

The Effect of Alkaline Media and Temperature on the Structure and Magnetic Properties of Magnetic Nanoparticles Modified with PEG

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Abstract–Magnetic nanoparticles were synthesized and coated by the situ-coprecipitation method with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ precursors in the presence of NH_4OH (or NaOH) reduction and PEG coated agent. Preparation of modified magnetic nanoparticles were performed at two different temperatures under the influence of different alkaline media. The effect of strength of alkaline media and reaction temperature of the magnetic properties (Magnetic saturation, Magnetic remanent, coercive force (of modified MNPs) were investigated. To study structure, morphology, optic and magnetic properties MNPs were characterized by XRD, FTIR, TEM and VSM analyzes. The results showed that modified magnetic nanoparticles have superparamagnetic properties and have high magnetic saturation and small coercive force, so the magnetic properties of the modified MNPs are depended to the strength of the alkaline remanent directly. The saturation magnetization of the synthesized sample in NH_4OH and NaOH at 80°C was determined as 60.94 and 49.39 emu/g, respectively. Also increasing temperature, improves magnetic properties coated MNPs) at temperatures below the blocking temperature. (The results of the XRD analysis showed that the structure of the modified magnetic nanoparticles is inverted spinel and the size of the nanoparticles synthesized in the ammonia media is smaller than the other media. The results of FTIR optical analysis revealed that the peaks at ~ 570 and $\sim 440\text{ cm}^{-1}$ indicates the bond Fe-O. TEM analysis indicated that the shape of the MNPs is pseudo-spherical. VSM analysis indicated that the magnetic nanoparticles synthesized in stronger alkaline media (ammonia) and high temperature showed better magnetic behavior by higher magnetic properties.

Keywords: Magnetic nanoparticles, superparamagnetic, magnetic properties, Magnetic saturation

1. Introduction

Magnetic nanoparticles (MNPs) can be considered as one of the most important groups in the field of nanoparticles. These nanoparticles have high physical and chemical properties therefore, they have been significantly noticed in various sciences. Major of these properties is due to their size and magnetic properties [1-5]. Magnetic nanoparticles have attracted the attention of many researchers due to their high specific surface area, good dispersibility, high absorption power and impressive superparamagnetic properties. These nanoparticles have high magnetic saturation and small size and are easily

separated by an external magnetic field; therefore, they have high magnetic capacity. The remarkable characteristics of magnetic nanoparticles have caused them to be used in various fields such as electronic memory, optics, medicine, high resonance imaging, magneto-optical and microwave devices, etc. [6-11].

Iron oxide is found in different forms, magnetite and hematite are the two most important and main forms in this field [12,13]. Magnetite and hematite MNPs have significant magnetic properties, which distinguishes them from other phases of oxidation. Magnetic nanoparticles can be fabricated by both physical and chemical methods. Although physical methods (from top to bottom) are scalable, cost-effective and capable of industrial production, in some methods, such as the steam condensation method, they have disadvantages such as exothermicity and oxidation. Also, a significant amount of mechanical, thermal or electrical energy is needed to transform materials into nanoparticles. The chemical method (from bottom to top) has a higher capability due to better control of

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synthesis parameters (temperature, molar ratio of raw materials, pH). So, the chemical method has a unique ability in the field of technology and science of nanostructured materials due to the arrangement of materials in nanometer conditions in order to achieve the desired properties, and most chemical methods follow the nucleation and growth mechanism. Sol-gel, sonochemistry, sonothermal, microemulsion and co-precipitation are the methods of chemical synthesis [14-18]. Co-precipitation method, due to the simplicity of the synthesis method, short reaction time, production of products with high purity is more suitable than other methods and is used in most experiments [19-22].

