Synthesis, Surface Modification and Characterization of Magnetic Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} Core-Shell Nanoparticles

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Abstract. The nanoparticles of the magnetic core-shell Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} were produced using a modified Stöber approach and functionalized with (3-amino-propyl) APTES triethoxysilane and ethylene-diamine-tetra-acetic acid (EDTA). Magnetic nano adsorbents exhibit many attractive opportunities for different purposes due to their easy removal and possibility of reusing these nanoparticles. The ligands grafting was chemically stable and did not affect the morphology or substrate structure appreciably. APTES-EDTA microspheres were formed for the removal from aqueous solution solutions of trivalent rare earth elements ions since the REEs have a strong oxygen affinity. The advantages of the SiO\textsubscript{2} shell that covers the magnetite nanoparticles include lower specific weight and a larger grafting density compared to other surfaces, improving the resistance to acidic environments. Different techniques have described the particle size, morphology, precise surface area and surface alteration including Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and vibrating sample magnetometer (VSM). The results show that the Fe\textsubscript{3}O\textsubscript{4} nanoparticles with an average particle size of 15 ± 3 nm were successfully synthesized at pH=11, at 25 °C temperature. Moreover, The nanoparticles prepared for Fe\textsubscript{3}O\textsubscript{4} were coated with amorphous SiO\textsubscript{2} and functionalized with amino and carboxylic groups.

Keywords: adsorption, Magnetic core-shell, Nano adsorbents, EDTA.

1. Introduction

Magnetic materials have received considerable attention due to their exceptional characteristics as Para magnetism or ferromagnetism, which can be easily modified and are non-toxic [1]. The magnetic iron oxide nanoparticles (NPs) Fe\textsubscript{3}O\textsubscript{4} hold tremendous assure in biomedical uses, such as regained catalysts and eclectic capture of metal ions, biosensors, drug delivery, and dual imaging compounds [2, 3]. Different regularization strategies have been founded in the literature to prepare the iron oxide nanoparticles, like coprecipitation, thermal decomposition in aqueous solutions, or hydrothermal synthesis, etc. The co-precipitation method could be used to prepare Fe\textsubscript{3}O\textsubscript{4} nanoparticles with such a high performance that yields very good quality and economy [4-6]. The core-shell nanoparticles can acquire significantly enhanced properties and it is slightly much more complicated in construction than the stereotypical nanoparticles [7-9]. The core is usually magnetite or cobalt that can be oxidized or degraded in an acidic medium. This core is covered with an inert cortex of ZrO\textsubscript{2}, TiO\textsubscript{2}, SiO\textsubscript{2}, graphene,
Numerous active sites could be produced due to the high surface area of Magnetite nanoparticles. However, the preparation of \( \text{Fe}_3\text{O}_4 \) nanoparticles played an important role in decrease the active sites through the agglomerate [13-15]. Inorganic capping reagent like silica (\( \text{SiO}_2 \)) has remarkable physical and chemical characteristics[15]. The \( \text{SiO}_2 \) shell conserves the core from oxidation or aggression by chemicals and is chemically stabilized in acid media. It may be moreover functionalized through linking of functional groups to the exterior [16, 17].

