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Review Article

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A review of industrial applications of iron oxide magnetic nanoparticles synthesized by different methods

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ABSTRACT

Today, the use of nanotechnology in various industries such as pharmaceutical, chemical, electronics, aerospace, environment, etc. has made great progress in facilitating the work process of these industries. One of the widely used materials in these industries is iron oxide, which is synthesized by various methods such as chemical vapor deposition and sol-gel, and is used on a nano scale. In this article at first, the introduction of nano iron oxide as a super paramagnetic material with unique mechanical and chemical properties has been discussed. After that, the synthesis methods of this substance are studied and investigated in different environmental conditions. In the next stage, the use of this material in the military and aerospace industries to make electromagnetic wave absorbing coatings, in the pharmaceutical industry to optimize the effect of anti-cancer drugs such as doxorubicin, and finally, the effect of this material as an effective catalyst in agricultural industries to remove wastes will be reviewed

Keywords: Iron Oxide, Synthesis Methods, Absorbing Coating, pharmaceutical, remove wastes

Introduction

Materials in nano dimensions have a wide range of chemical and physical properties, since the fraction of atoms on the surface and broken bonds is very high in the nano scale, it makes most materials able to have unique magnetic properties. In addition, it has antibacterial properties that make a significant impact in pharmaceutical treatments and environmental industries. In the last two decades, nanotechnology has attracted great interest in several areas of research for the development of nano scale materials which can be obtained through different techniques, such as physical or chemical methods. Due to their size (diameters ranging from 1 to 100 nm) nanoparticles present specific and controllable properties that are different from those they present on the macroscopic scale thus enabling unique Applications [1]. optical and magnetic properties for numerous applications such as production of inorganic pigments, magnetic storage media, development of gas sensors as well as electronic and optical devices, information storage, color imaging, magneto caloric refrigeration, bioprocessing, ferro fluid technology and wastewater treatment adsorbents Nano iron oxide (Fe_3O_4) is a group of synthesized metal oxides that can be used in many industries [2] and [3]. Iron oxide is a mineral compound which occurs abundantly in nature. It presents more than one crystal structure and also different structural and magnetic properties [4].

Synthesis by sol-gel method

Sol-gel synthesis methods usually refer to hydrolysis and condensation of metal alkoxides or alkoxide precursors, resulting in dispersions of oxide particles in “sol”, which is then dried or gelled by removing the solvent or by chemical reaction[5]. Due to their large surface-to-volume ratio, magnetic iron oxide nanoparticles possess

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high surface energies and therefore tend to agglomerate and form clusters thus resulting in increased particle size. Moreover, the naked iron oxide particles have high chemical activity and are easily oxidized in air, generally leading to loss of magnetism and dispersion. A strategy to prevent agglomeration is to promote the modification of surface nanoparticles by coating them with organic molecules, polymers, biomolecules or inorganic molecules,such as silica. Various polymers such as poly (vinyl alcohol), poly (lactide-co-glycolide), polyethyleneimine, polymethylmethacrylate and poly (ethylene glycol) as well as natural polymeric systems or proteins including gelatin, chitosan and dextrosan have been applied. Among inorganic coatings, silica, carbon and precious metals such as gold, silver and platinum are commonly used The solvent used in the sol-gel method is generally water and the precursors can be hydrolyzed by either an acid or a base. Reaction rates, temperature, nature of precursors and pH are parameters that affect the structures and size of iron oxide), for example, nanomaghemite, γ-Fe2O3 with particle size from 6 to 15 nm after heat treatment at 673 K [6] and [7]. Figure 1 shows a summary of the synthesis process of nano iron oxide by sol-gel method.

Synthesis by CVD method

During the research conducted by Sungu et al The Chemical Vapor Deposition (CVD) of iron and iron oxide films using H 2Fe[P(OCH 3) 3] 4 as precursors was investigated. CVD experiments were carried out in a cold-wall glass reactor with a bubbler-type precursor vessel maintained at 70-100 °C during the deposition process. The precursor was injected into the reactor with argon as a carrier gas with flow rate of 200-300 sccm. A liquid nitrogen trap was connected to the reactor to collect any reaction byproducts. Oxygen gas was leaked into the reactor separately when needed. No peaks were observed by XRD for the films deposited from H 2Fe[P(OCH$_3$) $_3$] 4 in the absence of any reactive gas such as H_2 or O_2 during the deposition process indicating that the films were amorphous. It was observed that both films were crystalline and exhibited no detectable Fe_3O_4 films [8]. Figure 2 shows the results of X-ray diffraction for nano iron oxide synthesized by the CVD method.
Table 1 shows the analysis sheet of nano iron oxide synthesized by CVD method.

