

Synthesis and Characterization of Magnetite Nanoparticles and the Effect of $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$ complex on its magnetic properties

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Abstract

A novel inorganic complex (shell)@metal oxide (core) was demonstrated by simple and highly efficient synthesis of Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$) coated by $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$ complex through one-pot reaction of prepared Fe_3O_4 nanoparticles and $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$. The Fe_3O_4 NPs structure was characterized by infrared spectroscopy (IR), scanning electron microscope (SEM) and energy dispersive X-rays (EDX) while the resulted $[\text{Fe}(\text{sac})_4(\text{H}_2\text{O})_2]@\text{Fe}_3\text{O}_4\text{NPs}$ was characterized using IR spectroscopy and XRD. The magnetic feature, which is one of physical properties of $\text{Fe}_3\text{O}_4\text{NPs}$ and the newly synthesized core-shell $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}$ were examined in order to study how the Fe in its complex effects on the magnetic properties of magnetite nanoparticles.

Keywords: Inorganic complex@metal oxide, Fe_3O_4 NPs, $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$ complex, $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4$ NPs, Magnetic properties.

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تحضير وتشخيص دقائق المغناتيت النانوية و تأثير المعقد على خصائصها

المغناطيسية $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$

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المخلص

تم عرض اول معقد لا عضوي (قشر) على اوكسيد فلز (لب) بواسطة طريقة تحضير بسيطة وكفاءة باستعمال دقائق Fe_3O_4 النانوية المغطاة بالمعقد $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$ اذ تم التفاعل ذو الدفعة الواحدة بين دقائق Fe_3O_4 النانوية و $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$. شخضت دقائق Fe_3O_4 النانوية بواسطة مطيافية الاشعة تحت الحمراء ومجهر المسح الالكتروني وكذلك مطيافية تشتت الطاقة بالأشعة السينية بينما المركب الناتج دقائق $[\text{Fe}(\text{sac})_4(\text{H}_2\text{O})_2]@\text{Fe}_3\text{O}_4$ النانوية شخضت باستعمال مطيافية الاشعة تحت الحمراء وحيود الاشعة السينية. اختبرت الخصائص المغناطيسية والتي هي احدى الخواص الفيزيائية لكل من دقائق Fe_3O_4 و $[\text{Fe}(\text{sac})_4(\text{H}_2\text{O})_2]@\text{Fe}_3\text{O}_4$ النانوية من اجل دراسة كيف يؤثر الحديد في معقداته على الخواص المغناطيسية لدقائق المغناتيت النانوية.

الكلمات الدالة: معقد لا عضوي @اوكسيد فلز، دقائق Fe_3O_4 النانوية، المعقد $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$ ، الخواص

المغناطيسية، $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4$ NPs.

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1. Introduction:

The nano structure of Fe_3O_4 with diameters (x,y,z) ranging from 1 and 100 nm and find an important nano material because it plays a main role in various fields as it was used as an adsorbent in micro solid phase extraction of metals or dyes [1, 2], data storage [3], biosensing [4] and drug delivery [5]. Magnetite nanoparticles (Fe_3O_4) can generally be separated from its reaction vessel by an external magnet such as neodymium magnet [6]. In recent times, the production of core-shell nanocomposites which may possibly be used as a catalysts for catalyzing organic reactions has been not far described [7]. Core-shell nanoparticles having a paramagnetic central material (core) such as iron or iron oxide are air and thermally stable and can be simply separated by an external magnet to evade old-style filtration methods [8]. Meanwhile, saccharin as a fake sweetener, the coordination chemistry of this heterocyclic amide have been extensively studied over the past 38 years [9]. There has been an important attention in the chemistry of metal ions bounded saccharine ligand over the past two decades ever since its demonstrations a varied kind of metal ion bonding fashions, and it is possibly useful as co-ligand in bioactivity studies. This ligand showed a variety of coordination modes to metals and was able to bind in a monodentate mode through either nitrogen atom via covalent bond, negatively charged or through the oxygen atom of carbonyl group. Furthermore, saccharine ligand has the ability to coordinate in a bidentate or even polydentate fashions with the contribution of the N- and O- donor atoms [9]. Saccharinate behaves as a monodentate ligand coordinates to the first row divalent metal ions through its deprotonated nitrogen atom [9-15]. In the present work, we report the preparation and characterization of inorganic core-shell nanoparticle containing $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$ as a shell and Fe_3O_4 nanoparticles as a core. Additionally, we report the magnetism properties of as-prepared inorganic core-shell nanoparticle.

