Original article

Synthesis and characterization of molecularly imprinted magnetite nanomaterials as a novel adsorbent for the removal of heavy metals from aqueous solution

Irshad Ahmad a,b,*, Weqar Ahmad Siddiqui a, Tokeer Ahmad b

a Department of Applied Science & Humanities, Faculty of Engineering & Technology, Jamia Millia Islamia University, New Delhi, 110025, India
b Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia University, New Delhi, 110025, India

ARTICLE INFO

Article history:
Received 17 July 2019
Accepted 18 July 2019
Available online 9 August 2019

Keywords:
EDTA
MI magnetite nanomaterials
SEM–EDX
FT-IR
VSM
Adsorption isotherm

ABSTRACT

For simultaneous water purification from both inorganic and organic pollutants, a novel multifunctional hybrid nanoadsorbent has been produced. Molecularly imprinted (MI) magnetic submicron-particles with iron oxide core and silica shell (Fe3O4/SiO2) were used as a substrate for immobilization of different functions. The activity towards heavy metals was provided via attachment of ethylene diamine tetra acetate (EDTA) silica-coated magnetite nanomaterials; then their use in the immobilization of MI magnetite nanomaterials (Fe3O4/SiO2/Thermosensitive/EDTA-CS) to the silica surface with subsequent chemical grafting of ethylene diamine tetra acetate (EDTA) on which coupling occurred via an chitosan bonding. XRD spectra revealed the cubic spinel nature of nanoparticles with an average particle size 20 nm and have phase stability besides. In addition to this, monodispersity of the nanoparticles was confirmed due to the size distribution of the particles. The EDX study also established the elemental ratio of EDTA functionalized silica coated magnetite nanoparticles (Fe3O4/SiO2/Thermosensitive/EDTA-CS). FT-IR spectral analysis revealed that the successful grafting of –COOH functional groups from EDTA on the surface of silica coated magnetite nanoparticles. Magnetic properties are found to be super paramagnetic at room temperature analyzed by VSM. The functionalization of EDTA on the surface of silica coated magnetite nanoparticles provides –COOH group and –NH2 group to be bonded with heavy metals from contaminated water by physicochemical interactions (physisorption and chemisorption). The effects of the adsorption process were studied with these parameters such as pH, contact time, adsorbent dose, temperature, and initial concentration (heavy metals). The Langmuir, Freundlich and Temkin adsorption isotherm models were applied to describe equilibrium data. The desorption study, as well as its reusability and recyclability, were accessible that indicates magnetite nanocomposites succeeding adequately.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

* Corresponding author.
E-mails: irshadahmad85@gmail.com, irs_chimisteetfrancais@yahoo.com (I. Ahmad).
https://doi.org/10.1016/j.jmrt.2019.07.034
2238-7854/© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
1. Introduction

Development of novel multifunctional nanoadsorbents for water remediation, both from organic and inorganic components, is a very important task for modern science and technology [1,2]. Recently, a number of adsorbents that are effective against some toxic metals and organic pollutants have been proposed [3,4]. Some of them are magnetic, and related to “green”, eco-friendly nanomaterials [5,6]. Unfortunately, no effective “green” nanomaterials have been reported so far for simultaneous removal of both organic and inorganic pollutants from water solutions [7-9].

Heavy metals are a class of promising environmental pollutants which is widely used as essential elements in both human and veterinary organisms [10]. The presence of heavy metals in the environment has been a major topic of concern recently. These heavy metals are released into aquatic environments by different ways, including domestic wastewater, hospital discharges, improper manufacturer disposal and sewage treatment plants also [11,12]. Compared with domestic sewage, hospital effluents generally exhibit higher detection frequencies and concentrations of heavy metals [13]. Heavy metals are being released in the aquatic environment since it is well-known for being non-biodegradable during conventional wastewater treatments [14]. The presence of these metals in the aquatic environment is worrying due to its known toxicity, endocrine disruption effects and bioaccumulation potential [15].

