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Improvement of Magnetic Property of CMC/Fe_3O_4 Nanocomposite by Applying External Magnetic Field During Synthesis

Niloofar Dehghani[a], Mohsen Babamoradi[a, *], Zoleikha Hajizadeh[b], Ali Maleki[b]

[a] Department of Physics, Iran University of Science and Technology, Tehran16846-13114, Iran

[b] Catalysts and Organic Synthesis Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran16846-13114, Iran

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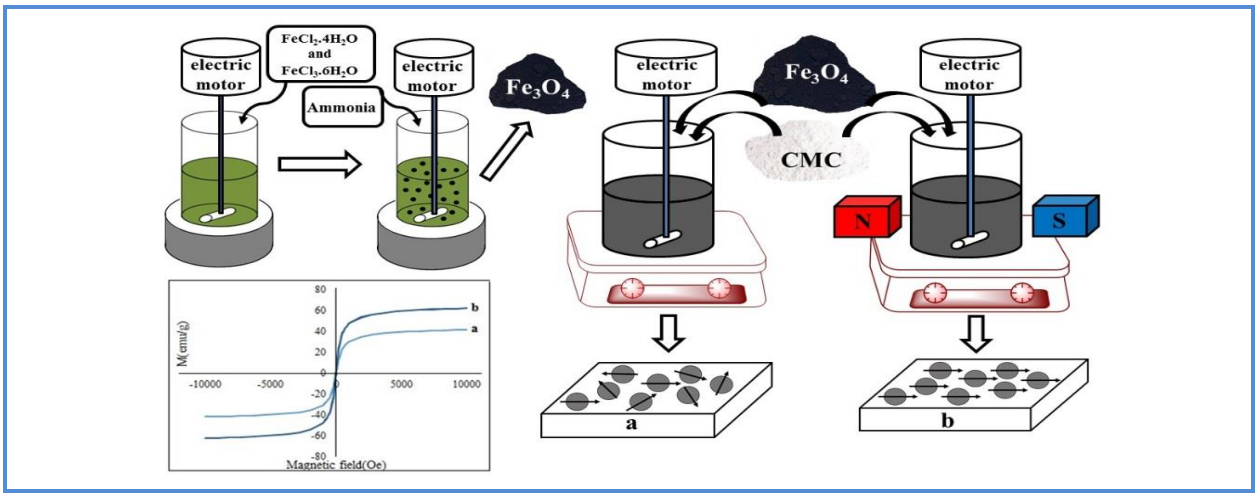
ABSTRACT

In this paper, magnetic nanocomposites were synthesized by embedding ferric oxide nanoparticles into carboxymethyl cellulose (CMC) using co-precipitation method. The properties of the synthesized nanocomposites in the presence of magnetic field were compared to the synthesized nanocomposite in normal condition. The magnetic properties of the nanocomposites were studied by a vibrational sampling magnetometer (VSM) to investigate the effect of the magnetic field on the magnetic properties. The results showed that the presence of magnetic field during the synthesizing, increased the saturation magnetization about 51%. X-ray diffraction (XRD) analysis confirmed the crystallinity of all samples. The SEM images revealed the nanoparticles homogenous dispersing in the composites. Infrared Fourier spectroscopy (FTIR) results confirmed the formation of iron oxide bonds in all samples. The increase of saturation magnetization can be attributed to the magnetic moment alignments by the magnetic field. Magnetic nanocomposites with higher magnetic properties can further develop their application.

