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Surface Modification of Fe_3O_4 as Magnetic Adsorbents for Recovery of Precious Metals

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Additional information is available at the end of the chapter

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Abstract

Magnetic nanoparticles such as magnetite have been studied intensively for their unique properties that are susceptible to a magnetic field, ready to coat with silica and able to modify with a variety of functional groups. The magnetite-silica core-shell system offers flexibility for extensive modification. The magnetic core is also important in the separation by the use of a magnetic field. The shell, meanwhile, is needed for protection of the magnetic core and further modification. Functional groups at the surface shell are critical in the reaction with target precious metal ions during application. In this contribution, we will have a comprehensive look at the preparation, characterization, and use of the magnetite core-shell modified with functional groups as a magnetic adsorbent. After adsorption, the materials together with the ions can be recovered by the use of magnet before further separation and purification.

Keywords: magnetic nanoparticle, recovery, silica, precious metal, adsorption, desorption

1. Introduction

Magnetic materials that are paramagnetic, ferrimagnetic, and ferromagnetic have received much attention because of their unique properties especially ready to modify and nontoxic [1, 2]. Magnetite (Fe_3O_4), one of many magnetic materials, is widely investigated for possible magnetic resonance imaging, sensor, and adsorbent. Magnetic nanoparticles typically consist of a magnetic core, a coating, and, in some cases, surface active modifiers.

The magnetite nanoparticles have a high surface area that yields numerous active sites. However, preparation of Fe_3O_4 nanoparticles is problematic since it can agglomerate, which

leads to the decrease in the active sites. Coating with organic or inorganic surfactants is one way to avoid the particle agglomeration. The organic surfactants act as capping agents, but at times, they can give bigger particle size. Inorganic capping agent such as silica (SiO_2) has exceptional physical and chemical properties. SiO_2 is chemically stable in acidic solution and tuneable for modification. Coating of Fe_3O_4 nanoparticles with SiO_2 will also avoid the agglomeration and protect them from dissolution in acidic solution. SiO_2 will cover the surface of each Fe_3O_4 nanoparticle to form $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticle core-shell system [3].

Morel et al. have coated Fe_3O_4 particles with SiO_2 to form core-shell having nanometer scale with an average diameter of 49 nm [4]. The success of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core-shell nanoparticle formation depends on the size of magnetite. However, stirring with the magnetic bar during the preparation causes condensation and agglomeration of the particles. The nonmagnetic mechanical stirring method was chosen for the preparation of Fe_3O_4 nanoparticle [5].

Many researchers used thiol group as an adsorbent for $[\text{AuCl}_4]^-$ ion with a better performance [2, 3, 6–9]. We have reported on the synthesis of the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticle core-shell modified with a thiol group. The $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticle core-shell preparation was performed by applying nonmagnetic stirring method. For improving adsorption capacity, modification with thiol group has been conducted. The thiol groups are of the soft bases.

On the other hand, the $[\text{AuCl}_4]^-$ ions are classified as weak acid species, thus provided specific interaction with each other based on Pearson's hard-soft acid-based concepts [10]. The adsorption kinetics, adsorption capacity, and interaction model for the adsorption of $[\text{AuCl}_4]^-$ ion in solution by $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticle core-shell adsorbent are reported. A recent review of the matter can be found elsewhere [11].

Figure 1 shows the schematic architecture of the magnetite-silica-functional groups. The core is magnetite to function as the important part for separation. The shell is silica, which can protect the magnetite from dissolution especially when it contacts with an acidic environment. Modification of the silica surface can be realized by silanization to give functional groups having an important function to react with the metal cations. The functional group must have a strong bond with the surface via complex formation.

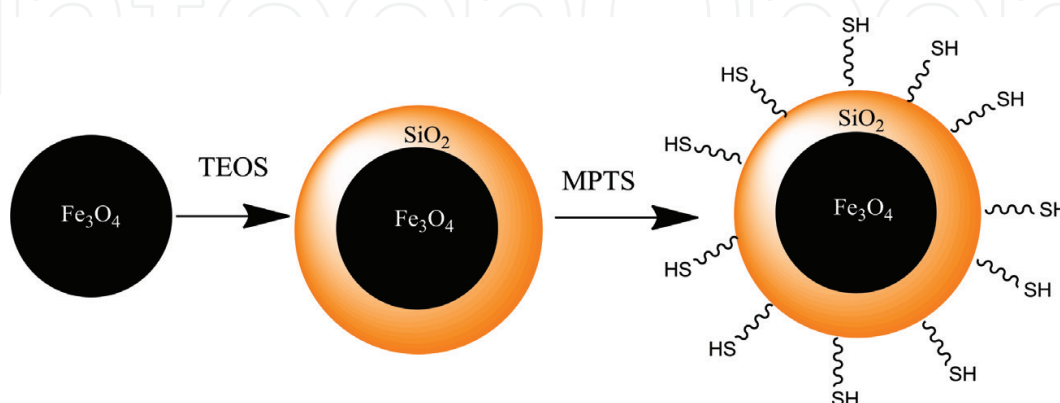


Figure 1. Step-by-step of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core-shell preparation and functionalization [3].

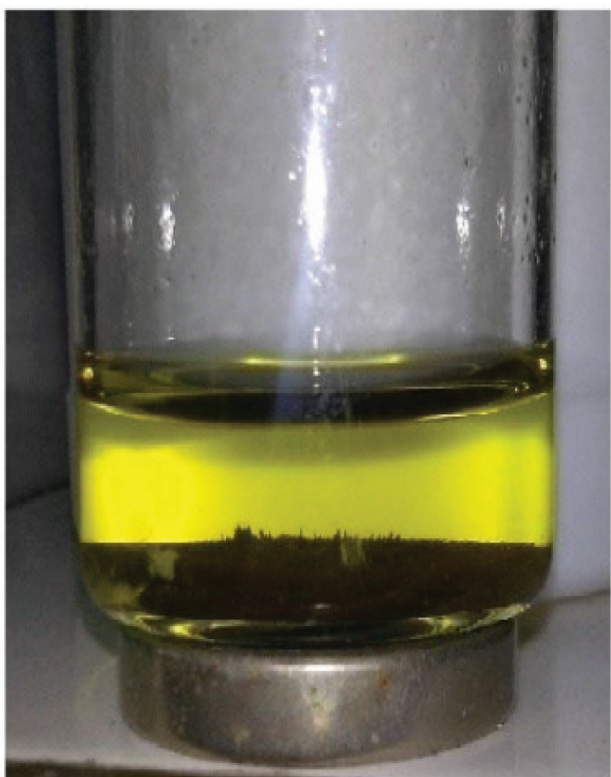


Figure 2. Image of simplified recovery technique of spent magnetic material after adsorption of precious metals [3].

Recovery of the magnetic material is key in the process following the adsorption. The spent adsorbent can be separated using a magnetic field. **Figure 2** shows how the used magnetic is separated by the external magnetic field. The magnetic adsorbent that has a high content of rare metals can be subject to dissolution and further separation. It is important to state that in the industrial purpose the powerful electromagnet system can be applied to do the job. In the purification, there are many possible green purification processes of metallurgy, starting from electrochemical separation to blast furnace.

