# Synthesis And Characterization of Polyethylene Amine (PEI) Coated with Superparamagnetic Iron Oxide Nanoparticals (Spions) By Using Co-Precipitation Method

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**Abstract**
This study aims to prepare and study the polyethylene amine (SPIONs-PEI) super-magnetic nanoparticles, considering that these nanomaterials are an important class because of their outstanding physical and chemical properties used in various applications such as medical, chemical, and biological applications.The supermagnetic iron oxide nanoparticles Fe3O4 coated with a biopolymer of polyethylene amine SPIONs-PEI was prepared by chemical method, which is the co-precipitation method by preparing Fe+2 and Fe+3 salts in an aqueous solution by precipitating NaOH and sodium citrate salt as a material. On the surface and inside a closed system, using an inert atmosphere for nitrogen gas N2 and in the packaging method, the preparation is ex-situ method, and this method is easy and inexpensive.The nanoparticles were diagnosed using a set of techniques, including X-ray diffraction, VSM analysis, ZP zeta potential, DLS zeta sizer , SEM scanning electron microscope, and transmission electron microscopy TEM analysis.Where the XRD technique showed that the supermagnetic nanoparticles coated with SPIONs-PEI polymer contain the crystal structure and that the polymer coating did not affect its crystal phase and it is within the nanomaterial ranges which is estimated at (~10nm), and the analysis of a sample technique Magnetic Vibration VSM It was found that the unwrapped magnetic nanoparticles coated with SPIONs-PEI polymer possess magnetic properties but it decreases with increasing PEI concentration by 20% which is sufficient to respond to the magnetic field. The results of the Zeta potential also showed that the nanoparticles before encapsulation were negative about (-33.16mV), and the polyethylene amine-coated polymer had a positive charge after coated of (28.49mV). Either the hydrodynamic size of the DLS was about (7.27 nm) for the uncoated particles and (9.85 nm) for the SPIONs-PEI coated particles. The results of SEM scanning electron microscopy diagnosis showed that nanoparticles before and after encapsulation retained spherical geometric shapes with sizes of about (~20 nm), and that the real size of particles before and after encapsulation was within the nanoscale using TEM technique was about (~18 nm).
Keywords: $Fe_3O_4$, SPIONs, Nanopartical , co-precipitation method , PEI \

## 1. Introduction

Magnetic nanoparticles (MNPs) attract them researchers in recent years have paid attention to them may be used for various applications. MNPs is solid colloidal particles ranging in size from 1 to 100 nm. MNPs are key scientists in the field of chemistry, biology, medicine and physics [1]. because of your comparable in size to cells, viruses, genes and proteins open up possibilities Interaction with basic biological applications [2-5]. Magnetic iron oxide nanoparticles (SPIONs) physically and chemically stable, biocompatible and environmentally friendly, thus unique characteristics of clinical applications [6]. In recent years, it has been very important to synthesis of different types of superparamagnets nanoparticles (SPIONs) as nanomedicine materials. These include engineered magnetic nanoparticles (MNP) oxides of iron, cobalt or nickel Special properties including high surface area to volume ratio ratio and high moment enabling potential operates by an external magnetic field [7]. In particular, MNPs fabricated with ferromagnets material, i.e,. superparamagnetic iron oxide Nanoparticles (SPION) made of magnetite (Fe3O4) Ideal biocompatibility with superparamagnetic properties that enable a wide range of biomedical applications, such as Targeted drug delivery, bioimaging, hyperthermia, Photoablation therapy, biosensors and theranostics apply [8,9].

In general, the synthesis of SPIONs is very critical Multi-stage process that needs to be optimized its early design stage because it is already very small Fluctuations that may occur in the production process significantly changed the expected results arrive.Therefore, both physical and chemical properties To do this, particles must be strictly controlled suitable for many different applications [10,11,12]. Various fabrication techniques have been reported SPIONs (Fe3O4) using different technologies such as Coprecipitation [13, 14], thermal decomposition [15, 16], micro irrigation, ultrasonic irradiation, etc. Hydrothermal synthesis

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[17]. Among the co-precipitation methods are SPIONs (Fe3O4). Synthesized from the ions Fe+3 and Fe+2 under alkaline conditions solution, under an inert atmosphere (N2) [18]. Some recent studies [19,23] show that Many parameters for the synthesis of SPIONs (Fe3O4). However, in this work an attempt was made to prepare and synthesis of SPION. (Fe3O4) co-precipitation method survey methods and results using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), vibrating sample magnetometer (VSM) and zeta potential analysis (Zp).

