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Preparation and characterization of smart hydrogels (magnetic field responsive)

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Abstract

Iron nanoparticles were prepared by using the co-precipitation process, and then used to fabricate magnetic field-responsive hydrogel films. The magnetic nanoparticles' structural, physical-chemical, morphological, and magnetic characteristics and the effect of hydrogel films' coating concentration were studied. The properties of the hydrogel film responsive to the magnetic field were investigated using Fourier analysis spectroscopy infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and a vibration sample magnetometer (VSM). The results indicated that all samples showed good inter-integration of the constituent materials and their functional groups. The hydrogel film samples which were polycrystalline, had broad diffraction peaks and showed constant particle size with nearly spherical particles with rounded edges. The SEM image of the magnetic nanoparticles with and without coating was established for the accumulation of numerous nanoparticles with a 17 nm mean diameter. In addition, the magnetic properties of the magnetic field-sensitive hydrogel films were evident and sufficient for drug delivery to the desired location.

Keywords: Magnetic nanoparticle; hydrogel; Polyvinyl alcohol; Smart hydrogels.

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1- Introduction

Smart hydrogels are hydrogels that instantly respond to signals or stimuli by sensing them and acting accordingly [1]. The cross-linked hydrophilic polymers that make up smart hydrogels are arranged in three dimensions and can change their characteristics in response to environmental factors including pH, temperatures, magnetic and electrical fields, light, as well as biomolecule concentration [2]. These stimuli-responsive hydrogels might be used for biomedical engineering, anticancer treatment, and improved drug delivery systems [3]. Smart hydrogels respond to external stimuli by abruptly changing both their macroscopic and physical characteristics [4]. These hydrogels' nonlinear feedback is what gives them their distinctiveness. They can respond to triggers by changing their phase volume in a reversible, intensity-scalable, repeatable, and predictable way, and they can return after the trigger has been withdrawn [5]. These changes involve modifications in the physical phase, solvent interactions, form and solubility, conduction, and hydrophobicity [6]. Smart hydrogels can be used in systems for drug delivery to decrease the number of doses needed, keep the optimum therapeutic dosage in a single dose, and lessen adverse effects by preventing drug buildup in tissues other than the target ones [7]. Polymer hydrogels are becoming more and more common in the field of controlled-release medication delivery. When dried, these polymers are typically glassy, but when water is absorbed, they expand to form an elastic gel [8]. The term "gel" is used to describe the elastic and semisolid material created by chemically bonding water-soluble polymers together in an aqueous solution [9]. Moreover, smart hydrogels are a great choice for drugs-included prolonged-release systems because of how simple they are to prepare [10]. One of the modern and important applications in the field of drug delivery is the use of hydrogel films (Magnetic Field Responsive). Iron oxide nanoparticles are crucial in many areas of chemical, physical, and materials research. Iron magnetic nanoparticles have attracted the most attention among nanoparticles because of their abundance, quick reaction, superparamagnetic, high competency, non-toxic, and increased stability [11]. Initially injecting MNPs into the circulation, directing them to the damaged area via an external magnetic field, and then concentrating them close to a magnet applied to the body's surface are the steps in the Magnetic Drug-Delivery System procedure. The low blood flow is crucial to this process since it distributes MNPs through the body before concentrating them with the aid of a magnetic field [12]. The primary characteristics of Polyvinyl alcohol (PVA), including its water solubility, are related to the degree to which acetate

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groups are replaced by hydroxyl groups (degree of hydrolysis) and the degree to which the polymer is formed. PVA is one of only a few high molecular-weight synthetic polymers that can be dissolved in water [13].

The size, shape, and structure of magnetic nanoparticles have a considerable impact on their characteristics. One of the hardest problems in contemporary material research is controlling the size and structure of nanoparticles [14]. The objectives of this research are to develop the preparation of hydrogel films with Fe_3O_4 nanoparticles (Magnetic field responsive).

2- Experimental work

2.1. Chemical materials

Table 1 shows all the chemical materials which were used in this research. The substances were employed without additional purification.