There are strong electromagnetic and van der Waals attraction forces between MNPs. These forces sometimes cause them to aggregate and become instability. This problem can be largely solved by reducing the size of MNPs or modifying their surface chemistry. Also, the type and method of using the coating agent during the synthesis process and choosing the appropriate alkaline media and temperature can be effective on controlling and adjusting the size of nanoparticles and their magnetic properties. In fact, by creating electrostatic or spatial repulsion forces between nanoparticles in the synthesis process, can be prevented them from agglomerating. Nanoparticle surface modification is done by using inorganic and organic agents [22-24].

So, Surface modification (Coatings) can aid the colloidal stability of the particles against aggregation and gravitational settling by reducing the inter-particle dipole-dipole interaction. The stability of the coated particles depends on the bond strength between the core and the coating. Polymers (organic coatings) have better capabilities due to biocompatibility and molecular biodegradability. PEG, PVA and PVP polymer coatings are the most suitable coatings in this field.

In 2017 Karimzadeh et al. modified MNPs via cathodic electrochemical deposition method. They investigated the properties of MNPs coated with PEG. In this research, the magnetic saturation value of modified nanoparticles was determined to be 37.5 emu/g [25].

In 2020, Antarnusa et al. synthesized coated magnetic nanoparticles by co-precipitation method and used $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ ammonium solution and PEG. The maximum saturation magnetization that they found was 60 emu/g. By applying 3g PEG, the amount of saturation magnetization was about 40 (emu g⁻¹) [26]. The final product contained different phases.

In this research, modified magnetic nanoparticles were synthesized by coprecipitation (in situ) method. PEG polymer agent was used to coat magnetic nanoparticles.

The effect of alkaline media and temperature on the structure, size, behavior and magnetic properties of modified magnetic nanoparticles were studied and investigated by XRD, FTIR, TEM and VSM analyses.

2. Materials and equipment

Ferrous chloride tetrahydrate (99%), ferric chloride hexahydrate (99%), Sodium hydroxide (98%), Ammonium solution (25%), chloric acid (37%), distilled water, polyethylene glycol 4000 (PEG-1000) was used to synthesize coated MNPs.

Equipment includes: a digital scale with an accuracy of 0.0001 g with the model KF3005, Heidolph magnetic stirrer HEI-TEC0147, Electrothermal EM100CE, HANNA digital PH meter HI 2211, an oven BM1200E and a digital thermometer STC-100A.

The structural study was performed by X-ray diffraction (XRD) and data with 2θ in the angle range ($80^\circ - 10^\circ$) with the type X-Pert Pro MPD, Cu-K α ($\lambda = 1.54060 \text{ \AA}$) was recorded. The transmission of the optical spectrum in the infrared spectrum (FTIR) was performed by a Spectrum RXI Infrared Fourier Transform Spectrometer manufactured by Perkin Elmer. The appearance and average size of nanoparticles were determined by transmission electron microscopy (TEM) with Zeiss EM-900 model (80 kv). The magnetic behavior of the samples was evaluated by a vibrating sample magnetometer (VSM) with Lake Shore 7300 model at room temperature.

3. Experiment

3.1. Synthesis of magnetic nanoparticles

For preparing of coated MNPs, at first a mixture of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), Ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) (2:1) and 2.9 g PEG were prepared in a three-necked flask, then it was dissolved in 20 cc hydrochloric acid (0.5 M) under a magnetic stirrer at 350 rpm at 80° C . Simultaneously, Sodium hydroxide solution (2M) was prepared in another flask and both of them were immersed under nitrogen atmospheric condition for 30 minutes. Then the mixture was added dropwise to the alkaline solution (2M). Gradually black nanoparticles were formed. Suspension magnetic nanoparticles were separated from the solution by external magnetic field at pH about 12. By using an external magnetic field, MNPs were separated from the solution. The resulting product was washed

several times with pure water to reach a neutral pH (PH=7). Then it was dried inside the oven at 50° C. In the next step, ammonium solution (2 M) was used instead of alkaline soda and the other synthesis steps were carried out similarly to the previous step. The resulting powders were prepared for different spectra, such as XRD, TEM, FTIR and VSM