The \( \text{SiO}_2 \) covered the surface of each \( \text{Fe}_3\text{O}_4 \) nanoparticles to form \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) core-shell nanoparticles which will also be avoiding from the clustering and protect them from degradation in acidic medium.[18, 19]. There are two general ways for silica coating, the first one was Stöber synthesis where, it may not be stratified to NPs that are insoluble in polar solution. And the second one the reverse microemulsion methods where it was a good alternate plan for silica coating of oil-dispersed NPs [20, 21]. To avoid the particle agglomeration there is one possibility, namely the coating with organic or inorganic surfactants. The organic surfactants act as capping reagents and they result in larger particle size[22, 23]. The core-shell and uniform NPs were could be functionalized by covalent binding, chemisorption, or electrostatic reactions of recruits on the surface [24]. Promising results have been found on functionalized siloxanes, as a result of hydroxyl groups that compose stronger covalent bonds with utmost oxide surfaces [25, 26]. The large amounts of commercial trialkoxyxilanes with various functional groups show individual potential for particular oxide nanoparticles surface modification [27]. A group of researchers recently discussed the adsorption capacity and selectivity of TMS-EDTA-functionalized \( \text{Fe}_3\text{O}_4, \text{TiO}_2, \) and \( \text{SiO}_2 \) nanoparticles in order to obtain a preferred understanding of the substrate effect on the surface reaction. [28-30]. It was revealed that TMS-EDTA functionalized \( \text{SiO}_2 \) nanoparticles implemented greater than the comparable \( \text{Fe}_3\text{O}_4 \) or \( \text{TiO}_2 \) nanoparticles. This may be due to high-density hydroxyl groups on \( \text{SiO}_2 \) surface providing a significant grafting density of functional TMS-EDTA groups. This intense layer of TMS-EDTA groups can connect a large number of rare-earth ions, but it also provides a good size-based selectivity.[31, 32]. It was presented that an intense layer of TMS-EDTA offers the best segregation between small and large size rare-earth ions[33]. Scandium is a rare and valuable metal, which has little richness in natural mineral deposits. It is oftentimes retrieved in as a byproduct material from industrial residuals like bauxite residue/red mud, accomplished with numerous quantities of other impurities like iron (Fe) and aluminium (Al) which the physicochemical properties are quite similar. Therefore, the recovery of Sc from industrial wastes faces the greatest challenges [34-36]. The rarity of Sc is the motivation for an inflated price of the Sc based on compounds such as scandium oxide (\( \text{Sc}_2\text{O}_3 \)) and alloy metal, the prices of which were round US$ 2.54 g\(^{-1}\) and US$ 155 g\(^{-1}\), respectively [37]. Among various sources of scandium, bauxite residue/red mud, a bountiful material gained as a risky by-product from the Bayer process, it is produced at a rate upon 130 million tons per year [38]. The modified core-shell structure nanoparticles show to be a promisingly adsorbent for Sc recovery, as they are mostly used adsorbents for heavy metals recovery because of their advantageous characteristics as high surface area, greatest adsorption efficiency and stability in an acidic medium [12, 20, 30]. To enhance the ion selectivity and recovery of these nanoparticles through complexation or coordination mechanism, different ligands are often immobilized on such support nanoparticles. The EDTA ligands consider cheap, available, and efficient for low ion concentrations. Moreover, the EDTA selectivity for different ions depends on adjusting of pH value of the solution [11]. This work led to the development of an environmentally friendly and economically efficient procedure for the production of nano adsorbents, The magnetic core-shell structure \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) nanoparticles was produced with updated Stöber ’s method and functionalized with (3-amino-propyl) triethoxysilane (APTES) as a binding agent and ethylene-diamine-tetra-acetic acid EDTA as a ligand capable of separating scandium metal ions Sc (III) from the aqueous medium model prior to application of these adsorbents in industry archives.
2. Experimental

2.1. Materials
All chemicals were of analytical grade and used as received without further purification. Ferrous chloride tetrahydrate (FeCl$_2$.4H$_2$O, 99%), ferric chloride hexahydrate (FeCl$_3$.6H$_2$O, 99%), tetraethyl orthosilicate (TEOS, 99%) and 3-aminopropyl triethoxysilane (APTES, 98%) was purchased from Sigma-Aldrich Co. Ammonium hydroxide (NH$_4$OH, 25%) was obtained from Merck Chemicals Co. Ethanol (C$_2$H$_5$OH, 96%), acetic acid (CH$_3$COOH, 20% v/v), sodium hydroxide (NaOH, 97%), and hydrochloric acid (HCl 37%) were purchased from VWR Chemicals BDH Co. All aqueous solutions were prepared with distilled water.

2.2 Instrumentation
Using the following instruments, the magnetic nanoparticles were analysed: TEM (JEM-1400 80 keV, JEOL Japan). Fourier transform infrared (FT-IR) spectra on a Bruker Vertex 70 spectrometer were measured between 4000 and 400 cm$^{-1}$. The XRD data was collected using an X-ray diffractometer (Shimadzu S-6000). Applied the Brunauer-Emmett-Teller (BET) system using Q Surf 1600 instrument, USA. Vibrating sample magnetometry (VSM) experiments conducted on a VSM Mag lab setup at 25 °C were used to obtain magnetisation results.