2. Materials and Methods:

The chemicals used in this work were obtained from Sigma Aldrich and Merck and used without further purification. FT-IR spectra were recorded in the range $400\text{--}4000\text{ cm}^{-1}$ with a Shimadzu 8400S spectrometer. The nanostructure of $\text{Fe}_3\text{O}_4\text{NPs}$ was characterized using a Philips Xpert X-ray powder diffraction diffractometer ($\text{Cu K}\alpha$, radiation, $\lambda = 1.54056\text{ \AA}$), at a scanning speed of $2^\circ/\text{min}$ with 2θ ranging 10° to 80° . A thermal method using ultrasonic equipment with probe (6mm) model UP200ht was used for homogenizing of the mixture. The

morphology of Fe_3O_4 was obtained using Oxford instruments (FESEM) Tech, scanning electron microscope. Magnetic properties of the prepared nanoparticles were recorded with a vibrating-sample magnetometer model VSM, PPMS-9T.

2.1 Preparation of Fe_3O_4 Nanoparticles:

Fe_3O_4 NPs were prepared by chemical co-precipitation. A solution of ferrous chloride tetra hydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) (2.58 g, 12.97 mmol), was added to an aqueous solution of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (7.20 g, 26.63 mmol). The resulting solution was stirred for 4 hours at 80 °C, under nitrogen. Thereafter, 25% ammonium hydroxide solution (15 ml) was inserted drop wise into the resulted mixture, under vigorous stirring. The mixture was stirred at room temperature for further 3 hours. Subsequently, the resulted mixture left at room temperature to cool and the magnetite nanoparticles were decanted by magnetic decantation using neodymium magnet and then washed several times with distilled water until the pH of decanted solution equal 7.4. Fe_3O_4 NPs was dried under vacuum at 75 °C. The resulting black powder of Fe_3O_4 NPs (2 g, 67%) was dispersed in dry ethanol under ultrasonic irradiation for 1 hour to use in the next step [16].

2.2 Preparation of $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$

A solution of ferrous chloride tetra hydrate (0.2550g, 1.1317mmol) in distilled water (20 ml), was added to a solution of sodium saccharinate (0.4643g, 2.2631mmol) in distilled water (15ml), a brown precipitate was immediately formed. Moreover, the mixture was refluxed for 1 hour and the resulted powder was filtered, washed with hot water and dried at 60 °C for 12 hours. Brown solid. Yield: 0.5024 g (74%). Molar conductivity in DMSO ($8.3 \Omega^{-1} \text{cm}^{-1} \text{mol}^{-1}$). IR (KBr, cm^{-1}): 3570vs $\nu(\text{H}_2\text{O})$, 3099s $\nu(\text{C-H})$, 2953s $\nu(\text{C-H})$, 1622vs $\nu(\text{C=O})$, 1577vs $\nu(\text{C=C})$, 1464m $\nu(\text{C=N})$, 1350vs, 1155vs $\nu(\text{SO}_2)$, 474m $\nu(\text{M-N})$ [15].

2.3 Preparation of $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@ \text{Fe}_3\text{O}_4$ NPs

$[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@ \text{Fe}_3\text{O}_4$ NPs were synthesized as follows. A mixture of an ethanolic solution of $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ (0.5103g, 1.000 mmol) in ethanol (50 ml) and Fe_3O_4 NPs (0.5101 g, 2.203mmol) in ethanol (50 ml) was refluxed for 30 hours. After cooling, the brown precipitate was isolated magnetically, washed thoroughly with hot ethanol, and dried under vacuum.

3. Results and Discussion:

3.1 Preparation and Characterization of the Nanocatalyst

The core-shell $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}$ was synthesized according to the procedure shown in Scheme 1. In the beginning, Fe_3O_4 NPs were synthesized through co-precipitation method by dissolving $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and refluxing in the presence of ammonium hydroxide, thereafter, the addition of $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]$ complex in ethanol afforded the $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}$.