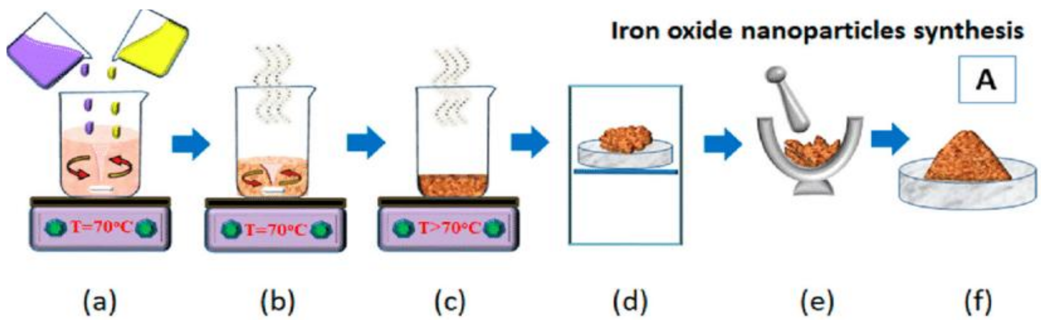

Fig. 1. Synthesis process of nano iron oxide

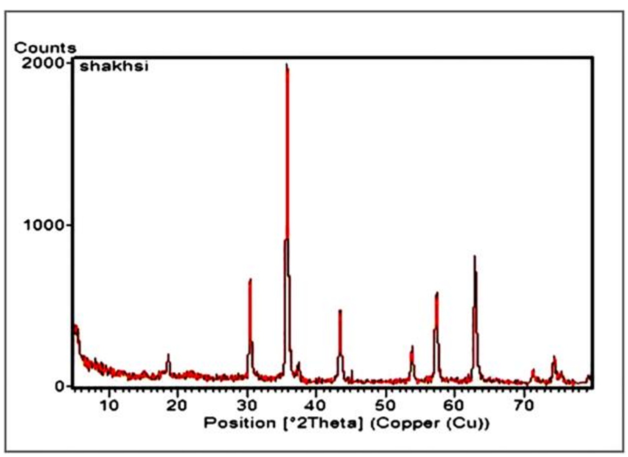

Fig. 2. XRD diffraction test for nano iron oxide

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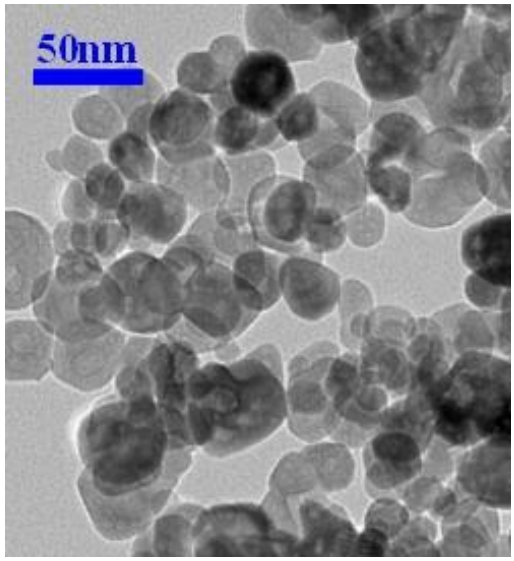

Fig. 3. SEM image of Fe_3O_4

Table 1. Physical and chemical characteristics of nano iron oxide

True Density	Bulk Density	Morphology	Color	SSA	APS	Purity
4.8-5.1g/cm^3	0.84 g/cm^3	Spherical	Dark brown	40-60m^2/g	20-30nm	+98%

Electromagnetic Absorbent Properties

The use of metal oxides on a nano scale, such as nano iron oxide, as the magnetic pole of an absorbent nano composite, can have a significant effect on increasing the absorption efficiency of radar evasive coatings in military industries. Nano powders as magnetic and dielectric poles for optimal performance in absorbent materials must be completely dispersed in the matrix so that complete distribution can be observed throughout the nanocomposite points. Figure 4 shows the proper dispersion process of nanomaterials in the epoxy matrix [9]. Nanotubes, zinc oxide and nano iron oxide in the resin matrix to produce an optimal nano composite in order to absorb electromagnetic waves, which has the ability to reduce radar reflection equal to -34.2 dB. It has a frequency range of 11.8 GHz. In this research, they were able to make this nano composite by using two magnetic poles that have unique properties. Figure 5 shows the reduction of radar reflectivity for 6 nano composite samples [10].