2. Preparation of Fe_3O_4

Magnetite is commonly prepared by co-precipitation of Fe(II) and Fe(III) salts with suitable bases. Sodium hydroxide and ammonia are both commonly used in the preparation of magnetite. There are many bases that can be used to help control the size and the shape of the particles. Magnetite nanoparticles can be prepared in the presence of carboxylate such as laurate, palmitate, linoleate, and so on. The addition of surfactant helps reduce the particle size and control the shape. The required shape is usually spherical with a diameter of the nanoscale.

For co-precipitation methods, the size, shape, and composition of the resulting nanoparticles very much depend upon the following [12]:

- a. The type of precursors' salts used, for example, chloride, sulfate, perchlorate, or nitrate
- b. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio
- c. The mixing orders
- d. The mixing rates
- e. The reaction temperature
- f. The pH value
- g. The ionic strength of the media

The remaining issue is that magnetite nanoparticles are easily oxidized to maghemite, so this method is often used to obtain nanoparticles of magnetite and maghemite with the small size of 4–20 nm. Grüttner et al. have listed the size, coating, heating behavior, and magnetic properties of some iron oxide nanoparticles produced by this method [13]. Nanoparticles are produced by this method range in size from 4 to 45 nm. For fixed-synthesis conditions, the quality of the magnetite nanoparticles is very reproducible. Although co-precipitation is unquestionably the easiest process and highly scalable, it is not without issues. Controlling the shape is not easy, and the nanoparticles can be more varied in size than that produced in some other methods [12].

Precursors for the Fe(II) include ferrous sulfate, ferrous nitrate, and ferrous chloride. Some use ferrous acetate and ferrous oxalate. The most used precursor is ferrous sulfate. For the Fe(III), we can use ferric chloride, ferric nitrate, and so on. Ferric nitrate is used a lot. Ferric acetate and ferric oxalate are also commonly used as Fe(III) precursors.

The Fe(II) to Fe(III) molar ratio must be controlled strictly at 1:2. Therefore, the concentration of the starting material must be fixed. The oxidation of the Fe(II) ion must be contained by controlling the atmosphere by the use of inert atmosphere. During the co-precipitation, the nitrogen gas must be kept flowing to reduce possible oxidation process. Other noble gases could be used, which give a better magnetite product.

There are various ways to prepare Fe_3O_4 nanoparticles, such as hydrothermal synthesis [14], co-precipitation [15], microwave irradiation [16], oxidation of $\text{Fe}(\text{OH})_2$ by H_2O_2 [17], and microemulsion [18]. The Fe_3O_4 nanoparticles synthesized by a hydrothermal method in the presence of sodium sulfate have a particle size of 160 nm [14]. Among various ways to prepare Fe_3O_4 , hydrothermal is one of the simple methods because it gives unique characters. The shape and size of nanoparticles have a good homogeneity and high degree of crystallinity [19].

The widespread method to produce Fe_3O_4 is by co-precipitation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ solution mixture with a molar ratio of 1:2 in alkaline solution [15, 20]. The reaction for Fe_3O_4 formation by co-precipitation method is shown in chemical Eq. (1). Although this method is well known for synthesis Fe_3O_4 , the molar ratio of reactant, pH, and temperature still need attention to get the proper size and morphology [15]:



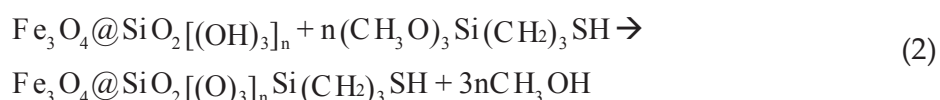
Microwave irradiation might be a promising method in processing materials due to its thermal and nonthermal effects. Microwave synthesis has the advantages of short reaction time, small particle size, and narrow size distribution. Aging under microwave irradiation in short period yields Fe₃O₄ nanoparticles with complete crystalline structure than those aged for 7 days at room temperature [16]. Yu et al. used H₂O₂ as an oxidizing agent to construct nano-sized superparamagnetic Fe₃O₄ powders with the size of 8–10 nm. The Fe(OH)₂ precipitates were partially oxidized to generate ultrafine Fe₃O₄ nanoparticles in the presence of surfactants [17]. Work on the control of the size of magnetite-silica via sol–gel method has also been reported [21].

Some researchers use capping agent to control crystal growth during Fe₃O₄ nanoparticle formation. Co-precipitation technique was used to prepare magnetite nanoparticles with diameter around 35 nm using 0.90 M NaOH solution as the precipitating agent and trisodium citrate as a capping agent. The precursors are ferric and ferrous chloride salts with predetermined Fe³⁺/Fe²⁺ molar ratio. The diameter of silica-coated magnetite nanoparticles synthesized by Stöber method was about 50 nm. Due to an electrostatic interaction between the Fe³⁺/Fe²⁺ ions of the Fe₃O₄ NPs and trisodium citrate surfactant, a stable magnetic fluid containing dispersed Fe₃O₄ NPs was produced [22]. A green and facile method for synthesis of magnetite nanoparticles was proposed [23]. Nano-sized polyhedral particles were synthesized by heating an aqueous solution of Fe²⁺, Fe³⁺, and urea at 85°C. The use of PVA in the synthesis system gives spherical magnetite nanoparticles with loose structure, unaggregated. The size of the microspheres can be tuned by changing the concentration of PVA. Upon addition of acetic acid to the system with PVA, microspheres with looser structure were produced. The size of the microspheres can further be tuned by changing the concentration of acetic acid. The co-precipitation of Fe²⁺ and Fe³⁺ in aqueous solutions under ultrasound irradiation results in smaller Fe₃O₄ NPs with a narrow size distribution (4–8 nm) than that produced without ultrasound irradiation [4]. Diethylene glycol (DEG) is also possibly used to control the particle size as reported earlier. This surfactant takes an important role in the preparation of magnetite/zinc oxide hybrid material [24].

3. Coating of Fe₃O₄ with SiO₂

The next step is coating magnetite with silica (SiO₂). It is usually performed via silanization reaction. The functional group that is ready to bond to iron oxide is methoxy silane (CH₃-O-Si-) or ethoxy silane (CH₃-CH₂-O-Si-). After the reaction, it forms a covalent bond of Fe-O-Si leaving the end group remains free. The leaving group is methane and ethane. The reaction is better to be done in an organic solvent. The silane group may have a spacer of long ethylene chain (-CH₂-). The ending of the silane may be carboxylic, an amine group, hydroxyl, and so on. The surface of the silica has different accesses to the organic functional groups [25].

For example, modification by the use of 3-mercaptopropyltrimethoxysilane (3-MPTS) [3] reaction is depicted as a chemical reaction (2). For further surface modification, we can use other silanization compounds [3]:



Iron oxide is not stable in acidic condition. After coating with silica, the magnetite core is usually stable in the acidic solution. It will come readily with a proton to give its corresponding ion either Fe^{2+} or Fe^{3+} . Dissolution of the magnetite will make the core-shell system unstable and break the bond between Fe-O-Si. To make sure that the magnetite is not dissolved in the acidic solution, we can test it by the use of an acid such as hydrochloric acid or nitric acid. The concentration of total iron as Fe^{2+} or Fe^{3+} can be an indicator if the magnetite is still strong. If high concentration of Fe^{3+} is found in the solution, we can say that the magnetite structure is collapsed and even broken down.