Table 1. List of Chemical Materials

Chemical	Molecular formula	Molecular weight(g/mol)	Purity (%)	Brand
polyvinyl alcohol	$(-C_2H_4O)_n$	14000	≥ 98	Aldrich
polyethylene glycol	$(C_2H_4OH)_nOH$	8000	99	Aldrich
glycerin	$C_3H_8O_3$	92.09382	99	Aldrich
starch	$(C_{12}H_{22}O_{11})_n$	342.30	99	Aldrich
Iron(III) chloride hexahydrate	$FeCl_3.6H_2O$	270.296	96	Merck
Iron(II) chloride dihydrate	$FeCl_2.2H_2O$	162.78	99.9	Merck
Sodium hydroxide	NaOH	40.0	99	Merck
Hydrochloric acid	HCl	36.458	99	BDH
Cetyltrimethylammonium bromide	CTAB	364.45	99	Merck

2.2. Preparation of Fe_3O_4 nanoparticles

The co-precipitation method was used to create magnetic nanoparticles. 1.7 mL of 12 M HCl was used to dissolve 10.4 g of FeCl3.6H2O and 3.27 g of FeCl2.2H2O. Distilled water was then added to bring the volume of the aqueous solution to 50 mL. The stock solution was continuously stirred in a beaker using a magnetic stirrer. A base solution was prepared by combining 4 g of NaOH (1M) with 100 mL of distilled water. Distilled water was then added to bring the volume of the 1.5 M base solution to 500 mL. Next, a 500 mL solution of 1.5 M NaOH was heated to 80°C in a beaker, and the temperature of the solution was maintained there for 30 min while the stock solution was progressively added and stirred. The black precipitates of magnetic nanoparticles were eventually retrieved by a strong magnetic field and suspended in distilled water after being repeatedly cleaned with 500 mL of distilled water. The magnetic suspension was held steady for at least a month.

2.3. Synthesis of hydrogels' films with Fe_3O_4 nanoparticles

Due to its ease of use and simplicity, blending is a frequently used technique to prepare magnetic hydrogel. First, magnetic nanoparticles were synthesized. A starch solution was prepared by dissolving 1.5 g of starch in 10 mL of distilled water with continuous stirring at 50 °C for 30 minutes. On the other hand, the aqueous PVA/PEG solution was prepared by dissolving 2.5 g of PVA in 30 mL of distilled water at 80 °C with a magnetic stirrer for 30 minutes, then 2 g of PEG was mixed with the PVA solution with 1 g of glycerin and stirred for 30 minutes. The resultant solution was heated in the microwave for 45 s until it became clear and transparent. Then the two solutions were mixed for 30 minutes at room temperature until a homogeneous solution was obtained. To make the CTAB solution, 0.5 g of CTAB was mixed with 250 mL of distilled water. Then, at a ratio of 1/1, 1/2, 1/3 (V/V), the produced MNPs and 0.2% w/v CTAB with a proportion of 1/1 (V/V) were added immediately and poured into the polymer blend solution that had already dissolved. The MNPs were sonicated to ensure they diffused uniformly throughout the polymer solution. The homogenized hydrogel was slowly stirred and poured onto six glass slides, which were left to dry at room temperature for 24 hours. The hydrogel films underwent an annealing process, one of the techniques for physical crosslinking, during the final stage of preparation which involved placing them in an electric oven for 20 min at a temperature of 90°C. After that, the films were allowed to cool at ambient temperatures. The efficiency of the produced films will be examined using several tests.

2.4. Characterization of hydrogel films (magnetic field responsive)

A. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra are frequently used to identify the kind of chemical covalent bonds resulting from physical cross-linking present in the samples to examine the functionalization of hydrogel films (Magnetic field responsive) of Fe_3O_4 nanoparticles of the polymer coated. The functional groups of hydrogel films were examined using ALPHA II FTIR - ATR from BRUKER with a wave number range (400-4000 cm^{-1}) at the facilities of the Ministry of Science and Technology.

B. X-ray diffraction (XRD)

All synthetic hydrogel films that responded to the magnetic field were examined for crystallinity using XRD. Samples' X-ray diffraction patterns were obtained at 40 kV and 40 mA utilizing the Cu-Ka radiations (λ = 1.54178 Å) with a Bruker AXS D8 Automatic powder diffractometer. The data were recorded for the 2 theta

range from 20 to 80 degrees at a scanning speed of 5 degrees per minute.

C. Scanning electron microscopy (SEM)

SEM is a kind of microscope that generates high-resolution pictures by scanning a sample's surface with a concentrated stream of electrons. These images show the morphology and structural characteristics of the magnetic field-responsive hydrogel. High-resolution FESEM measurements were made utilizing the FESEM JSM-671F at 1 nm (15 kV) and 2.2 nm (1 kV), with an objective lens aperture size of uncharged and a maximum probe current of 2 nA. Before analysis, the samples were sputter-coated with platinum.