4. Results and discussion

4.1. XRD analysis

XRD spectra was carried out to characterize the modified MNPs crystal structure, particle size and phases in the samples. Figure 1 represents the XRD spectra of pure and modified magnetic nanoparticles in two alkaline media, ammonium and soda. As it is clear from the Figure, in both cases, the crystal structure of the modified magnetic nanoparticles was the same as that of Fe₃O₄ magnetic nanoparticles "face center cubic (FCC)," and the molecular structure was "inverse spinel. The unit cell structure consists of tetrahedral and octahedral sites in which oxygen and iron ions are placed. The unit cell contains 32 O₂⁻ ions and 8 Fe⁺³ ions in tetrahedral sites and 16 iron ions in octahedral sites (8 Fe⁺² and 8 Fe⁺³).

The peaks observed in the XRD analysis at the angles of 2θ were 30/3° (220), 35/5° (311), 43/2° (400), 53/5° (422), 57/6° (511), and 62/8° (440), indicating that the Magnetite phase. According to the card number JCPDS-19629, these data confirm the crystal structure of magnetite. The size of the nanoparticle was calculated by Scherer's

Eq. (1) using reference peak specifications (311) [27]. The crystal size of the coated MNPs in two alkaline media, sodium and ammonium, was about 9.8 nm and 10.2 nm, respectively.

$$d = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

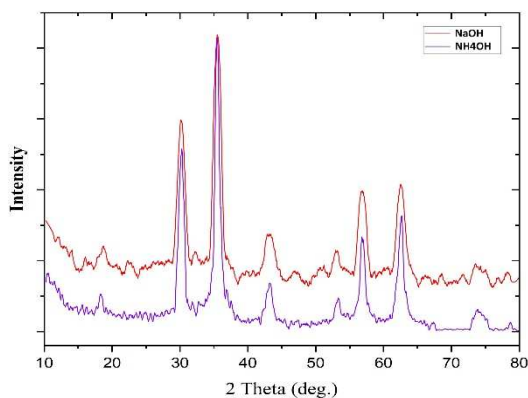


Fig.1. XRD spectrum of modified MNPs with PEG at the presence of NH₄OH and NaOH.

As can be seen, except for the PEG polymer agent that prevents the growth of magnetic nanoparticles, the alkaline media also has an effect on the size growth of nanoparticles.

4.2. Ftir analysis

FTIR analysis was used to determine the functional group and vibration bands. Figure 2 shows the transmission rate of samples in the co-precipitation method. In FTIR spectra of both modified samples, the peaks at ~570 cm⁻¹ and ~440 cm⁻¹ are related to the ν₁ and ν₂ Fe-O bonds, respectively. The presence of peaks in the range of 874 cm⁻¹ to 1384 cm⁻¹ indicates the placement of PEG polymer agent on the surface of MNPs while the peaks at ~1120 cm⁻¹ and ~1360 cm⁻¹ are attributed to the C-O-C ether stretch and vibration bands [26,28]. Also, the absorption peaks at ~2900 cm⁻¹ and ~960 cm⁻¹ are related to -CH stretching vibrations and its out-of-plane bending vibrations, respectively and the peak at ~1470 cm⁻¹ is attributed to the -CH₂- groups bending.

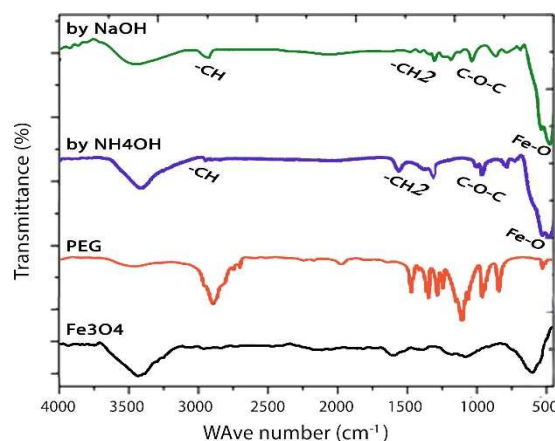


Fig.2. FTIR spectrum of modified MNPs with PEG at the presence of NH₄OH and NaOH.