FTIR spectrum of $\text{Fe}_3\text{O}_4\text{NPs}$ Fig. 1A, displays intense band at 588 cm^{-1} referring to the $\nu(\text{Fe}_{\text{tetra}}-\text{O})$ of iron-oxygen at tetrahedral site. The two bands at 3433 and 1637 cm^{-1} correspond to the stretching and bending modes of hydroxyl group of water molecules, respectively, that adsorbed due to high surface area of the prepared $\text{Fe}_3\text{O}_4\text{NPs}$ [18,19].

The particle morphology of the prepared $\text{Fe}_3\text{O}_4\text{NPs}$ was categorized by SEM Fig. 2. The (SEM) result of the prepared $\text{Fe}_3\text{O}_4\text{NPs}$ shows that the particle size were less than 40 nm with spheres-shaped in form. EDX of magnetite nanoparticle Fig. 3 shows oxygen and iron signals at 0.5 and $6.3, 0.6\text{ keV}$ of Fe_3O_4 nano-particles. It also shows that the elemental ratio of Fe:O is $68:26\%$ which is in agreement with the calculated ratio ($72:27\%$).

FT-IR spectrum of $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ shows a characteristic bands at $3570, 1622$ and 1464 cm^{-1} which corresponds to the stretching vibrations of (O-H, H_2O), C=O and C=N groups, while the two bands at 1350 and 1155 cm^{-1} attributes to the asymmetrical and symmetrical stretching vibration of SO_2 group Fig. 1B. In the core-shell $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}$ spectrum, the absorptions of $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]$ are observed, along with a virtual broad band at 590 cm^{-1} assigned to the stretching vibration of the Fe-O group, indicating that the magnetic $\text{Fe}_3\text{O}_4\text{NPs}$ are coated by $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]$ Fig. 1C. To confirm the presence of Fe_3O_4 as a core, the structures of the newly prepared magnetic nanoparticles was characterized by (XRD), as shown in Fig. 4. There are six diffraction peaks at 2θ about $30.11^\circ, 35.50^\circ, 43.21^\circ, 53.03^\circ, 57.13^\circ,$ and 63.25° corresponding to the (2 3 0), (3 2 1), (4 0 0), (4 2 2), (5 1 1), and (4 5 0) planes [20] in the core-shell NPs, which is the standard pattern for crystalline magnetite with cubic structure. The diffraction pattern also shows diffraction peaks at $25.01^\circ, 39.4^\circ, 47.5^\circ$ and 69.33° which attributed to the shell.