Molecularly imprinted (MI) magnetite nanomaterials have been extensively used due to its scientific aspects and technological curiosity also shown enormous potential in environmental application apart from such type of applications in biomedicine, drug designs, molecular imaging, biosensing, electro-optics, electronics (conductors and semiconductors), drug delivery, etc. [16-18]. The unique features of molecularly imprinted nanoparticle (MI-Fe₃O₄) and its surface modified with inorganic/organic moieties are associated with its high surface area to volume ratio, biodegradable, biocompatible, non-toxic easy to synthesize and renewable; readily isolated from solutions by the application of an external magnetic field [19-23]. The major advantages of these nanomaterials (MI-Fe₃O₄) for purification of water which is absolutely dependent in fact that they do not retains magnetism, after the removal of external magnetic field; therefore, that they have been widely investigated (especially magnetite and its composites) in industrial applications, as a combination of adsorption and magnetic carrier technology (MCT) [24,25].

Several promising options for the removal of toxins (heavy metals) from the water are accessible, and many technologies such as ozonation, nanofiltration, reverse osmosis, oxidation and adsorption are employed [26]. Amongst various predictable methods to eliminate contaminants from aqueous solution, only adsorption method [27] is the most versatile and widely used; as a capable one for the removal of toxins (heavy metals) from wastewater due to its aspects having less expensive, more-efficient and feasibility, also especially easily-facile operational method. So far, various types of adsorbents such as activated carbon, clay minerals, chelating materials, chitosan or natural zeolites have been developed as a sorbents to eliminate toxins from aqueous solution [28]. Although traditional sorbents could adsorb heavy metals from aqueous solution but problem is that their sorption capacities and efficiency limits their application at commercial level [29]. Recently, the magnetic nanoparticles have been used in the treatment of wastewater because of their main advantages like easier manipulation of the adsorbent by an external magnetic field, fast kinetics, small particle sizes and high surface areas [30]. Unfortunately, the susceptibility to auto-oxidation, tendency to agglomerate and concerns over its toxicity are the main challenges in real life water treatment applications of bare magnetite nanoparticles [31,32]. The coating of silica can lead to its stability, and easily functionalized of it to adsorb highly selective pollutants with a wide range of small organic ligands and also large macromolecules using surface modification techniques [33]. Also, considering their combined advantages, thermo sensitive polymeric adsorbents are of particular interest [34]. At temperatures lower that of the LCST (lower critical solution temperature) which is considered as the threshold temperature, the thermosensitive polymeric adsorbent is soluble in water [35]. Above the LCST, it converts to a non-soluble state, rendering more favourable polymer–water separation [36].

There is a solid solution to overcome these problems in the form of nanomaterials, which were used as a novel and potential substitute to eradicate heavy toxic metals from waste water. Nanomaterials with particle size 1–100 nm exhibiting exclusive physico-chemical properties have been comprehensively investigated over a decade’s [37]. Contemporary succession in nanoscience and nanotechnology [38] has been shown a significant prospective for the remediation of ecological dilemmas. Nano-structured sorbents [39] are far better to predictable sorbents in terms of more efficiency and more feasibility of separation of contaminants from the waste water due to their novel size-shape dependent possessions. Generally most of the dissolved contaminants have repellant and thus could not take action to external applied magnetic field. Molecularly imprinted (MI) magnetite nanomaterials [40] with bulky surface area as well as distinctive magnetic properties in addition to its surface customized throughout particular functional ligands with affinities for target contaminants which were bonded with these ligands have feasible application in removal of contaminants from aqueous solution [41]. Recently researchers have been explored on magnetite nanomaterials and its composites in withdrawal of heavy metals from aqueous solution. Several preparation methods such as physical and chemical methods for magnetite nanomaterials and its composites were analyzed [42]. It has been implicated that successful relevance of nanomaterials in environmental remediation as well as in biological fields like that – biomedicine, drug designs, molecular imaging, biosensing, opto-electronics) depends on the homogeny in size and shape, stability, hydrophobicity/hydrophilicity of reactive surface groups and biocompatibility [43,44].