4.3. TEM analysis

TEM analysis was performed to determine the precise size and appearance of the magnetic nanoparticles. Figure 3 shows the TEM analysis of coated MNPs in two alkaline media, ammonium and soda at 80 °C. the shapes of the nanoparticles were almost spherical, and they were somewhat attached, which was due to the electrostatic repulsion and steric hindrance force [29,30]. The mean size of modified magnetic nanoparticles in alkaline ammonium and sodium media from size distribution histograms of Figure 4 modified MNPs was determined to be 10.3 nm and 9.8 nm, respectively. There is a critical size which define the superparamagnetic region, for calculation of this

parameter one can use the following expression, $V_p \approx 25kT/K$; where k is Boltzmann constant, K denotes anisotropy constant (for $Fe_3O_4 = 1.35 \times 10^4 \text{ J/m}^3$) and T is the absolute temperature [30,32]. At room temperature, 300 K, the critical size is equal to 27 nm. The coated MNPs prepared in this study have sizes around 9 to 11 nm which are below this critical size, this matter ensures the superparamagnetic behavior of prepared the coated MNPs.

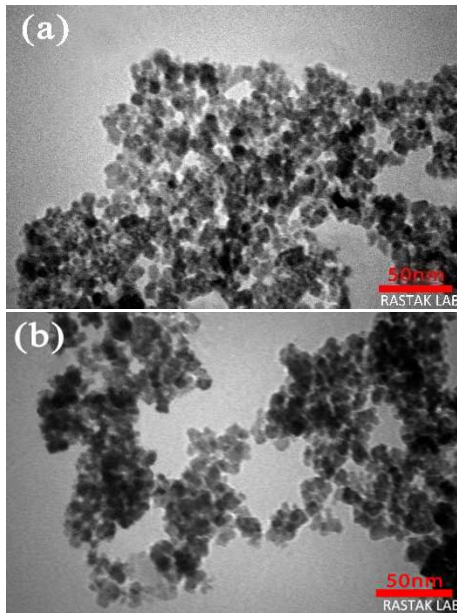


Fig.3. TEM micrographs of modified MNPs with PEG at the presence of (a) ammonium and (b) soda.
mean and StDev: 10.33 and 2.89

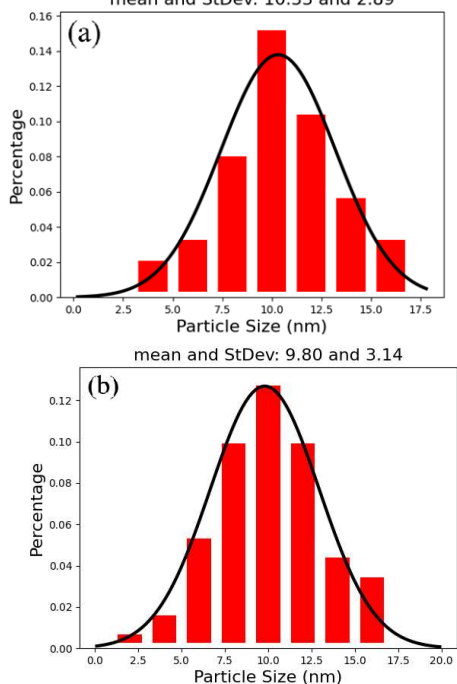


Fig.4. Size distribution histograms of modified MNPs with PEG at the presence of (a) ammonium and (b) soda.