The visual indication can be seen from the color of the dispersion of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell. The solution of Fe^{3+} in the solution is pale yellow. If the dispersion color is pale yellow, it can be concluded that magnetite does dissolve. The color is getting dark when the more magnetite dissolved in the dispersion. A combination of atomic absorption spectrometry and visual observation helps us make sure the magnetite core is still strongly intact.

$\text{Fe}_3\text{O}_4/\text{SiO}_2$ core-shell nanoparticles were obtained by dispersing Fe_3O_4 into the mixture solution of 80 mL of ethanol, 20 mL of deionized water, and 1.0 mL of concentrated aqueous ammonia solution (28 wt.%). After this, the mixture solution was homogenized by ultrasonication for 30 min to form a uniform dispersion. Subsequently, a certain amount of tetraethoxysilane (TEOS) was added dropwise into the solution with vigorous stirring. After stirring at room temperature for 6 h, the product was separated with a magnet bar, washed with deionized water for three times, and dried in vacuum at 50°C for 12 h. A series of $\text{SiO}_2@\text{Fe}_3\text{O}_4$ particles were prepared with 1–9% SiO_2 content [26].

The silica coating used on a core particle has several advantages. The essential advantages of the silica coating compared with another inorganic (metal or metal oxide) or organic coating are as follows: It reduces the bulk conductivity and increases the suspension stability of the core particles. Also, silica is the most chemically inert material available; it can block the core surface without interfering in the redox reaction at the core surface [27]. There are two methods for coating Fe_3O_4 with silica, by acidic hydrolysis of silicate in aqueous solutions and the modified Stöber process [4, 28].

The Stöber method consists of the alkaline hydrolysis of tetraethyl orthosilicate (TEOS) in ethanol/water mixture in the presence of Fe_3O_4 NPs [28]. The Stöber process is applied to the classic sol–gel process [29]. The Stöber synthesis has the advantage of being easy to scale up for commercial applications and the possibility to effortlessly transfer the nanoparticles into aqueous solutions [30]. Some methods that lead to the synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ are shown in **Table 1**.

About the modification and application of magnetic materials, a coating of Fe_3O_4 by the use of various materials has been reported elsewhere. $\text{TiO}_2@\text{Fe}_3\text{O}_4$, $\text{TiO}_2@\text{Fe}_3\text{O}_4@\text{chitosan}$, and methyl pyrazolone-functionalized $\text{TiO}_2@\text{Fe}_3\text{O}_4@\text{chitosan}$ were prepared for photocatalytic degradation of dyes [32]. They found that the core is important for separation and the shell is an active catalyst. The degradation of dye using these catalysts can reach up to 98–99%.

Thioctic acid-modified silica-coated magnetite nanoparticles, $\text{RS-SR-NH-SiO}_2@\text{Fe}_3\text{O}_4$, have been prepared, and its ability for the recovery of Au(III) in aqueous solutions was evaluated [31]. The Au(III) adsorption capacity of the produced adsorbent is about 25 mg/g. The possible

Core		Shell	
Method	Precursors	Method	Basic reagent
Wet chemical reaction	$\text{FeCl}_3, \text{N}_2\text{H}_4$	Sol-gel	TEOS
Wet chemical reaction	$\text{FeCl}_3, \text{FeSO}_4$	Hydrolysis	Na_2SiO_3
Wet chemical reaction	$\text{FeCl}_3, \text{FeSO}_4$	Hydrolysis	Commercial SiO_2
A chemical reaction in microemulsion	$\text{FeCl}_3, \text{FeSO}_4$	Sol-gel reaction in microemulsion	TEOS

Table 1. Methods for synthesis of Fe_3O_4 coated with SiO_2 .

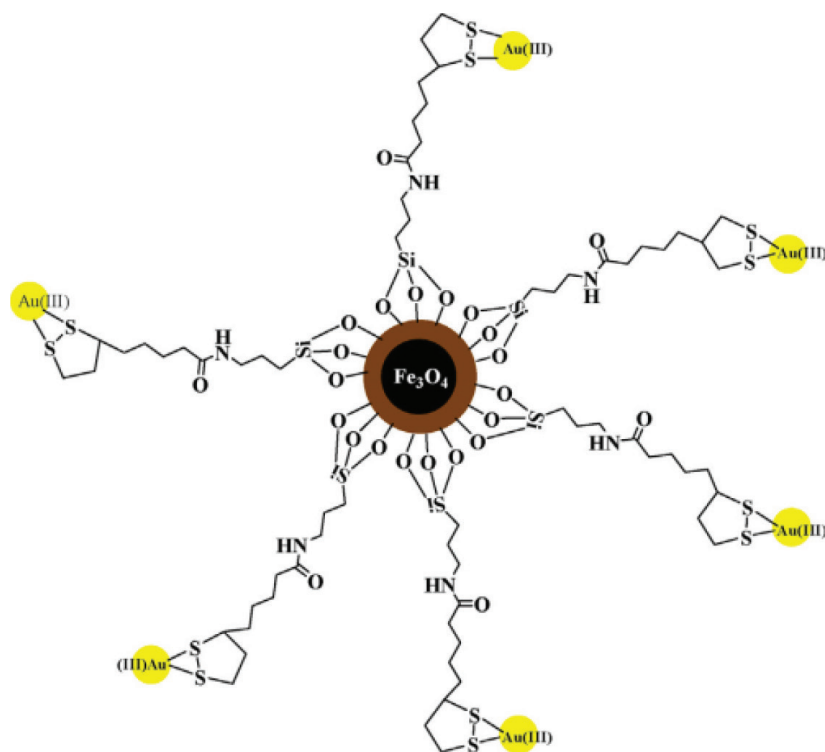


Figure 3. Possible interaction between $\text{RS-SR-NH-SiO}_2@\text{Fe}_3\text{O}_4$ and Au(III) ions [31].

interaction is shown in **Figure 3**. Another study shows the success of recovery of gold from copper anode slime by means of magnetite nanoparticles [33]. The surface of magnetite was also modified with oleic acid, methyl methacrylate, and ethylenediamine ($\text{EDA-MMA-OA}@\text{Fe}_3\text{O}_4$) giving the adsorption of indium of about 54 mg/g [34].

An interesting example of functionalization of Fe_3O_4 is by the use of dithiocarbamate, and it is applied as a magnetic nano-adsorbent for recovery of precious metal nanoparticles by contacting the nano-adsorbent with Au, Ag, Pd, or Pt hydrosols [35]. The magnetic particles are very efficient for Au due to strong affinity of sulfur-containing groups at the magnetite surfaces with this metal. Since Au colloids are used in laboratory and industrial contexts, the material could have an impact on the development of nanotechnology to recover precious

metals like Au [35] and Ag. Another trial is modification using chitosan and EDTA. It shows more selective for the quasi-precious metal of Cu than Cd and Pb [36].

4. Surface functionalization of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-X}$

In reaction (1), we can see the steps of surface modification of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell to form $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-X}$, where X is a functional group. The layer of SiO_2 was usually coated on the surface of Fe_3O_4 using the Stöber method. The prepared Fe_3O_4 nanoparticles were used as cores and dispersed in ethanol, and it was added to a three-neck round-bottom flask in ethanol and deionized water. The solution of the concentrated ammonia solution was added. After 15 min, TEOS was added dropwise in 10 min. The mixture was allowed for mechanical stirring for 8 h to perform the silica coating. The produced $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was separated and washed with deionized water and ethanol [37].