*Corresponding author: E-mail: babamoradi@iust.ac.ir, Department of Physics, Iran University of Science and Technology, Tehran16846-13114, Iran, Tel: +98021 73225871; Fax: +98 02177240497

Graphical Abstract



Introduction

In recent years, metal oxide nanoparticles have been highly regarded as one of the most important classes of nanostructures in a wide range of industries due to their optical, magnetic, and electrical properties. Among the various types of magnetic nanoparticles, iron oxide nanoparticles can be named as the most common and the most used category. Iron oxide nanoparticles can be applied in many fields same as in biomedicine as an anticancer and in coating fields as protection against corrosion [1, 2]. The properties of iron oxide nanoparticles depend on the size and structure of the particles, and up to now, many researches have been done to improve the magnetic properties of the iron oxide nanoparticles [3-9]. Due to the attraction between the magnetic nanoparticles, the magnetic nanoparticles have ability to aggregation. The aggregation decreases the performance of the magnetic nanoparticles [10]. One solution to this problem is the use of composites. Carboxymethyl cellulose (CMC) is a white, odorless, and soluble substance in water. It is one of the cellulose derivatives that has been widely considered for its biocompatibility and low cost properties [11]. Extensive uses of this material range from edible and pharmaceutical consumption to textile, dye and detergent use [12].

Magnetic iron oxide nanocomposites with carboxymethyl cellulose (CMC) due to the special ability of CMC to change the surface of magnetic nanoparticles have attracted attentions. They have been studied in the elimination of cancer cells, diagnosis of liver cancer by magnetic resonance imaging (MRI), targeted drug delivery system in medicine and removal of organic and inorganic pollutants from water in the environment [13-20].

Magnetic particles can be attached to drug molecules, proteins, and enzymes, and reached the target tissue using an external field. Bio compatible magnetite-carboxymethyl cellulose nanocomposite have

been studied by other groups. Modified co-precipitation synthetic pathways were successfully employed to prepare CMC-conjugated Fe_3O_4 nanoparticles by Habibi *et al.* [19]. The CMC-Fe_3O_4 hydrogel have been studied for the removal of organic and inorganic pollutants and its capability to adsorb both MB and Cd (II) in deionized water was shown [20]. In other work, Fe_3O_4 magnetic nanoparticles were coated with carboxymethyl cellulose prepared by co-precipitating method and their application in MRI were studied [16]. Improvement of CMC/Fe_3O_4 properties need more studies as a bio composite and then it will be used more in industry. According to our best knowledge, the effect of magnetic field on the improvement of magnetic property of CMC/Fe_3O_4 has not been studied yet.

In this study, CMC which is used as an adjuvant for the placement of iron oxide magnetic nanoparticles is also a factor in preventing the aggregation of magnetic nanoparticles, as well as the properties of biocompatible magnetic composites. The increase of magnetic property of the nanocomposites by this method can be used for their development.

Experimental

Materials and apparatus

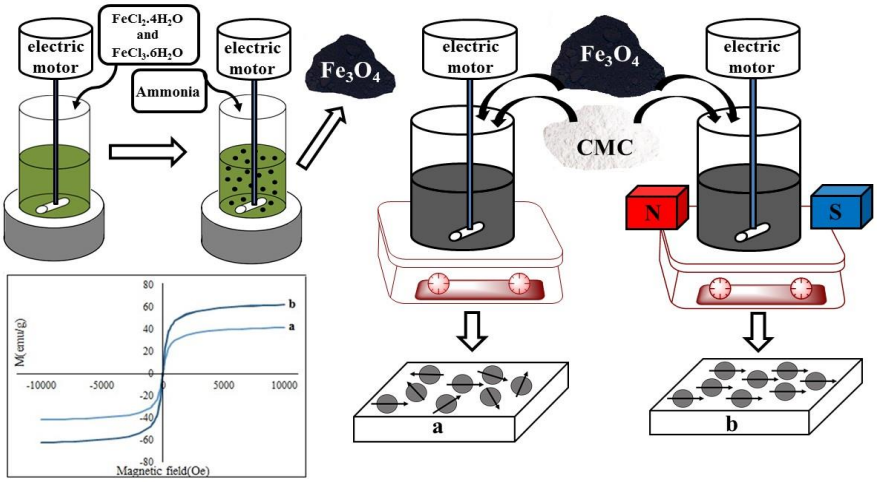
Ferric chloride ($FeCl_3.6H_2O$), ferrous chloride ($FeCl_2.4H_2O$) and ammonium hydroxide (NH_4OH) are purchased from Merck. Also, carboxymethyl cellulose (CMC) were obtained from the UK Sigma Aldrich company. The XRD pattern was characterized by DRON-8 operating at 40 mA, 40 kV with radiation wavelength as 1.54 Å. Magnetic properties were measured by Lake Shore VSM 7410 MDK model. The Tescan Vega 2 model instrument was used for taking SEM images. To obtain the SEM images, a thin layer of gold was coated on the samples by a desktop sputtering system (DSR 1; Nanostructure Coating, Iran). IR spectra was recorded on a Shimadzu FTIR-8400 S model manufactured by Shimadzu Corporation. The FTIR measurements were performed in transmission mode.