In recent research efforts, a co-precipitation method [45] was used to acquire the liquid based colloidal magnetite nano-particles due to having less expensive and easily-facile method. It is the most frequently method used because of reaction parameters during synthesis can be easily controlled.
such as temperature, pH, sonication, contact time, etc. The particle size can be controlled adequately by adding surfactants, such as – oleic acid or polyethylene glycol as well as to avoid agglomeration [46]. Chemical co-precipitation procedure produces high purity, spherical, stoichiometric particles with single and multi component metal oxides. It has been observed that if reaction parameters such as temperature, solution pH, magnificient rate, solute concentration, surfactant concentration were cautiously controlled it was notable that to obtain nanoparticles with desire size, shape and magnetic property [47–49]. Silica coating was done on the surface of magnetite through sol–gel hydrolysis of the TEOS followed by functionalization of EDTA to obtain EDTA functionalized silica-coated magnetite nanocomposites used as a nanosorbents in elimination of heavy toxic metals from aqueous solutions. Being hexadentate ligand, EDTA (ethylene-diamine tetra acetic acid) has a higher rate of chelation or complexation with toxic metals thus enhancing the removal efficiency of nanosorbents. EDTA was functionalized on the surface of Si-coated magnetite nanoparticles in acidic medium (pH= 4.5–5) through a complex reaction mechanism. The silica-coated magnetite nanocomposites were used as a best nanosorbents in the elimination of toxic heavy metals from wastewater and industrial effluents. The sol–gel technique is the most common method for silica coating on the surface of magnetite nanoparticles. It involves the concurrent hydrolysis and condensation reaction of the metal alkoxide [50]. Kolbe in 1956 observed the formation of silica coating on the nanoparticles by reacting TEOS in alkali solution with water in the presence of certain bases (NaOH) [51]. It is essential to have silica nanoparticles of a narrow size particle distribution with high purity; depending on the synthesis nature, the structure of colloidal particles may vary from isolated spherical particles to agglomerates form complex structures [52–54]. The purpose of the present study was to investigate different solvents and their effects in preparing monodispersed silica coating on the surface of magnetite nano-particles [55–59].

2. Experimental procedure

2.1. Materials and reagents

The chemicals used in the experiment were of analytical reagent grade or the highest purity purchased from Sigma Aldrich (Merck) Bangalore, India. The company name details as ©2015 Sigma-Aldrich Co. LLC. All rights reserved. SIGMA-ALDRICH is trademarks of Sigma-Aldrich Co. LLC, registered in the US and other countries. But I have purchased these chemicals from Bangalore, India namely such as – ferrous chloride (FeCl₂) and ferric chloride (FeCl₃), ammonium hydroxide (NH₄OH), ethanol (C₂H₅-OH), tetraethoxysilane (TEOS), glacial acetic acid, and PVA (5%), n-vinyl caprolactam (C₆H₁₁NO), 3-(trimethoxysilyl)-1-propanethiol (C₃H₇O₂SSi), EDTA, trinitro-toluene (C₇H₄N₃O₆), methanol (CH₃OH), azobis-isobutyronitrile ([CH₂]₂Cl₂N₂), methylmethacrylate-MMA (CH₂=C(CH₃)COOCH₃), ethylenediamine (C₆H₁₂N₂), acetate buffer, acetic acid. Distilled water (18.2 MΩ cm at 25 °C) was used throughout the experiment. The stock solution 0.1 M (M¹²·6H₂O) for adsorption study was prepared, by dissolving calcuated amount of M¹² hexahydrate in deionized water and different concentrations of solution were obtained by diluting the stock solution. All the adsorption experiments were replicated thrice and the mean values were considered as the final results.

2.2. Instrumentation

The test instruments used in this experiment, viz. namely – Magnetic Stirrers, Centrifuge, UV–Visible Spectrophotometer, XRD, SEM, EDX, FTIR, and VSM. The Magnetic Stirrer and Centrifuge instruments were performed by REMI 2MLH. The crystal structure of the synthesized materials was determined by an XRD (38066 Riva, d/G.Via M. Misone, 11/D (TN) Italy) at ambient temperature. The structure, morphology and size of the nanomaterials were characterized using SEM (SEM–EDX, XL30 and Philips Netherlands). The magnetic properties of the synthesized nanomaterials were measured using a vibrating sample magnetometer (VSM, 4 in. Daghigh Megh natis Kashan Co., Kashan, Iran). FT-IR spectra (4000–400/cm) in KBr were recorded on Perkin Elmer, spectrum 100, FT-IR spectrometer. The contents of heavy metals were measured using a UV–Vis spectrophotometer (Shimadzu UV-2600/2700 spectrophotometer, Japan). The instrument was controlled by UV-2600/2700 operation software.