Direct modification by the use of organic compound is also studied, without first modification by silica. Magnetic nanoparticles modified with third-generation dendrimers followed by ethylenediaminetetraacetic acid (EDTA) were prepared and tested for their performance for recovery of precious metals that are Pd(IV), Au(III), Pd(II), and Ag(I) in the aqueous system [38]. It is interesting that high valence Pd(IV) and Au(III) exhibit relatively better adsorption efficiency than that of Pd(II) and Ag(I) with lower valence. It suggests that the adsorption of precious metals by this type of materials modified with EDTA is a function of valence. When the competing ion such as Zn(II) presents, the adsorption efficiency of the adsorbent for all four precious metals, which are Pd(IV), Au(III), Pd(II), and Ag(I), reduces much.

Magnetite nanoparticles could be directly modified with an organic compound of oleic acid. Iron oxide surface possibly bonds to carboxylic end of lauric acid [21]. However, this method of functionalization might not produce an acid-resistive magnetic adsorbent. The bond between lauric acid and magnetite could be easily damaged when the acidic solution is used. Therefore, the magnetite modified with lauric acid may find application in biological systems since both lauric acid and magnetite are biocompatible.

Silane compound such as (3-aminopropyl)trimethoxysilane (APTMS) could be used to coat magnetite nanoparticles. The product can be described as $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CH}_3\text{-NH}_2$. Further surface modification by alginate gives $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CH}_3\text{-NH}_2\text{-AA}$. The alginate forms the outer shell of the magnetite by electrostatic interaction with amine [39]. **Figure 1** shows a step-by-step extension of magnetite coating and functionalization. Silica coating will allow further functionalization via silanization, extension (additional of the spacer), and functional group attachment. The functional groups should be free to bond the metal ion either by an ionic or covalent coordination bond. Directed functional groups allow selective reaction with certain cation.

5. Characterization

Characterization of the magnetite can be done by at least five methods, which are vibrating sample magnetometer, powder X-ray diffraction, electron microscopy, elemental analysis,

and infrared (IR) spectroscopy. The vibrating sample magnetometer (VSM) can reveal the magnetic properties of the magnetic materials. The microscopic images can be obtained commonly by the use of scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). Nanomaterials are best to characterize by TEM and AFM. The IR spectroscopy is useful to detect the functional groups present on the magnetite surface. The IR spectroscopy is one of the methods to make sure that functionalization of the surface is successful.

For elemental analysis, a nondestructive energy dispersive X-ray spectrometry (EDS) can be used to estimate the chemical composition. The SEM is usually equipped with EDS system. The EDS results may lack precision and accuracy; however, it can detect the chemical composition in situ. The destructive methods such as atomic absorption spectrometry, UV-Vis spectrometry, and so forth may be used in place of EDS method. The destructive methods are usually not of choices for this type of materials.

One major analytical method in the magnetite characterization is powder X-ray diffraction. **Figure 4** shows the XRD patterns of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{SiO}_2$ solid nanoparticle core-shell. The Fe_3O_4 diffraction patterns have five main peaks at 2θ values of 30.1° , 35.5° , 43.3° , 57.1° , and 62.5° . The Fe_3O_4 has a cubic system as confirmed by JCPDS Card No. 88-0315. The magnetite phase can be detected with certainty by XRD. However, when it is coated with silica, the intensity of the XRD peaks will be much diminished since silica is an amorphous solid. Further decrease in the XRD is expected after organic modification on top of the silica layer.

The FT-IR could also be useful for more characterization of magnetic materials. It can offer details of the bond between the core, the shells, and the surface modifiers. Here is the example, the FT-IR spectra of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticle core-shell are presented in **Figure 5**. Both spectra have a broad peak at 586 cm^{-1} . The peak is attributed to the Fe-O stretching mode of magnetite. The peak at 3400 cm^{-1} is due to the O-H stretching mode. The sharp peak at 1100 cm^{-1} can be attributed to the Si-O-Si stretching mode. The Si-O bending vibration

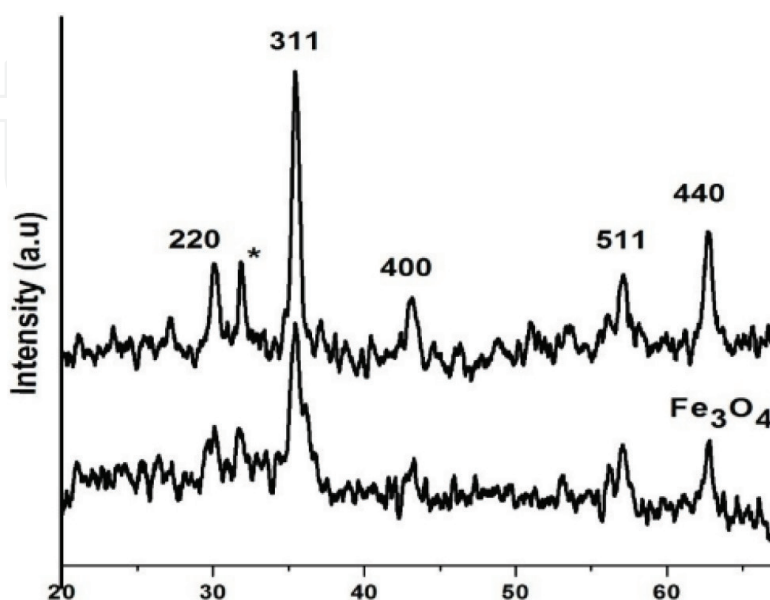


Figure 4. XRD patterns of Fe_3O_4 (top) and $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticle core-shell modified with a thiol group (bottom) [3].

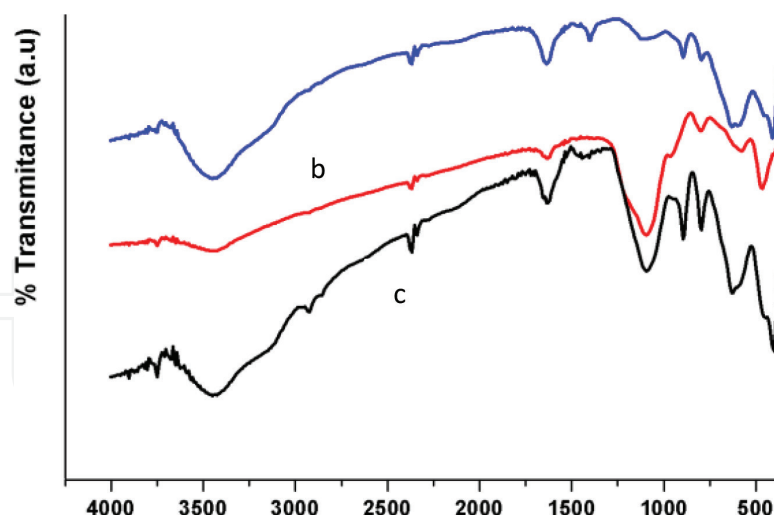


Figure 5. FT-IR spectra of resulted Fe_3O_4 (a), $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticle core-shell (b), and $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticle core-shell modified with a thiol group (c) [3].

mode of the silanol group is seen at 964 cm^{-1} . It indicates that the silica has coated well the outer surface of Fe_3O_4 particles [3]. The surface modification of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles by thiol groups can give a better interaction with $[\text{AuCl}_4]^-$ ions in the solution. The FT-IR spectra of the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticle core-shell after modification with thiol group are shown in **Figure 5**. The peak at 686 cm^{-1} is attributed to the C-S bending vibration mode. The peak at near $2570\text{--}2590\text{ cm}^{-1}$ is attributed to the stretching vibration mode of S-H. The S-H stretching vibration mode is not usually detected [2]. The band at around $2850\text{--}2900\text{ cm}^{-1}$ is due to the stretching vibration of C-H of methylene. This result suggests that the surface modification of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticle core-shell is successful.