2.3 Iron Oxide Magnetic Nanoparticles Preparation
The protocol on co-precipitation was used as a method was used to prepare MNPs[7]. Where (4.4, 1.98) grams of FeCl$_3$.6H2O and FeCl$_2$.4H2O were dispersed consecutively in 60 mL de-aerated water. But the mixture was purged with nitrogen for 30 min to avoid the oxidation of Fe$_2$ + ions. In order to prepare and get the best morphology and nanoscale dimensions of iron oxide magnetic nanoparticles, the addition of NH$_4$OH solution was carried out at two pH=10 and pH=11. A 140 mL 0.8 M NH$_4$OH was applied to the solution under continuous stirring at 25 °C temperature, and 0.1 mol / L HCl changed the pH. At the same time, the solution color was seen to change from brown to black during NH$_4$OH add-on. Furthermore, the black iron oxide product was trying to conform to a magnetic field as predicted. This property is useful when extracting particles from the solution for the reaction.

2.4 Preparation of iron oxide nanoparticles with core-shell structure
The modified Stöber protocol was used method of coating, where the iron oxide nanoparticles synthesized at pH=10 and pH=11, (100 mg) was dispersed in ethanol of 40 mL volume. Later on, with continually stirring, NH$_4$OH and TEOS were added to the iron oxide mixture by 3 mL of 25 wt % NH$_4$OH, 7 mL of distilled water and 300 µL of TEOS. By using a magnetic stirrer to stir for 2 h, the solution then was ultra-sonicated for 10 min. The nano-particles were isolated by magnetic attraction force from the liquid then released in 30 mL of ethanol. This was done twice to obtain triple coated nano-particles. The number of coating times depends on the application required for Fe$_3$O$_4$@SiO$_2$ nanoparticles. In order to improve the Si – O – Fe connection, two separation and washing courses were performed using magnetic bar and alcohol, the particle solution was kept in the water bath at 60 μC for 2 hours. After that, the coated molecules were broken down through the magnetic domain from the solution.

2.5 Functionalization with amino and carboxyl groups
Amino groups were first used to functionalized Fe$_3$O$_4$@SiO$_2$ nanoparticles by using APTES, since alkoxide groups of APTES were expected to react with OH groups on the silica surface of the Fe$_3$O$_4$@SiO$_2$. After functionalizing the nanoparticles, the silanization procedure would begin by adjusting the pH value at 4.5 with 1 mol/L of HCl and then dispersing 100 mg of nanoparticles in 40 mL EtOH/H$_2$O solution of 85:15 ratio. The next step was putting the solution in an ultrasonic bath for 10 min then added 700µL APTES both with a little drop of acetic acid. The solution was refluxed at 60 °C temperature for 4 h with stirring. The particles were separated from the liquid using a small magnet and rinsed once with water and once with acetone. The modified nanoparticles Fe$_3$O$_4$@SiO$_2$-NH$_2$ were functionalized with carboxyl functional groups by using EDTA through the formation of amide bonds.
Where the nanoparticles dispersed by the sonication process in 0.3 mol/L of EDTA solution. The solution was refluxed at 60 °C temperature for 2 h with stirring. Finally, the nanoparticles were dried at 50 °C for 60 min resulting in Fe₃O₄@SiO₂-COO as shown in figure 1.

Figure 1. A schematic illustration of the preparation and functionalization of Fe₃O₄@SiO₂ nanoparticles

3. Results and discussion
To prepare the best magnetic nanoparticles with an optimum morphology before coating with a silica shell, the iron oxide nanoparticles were prepared at pH = 10 and pH = 11. The TEM images in figure 2 show the iron oxide nanoparticles that were prepared at pH = 10, the observed particles under TEM showed the multiphase of iron oxide nanoparticles, spheroidal magnetite (Fe₃O₄) and goethite nanorods (α-FeOOH). Moreover, the spheroidal magnetite represents the most with an average particle size of 28 nm. The TEM image in Figure 3 shows the iron oxide nanoparticles synthesized at pH = 11, the observed particles under TEM showed the one phase of iron oxide nanoparticles were spheroidal magnetite (Fe₃O₄), regular in shape, and uniform in size with an average particle size of 15 nm.