Absorbtion Equations

According to the relationships between the magnetic and electric fields from Maxwell's theory, the wave impedance is extracted from equation (1):

$$\frac{E}{H} = \frac{\omega\mu}{K} = \frac{\sqrt{\mu}}{\varepsilon} = z \qquad (1)$$

where K is the direction of wave propagation vector. In the far field, the wave is expressed as a plane wave, because in the far field, electromagnetic waves essentially lose their curvature and the surface that includes E and H becomes flat. When a wave hits the surface of an object, it either reflects from the surface or penetrates into it. Its reflection depends on the material of the surface and the frequency of wave propagation. The reflection coefficient (R) for normal radiation with normalized impedance is calculated from the following equation (2):

$$RL = \frac{-1+\frac{z}{z_0}}{1+\frac{z}{z_0}} \qquad (2)$$

Electromagnetic absorption and transmission can be related to the scattering matrix (reflection, absorption and transmission) in this matrix, where S_{11} represents the reflection value towards the wave input port, and S_{21} value is equal to the transmission, which is extracted from equation 3[11]:

$$Scattering = \begin{bmatrix} S11 & S12 \\ S21 & S22 \end{bmatrix} \qquad (3)$$

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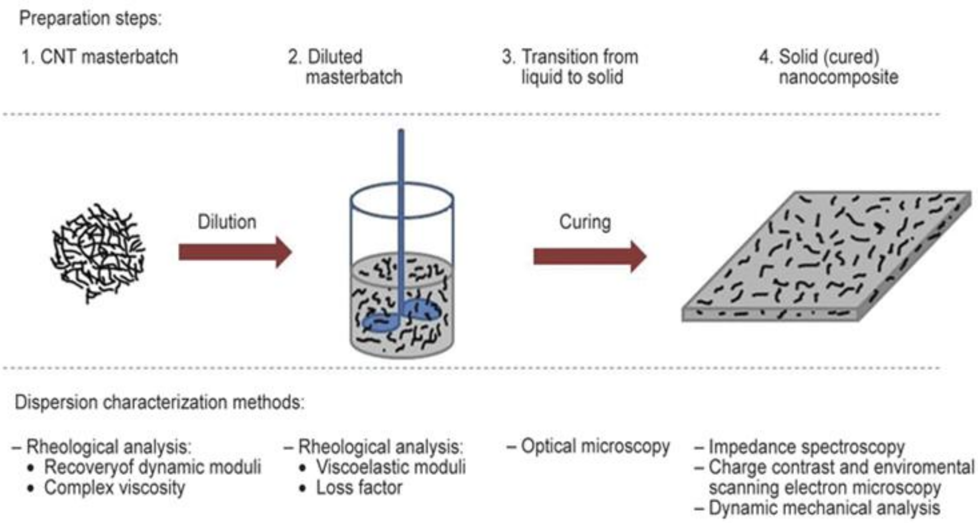

Fig. 4 The process of diffusion of nano materials in the matrix

Ahmad Taufiq and colleagues during research using nano materials such as multi-walled carbon