## 2. Experimntal part

### 2.1: Fabrication Techniques

The general structure of the ready-made feedback system SPIONs and schematic are shown in Figure 1.

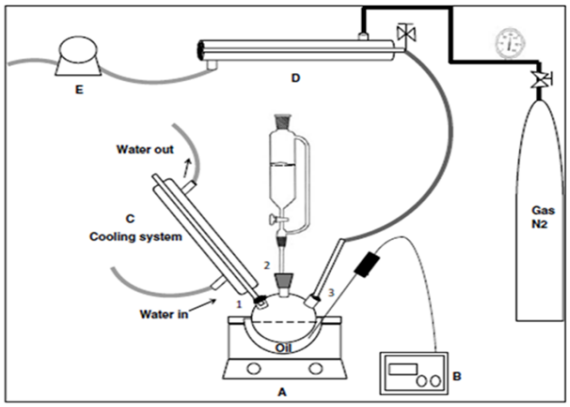



*Fig. 1: Schematic structure of the reflux system for synthesis of (SPIONs).*

## 3. Materials

We dissolve (0.69) by weight of iron sulfate II ($FeSO_4.7H_2O$) in (10 ml) of deionized water, and we dissolve (1.35) by weight of iron chloride III ($FeCl_3.6H_2O$) in (10 ml). Of deionized water the molar ratio is (1:2). And dissolve (1.2 g) of sodium hydroxide (NaOH) in (10 ml) of deionized water, and dissolve (1.77) g of sodium nitrate ($Na_3C_6H_5O_7$) in (10 ml) of deionized water.

### 2.3: Chemical Synthesis and Material

Pure magnetite nanoparticles were synthesized using the chemical co-precipitation method. This cycle involves the combined precipitation of iron and iron salts in an alkaline solution such as sodium hydroxide (NaOH) in the presence of trisodium hydroxide as a surfactant in an environment under $N_2$ flow as with the following chemical [24, 25]:

After preparing the nanoparticles and washing them twice with ethanol and twice with deionized (DI $H_2O$) water, then (20ml) of (DI $H_2O$) water is added to a concentration of (8 mg/ml) (g10) of the branched polymer polyethylene amine (PEI) was used. (Branched), and then dissolving it in (100ml) deionized water, taking into account the pH of the substance , which should be (7.9), where three concentrations of nanoparticles were used with proportions of (R =10,30,50) And polymer coating (PEI), and by applying the law of concentrations to find the value of $Fe_3O_4$ , which in the three concentrations is (12.5ml), and by applying the law of concentrations $R = \frac{PEI}{Fe_3\ O_4}$ to find the values of PEI and the law for the volume of $v_1 x\ c_1 = v_2 x\ c_2$and it was The result of the first concentration (%10) is (0.5 ml) and is supplemented with deionized water to reach (5 ml), and the ratio of the second concentration (%30) is (1.5 ml) to be supplemented with deionized water, and the ratio of the third concentration (%50) is (2.5 ml) Supplement with water. According to the packaging method used, which is an ex-situ method, that is, encapsulation of nanoparticles with a polyethylene amine polymer after the co-precipitation process.

$Fe^{+2} + 2Fe^{+3} + 8OH^{-1} \rightarrow Fe_3O_4 + 4H_2O$ (1)

The dependence of the control on the shape and size of nanoparticles depends on the ratio of $Fe^{+3}$ and $Fe^{+2}$, as well as on the type of salts (for example, chlorides, sulfates), and on the acidity of the medium.Figure 2 shows the flowchart for the synthesis of SPIONs by the co-precipitation method in the present work.

