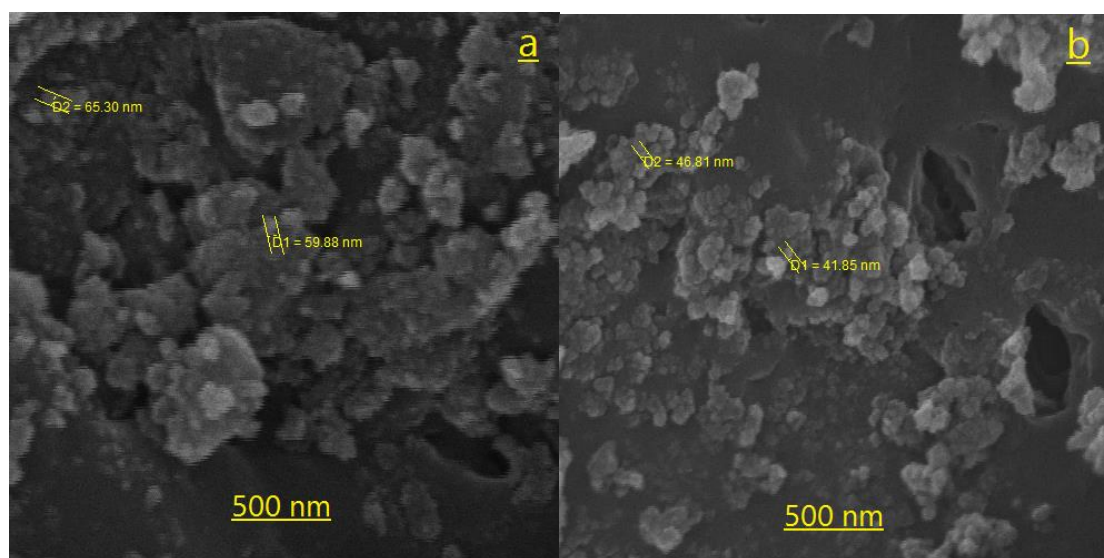


**Figure 3.** SEM images of: (a) agar/Fe$_3$O$_4$ nanocomposite in an external magnetic field, (b) in absence of an external magnetic field

The magnetic properties of nanocomposites are characterized by vibrating sample magnetometer (VSM) at room temperature. The Figure 4 shows the plot of the magnetization 'M' versus applied magnetic field (from -10000 Oe to 10000 Oe). The magnetization and applied magnetic field can be described by Langevin equation as: *M=M$_s$(Coth y-1)* and *y=mH/kT*. Where M$_s$ is the saturation magnetization of nanoparticles in the composites, m is the average magnetic moment of nanoparticles and k is the Boltzmann constant. The VSM curve reveals that the synthesized nanoparticles are super paramagnetic [15]. The superparamagnetic behavior is concluded from the hysteresis loop for Fe$_3$O$_4$ nanoparticles passing from the zero point and zero coercivity and remanence values. The VSM curve of the sample synthesized in absence of an external magnetic field is the same as the one for the synthesized sample in the presence of an external magnetic field. By increasing the applied field from 0 to 5000 Oe, the M (magnetization) increases sharply and at about the 5000 Oe it reaches about its saturation value. The saturation magnetization (M$_s$) value for the sample 1 is 33.92 emu/g and for the sample 2 is 38.92 emu/g. By applying an external magnetic field, the magnetic nanoparticles are aligned to the external magnetic field direction. The aligned magnetic dipoles attract each other and then a greater magnetic domain is formed. The greater domains cause more magnetic properties of nanocomposites and higher M$_s$ in VSM studies. The reported value of M$_s$ for the Fe$_3$O$_4$ nanoparticles is 80.7 emu/g [15]. The difference of M$_s$value in our study and other groups is because of the synthesizing conditions. In this study, we have only focused on the effect of external magnetic field on the magnetic properties of nanoparticles in the composites for the first time. By applying this method for increasing the saturation magnetism of nanoparticles to the reported methods with the highestM$_s$, the M$_s$ valueof even higher than 80.7 emu/g can be reached. Otherwise, the nanomagnetic particles in the composites are affected by the surrounding area (matrix) and therefore the saturation magnetism is different from pure magnetic nanoparticles.
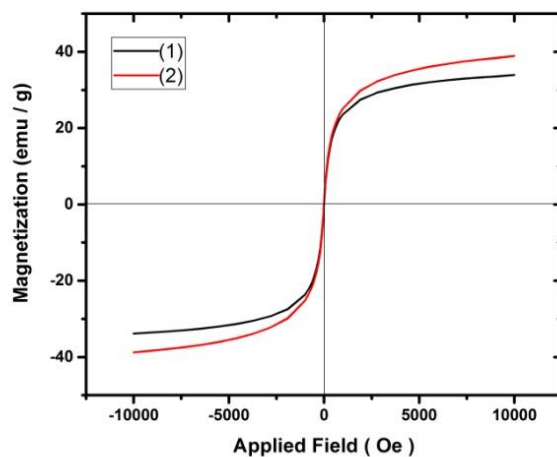