D. Vibrating sample magnetometer (VSM)

Utilizing a vibrating sample magnetometer (VSM) (Lake Shore 7303-9309 VSM), the magnetic characteristics of the solids under investigation were assessed at room temperature. Faraday's law of induction provides the foundation for the operation of a vibrating sample magnetometer. The electric field is measured to find the coil's induced magnetic field (EMF), which is caused by a shift in flux coupling to determine how a magnetic field changes.

3- Results and discussions

3.1. Fourier transform infrared spectroscopy (FTIR)

The FT-IR spectroscopy was used to study chemical bonds (functional group) among molecules as illustrated in Fig. 1. Fig. 2 corresponds with the obtained outcomes and shows the spectra of uncoated IONPs, which include the absorption peak at 3403 cm^{-1} that is related to O-H stretching (v) vibrations. The peak at 1630 cm^{-1} is related to H-O-H bending (δ) vibrations because the water was adsorbed on the surface of uncoated IONPs [15]. The spectra of IONPs coated with hydrogel films in the ratios of 1:1, 1:2, and 1:3 reveal absorption peaks at 3375 cm^{-1} which is attributed to the stretching vibration of the O-H band (alcohol).

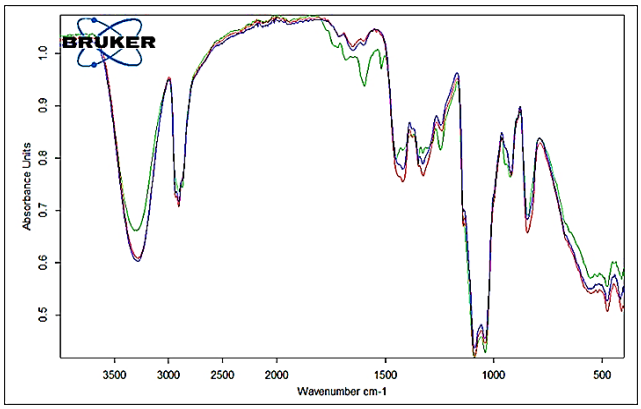

Fig. 1. FTIR for Hydrogels' Films (Magnetic Field Responsive) in the Ratios of 1:1, 1:2 and 1:3

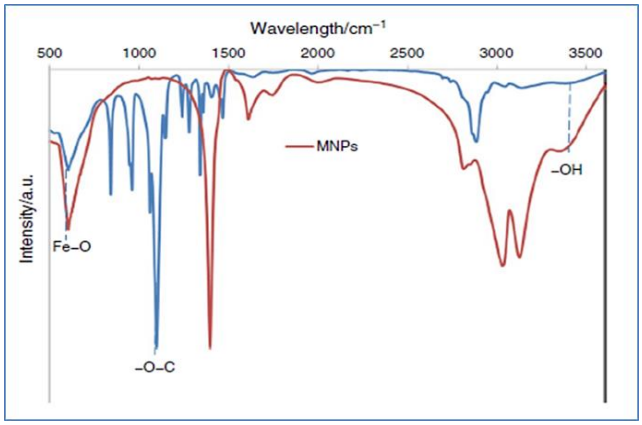

Fig. 2. FTIR for Iron Oxide Nanoparticles IONPs

The extra peak at 2853 cm^{-1} is caused by the symmetric C-H stretching vibration, while the band at 2926 cm^{-1} is due to the asymmetric CH2 stretching vibration. The H-O-H bending (δ) vibrations caused by adsorbed water are seen by the absorption peak at 1630 cm^{-1} [16].

3.2. X-ray diffraction (XRD)

The diffraction patterns of synthesized hydrogel film samples were scanned, and their accuracy was verified by contrasting their diffraction patterns with those of a reference sample. The XRD pattern of the generated hydrogel sheets is shown in Fig. 3, whereas the pattern of the IONPs is shown in Fig. 4. Comparison shows that the result of the preparation method agreed with the crystal structure of IONPs, indicating that natively synthesized and high-quality magnetic hydrogel films are produced by the preparation procedure.

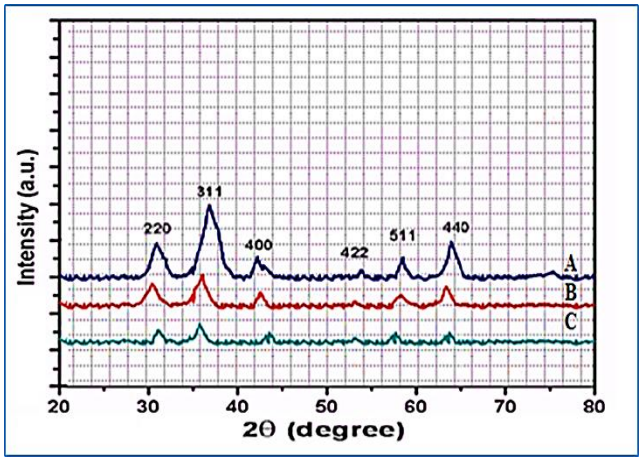

Fig. 3. XRD Pattern for Hydrogels' Films at a Ratio of 1/1, 1/2 And 1/3 (V/V) is (A, B and C) Respectively