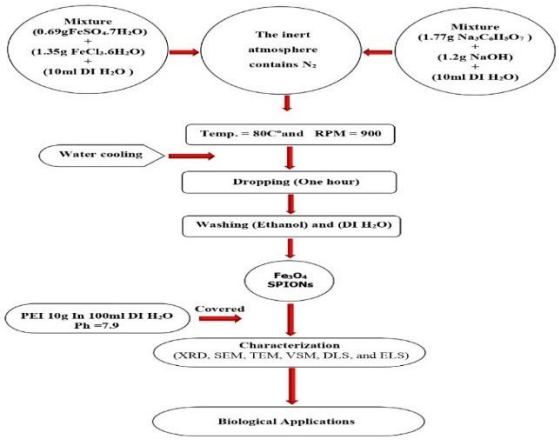



*Fig. 2: shows a complete scheme for the preparation and application of the biologics of PEI-coated SPIONs by the co-precipitation method.*

### 2.4: Characterization:

The X-ray diffraction patterns of the samples were determined using a CuKa radiation X-ray diffractometer (1.5418 Å) as the source.TEM is a versatile technique for analyzing nanoparticle sizes, crystal structure, and morphology distribution through imaging and diffraction techniques. The image produced by the SEM was projected onto the CRTs in the electronic control unit, and the captured images were digitally saved or printed directly. The magnetic properties characterization (VSM) of the prepared SPIONs was used in this work. Magnetic selection was carried out according to Faraday's laws so that an alternating current voltage is achieved in the mains and is equal to the rate of development of the electric current. The magnetic flux to which the circuit is connected, and the magnitude of the moment inside the sample due to the magnetic field. that the sample is bobbing in a vertical direction near

the detection coil if the sample oscillation makes the AC signal at a specific frequency. Measurements of colloidal particles were used, in most cases, negative or positive electrostatic charge. when the electricity the field is cast as the particles are scattered, and the particles travel in two directions and are charged in the opposite direction. Doppler shift occurs when particles are exposed to radiation while traveling as a coil as a result of the scattering of light according to the movement of electrophoresis. The Nano Brook program calculates the amount of the Doppler shift, followed by the zeta potential and electric motion, by combining an inhomogeneous array and a photon-to-dynamic subscription path. It is a device that detects the size of hydrodynamic nanoparticles.The surface of nanoparticles occurs in a variety of interactions with solvent particles and ions when nanoparticles are surrounded by feedstock[26,30].

## 4. 3. Results and discussion

### 3.1: X-ray diffraction analysis of SPIONs $Fe_3O_4$ Structure

Fig. 3: shows the X-ray diffraction (XRD) pattern of magnetite MNPs Fe3O4.

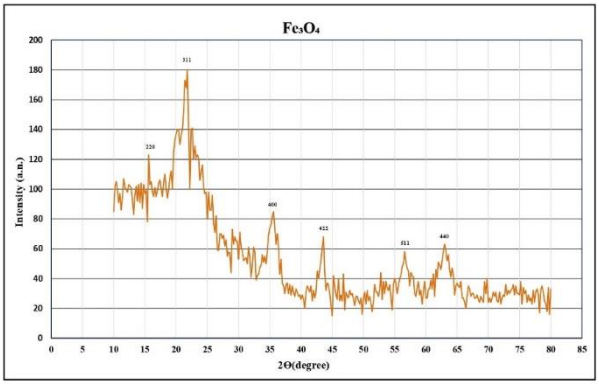



*Fig. 3: X-ray diffraction analysis of uncoated supermagnetic iron oxide nanoparticles. $Fe_3O_4$ .*

Fig. 3 shows that the supermagnetic iron oxide nanoparticles uncoated SPIONs show in X-ray diffraction analysis the presence of black iron oxide ($Fe_3O_4$) within the crystal structure according to Miller's coefficients indicated in the detector angles ($\Theta_2$) obtained from the results The study showed that the average crystal size of uncoated iron oxide calculated using the Debye-Scherrer equation is about (~10 nm).

$D = K\lambda / (\beta \cos \Theta)$ (2)

λ is the X-ray wavelength (5.03 nm), where K is the Scherrer constant (0.92), and Θ is the Bragg diffraction angle, β is the peak full width at half maximum (FWHM) of the reflection [29].