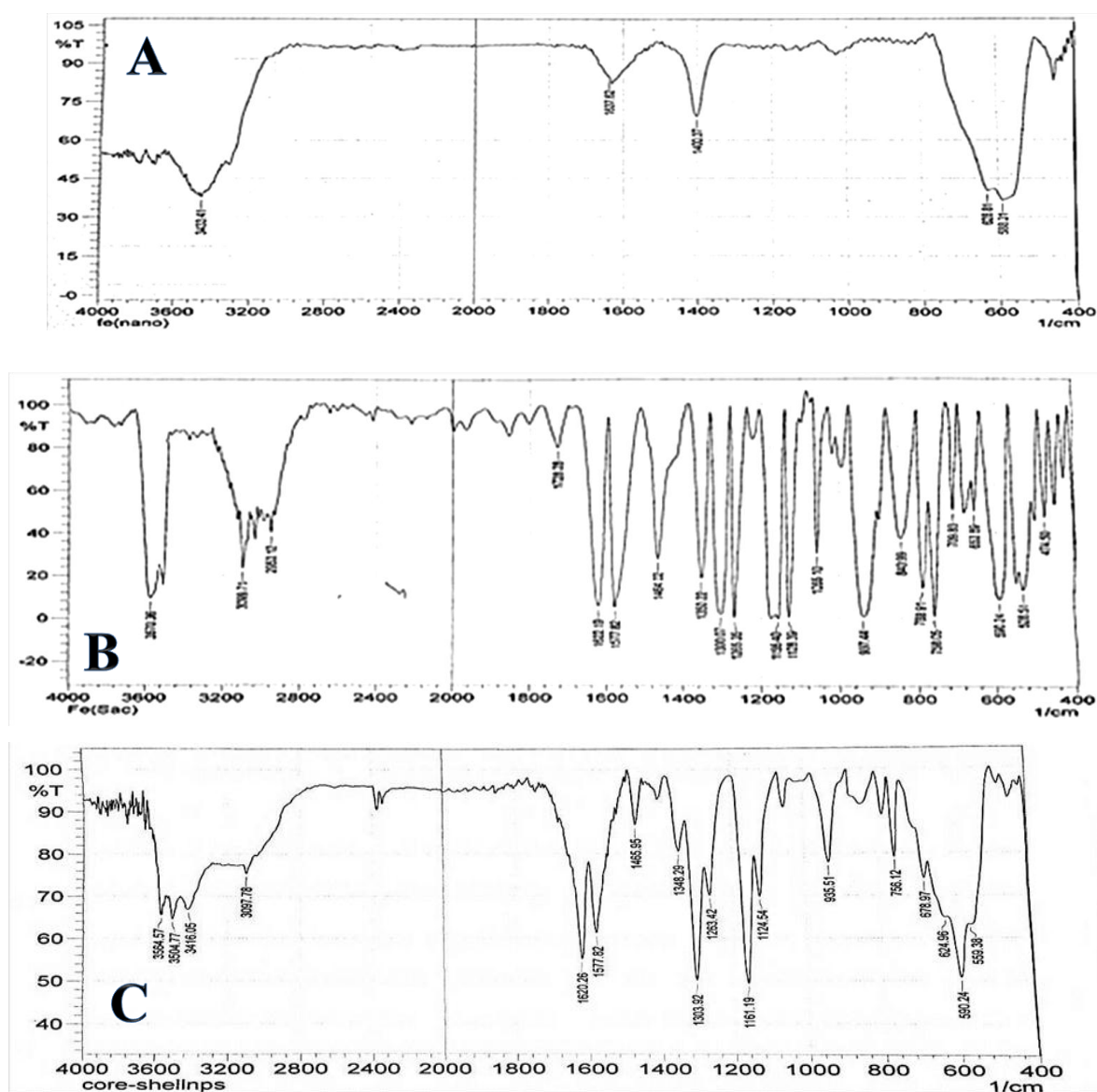
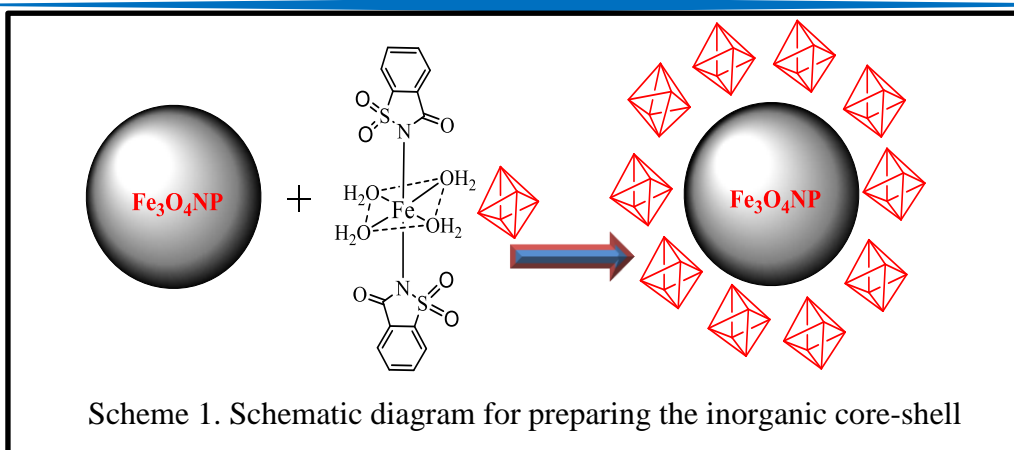


Fig. 1: IR spectra of (A): $\text{Fe}_3\text{O}_4\text{NPs}$, (B): $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ and (C): $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@ \text{Fe}_3\text{O}_4\text{NPs}$.