2.3. Methods for preparation of molecularly imprinted magnetite nanomaterials

Magnetite nanoparticles (Fe₃O₄) were synthesized by a simple chemical co-precipitation method and silica-coating on its surface was done by hydrolysis of precursor tetra ethoxy silane (TEOS) followed by condensation to form silicone polymers to bind with the exposed hydroxyl group of magnetite nanoparticles [60,61]. It has several steps for the preparation of molecularly imprinted magnetite nanomaterials recorded as below.

2.3.1. Synthesis of silica-coated magnetite (Fe₃O₄/SiO₂) nanomaterials

In this study for the preparation of magnetite nanomaterials the chemical co-precipitation technique, a mixture of FeCl₃·6H₂O (10 mmol) and FeCl₂·4H₂O (5 mmol) in 2:1 molar ratio were dissolved in 70 ml deionized water under nitrogen atmosphere, was used. The chemical reaction during the co-precipitation of ferrous and ferric salts occurs as follows:

\[ \text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} \]

Ammonium hydroxide 25% (v/v) was added drop wise under vigorous stirring and the pH of the solution was adjusted to 10–11 at which the colour of solution changed to black immediately. After stirring for an hour, 80 ml ethanol and either 40 ml tetra ethoxy silane (TEOS) were slowly added and stirred for 24 h. The magnetite nanomaterials were washed thoroughly with distilled water 3–4 times and then dried under vacuum.

Ammonium hydroxide 25% (v/v) was added drop wise under vigorous stirring and the pH of the solution was adjusted to 10–11 at which the colour of solution changed to
black immediately. After stirring for an hour, 80 ml ethanol and either 40 ml tetraethoxysilane (TEOS, 10% v/v) were slowly added followed by adding adhesive agent PVA (5%) as a stabilizer simultaneously and kept back for 24 h on stirring. Glacial acetic acid is used in slightly acidic medium for adjusting pH (4.5–5.2) of the suspension as a catalyst for hydrolysis and poly-condensation reactions occurs simultaneously [62]. After that, the suspension was kept for stirring and heating for six hours at 600 °C temperature to obtained crude suspension. The magnetite nanomaterials were washed thoroughly with deionized water and ethanol simultaneously till pH remains neutral (6.5–7.2) and then dried under vacuum.

2.3.2. Effects of coating on magnetite by the silica 
(Fe$_2$O$_4$/SiO$_2$) nanomaterials
The growth of silica shells on iron oxide (Fe$_2$O$_4$) nanoparticles involved the acid catalyzed hydrolysis of TEOS and subsequent condensation of silica onto the surfaces of iron oxide (Fe$_2$O$_4$) cores. The core–shell nanoparticles could be separated from the reaction medium by magnetically and then re-dispersed into deionized water. Due to the presence of negative charges on the surface of silica shells, these magnetite nanoparticles having a core–shell structure could form very stable dispersions in water without adding other surfactants [63]. The ratio between the concentrations of iron oxide (Fe$_2$O$_4$) nanoparticles and TEOS had been optimized to avoid the homogeneous spheres.

Several parameters (such as the growth time and the concentration of ammonia catalyst or water) could be employed to control the thickness of silica shell; it is the most convenient and reproducible to adjust the shell thickness by changing the concentration of TEOS precursor with respect to the concentration of magnetite nanoparticles. Synthetic route for silica coated magnetite nanocomposites is shown in Fig. 1.

2.3.3. Modification of silica coated magnetite (Fe$_2$O$_4$/SiO$_2$) with 3-(trimethoxysilyl)-1-propanethiol
(Fe$_2$O$_4$/SiO$_2$/Thermosensitive)
The perspective of non-covalent imprinting has been developed by Mosbach and his subordinates, is easier regarding the choice of possible target molecules (functional monomers) and the consumption of the imprinted nanomaterials [64]. In addition, the yield of binding sites to be relative with the amount of imprint molecules used which will be more than non-covalent protocols. The well defined perspective mechanism of the molecular imprinting has been extended primarily by Wulff and co-workers as shown in Fig. 2.