### 3.2: Magnetic Properties Characterization (VSM) Analysis

Vibration sample magnetometer (VSM) was used to study the magnetic properties of iron in supermagnetic iron oxide nanoparticles uncoated and coated with SPIONs prepared by co-precipitation method at conditions (temperature 80°C and rotation speed (RPM) 900 cycles). per minute in the presence of nitrogen gas $N_2$).

Fig. 6: shows the magnetic properties of the supermagnetic SPIONs iron oxide nanoparticles and envelope SPIONs-PEI that showed saturation magnetization (Ms) when the magnetic field applied to the object was increased.

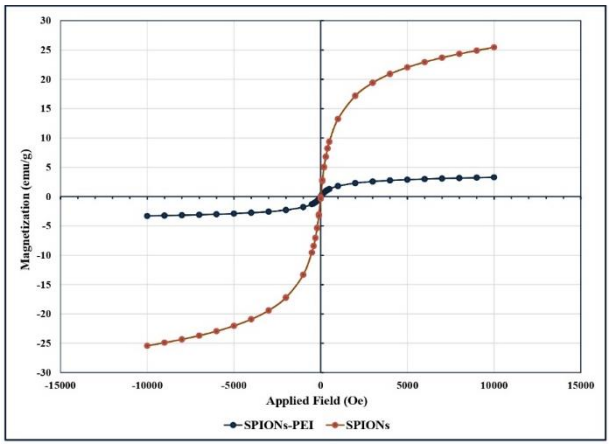



*Fig. 4: DLS zeta size of iron oxide supermagnetic nanoparticles (a) non-coated SPIONs(b) supermagnetic iron oxide nanoparticles with a concentration of PEI 10%*

The results of the examination with Vibration Sample Magnetometer (VSM) technique of the supermagnetic nanoparticles of uncoated iron oxide (SPIONs) prepared by co-precipitation and Ex-situ method show that the saturation magnetization Ms of uncoated iron oxide is about (~25emu/g). After encapsulating the nanoparticles with SPIONs-PEI polymer and at a concentration of PEI (30%), it was found that the saturation rate Ms of the uncoated iron oxide is about (~3.5emu/g).

$$D_m = \left(\frac{18k_BT\chi_i}{\pi\rho M_S}\right)^{1/3} \quad (3)$$

where Dm is the size of the magnetic particles, $K_B$ is the Boltzmann constant, T is the temperature in Kelvin 300 K, ρ is the density of black iron and is estimated at (5.18g/cm3), $\chi_i=(dM/dH)_{H\to 0}$It is the magnetic susceptibility where the size of the uncoated magnetic particles (Dm) is about (7nm), SPIONs-PEI is coated with a polyethylene (9nm).

### 3.3: Zeta Dynamic light scattering (DLS)

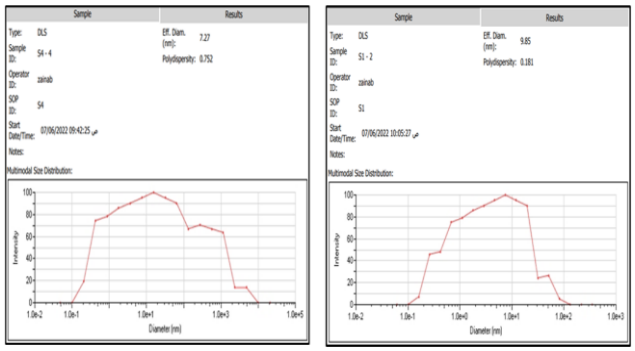


*Fig. 5: The zeta potential (a) shows the zeta potential of the supermagnetic nanoparticles of uncoated iron oxide SPIONs. (b b) zeta potential at a ratio and concentration of polyethylene amine PEI 10%..*