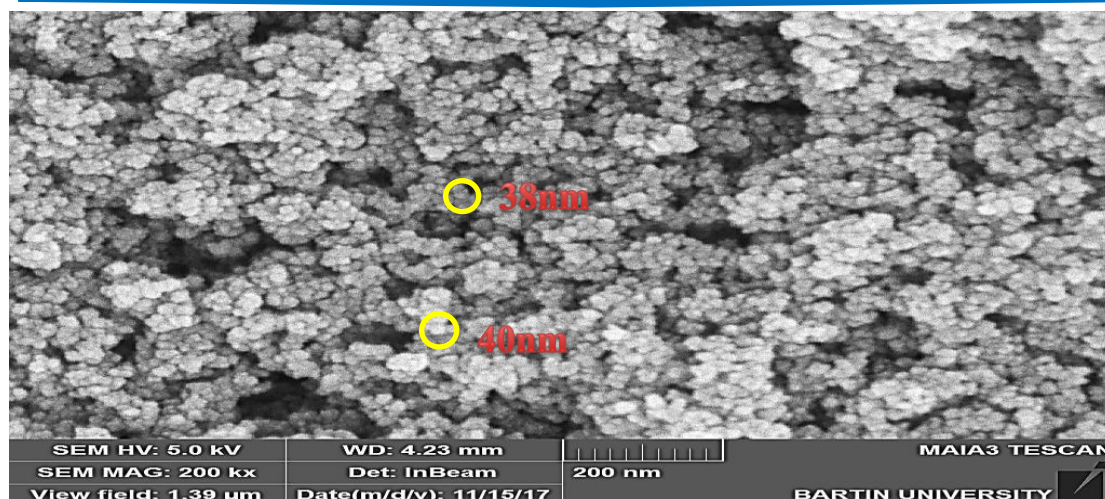


Fig. 2: SEM of Fe₃O₄NPs.

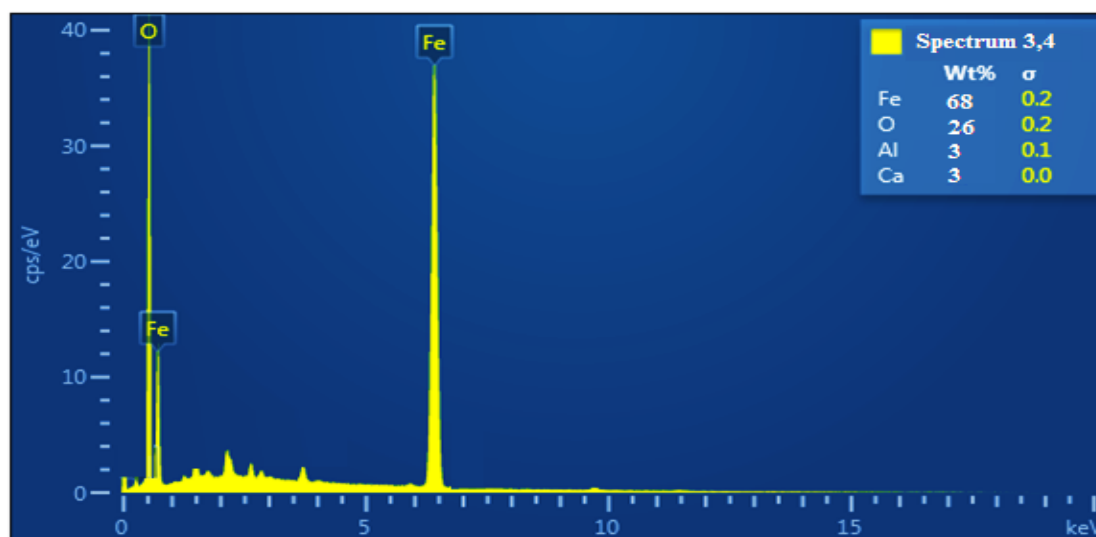


Fig. 3: EDX of Fe₃O₄NPs.