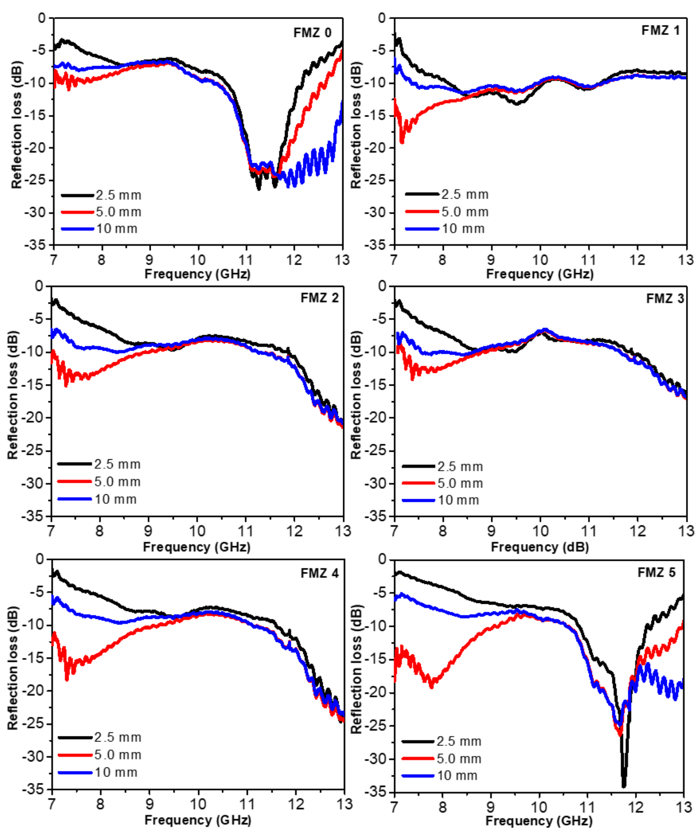

Fig. 5. Reflection loss of the Fe_3O_4/MWCNT/ZnO NCs with thickness variation.

Medicinal And Therapeutic Properties

Nano iron oxide, like other metal oxides, play a significant role in making and optimizing the effectiveness of many anti-cancer drugs. During a research, Khakbaz et al investigated the synthesis of porous nano iron oxide particles and the use of these nanoparticles in increasing the effectiveness of the drug doxorubicin, which is a chemotherapy drug.

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Experimental Synthesis

In this research, 0.1 molar iron sulfate orange solution was prepared and stirred at a temperature of 100 °C at a speed of 10,000 rpm and 4 molar soda solution was added to it until saturation. It was observed that the secondary color of the solution turned black, which was caused by the formation of iron nanoparticles. After this step, the solution is passed through a strainer three times and the sediment is washed twice with deionized water and once with acetone to ensure that no impurities are present. Iron oxide deposition is observed.After this step, the nanoparticles were placed for further oxidation in the presence of oxygen conversion reagents (trimethylamine) at high temperature, which caused structural defects and then the formation of hollow nanoparticles with a core containing crystalline nano iron oxide grains.In the next step, a chemotherapy drug called doxorubicin was loaded onto this porous nanoparticle by physical adsorption. After being coated with PEG, the porous nanoparticles showed a very good dispersion, which showed the binding of doxorubicin soluble in water to The internal parts of the nanostructure facilitated, compared to pure doxorubicin, doxorubicin loaded in porous nanoparticles provided much more control over the release behavior and less cytotoxicity towards 3-SK-BR cancer cells, as shown in Figure 6 [12].

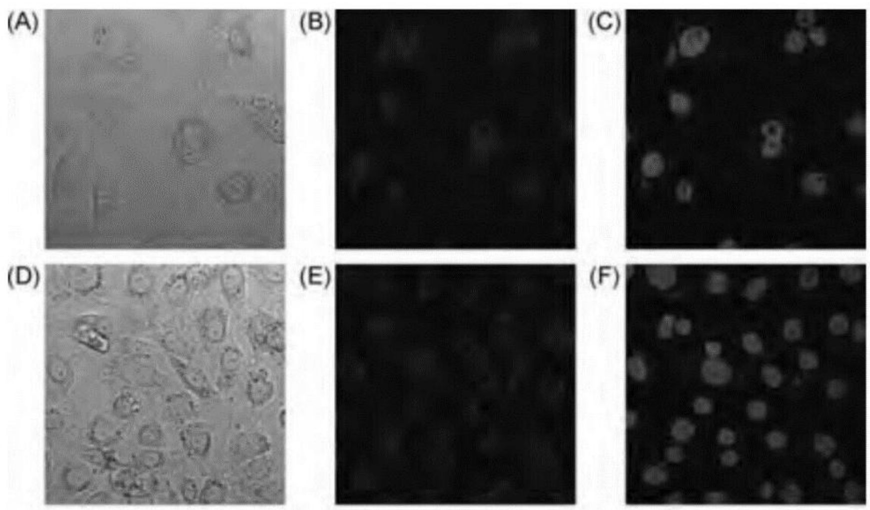

Fig. 6. (A,B,C) Observing the behavior of pure doxorubicin, (D,E,F) Observing the behavior of doxorubicin loaded inside porous nanoparticles

Environmental Properties

Another property of iron oxide nanoparticles is to use them in various compounds to remove environmental pollutants, industrial effluents and as a catalyst to remove heavy metals. During the research of Shafi Rehman and colleagues, using an efficient synthesis method, they were able to use nanoparticles of iron oxide in the direction of disinfection of industrial effluents. The aim of the present work was to synthesize magnetite (Fe3O4) nano hollow spheres (NHS) via simple, one-pot, template-free, hydrothermal method. The structural, morphological, and surface analysis of Fe_3O_4 NHS were studied by scanning electron microscopy (SEM), x-ray diffraction technique (XRD), Fourier transform infrared spectroscopy FTIR and burner-Emmett-teller (BET).