Preparation of Fe_3O_4/CMC nanocomposites

The nanoparticles were prepared by co-precipitation method [19] as the following steps: The materials $FeCl_3.6H_2O$, $FeCl_2.4H_2O$ and NH_4OH were used. At first, 4.7 g of $FeCl_3$ (0.2 molar) and 2.7 g of $FeCl_2.4H_2O$ (0.1 molar) were prepared separately; Then two powders were added in 100 cc distilled water at 80 °C and stirred for 1 h with a mechanical stirrer to completely dissolve in water. After 1 h, a clear yellow solution was appeared. In the next step, using 25% of ammonium hydroxide solution, we diluted the pH to 11. For this aim, we diluted 10 cc of ammonia with 10 mL distilled water and added drops to the solution for 10 min. Upon the addition of the first open droplet, a black solution was formed in the sedimentary solution. After 10 min, the total amount of ammonium hydroxide was added to the solution. After 30 min, we stopped the kneading and allowed the precipitate to settle. In order to adjust

the pH of the solution to 7, the solution was washed several times by distilled water. Then the precipitate was removed from the solution with the help of a conventional magnet, and heated for 12 h in an oven at 80 °C to obtain an iron oxide nanoparticles powder.

In the next step, CMC powder and Fe_3O_4 nanoparticles were mixed with weight ratio 1:2 in 20 cc distilled water at 80 °C for 30 min. After that, the solution became in jelly-mode. The solution was poured equally to two beakers. One of the beakers was put in the usual conditions at 70 °C and the other one, was put under the influence of a magnetic field of about 0.4 T. The stirring conditions and temperature values for the both samples were same as each other. The synthetic of Fe_3O_4 nanoparticles and CMC/Fe_3O_4 composites in the absence and presence of magnetic field are illustrated in Scheme 1.



Scheme 1. The synthesis of Fe_3O_4 nanoparticles and CMC/Fe_3O_4 composites in the presence and absence of magnetic field

Results and discussion

XRD (X-ray diffraction) analysis was used to identify the crystalline structure of the samples, as well as to confirm the formation of the phases and the absence of impurities. The XRD results of samples synthesized in normal conditions and in the presence of a magnetic field are shown in Figure 1. The XRD patterns of two samples in the Figure 1 were confirmed by a reference sample (JCPDS 19-0629). The typical X-ray diffraction patterns of magnetite (Fe_3O_4) and the cubic structure of magnetite nanoparticles is perfectly consisted. The crystalline peaks which are observed at the diffraction angles (2θ) of 30.3, 35.8, 42.2, 57.3 and 62.7 degrees are related to the (220), (311), (400), (511) and (440) crystallographic planes, respectively.

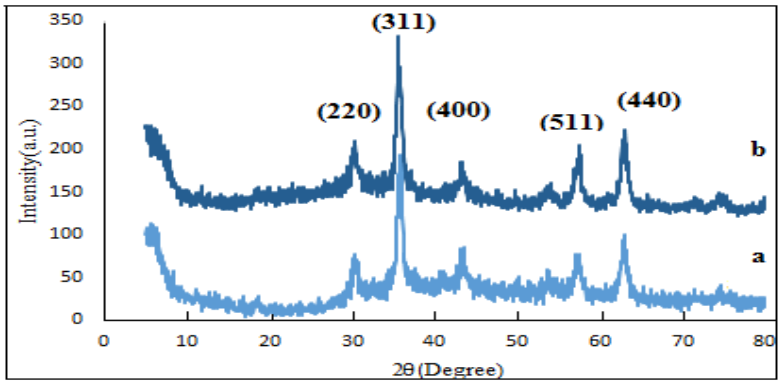


Figure 1. XRD patterns of CMC/Fe_3O_4 composites synthesized in the absence of magnetic field (a) and in the presence of magnetic field (b)