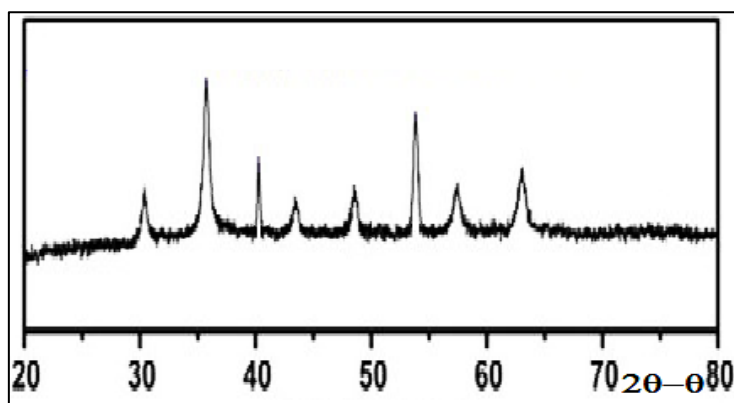


Fig. 4: XRD pattern of [Fe(sac)₂(H₂O)₄]@Fe₃O₄NPs.

3.2 Magnetic Properties of the Nanoparticles:

The magnetometer can be used as a field calculating device by using a paramagnetic material. A vibrating sample magnetometer (VSM) depends on Faraday's law of induction, which informs that a changing magnetic field will produce an electric field. This electric field can be measured and provide us information about the changing magnetic field. The magnetization of Fe_3O_4 and $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}$ was measured and the results are shown in Fig. 5A-D. The results show an increase with an intensification in the magnetic fields and the saturated magnetization were 60.00 [21] and 39.96 emu g^{-1} for Fe_3O_4 and $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}$, respectively. The comparatively high VSM value indicates good superparamagnetism of $\text{Fe}_3\text{O}_4\text{NPs}$ and $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}$ and the results show that the addition of ferrous-saccharine complex reduced the magnetism properties of the prepared Fe_3O_4 NPs.

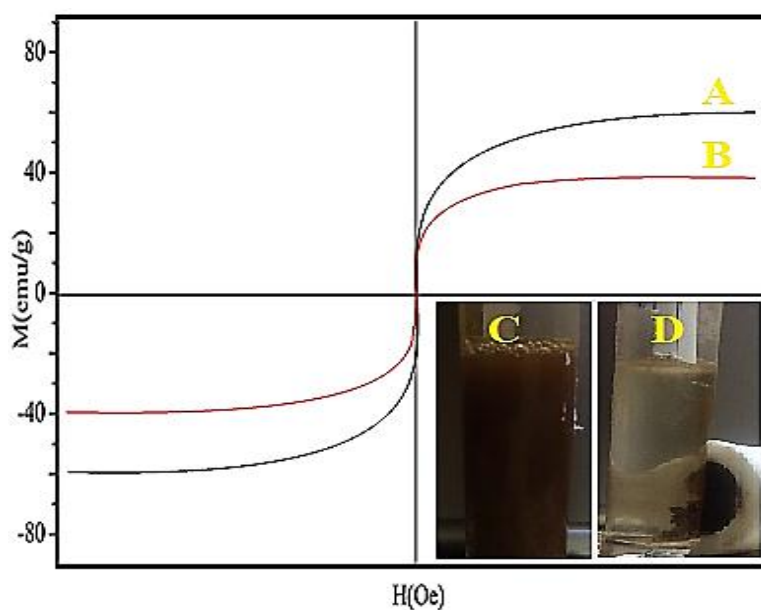


Fig. 5: VSM of (a) Fe_3O_4 (b) $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}$ (c) well-dispersion of the $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}$ in water (d) isolation of the $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}$ by neodymium magnet.

4. Conclusions:

In this study, the first inorganic core-shell nanoparticle that containing a complex of Fe(II) ion with saccharine ligand as a shell and Fe_3O_4 nanoparticles as a core has been successfully prepared and characterized. The yields of each step are high, and isolation of product from the

reaction mixture is so easy using out magnetic field. This novel nano core-shell has been used to study the magnetism properties and to make a comparison with the core material as a first attempt to determine the effect of complexes in the magnetic properties of chose iron oxide. The results show that the magnetic properties of Fe₃O₄NPs have been reduced after addition of a complex but the material still effected by magnetic field.

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