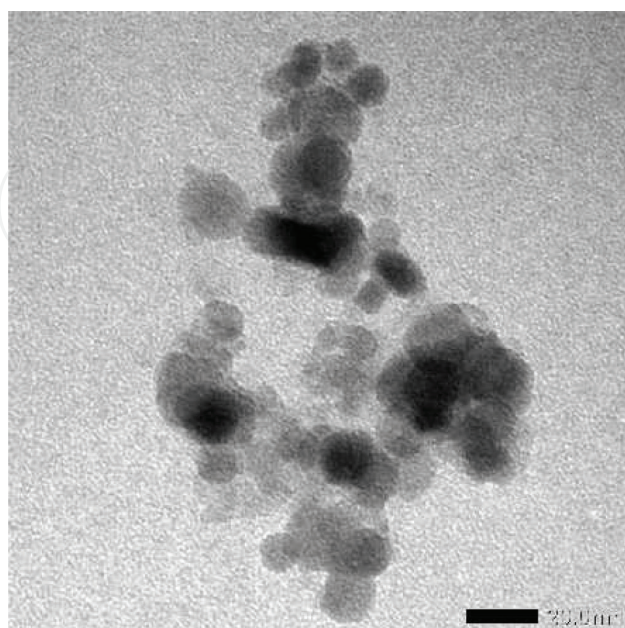


Figure 6. TEM image of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticle core-shell [3].

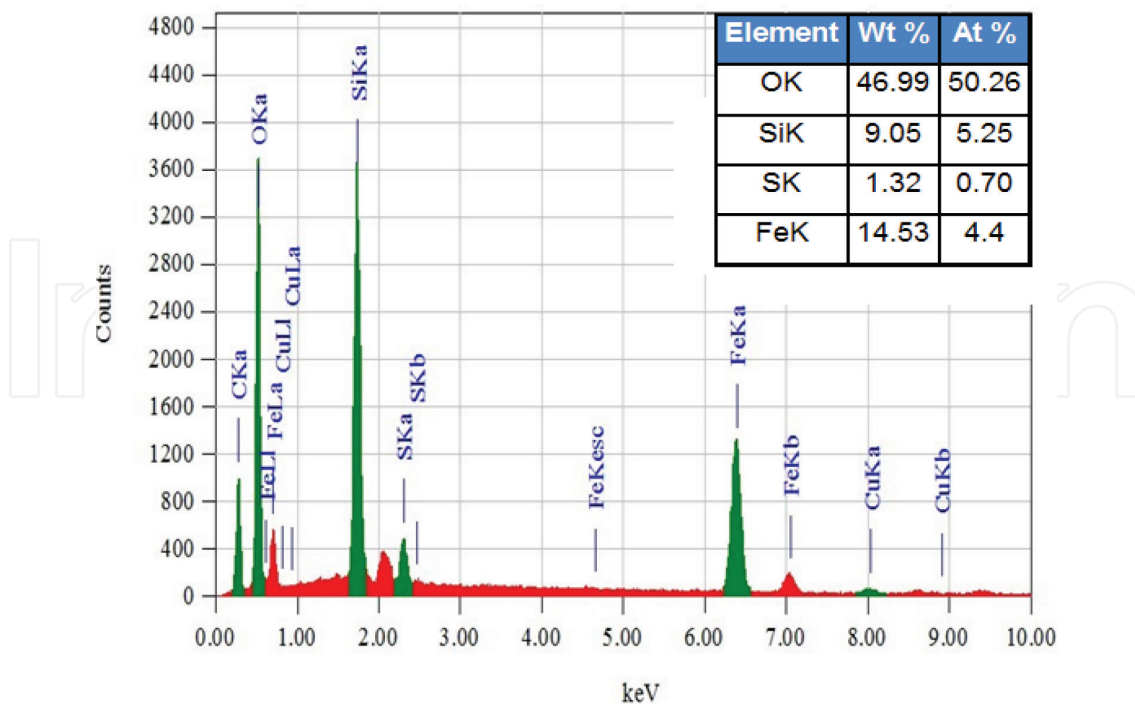


Figure 7. EDX spectra of Fe₃O₄/SiO₂ nanoparticles modified with thiol group [3].

The covering of Fe₃O₄ nanoparticle core-shell by using silica does not only protect the magnetite core from dissolution in acid but also control the agglomeration of Fe₃O₄ particles. Silica acts as a capping agent for each Fe₃O₄ nanoparticle to form Fe₃O₄/SiO₂ core-shell. **Figure 6** shows the TEM images of Fe₃O₄/SiO₂ nanoparticle core-shell. The Fe₃O₄/SiO₂ nanoparticle core-shell has a size of approximately 10–20 nm. The size of Fe₃O₄/SiO₂ core-shell can be observed. These results prove that the synthesis of Fe₃O₄/SiO₂ nanoparticle core-shell is successful.

In situ analysis of adsorbent is preferable to understand the chemical composition of the product without a change in its nature. **Figure 7** shows the EDX spectra of modified Fe₃O₄/SiO₂ solid nanoparticle core-shell. The sulfur content is 1.32% (w/w). It suggests that thiol group is present on the surface of Fe₃O₄/SiO₂ nanoparticle core-shell material. It confirms the FT-IR spectra. The modification of Fe₃O₄/SiO₂ solid nanoparticle core-shell by 3-MPTS will give free thiol groups on the nanoparticles' surface. The thiols are expected to form covalent coordination bond with the target ion.

The EDX may also give details of atomic mapping across the sample, especially that of the functional group. For example, sulfur atom in the thiol group is mapped by the EDX method nicely. Functional groups such as amine, thiol, sulfonate, and phosphate may be better detected by EDX rather than destructive methods such as UV-Vis spectrophotometry.

6. Adsorbent performance

Table 2 shows a comparison of adsorbent performance for adsorption of precious metals especially gold and palladium [3, 38]. The first two rows show the adsorption performance of

Adsorbents	Adsorption capacity (mg/g)			Reference
	Au(III)	Pd(II)	Ag(I)	
Magnetite nanoparticles/thiolated	115	—	—	[3]
Magnetite nanoparticles/dendrimer	3.58	2.71	—	[38]
Magnetite nanoparticles/thiourea	118.5	111.6	—	[40]
Magnetite nanoparticles/chitosan	709.2	—	226.5	[41]
Magnetite nanoparticles/chitosan	59.5	—	—	[42]
Primary amine-lignin	384	40.43	—	[43]
Ethylenediamine-lignin	606.76	22.66	—	[43]

Table 2. Comparison of adsorption capacities (q_{\max}) of some adsorbents for selected precious metals from aqueous solution. Data presented here are based on the Langmuir isotherm.

magnetic material modified with thiol and dendrimers. It shows that functionalization of the magnetite is very important to increase the adsorption capacity. Thiol group on the surface of magnetite produces high affinity toward Au(III). As we know, thiol can strongly react with gold to form a covalent bond. However, the adsorption capacity of magnetite is still far below that of adsorbent produced by the use of lignin as a precursor.