Figure 2. TEM image of multiple iron oxide nanoparticles (goethite nanorode and spherical magnetite) prepared at pH 10
3.1 Mechanism of formation for the Fe₃O₄ nanoparticles

Within the deposition of Fe₃O₄ from Fe²⁺ and Fe³⁺ salts mixtures, two separate reactions might take place next to the ammonium hydroxide addition to monitor and adjust the precipitation of Fe₃O₄ metal nanoparticles (MNPs). It is familiar that Fe (OH)₂ and Fe (OH)₃ compose at pH ~ 11 through the hydroxylation of the ferrous and ferric ions within an anaerobic environment. Thus, the forming of Fe₃O₄ MNPs performed with black color precipitate. The formation reactions for Fe₃O₄ MNPs are considered by the following equations:

\[
Fe^{+3} + 3OH^- \rightarrow Fe(OH)_3 \quad (1)
\]

\[
Fe(OH)_3 \rightarrow FeOOH + H_2O \quad (2)
\]

\[
Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2 \quad (3)
\]

\[
2FeOOH + Fe(OH)_2 \rightarrow Fe_3O_4 \downarrow + 2H_2O \quad (4)
\]

Next to the iron source addition, the reaction occurred in higher yield and magnetite crystals are observed immediately. Moreover, oxygen is released from the whole reaction mixture and magnetite may be oxidized to maghemite (γ-Fe₂O₃). The large particle sizes can further be earned through the aggregations of small crystallites during synthesis [25].

3.2 Mechanism of surface modification

The chemical properties of the silica surface are mainly determined by the density of silanol per unit mass of silica. On the surface, the structure closed by either a siloxane group (Si-O-Si) with the oxygen or one of the various forms of silanol groups (Si-OH). Through the hydrolysis, the alkoxide groups (OC₂H₅) of APTES were exchanged by hydroxyl groups (OH) to compose reacting silanol groups that concentrate with other silanol groups to form siloxane bonds (Si-O-Si) to produce a silane polymer.
After that, the polymers laminated the nanoparticles to obtain a covalent bond with OH groups [39]. Next to APTES coating, the nanoparticles were functionalized with amino groups. Then, EDTA was linked to the APTES coated nanoparticles. The covalent bonding of EDTA to particles was attained through the forming of amide bonds among the carboxylic acid groups of EDTA and amino groups supplied from the APTES coating [28].

3.3 Characterization of core-shell structure of iron oxide nanoparticles

Figure 4. Shows the TEM images and elemental map of core-shell structure of multiphase iron oxide nanoparticles Fe₃O₄@SiO₂ and a-FeOOH@SiO₂. The TEM images showed the shell thickness of the magnetite spherical nanoparticles (Fe₃O₄) varied 1.3 -1.7 nm while the shell thickness of the goethite nanorods (a-FeOOH-) 3.9 - 4 nm.

![TEM images and elemental map](image)

**Figure 4.** TEM images and elemental map of core-shell structure of multiphase iron oxide nanoparticles Fe₃O₄@SiO₂ and a-FeOOH@SiO₂

The TEM images of the nanoparticles shown in figure 5. confirm the core-shell structure of Fe₃O₄@SiO₂ magnetite nanoparticles. Moreover, the images showed the morphology were spherical, regular in shape, and uniform in size, and the SiO₂ coating layer was uniform with ~7nm in thickness. On other hand, the elemental map by TEM confirmed the distribution of iron and silica of Fe₃O₄@SiO₂ nanoparticles as shown in figure 5. The measured BET surface areas are listed in Table1. Due to the effect of the coating
by amorphous silica shell that has a thickness of ~6-8 nm, the surface area increased from 117 to 300.8 m$^2$/g. The surface area decreased after surface modification with APTES and EDTA. This is due to the functional groups attached to the amorphous silica surface. The surface area determined by BET method and the average particle sizes determined by TEM of these nanoparticles are listed in Table 1.

Figure 5. TEM images and elemental map of Fe$_3$O$_4$@SiO$_2$ nanoparticles
Table 1. Selected properties of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-NH₂ and Fe₃O₄@SiO₂-COO nanoparticles.

| Sample                     | BET surface area (m²/g) a | Particle size (nm) b |
|----------------------------|---------------------------|----------------------|
| Fe₃O₄                     | 117.0                     | 15                   |
| Fe₃O₄@SiO₂                | 300.8                     | 22                   |
| Fe₃O₄@SiO₂-NH₂            | 203.6                     | 27                   |
| Fe₃O₄@SiO₂-COO            | 101.3                     | NA c                 |

a Determined by N₂ adsorption using the Brunauer–Emmett–Teller (BET) method

b Average particle size observed from the transmission electron microscopy (TEM) images

c Not available

The saturation magnetization values were measured by vibrating sample magnetometer VSM. Those were 79.0 emu/g for Fe₃O₄ and 60.2 emu/g for Fe₃O₄@SiO₂ respectively. Although the saturation magnetization reduced after silica coating of the Fe₃O₄ core surface, full magnetic separation of Fe₃O₄@SiO₂ samples was accomplished within 2 min by putting the magnet nearby the containers holding the aqueous dispersions of nanoparticles as shown in Figure 6.