The as obtained magnetic (Fe_3O_4) NHS were used as an adsorbent for treating industrial trinitrotoluene (TNT) wastewater to reduce its Chemical Oxygen Demand (COD) values. Adsorption capacity (Qe) of the NHS obtained is 70 mg/g, confirming the attractive forces present between adsorbent (Fe_3O_4 NHS) and adsorbate (TNT wastewater). COD value of TNT wastewater was reduced to >92% in 2 h at room temperature.

The adsorption capacity of Fe_3O_4 NHS was observed as a function of time, initial concentration, pH, and temperature. The applied Fe_3O_4 NHS was recovered for reuse by simply manipulating its magnetic properties with slight shift in pH of the solution. A modest decrease in Qe (5.0–15.1%) was observed after each cycle.

The novel Fe_3O_4 NHS could be an excellent candidate for treating wastewater generated by the intermediate processes during cyclonite, cyclotetramethylene-tetranitramine (HMX), nitroglycerin (NG) production and other various environmental pollutants/species [13].

For the synthesis of Fe3O4 (NHS), 0.05 g of CTAB, 1.25 g of [K3 Fe (CN)6], 3.5 g of (NH4)2S2O8, and 0.05 g of 0.02 M NaH2PO4 solution were dissolved in 250 mL de-ionized water.

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The solution was magnetically stirred at room temperature in the presence of nitrogen gas until the solution turned visibly yellow in color. The solution was then poured into a 250 mL Teflon cup, sealed properly in an autoclave, and kept for calcination in an oven and 8 h at a temperature of 120 ◦C, 160 ◦C and 180 ◦C, respectively. The impact of these process parameters on the shape and morphologies of the catalyst was determined. After the completion of hydrothermal treatment, the solution was centrifuged at 4000 rpm for 30 min and washed three times with de-ionized water and ethanol systematically. The dark brown solution was filtered and then dried in a vacuum oven overnight at 45 ◦C (Figure 7)

Figure 8 shows the SEM of synthesized Fe_2O_3 and Fe_3O_4:

Figures 9 and 10 show X-ray diffraction images for Fe_2O_3 and Fe_3O_4 at an angle between 0 and 90 degrees:

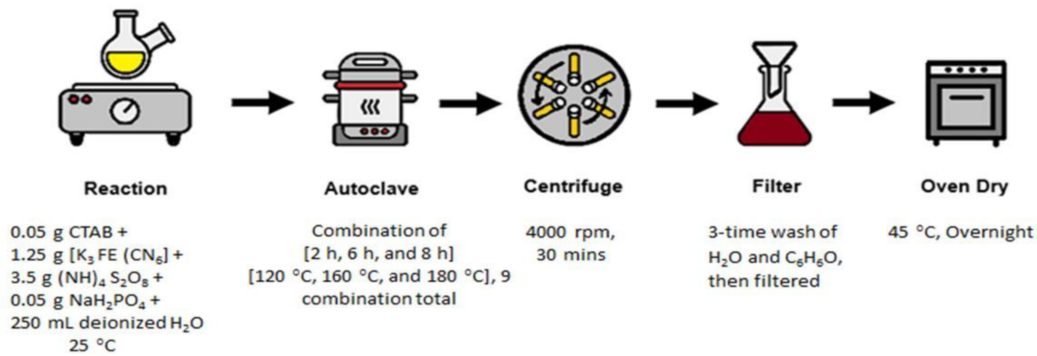

Fig.7. Schematic of the synthetic strategy employed to synthesize α-Fe_2O_3 and Fe_3O_4 (NHS), with synthetic parameters for each step listed