An adsorbent of magnetic nanoparticles modified by thiourea for effective and selective adsorption of precious metals like gold(III), palladium(II), and platinum(IV) in aqueous acid solution has also been reported. It needs contact time of less than 30 min to reach maximum capacity. Its maximum adsorption capacity of precious metals as determined by Langmuir model was 43.34, 118.46, and 111.58 mg/g for Pt(IV), Au(III), and Pd(II), respectively, at pH 2 and 25°C [40]. The adsorption is selective for Au(III) even in the presence of high concentrations of interfering ion Cu(II). The recycling was achieved by the use of a solution containing 0.7 M thiourea and 2% HCl. The result of the adsorption–desorption test shows that the adsorbent is reusable for the recovery of precious metals.

In general, the adsorption capacity of the magnetite-based adsorbent can reach up to 118.46 mg/g, which is very promising. It may still be less than that of lignin derivatives. For chitosan-modified magnetite, it even can reach the capacity for gold(III) of 707 mg/g [41]. The core-shell-modifier based adsorbent may not have such a high adsorption capacity. The modification step was done through the reaction between chitosan and polymeric Schiff's base of thiourea/glutaraldehyde in the presence of magnetite.

After adsorption test, desorption of the adsorbed cation must also be examined. Complete desorption of the adsorbed cation indicates a better adsorbent performance. In most cases, the acids can desorb adsorbed ion from the surface. The desorption process may use strong acids such as HCl, H_2SO_4 , and HNO_3 . The cation is believed to form complex coordination bonds with the surface, and leaching them is difficult.

On the other hand, application of concentrated acid solution may damage the structure of adsorbent. Therefore, mildly acidic solutions are usually employed to release the cation from

the adsorbent's surface. People use a complexing agent to release the adsorbed metal cations. Thiourea and EDTA are of important environmentally friendly complexing agents.

Thiourea solution in 1 M HCl was employed to liberate $[\text{AuCl}_4]^-$ ions that had been adsorbed by the material [3]. Thiourea has a better affinity than that of thiol and amine groups. It can form a complex ion with $[\text{AuCl}_4]^-$ ion to dissolve back into the solution. According to the HSAB theory, both thiol and $[\text{AuCl}_4]^-$ ion are among the weak bases. A strong coordination bond forms between thiourea and $[\text{AuCl}_4]^-$ ion.

Figure 8 depicts the curve of desorption of $[\text{AuCl}_4]^-$ ion by thiourea in 1 M HCl solution at various concentrations following adsorption by the magnetite modified with a thiol group. Dilute thiourea solution can only desorb 43 mg/g $[\text{AuCl}_4]^-$ ion of initially adsorbed 68 mg/g or 60% of the total $[\text{AuCl}_4]^-$ ions bond to the surface. **Figure 9** displays schematic adsorption

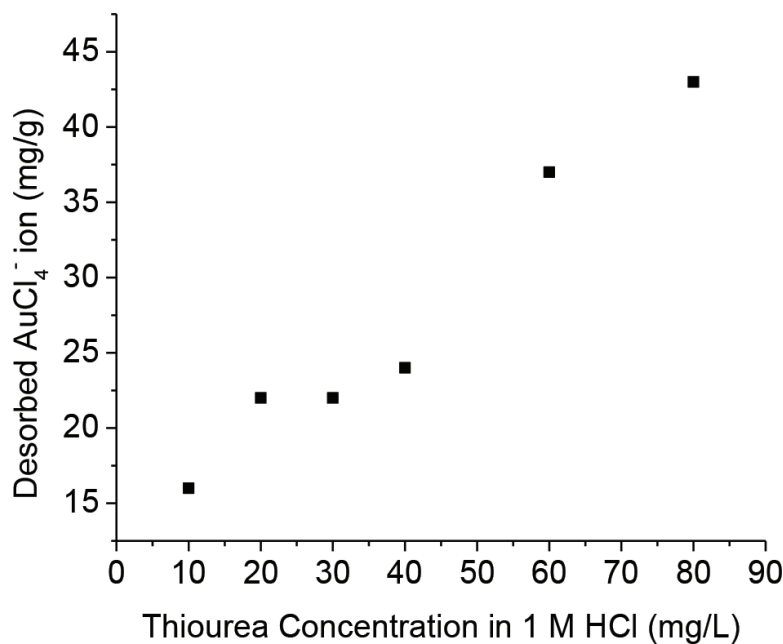


Figure 8. Profile of $[\text{AuCl}_4]^-$ ion desorption by HCl/thiourea at various concentration [3].

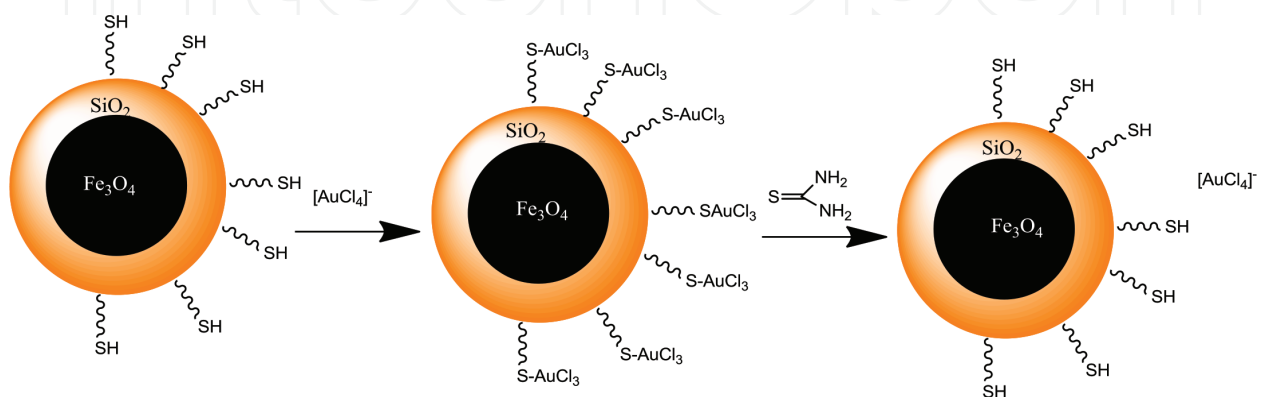


Figure 9. Adsorption and desorption of $[\text{AuCl}_4]^-$ ions by magnetite nanoparticles modified with a thiol group [3].

of $[\text{AuCl}_4]^-$ ion by magnetite modified with a thiol group and desorption. The desorption is done by applying thiourea in HCl solution. The concentration of the thiourea is low. The thiol group may form a covalent coordination bond with $[\text{AuCl}_4]^-$ ion on the adsorbent surface.