Figure 6. The magnetic curve of Fe₃O₄ and Fe₃O₄@SiO₂ nanoparticles

The crystalline structures of the nanoparticles were identified with XRD. The XRD patterns of the Fe₃O₄ and Fe₃O₄@SiO₂ are shown in Figure 7. A set of characterization peaks were noticed in the XRD patterns at 2θ of 30.2°, 35.6°, 43.2°, 53.9°, 57.3°, 62.9° and 74.7° identical to the diffractions of [2 2 0], [3 1 1], [4 0 0], [4 2 2], [5 1 1],[4 4 0] and [5 3 3] crystal planes of a cubic spinel unit cell that in good agreement with the standard Fe₃O₄ pattern [28, 29]. For Fe₃O₄@SiO₂ nanoparticles, the characteristic peaks were comparable to that of Fe₃O₄ nanoparticles unless for the peak about 24°. The peak near 24° might be assigned to the silica shell [3]. There are no peaks for any other phases that were noticed in the XRD patterns which refers to the product with high purity.
**Figure 7.** XRD-pattern of Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$ nanoparticles

The FTIR spectra of modified Fe$_3$O$_4$@SiO$_2$ nanoparticles are compared in Figure 8, to prove the silica coating and the functionalization of amino and carboxylic groups on the surface of Fe$_3$O$_4$ nanoparticles. Concerning all three nanoparticles, absorption peaks at 575 cm$^{-1}$ were noticed as shown in Figure 6, corresponding to the Fe–O vibration from the magnetite phase. The curve (B) of Figure 8 shows the FT–IR spectrum of Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanoparticles, at 794 cm$^{-1}$ and that near 1082 cm$^{-1}$ indicated to the Si–O–Si stretching vibration, the Si–O–H stretching vibration and the Si–O vibration, respectively [31]. Moreover, new bands observed at 1425 and 1528 cm$^{-1}$ were attribute to N–H bending vibration of amine groups. The peak at 3420 cm$^{-1}$ was due to O–H stretching band of the surface of silanol groups and the residual adsorbed H$_2$O molecules. figure 6C shows the FT–IR spectrum of Fe$_3$O$_4$@SiO$_2$-COO nanoparticles, at 1725 cm$^{-1}$ corresponding to the C=O vibration of carboxylic groups [31, 32]. That results proved that the silica coating and the next amino and carboxylic groups functionalization on the surface of Fe$_3$O$_4$ nanoparticles were effective.

**Figure 8.** FTIR of (A)Fe$_3$O$_4$, (B) Fe$_3$O$_4$@SiO$_2$-NH$_2$ and (C) Fe$_3$O$_4$@SiO$_2$-COO nanoparticles
4. Conclusions

In this study, with metal-coordinating APTES-EDTA groups, Fe₃O₄@SiO₂ magnetic nanoparticles with core-shell structure were synthesized and successfully functionalized. The idea was that the benefit of magnetic retrieval (Fe₃O₄ core) could be combined with the higher compatibility observed when APTES-EDTA was attached to SiO₂. The iron oxide magnetic nanoparticles were synthesized by co-precipitation protocol at pH=11 and temperature. According to the TEM, thin and homogeneous SiO₂ shells (7 ± 1 nm thick) were grown around Fe₃O₄ cores (15 ± 3.0 nm diameter) using a modified Stöber method. Moreover, the distribution of iron and silica of Fe₃O₄@SiO₂ nanoparticles was proved. The functionalization of Fe₃O₄@SiO₂ by amino and carboxylic groups was confirmed by FTIR spectra. The saturation magnetization of the Fe₃O₄ nanoparticles was 79 emu/g, while that of the Fe₃O₄@SiO₂ composite nanoparticles was 60.2 emu/g. This difference could be attributed to the SiO₂ coated layer. The XRD pattern peaks confirmed the crystalline structures of the nanoparticles except for the peak around 24° which can be attributed to the silica shell. This synthesis protocol called for the synthesis of nanoparticles of high-quality Fe₃O₄@SiO₂(APTES-EDTA). The goal of carboxyl group functionalization of nanoparticles was the selective adsorption of rare earth element ions from aqueous solutions due to the high affinity of the REEs for oxygen. We'll deal with this job in our next article.

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