The crystallinity for the sample synthesized under the magnetic field has increased. This can be related to the increasing of the saturation magnetization. The magnetic field aligns magnetic nanoparticles to its direction and therefore more magnetic moment causes more crystallinity. The average size of the nanoparticles according to the Scherrer formula was calculated as about 15 nm. The magnetic properties of magnetic iron oxide nanoparticles were investigated by vibrating magnetic sample (VSM) instrument. In Figure 2, a typical magnetic resonance curve is observed on the ferromagnetic behavior. The magnetization curves of the composites pass through the source, and the field of formation and magnetization of the residual are also not observed, so it can be said that the composites are synthesized of the super paramagnetism [21].

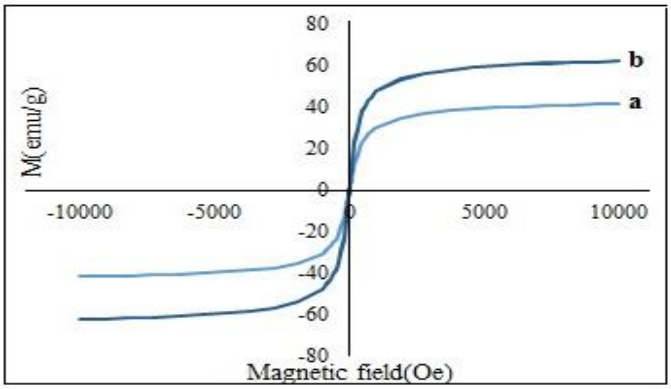


Figure 2. VSM results for CMC/Fe_3O_4composites synthesized in the absence of external magnetic field (a) and in the presence of external magnetic field (b)

The curve b shows the magnetic property of the synthesized composite in the presence of the magnetic field. Saturation magnetization (M_s) was increased from 41 emu/g (under normal construction conditions) to 62 emu/gr for the sample synthesized in the presence of a magnetic field. Chang *et al.*

reported the saturation magnetism of CMC/Fe_3O_4 as 35.75 emu/gr [22] and in similar work Foroutan *et al.* reported its value for CMC-g-HAp/Fe_3O_4 nanobiocomposite as 28.735 emu/g [23]. Our result for saturation magnetism value for synthesized sample without applying magnetic field showed the better than the other pervious works. Meanwhile, synthesizing in the presence of magnetic field increased the saturation magnetism value significantly.

Actually, CMC has immobilized the magnetite particles to remain constant in the presence of the magnetic field to perform particle analysis, and this field does not affect the sample. This result is due to the momentum introduced into the formed nuclei, which has a magnetic component. By increasing the diameter of the magnetic nuclei, reducing the percentage of surface atoms, increasing the crystallinity; the magnetic moment of the formed nuclei increases and a stronger momentum is introduced into them. In fact, with the improvement of the crystallinity of the non-magnetic layer, we will have a thinner surface that causes a cationic distribution with a narrower range, so that magnetism is more saturated when it is formed in the presence of the field.