7. Summary

Modified magnetic adsorbents have been synthesized and used in the recovery of precious metals from aqueous solutions. Among the magnetic materials, magnetite is studied widely. Surface modification of nanoscale magnetite core is crucial to have a better adsorption capacity, stability, and turnover. The key issues of the magnetic adsorbent include size and shape of the core, choice of surface modification, adsorption capacity, stability, and recyclability. The size of the magnetite core is also better if it is in the nanoscale rather than in micron scale. It will improve the contact between pursued ions and adsorbent surface. The surface modification must have a good affinity toward certain precious metal cations. Many researchers attempt to combine adsorption capability and magnetic properties of the magnetite-based adsorbent for certain metal recovery from the solution. Selective adsorbents are also of interest for separation of precious metals from a complex system such as industrial waste. Adsorption selectivity is highly considered for complex matrices. Magnetite core has low stability in strongly acidic aqueous media. Coating with silica has two advantages, for protection against the acidic environment and a binding site for further functionalization. A suitable modification of the magnetic particles by coating or functionalization using inorganic components or organic molecules is usually needed.

The synthesis of magnetite as the core material has been established. The use of salts of Fe(II) and Fe(III) with careful stoichiometric calculation is a must. The pH of the magnetic formation should also be controlled, either by the use of sodium hydroxide or ammonia solution. In many cases, ammonia can give better homogeneous particles. It may be better to add a stabilizing agent for reducing aggregation of the magnetite nanoparticle and improve the stability of the colloid. Coating of magnetite with silica has also been well understood. TEOS and TMOS are the main choices for the outer shell of the magnetite, although sodium silicate may work. Silica is a preferable coating since it is resistant to acid and base, which will protect the magnetite core.

The final surface modification is functionalization of the silica with ligands that will strongly bind the cations. The end of the modification chain must have a special interaction with the cations, especially through coordination bonds. The functional groups could be an amine, carboxylate, thiol, sulfonate, amide, hydroxyl, and so on. Based on reagent availability, the functional groups determine the selectivity toward certain precious metal cations.

The release of the adsorbed metal cations after being concentrated in the adsorbent can be realized using acids and strong complexing agents. The acids are usually not desirable since they can cause the magnetite core to dissolve. Dissolution will damage the structure of the magnetite, which may not be possible to reuse. Complexing agents such as thiourea and EDTA can give a better option to minimize the damage to the magnetite-based adsorbents.

Purification of the recovered metals may be done through well-known processes. Electrochemical process is the best choice of metallurgy. Other methods by the use of chemical reduction could also be selected. In the large scale, we can consider blast furnace combined with a redox reaction. One important point to consider, the use of environmentally friendly reprocessing of the metals must always be prioritized.

8. Future recommendation and direction

The conventional metal reprocessing uses chemicals that are not environmentally friendly. The magnetite-based adsorbents offer technology that can reduce the application of toxic chemicals. The adsorbents give the possibility to reduce, reuse, and recycle for a few times. The magnetic core of the adsorbent is also readily synthesized with environmentally benign precursors. The coating with silica protects against acid and base media during application and recycle. The silica coating can also facilitate the attachment of the functional groups, which is critical in the modification step.

The current advanced electronic devices utilize the precious metals in their important components. The waste of electronic devices grows rapidly along with an increase in smartphone and PC use. Computer parts like processors, memories, motherboards, hard drives, and CD/DVD drives contain gold and other precious metals such as silver, palladium, and so on. The conventional gold recovery process uses cyanide ions for complex ion formation and electrolysis. The current technology attempts to recover gold and other precious metals from computers' and smartphones' components by utilizing magnetite nanoparticles. The new magnetic materials are effective yet environmentally friendly to recover precious metals. The magnetic adsorbents could also be the future of reclaiming precious metals from the waste of the other industries.

In the magnetic adsorbent development, the magnetite core could be possibly substituted with other oxides of transition metals such as manganese, cobalt, or nickel if they maintain strong magnetic characters. However, silica is the main choice for easy coating of the magnetic core, which also helps protect the magnetic core from dissolution in the acidic and basic media. The presence of the ligands on the surface of the magnetite-silica core-shell is critical for adsorption process. The environmentally safe polymers and simple molecules may be used to facilitate coordination bond with the target cations. The desorption process must be done using suitable solutions. The solution for desorption should leave the adsorbent in good shape for further reuse and turnover. The present technology available for purification of the recovered metals may apply electrochemical, chemical, and thermal processes.

Symbols and abbreviations

AFM	atomic force microscopy
APTMS	aminopropyl trimethoxysilane

DEG	diethylene glycol
EDTA	ethylenediamine tetraacetate
EDA-MMA-OA	ethylenediamine, methyl methacrylate, and oleic acid
EDX	energy dispersive X-ray spectroscopy
JCPDS	Joint Committee on Powder X-ray Diffraction Standards
MPTS	mercaptopropyltrimethoxysilane
NPs	nanoparticles
PVA	polyvinyl alcohol
q_e	maximum capacity of adsorbent (mg/g)
SEM	scanning electron microscopy
TEOS	tetraethyl orthosilicate
TEM	transmission electron microscopy
VSM	vibrating sample magnetometer

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References

- [1] Haw CY et al. Hydrothermal synthesis of magnetite nanoparticles as MRI contrast agents. *Ceramics International*. May 2010;**36**(4):1417-1422
- [2] Zhang S et al. Thiol modified $\text{Fe}_3\text{O}_4@\text{SiO}_2$ as a robust, high effective, and recycling magnetic sorbent for mercury removal. *Chemical Engineering Journal*. Jun. 2013;**226**:30-38
- [3] Roto R, Yusran Y, Kuncaka A. Magnetic adsorbent of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles modified with thiol group for chlorauric ion adsorption. *Applied Surface Science*. 2016;**377**:30-36
- [4] Morel A et al. Sonochemical approach to the synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ Core-Shell nanoparticles with tunable properties. *ACS Nano*. 2008;**2**(5):847-856

- [5] El-kharrag R, Amin A, Greish YE. Low temperature synthesis of monolithic mesoporous magnetite nanoparticles. *Ceramics International*. Jan. 2012;**38**(1):627-634
- [6] Lin J, Lai Q, Liu Y, Chen S, Le X, Zhou X. Laccase–Methacryloyl functionalized magnetic particles: Highly immobilized, reusable, and efficacious for methyl red decolourization. *International Journal of Biological Macromolecules*. 2017;**102**:144-152
- [7] Peng L et al. Modifying Fe_3O_4 nanoparticles with humic acid for removal of Rhodamine B in water. *Journal of Hazardous Materials*. 2012;**209-210**:193-198
- [8] Nigam S, Barick KC, Bahadur D. Development of citrate-stabilized Fe_3O_4 nanoparticles: Conjugation and release of doxorubicin for therapeutic applications. *Journal of Magnetism and Magnetic Materials*. 2011;**323**(2):237-243
- [9] Zhang JM, Zhai SR, Zhai B, Da An Q, Tian G. Crucial factors affecting the physicochemical properties of sol-gel produced $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ core-shell nanomaterials. *Journal of Sol-Gel Science and Technology*. 2012;**64**(2):347-357
- [10] Hakami O, Zhang Y, Banks CJ. Thiol-functionalised mesoporous silica-coated magnetite nanoparticles for high efficiency removal and recovery of hg from water. *Water Research*. 2012;**46**(12):3913-3922
- [11] Aghaei E, Alorro R, Encila A, Yoo K. Magnetic adsorbents for the recovery of precious metals from leach solutions and wastewater. *Metals (Basel)*. 2017;**7**(12):529
- [12] Narayan R editor. *Nanobiomaterials: Nanostructured Materials for Biomedical Applications, Magnetic Nanoparticle Synthesis*. Amsterdam: Elsevier Ltd; 2017. Chapter 8. p. 197-229
- [13] Grüttner C, Müller K, Teller J, Westphal F. Synthesis and functionalisation of magnetic nanoparticles for hyperthermia applications. *International Journal of Hyperthermia*. 2013;**29**(8):777-789
- [14] Ni S et al. Hydrothermal synthesis of Fe_3O_4 nanoparticles and its application in lithium ion battery. *Materials Letters*. 2009;**63**(30):2701-2703
- [15] Valenzuela R et al. Influence of stirring velocity on the synthesis of magnetite nanoparticles (Fe_3O_4) by the co-precipitation method. *Journal of Alloys and Compounds*. Nov. 2009;**488**(1):227-231
- [16] Mahmoud ME, Amira MF, Zaghloul AA, Ibrahim GAA. Microwave-enforced sorption of heavy metals from aqueous solutions on the surface of magnetic iron oxide-functionalized-3-aminopropyltriethoxysilane. *Chemical Engineering Journal*. 2016;**293**:200-206
- [17] Yu LQ, Zheng LJ, Yang JX. Study of preparation and properties on magnetization and stability for ferromagnetic fluids. *Materials Chemistry and Physics*. 2000;**66**(1):6-9
- [18] Zhang DE, Tong ZW, Li SZ, Zhang XB, Ying A. Fabrication and characterization of hollow Fe_3O_4 nanospheres in a microemulsion. *Materials Letters*. 2008;**62**(24):4053-4055
- [19] Zhang H, Zhu G. One-step hydrothermal synthesis of magnetic Fe_3O_4 nanoparticles immobilized on polyamide fabric. *Applied Surface Science*. 2012;**258**(11):4952-4959