was used to determine a hydrodynamic size of SPIONs $Fe_3O_4$ at different rotational speeds RPM and variation concentrations of NaOH with a constant temperature of 80 °C. The optimum results have been observed for the Fig8, and Table 2.Size (DLS) Analysis. Where the value of the effective diameter of the zeta size of the uncoated supermagnetic nanoparticles (SPIONs 7.27 nm)) appeared. As for the results of the zeta volume analysis of ultra-magnetic iron oxide nanoparticles coated with SPIONs-PEI polymer, which plays an important role in increasing the zeta volume according to the bonding strength between PEI and the surface of the SPIONs nanoparticles, which was prepared by co-precipitation method at a constant rotation speed (RPM). 900 revolutions per minute and a constant temperature of 80 degrees Celsius, as the packaging was done by Ex-Situ Method with different concentrations of polyethylene amine (PEI R =10%,30%,50%) . Where the size of the zeta DLS of the supermagnetic iron oxide nanoparticles SPIONs-PEI coated with concentrations, respectively, was (9.85 nm), (18.70 nm), and (26.39 nm).

(a) (b)

## 3.4: Zeta Potential Analysis

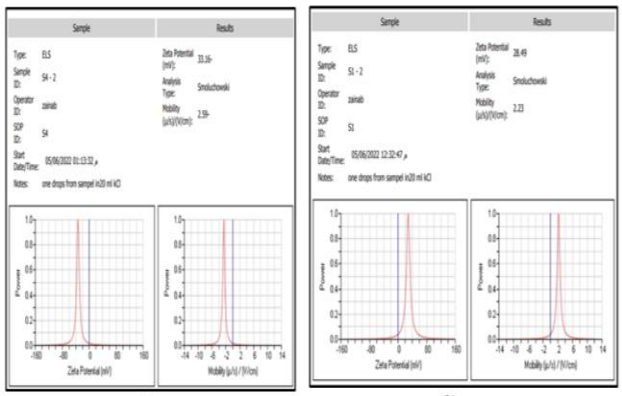
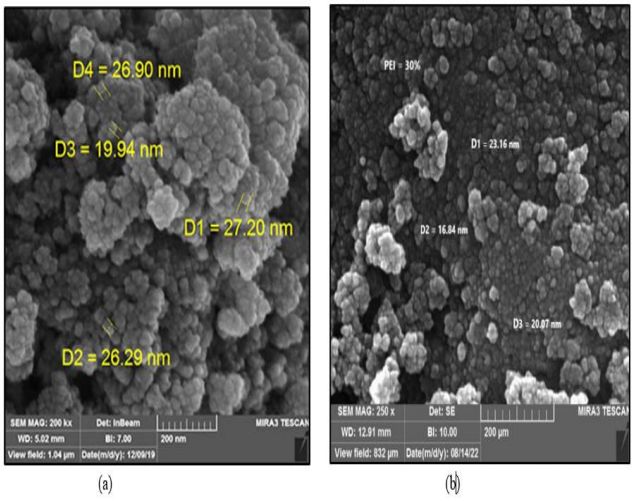


*Fig. 6: Magnetic properties of supermagnetic iron oxide nanoparticles SPIONs and SPIONs-PEI coated (hysteresis ring) at 30% concentration of PEI.*

Colloidal stability plays a very important role in the zeta potential (ZP) analysis of magnetic nanoparticles of uncoated iron oxide (SPIONs) As for the results of the zeta potential (Zp) for uncoated supermagnetic nanoparticles, the zeta potential of SPIONs is about (-33.16 mV), which is a negatively charged particle. And the zeta potential (ZP) for ultra-magnetic nanoparticles coated with polyethylene amine SPIONs-PEI in different ratios and concentrations (R = 10,30,50) used in coating the surface of nanoparticles, and surface coating is to increase the surface stability of the particles and reduce the repulsive force between the nanoparticles. As it was shown in the previous pictures that the result of the ratios and concentrations of the particles was as follows: 10% is about (28.49), 30% is (45.88), 50% is (48.55) and these percentages indicate that the higher the percentage of concentrations, the greater the positive charge.