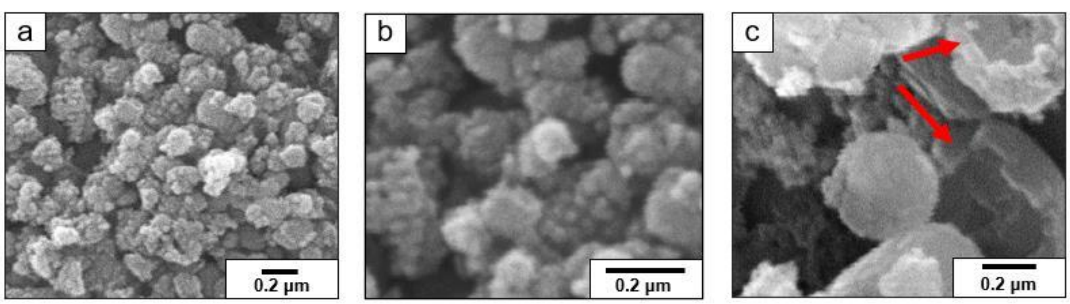

Fig.8. SEM images of α-Fe_2O_3 particles autoclaved for 2 h at 120 ◦C (a), 6 h at 160 ◦C (b), and Fe_3O_4 (NHS) autoclaved for 8 h at 180 ◦C (c) Red arrows point to areas where the hollow cavity of the particles can be observed in Fe_3O_4 (NHS).

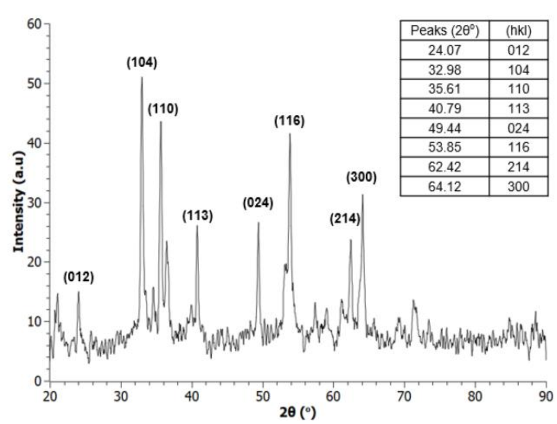

Fig .9. XRD spectra of α-Fe2O3 (hematite), autoclaved at 160 ◦C for 6 h.

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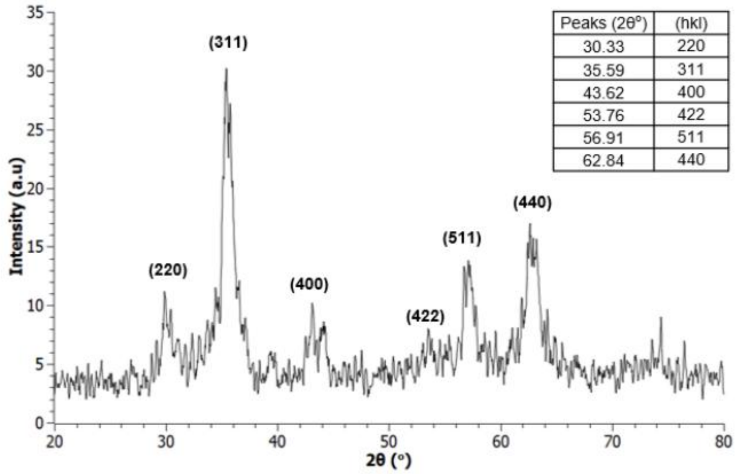

Fig .10. XRD spectra of Fe3O4 NHS (magnetite), autoclaved at 180 ◦C for 8 h

Conclusion

In this research, different synthesis methods of nano iron oxide, such as sol-gel method and CVD method, were reviewed. In general, the synthesized nano iron oxide can be used as an effective magnetic pole in the manufacture of nano coatings that absorb electromagnetic waves. They record a return drop above 10 dB to be effective. In addition, the optimal effect on the structures of chemotherapy drugs such as doxorubicin, which can significantly increase the efficiency of the drug, as well as the use of nano iron oxide synthesized hematite and magnetite by hydrothermal method for disinfection of industrial effluents and wastewaters, which can reduce the amount of CO It was investigated to reduce it by 92%. In general, the use of nano scale materials can be very fruitful in various industries due to the change in morphological properties and the distribution of particles throughout the material. In the next researches, it is possible to review and experimentally examine other metal oxides such as zinc oxide and titanium oxide and the effects of these materials synthesized in different ways in different industries and choose the most optimal materials.

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