4.4. VSM analysis

VSM analysis was used to determine the magnetic behavior and properties of the modified MNPs. The amount of the saturation magnetism (M_s), magnetic remanent (M_r) and coercive force (H_c) of each sample was analyzed. The analysis shows that the coated MNPs have superparamagnetic properties (Figure 5). The reduction of particle size, the breaking of a large number of atomic bonds on the surface, and the use of polymer agents have led to a decrease in magnetic saturation compared to its bulk state [33-35]. The small thickness of the coating agent and the engineering design and selection method have minimized this reduction and prevented the agglomeration of MNPs. Also, the alkaline media where the synthesis process is carried out also plays an important role in the magnetic properties of coated MNPs. While increasing the temperature and slightly reducing the size of the coated magnetic nanowire causes the surface defects to disappear, it leads to the improvement of the magnetic properties (magnetic saturation).

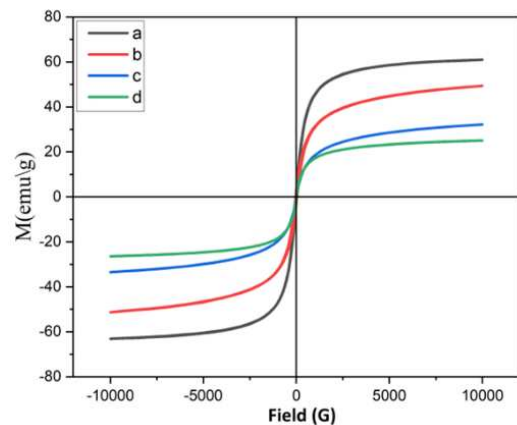


Fig.5. VSM analysis of modified MNPs with PEG at the presence of ammonium at (a) 80°C, (b) 20°C and at the presence of soda at (c) 80°C and (d) 20°C.

The Figure 6 shows that the increase in temperature (below the Curie temperature) directly increase the M_s of coated MNPs. The amount of saturated magnetization is significantly higher when ammonium is used. The Figure 7 shows that the effect of alkaline media and temperature on the M_r .

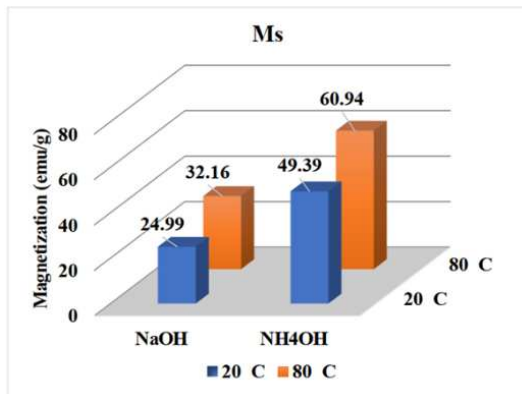


Fig. 6. Investigation of the effect of alkaline media and temperature on saturation magnetism.

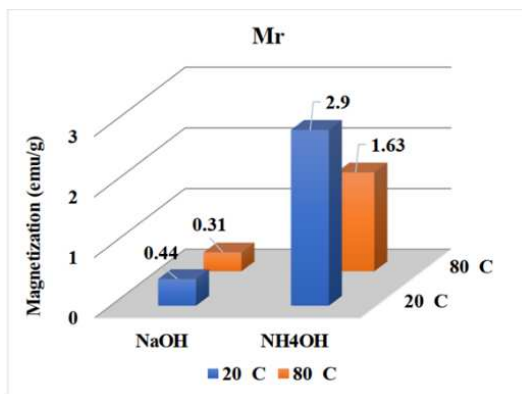


Fig.7. Investigation of the effect of alkaline media and temperature on magnetic remanent

5. Conclusions

Magnetic nanoparticles were successfully synthesized and coated with PEG polymer agent by in situ coprecipitation method. Effect of alkaline media and temperature on the structure, size and magnetic properties of modified MNPs were investigated. Polymeric agent caused the stability of magnetic nanoparticles. Ammonium and soda had effect on the magnetic properties of coated MNPs and to some extent on their size and did not affect their structure. The modified nanoparticles had higher magnetic saturation in the presence of ammonium. The results also indicated that by an increase in the temperature the magnetic saturation of the coated magnetic nanoparticles was increased.

The modified magnetic nanoparticles had a smaller size in the presence of sodium.

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