The peaks at the lattice planes (220), (311), (400), (511), and (440) match the typical pattern [17] for the predominant magnetite nanoparticles phase (Fe_3O_4). Because the crystallites in all the samples are Nano-scale, the XRD pattern indicates that they were all polycrystalline and had wide diffraction peaks.

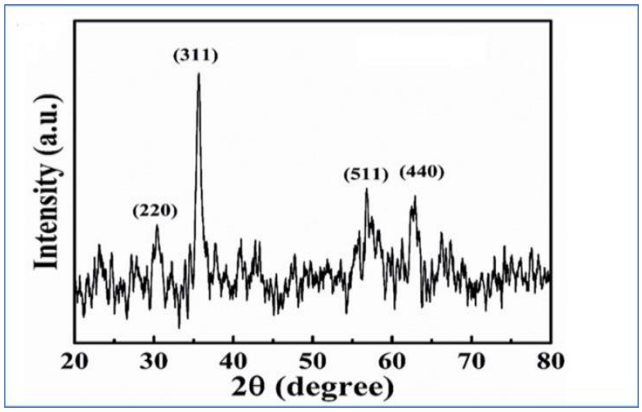

Fig. 4. XRD Pattern of the IONPs

3.3. Scanning electron microscopy (SEM)

The SEM technique to characterize the synthesized Fe3O4 MNPs with and without coating. Fig. 5 displays the samples' SEM images. For the aggregation of many nanoparticles, magnetic nanoparticles with and without hydrogel-coating. The equally dispersed size of MNPs was shown by the very porous appearance. The SEM images of hydrogel films exhibited a consistent particle size with practically spherical particles that have rounded edges and agreed with the literature [18].

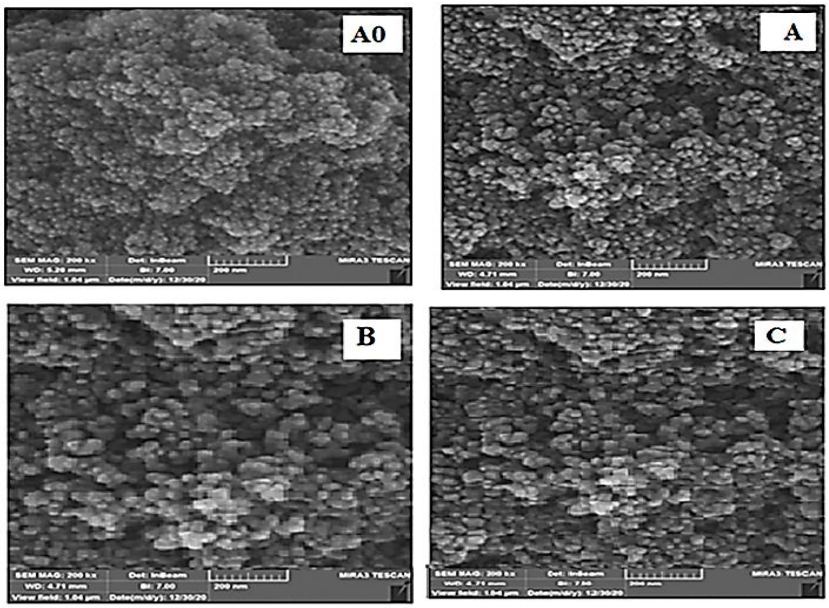

Fig. 5. SEM Image of Fe3O4 Nanoparticles (AO) and Hydrogels' Films (Magnetic Field Responsive) at a Ratio of (1/1, 1/2 And 1/3) (V/V) is (A, B, and C) Respectively

3.4. Vibrating sample magnetometer (VSM)

The magnetic analysis of all samples demonstrates that the IONPs displayed superparamagnetic behavior, as shown by the absence of remanence and coercivity on hysteresis curves. The remarkable magnetic responsiveness of these particles was due to their predicted size-dependent magnetic characteristics. When the particles are tiny enough, a new feature known as "single super spin" develops from the presence of a single magnetic domain in the IONPs complex. The saturation magnetization (Ms) of coated and uncoated IONPs was observed at an applied field of 10000 Oe. Fig. 6 illustrates the rapid decrease in Ms with increasing concentrations of the hydrogels of the polymer coating. Hydrogels coated IONPs, Ms was found to be significantly reduced to values of 65.02, 55.19, and 42.17 (emu/g), for the suspension MNPs solution to the polymer solution at a ratio of 1/1, 1/2, and 1/3 (V/V) respectively which is caused by radical (-OH) group in PVA and the diluting effect of adsorbed water [19]. When IONPs are steered magnetically, the observed magnetic properties of these particles are enough for delivering the medication to the target spot.