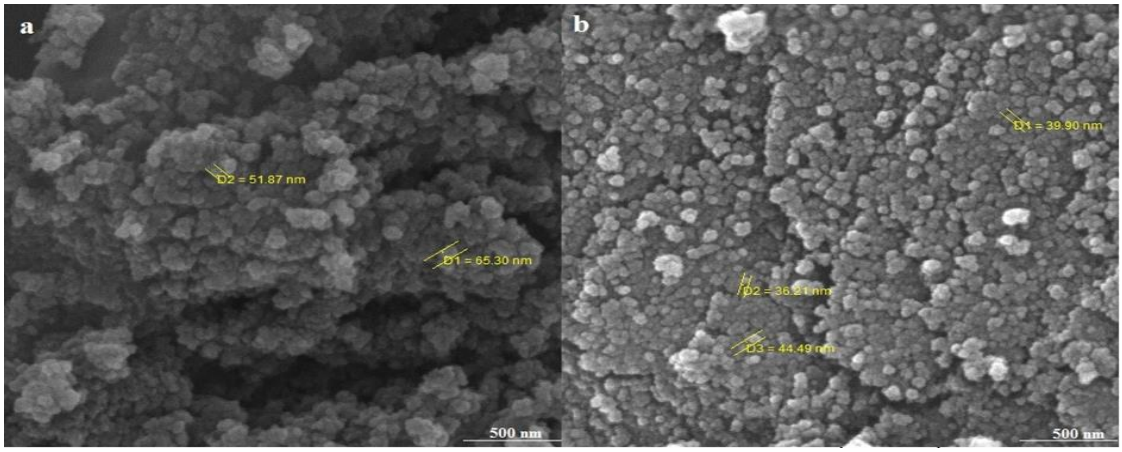


Figure 3. SEM images of CMC/Fe_3O_4 composites synthesized in the absence of external magnetic field (a) and in the presence of external magnetic field (b)

Figure 3 shows the SEM (scanning electron microscopy) images and morphologies of the nanocomposites. As can be seen in the Figure 3, the sizes of particles are decreased in the synthesized sample in the presence of magnetic field. In addition, the particle shapes have become even more uniform and, in general, particles with smaller dimensions are produced. Particles removed from the aggregation state also have a more homogeneous and spherical shape.

The Figures 4 a, and b show the Fourier transform infrared spectroscopy (FT-IR) spectrum constructed in normal conditions and in the presence of magnetic field, respectively. In this Figure, the peak or absorption bond of Fe-O which has the range of 550 cm^{-1} to 600 cm^{-1} is observed corresponding to inherent stretching vibrations of metal-oxygen at tetrahedral site (Fe_{tetra}-O) [24]. The second peak is

about 3367 cm^{-1} which is due to strong stretching vibration by the hydrogen bond formed with hydroxyl groups (OH) which is adsorbed from the environment by the sample. Also, a medium-intense peak at 1608 cm^{-1} in Figure 4 a and 1595 cm^{-1} in Figure 4 b is derived from the asymmetric stretching of carboxylate groups.

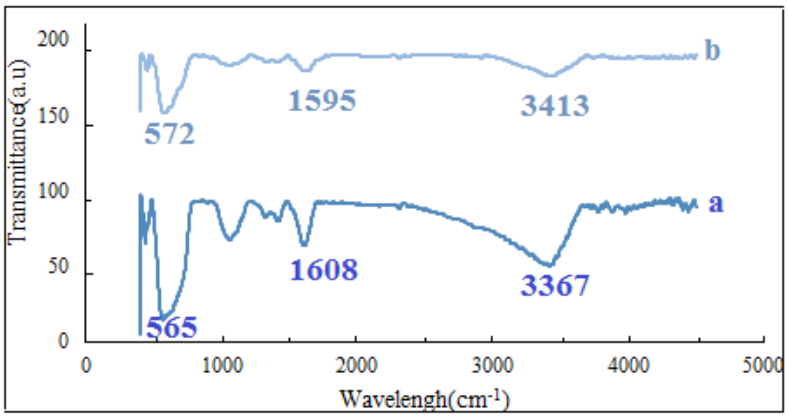


Figure 4. FT-IR spectra of CMC/Fe_3O_4 composites synthesized in the absence of magnetic field (a), inthe presence of the magnetic field (b)

Conclusions

Nanoparticles of iron oxide were prepared by chemical co-precipitation method. The CMC/F_3O_4 nanocomposites were synthesized in the presence of magnetic field. X-ray diffraction results confirmed the crystallinity of the nanocomposites. From the scanning electron microscope images, it can be seen that the particles cling together to a smaller magnetic field due to orientation in the direction of the magnetic field. In particular, the results of the VSM analysis showed that the production of nanocomposites in the magnetic field caused 51% increase in the saturation magnetization value. FTIR analysis also showed that the magnetite nanoparticles coated by carboxymethyl cellulose retained magnetite bonds. These results, which have been found for the first time, can be used for the desired parameters required by researchers for magnetic nanocomposites development.