- [20] Liao M-H, Chen D-H. Preparation and characterization of a novel magnetic nano-adsorbent. *Journal of Materials Chemistry*. 2002;**12**(12):3654-3659
- [21] Mahdavi M et al. Synthesis, surface modification and characterisation of biocompatible magnetic iron oxide nanoparticles for biomedical applications. *Molecules*. 2013;**18**(7):7533-7548
- [22] Khosroshahi ME, Ghazanfari L. Preparation and characterization of silica-coated iron-oxide bionanoparticles under N₂ gas. *Low-dimensional systems and nanostructures*. 2010;**42**(6):1824-1829
- [23] Yang C, Yan H. A green and facile approach for synthesis of magnetite nanoparticles with tunable sizes and morphologies. *Materials Letters*. 2012;**73**:129-132
- [24] Feng X, Guo H, Patel K, Zhou H, Lou X. High performance, recoverable Fe₃O₄ ZnO nanoparticles for enhanced photocatalytic degradation of phenol. *Chemical Engineering Journal*. 2014;**244**:327-334
- [25] Habila MA, Alothman ZA, El-Toni AM, Labis JP, Soylak M. Synthesis and application of Fe₃O₄@SiO₂@TiO₂ for photocatalytic decomposition of organic matrix simultaneously with magnetic solid phase extraction of heavy metals prior to ICP-MS analysis. *Talanta*. 2016;**154**:539-547
- [26] Liu H, Jia Z, Ji S, Zheng Y, Li M, Yang H. Synthesis of TiO₂/SiO₂@Fe₃O₄ magnetic microspheres and their properties of photocatalytic degradation dyestuff. *Catalysis Today*. 2011;**175**(1):293-298
- [27] Ghosh Chaudhuri R, Paria S. Core/shell nanoparticles: Classes, properties, synthesis mechanisms, characterization, and applications. *Chemical Reviews*. 2012;**112**(4):2373-2433
- [28] Stober W, Fink A. Controlled growth of Monodispersed silica spheres in the Micron size range. *Journal of Colloid and Interface Science*. 1968;**26**:62-69
- [29] Liu J et al. Extension of the stöber method to the preparation of monodisperse resorcinol-formaldehyde resin polymer and carbon spheres. *Angewandte Chemie, International Edition*. 2011;**50**(26):5947-5951
- [30] Gholami T, Salavati-niasari M, Bazarganipour M. Superlattices and microstructures synthesis and characterization of spherical silica nanoparticles by modified Stöber process assisted by organic ligand. *Superlattices and Microstructures*. 2013;**61**:33-41
- [31] Abd Razak NF, Shamsuddin M, Lee SL. Adsorption kinetics and thermodynamics studies of gold(III) ions using thioctic acid functionalized silica coated magnetite nanoparticles. *Chemical Engineering Research and Design*. 2018;**130**:18-28
- [32] Abdelwahab NA, Morsy EMH. Synthesis and characterization of methyl pyrazolone functionalized magnetic chitosan composite for visible light photocatalytic degradation of methylene blue. *International Journal of Biological Macromolecules*. 2018;**108**:1035-1044
- [33] Ranjbar R, Naderi M, Omidvar H, Amoabediny G. Gold recovery from copper anode slime by means of magnetite nanoparticles (MNPs). *Hydrometallurgy*. 2014;**143**:54-59

- [34] Chiou CS, Chuang KJ, Chen HW, Chen YC. Magnetite modified with amine polymer to adsorb indium ions. *Powder Technology*. 2015;**279**:247-253
- [35] Lopes JL, Marques KL, Girão AV, Pereira E, Trindade T. Functionalized magnetite particles for adsorption of colloidal noble metal nanoparticles. *Journal of Colloid and Interface Science*. 2016;**475**:96-103
- [36] Ren Y, Abbood HA, He F, Peng H, Huang K. Magnetic EDTA-modified chitosan/ SiO_2 / Fe_3O_4 adsorbent: Preparation, characterization, and application in heavy metal adsorption. *Chemical Engineering Journal*. 2013;**226**:300-311
- [37] Habila MA, Alothman ZA, El-Toni AM, Labis JP, Soylak M. Synthesis and application of $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{TiO}_2$ for photocatalytic decomposition of organic matrix simultaneously with magnetic solid phase extraction of heavy metals prior to ICP-MS analysis. *Talanta*. 2016;**154**:539-547
- [38] Yen CH, Lien HL, Chung JS, Der Yeh H. Adsorption of precious metals in water by dendrimer modified magnetic nanoparticles. *Journal of Hazardous Materials*. 2017;**322**: 215-222
- [39] Yang L et al. Modification and characterization of Fe_3O_4 nanoparticles for use in adsorption of alkaloids. *Molecules*. 2018;**23**:562
- [40] Lin TL, Lien HL. Effective and selective recovery of precious metals by thiourea modified magnetic nanoparticles. *International Journal of Molecular Sciences*. 2013;**14**(5): 9834-9847
- [41] Donia AM, Atia AA, Elwakeel KZ. Recovery of gold(III) and silver(I) on a chemically modified chitosan with magnetic properties. *Hydrometallurgy*. 2007;**87**(3-4):197-206
- [42] Chang YC, Chen DH. Recovery of gold(III) ions by a chitosan coated magnetic nano-adsorbent. *Gold Bulletin*. 2006;**39**(3):98-102
- [43] Parajuli D, Kawakita H, Inoue K, Funaoka M. Recovery of gold(III), palladium(II), and platinum(IV) by aminated lignin derivatives. *Industrial and Engineering Chemistry Research*. 2006;**45**(19):6405-6412