**Figure 4.** VSM results 1) synthesized sample in absence of an external magnetic field and 2) synthesized sample in presence of an external magnetic field

The thermal stability of the nanocomposite was studied by thermogravimeteric (TG) analysis at heating rate of 15 °C/min in the air atmosphere. The thermogravimeteric (TG) and derivative thermogravimeteric (DTG) curves of the agar/$Fe_3O_4$ are shown in Figure 5. The losing of weight around 150– 200 °C is attributed to the removal of the surface adsorbed water. As revealed by the DTG curve, the agar exhibited a peak at about 300 °C which is the temperature of maximum mass loss rate. According to the TG and DTG results, the agar mass ratio in the composite is 39%.
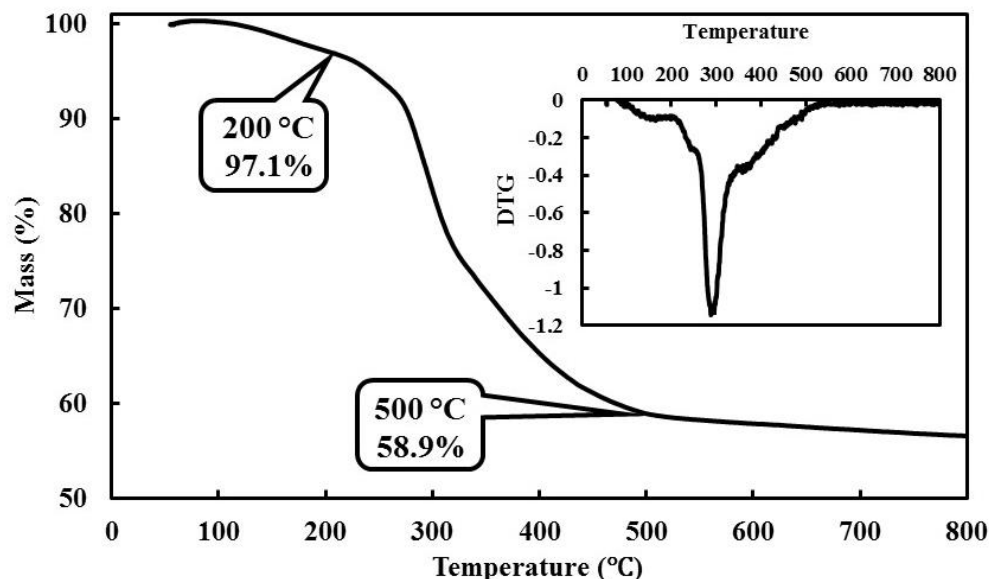


**Figure 5.** TG and DTG (inset) curves of agar/$Fe_3O_4$ composite

## Conclusion

Agar, a biopolymer as matrix, and $Fe_3O_4$ magnetic nanoparticles were used for synthesis of magnetic nanocomposite. The main advantages of agar include the prevention of magnetic nanoparticles to aggregation and synthesizing a green composite.

It is for the first time that the synthesis of $Fe_3O_4$/agar nanocomposites is carried out in the presence of external magnetic field. FT-IR and XRD analysis confirmed the magnetic nanoparticles synthesized in the presence and absence of magnetic field. The results of VSM showed that the saturation magnetism increased at about 15% by applying the magnetic field during the synthesis. This result can be used to increase the magnetic property of nanocomposites and to produce permanent magnetic composites.

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