Conflict of Interest

We have no conflicts of interest to disclose.

References

[1] Giri M.N., Agarwala V. *J. Bionanosci.*, 2015, **9**:276

[2] Wu W., He Q., Jiang C. *Nanoscale Res. Lett.*, 2008, **3**:397

[3] Reddy A.V.B., Yusop Z., Jaafar J., Reddy Y.V.M., Arisa A.B., Majid Z.A., Talib J., Madhavi G. *J. Environ. Chem. Eng.,* 2016, **4**:3537

[4] Wang X., Liao Y., Zhang D., Wen T., Zhong Z. *J. Mater. Sci. Technol.,* 2018, **34**:1259

[5] Lisjak D., Mertelj A. *Progress Mater. Sci.*, 2018, **95**:286

[6] Ziabari S.A.M., babamoradi M., Hajizadeh Z., Maleki A. *Iran. Chem. Commun.*, 2019, **7**:512

[7] Sharma G., Kumar A., Sharma S., Naushad M., Dwivedi R.P., ALOthman ZA, Mola G.T. *J. King Saud Uni. Sci.*, 2017, **31**:257

[8] Rios A., Zougagh M. *Trends Anal. Chem.,* 2016, **84**:72

[9] Simonsen G., Strand M., Øye G. *J. Petrol. Sci. Eng.*, 2018, **165**:488

[10] Behrens S. *Nanoscale*, 2011, **3**:877

[11] Biswal D.R., Singh R.P. *Carbohydr. Polym.*, 2004, **57**:379

[12] Shanker G., Kumar C.K., Gonugunta C.S., Kumar B.V., Veerareddy P.R. *AAPS Pharm. Sci. Tech.*, 2009, **10**:530

[13] Miller M.M., Prinz G.A., Cheng S.F., Bounnak S. *Appl. Phys. Lett.*, 2002, **81**:2211

[14] Veiseh O., Gunn G.W., Zhang M. *Adv. Drug Delivery Rev.*, 2010, **62**:284

[15] Gang L., Zhiyong W., Jian L., Chunchao X., Fabao G., Qiyong G., Bin S., Xuna Z., Xintao S., Xiaoyuan C., Hua A., Zhongwei G. *Biomater.*, 2011, **32**:528

[16] Sitthichai S., Pilapong C., Thongtem T.,Thongtem S., *Applied Surface Science*, 2015, **356**:972

[17] Gallo J., Genicio N., Penadés S. *Adv. Healthcare Mater.*, 2012,**1**:302

[18] Pilapong C., Keereeta Y., Munkhetkorn S., Thongtem S., Thongtem T. *Colloids Surf. B. Biointerfaces*, 2014, **113**:249

[19] Habibi N. *Spectrochim Acta Part A Mol. Biomol. Spectrosc.*, 2014, **131**:55

[20] Uva M., Tambasco M., Grassi G., Corsi I., Protano G., Atrei A. *J. Environ. Chem. Eng.*, 2017, **5**:3632

[21] Maity D., Agrawal D.C. *J. Magnet. Magnet. Mater.,* 2007, **308**:46

[22] Chang P.R., Yu J., Ma X., Anderson D.P. *Carbohyd. Polym.,* 2011, **83**:640

[23] Foroutan R., louydarab M.A., Ramavandi B., Mohammadi R. *J. Environ. Chem. Eng.,* 2018, **6**:6049

[24] Hajizadeh Z., Maleki A. *Molecul. Catal.,* 2018, **460**:87

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