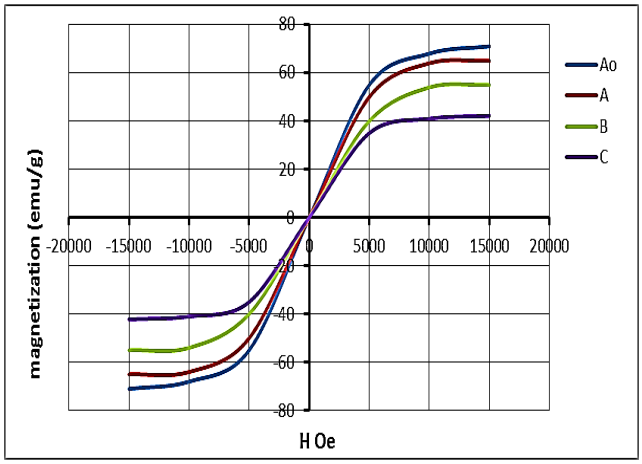

Fig. 6. Magnetic Profile of Uncoated IONPS (AO) and Hydrogels' Films (Magnetic Field Responsive) at A Ratio of (1/1, 1/2 and 1/3) (V/V) is (A, B, and C) Respectively

4- Conclusions

According to the findings, the SEM pictures of the hydrogel films which are sensitive to magnetic fields show a consistent particle size with almost spherical particles and rounded edges. The hydrogels' magnetic field-responsive functional groups were found by the FTIR, indicating a strong interfacial integration of the component materials and their functional groups. The conclusion drawn from the preparation process is that magnetic hydrogel films are synthesized with high quality; the crystallites in all the samples were nanoscale, and the XRD analysis shows that they were all polycrystalline and had wide diffraction peaks. The preparation of hydrogel films (Magnetic Field Responsive) was consistent with the crystal structure of IONPs. As per the findings, the magnetic studies of all samples demonstrated that IONPs displayed superparamagnetic behavior. Additionally, the magnetic characteristics of hydrogel films, which were responsive to magnetic fields, were enough for the delivery of medication to the intended site.

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تحضير وتوصيف لهلاميات المائية الذكية (المستجيبة للمجال المغناطيسي)

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الخلاصة

تمت دراسة الخصائص الهيكلية والفيزيائية والكيميائية والمورفولوجيا والمغناطيسية للجسيمات النانوية المغناطيسية، بالإضافة إلى تأثير تركيز طلاء أفلام الهيدروجيل. تم تحضير جسيمات الحديد النانوية باستخدام عملية الترسيب المشترك، ثم استخدامها لتصنيع أفلام هيدروجيل مستجيبة للمجال المغناطيسي. تم فحص خصائص أفلام الهيدروجيل المستجيبة للمجال المغناطيسي باستخدام تحليل فورييه الطيفي للأشعة تحت الحمراء (FTIR)،وحيود الأشعة السينية (XRD)، والمجهر الإلكتروني الماسح (SEM)، ومقياس مغناطيسية عينة الاهتزاز (VSM). تشير النتائج إلى أن جميع العينات أظهرت تكاملاً جيداً بين المواد المكونة ومجموعاتها الوظيفية. كانت عينات فيلم الهيدروجيل متعددة البلورات، ولها قمم حيود واسعة، وأظهرت حجم جسيم ثابت مع جزيئات كروية تقريبًا ذات حواف مستديرة. تم إنشاء صورة SEM للجسيمات النانوية المغناطيسية مع وبدون طلاء لتراكم العديد من الجسيمات النانوية بمتوسط قطر ١٧ نانومتر. بالإضافة إلى ذلك، كانت الخصائص المغناطيسية لأفلام الهيدروجيل الحساسة للمجال المغناطيسي واضحة وكافية لتوصيل الدواء إلى الموقع المطلوب.

الكلمات الدالة: الجسيمات النانوية المغناطيسية، الهيدروجيل، بولي فينيل الكحول، الهلاميات المائية الذكية.