## 3.5: Scanning Electron Microscope

Scanning electron microscopy (SEM) of non-encapsulated supermagnetic iron oxide nanoparticles (SPIONs) demonstrates the nature of the particle surface, particle size, shape and distribution method. Where samples of supermagnetic iron oxide nanoparticles prepared by co-precipitation method at a temperature of 80 °C and a rotation speed of 900 rpm were examined. We find that the uncoated SPION nanoparticles tend to aggregate in spherical shapes into groups with an average diameter of ~25 nm. And after super-magnetic iron oxide nanoparticles were coated with a polyethylene amine (SPIONs-PEI) polymer using Ex-Situ method, at a concentration of R =30% . (Fig. 7) indicates that the nanoparticles were spherical with an average diameter of about (~ 20 nm) as shown by the results of the scanning electron microscope (SEM) technique. We noticed from the previous figure that adding a layer of PEI to the nanoaggregates did not affect the surface morphology of the particles.




(a) (b)

*Fig. 7: Scanning electron microscope image of iron oxide nanoparticles (a) non-coated supermagnetic iron oxide nanoparticles (b) coated with polyethylene amine (SPIONs-PEI PEI=30%).*

## 3.6: Transmission Electron Microscopic (TEM) Analysis

Transmission electron microscopy (TEM) analysis showing the actual size of supermagnetic nanoparticles without encapsulating SPIONs, which were prepared by co-deposition method, after preparation (temperature 80 °C and rotational speed (RPM) 900 . After using the image analysis program ImageJ and the Origin Lab program, it was found that the size of nanoparticles is equal to (5 nm) , which is compatible with the result of X-ray diffraction technique (XRD) in the study. As for the results of the analysis of the ultra-magnetic nanoparticles of iron oxide coated with SPIONs-PEI polymer, with a concentration of 30% of the proportion of PEI is about (18nm) separated and homogeneously distribute Fig. 5: The results of a transmission electron microscope (TEM) can be

illustrated. Table 1 show the comparison particles Size in deffreint techniques between XRD, SEM, TEM, and VSM.

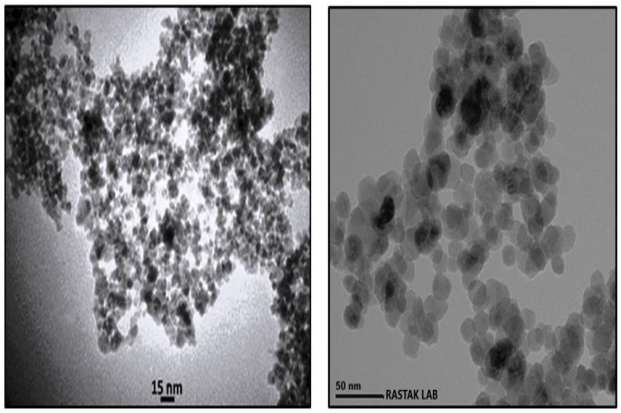



*Fig. 5: Transmission electron microscopy (TEM) image of supermagnetic nanoparticles. After encapsulation SPIONs-PEI at a concentration (R=30%) of PEI.*

| التقنية | XRDnm | VSMnm | SEMnm | TEMnm |
|---|---|---|---|---|
| SPIONs | 10 | 7 | 25 | 5 |
| SPIONs-PEI | - | 9 | 20 | 18 |

## 5. Conclusions

In our study there are some conclusion, XRD technique showed that the nanoparticles of pure black iron oxide Fe3O4 are within the crystalline structure of standard nanoparticles and within the nanoscale. Analysis of VSM technique showed that the nanoparticles coated with polyethylene amine SPIONs-PEI have magnetic property, but it decreases with increasing concentration of polyethylene amine, but it is sufficient to respond to the magnetic field. Zeta potential analysis of the surface charge was negative for supermagnetic iron oxide nanoparticles before encapsulation and was positive after encapsulation with SPIONs-PEI Polyethylene. The SEM analysis of the supermagnetic nanoparticles before and after encapsulation kept the spherical geometry. The actual size of SPIONs before and after encapsulation was within the nanoscale using TEM technique. The particles prepared by co-precipation method are nanoparticles whose sizes are (<100 nm) and after encapsulation with PEI polymer, they remain magnetic and nanoscale.The prepared particles coated with PEI polymer can be prepared in large quantities and at low cost for use in biological applications.

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