The silica coated magnetites were suspended in 3-(trimethoxysilyl)-1 propanethiol (C$_6$H$_5$O$_2$SSi) 5% in anhydrous toluene [65]. The resulting mixture was refluxed at 80 °C for 48 h. Modified magnetic nanomaterials were washed sequentially with trinitrotoluene (TNT) and ethanol water after washing it dried properly at room temperature as shown in Fig. 2.

2.3.4. Molecularly imprinted nanomaterials
(Fe$_2$O$_4$/SiO$_2$/Thermosensitive/EDTA)
The modified magnetite molecularly imprinted nanomaterials (Fe$_2$O$_4$/SiO$_2$/Thermosensitive) were refluxed in the solution of 40 ml ethanol (C$_2$H$_5$OH), 1 g n-vinyl caprolactam (C$_6$H$_13$NO) as a thermosensitive agent and 10 ml allylamine were heated at 60–65 °C for 8 h then kept under N$_2$ atmosphere [66]. After that, 6.25 ml of 3.3% aqueous solution of ethylene di-ammine tetra acetic acid (EDTA) were added in this suspension. Acetic acid solution of 15 m mole is used for maintaining pH 4.5–5 (slightly acidic medium) of the reaction medium. Afterward, the modified magnetite molecularly imprinted nanomaterials were washed several times with ethanol and vacuum dried at room temperature. This reaction was done at the presence of Azobis isobutyronitrile (AIBN) as a radical initiator. It should be noted that for the efficient homogenous functionalization of EDTA, the ratio of silica coated magnetite and EDTA is optimized (2:1). The schematic representation of EDTA functionalized with silica coated magnetite nanomaterials (Fe$_2$O$_4$/SiO$_2$/Thermosensitive/EDTA) as a nanosorbents are shown in Fig. 3.

2.3.5. Grafted of functionalized EDTA onto thermosensitive modified magnetite molecularly imprinted nanomaterials
The surface coating of G$_0$ generation on nanomaterials was carried out with functionalized EDTA through Michael reaction. 10 ml of methyl metaacrylate in 150 ml methanol solution was added to obtained G$_0$ generation, and the suspension was refluxed at 60 °C temperature for 7 h under a nitrogen atmosphere. After being refluxed, nanomaterials were eluted by magnetic decantation and washed with methanol. Then, 15 ml ethylene diamine in 150 ml methanol solution was added, and suspension was refluxed for 3 h. The nanomaterials were washed three times with methanol through magnetic decantation.
2.3.6. Coupling of chitosan (CS) on functionalized EDTA grafted thermosensitive modified magnetite molecularly imprinted nanomaterials

The method for chitosan (CS) covalent immobilization onto EDTA-functionalized magnetite nanoparticles surface is presented. Covalent binding of CS to the magnetite surface proceeds using a free -CH$_2$-COOH group of CS and a NH$_2$-group of molecularly imprinted magnetite which immobilizes EDTA as a cross-linker [67]. The Coupling of chitosan (CS) on EDTA-functionalized grafted thermosensitive modified magnetite molecularly imprinted (Fe$_3$O$_4$/SiO$_2$/Thermo-sensitive) nanomaterials was carried out in acetate buffer. Then, 0.5 g of chitosan was added to 50 ml acetate buffer at 40 °C for 24 h. The resulting product (Fe$_3$O$_4$/SiO$_2$/Thermo-sensitive/CS) was washed several times with 2% acetic acid and double-distilled water.

2.3.7. Specific mechanism for the sorption of toxins onto modified magnetite molecularly imprinted nanomaterials

Molecularly imprinting of manmade polymeric materials (Fe$_3$O$_4$/SiO$_2$/Thermo-sensitive nanomaterials) are functionalized by the cross-linking of monomeric molecules (heavy metals) which are processed by copolymerization of monomers in the light of an analyte (imprint molecule), which react as a molecular template [68]. The functionalized monomeric materials at first composed a complicated compound with an imprint molecule and then followed by the polymerization their functional groups are linked by the highly cross-linked
polymeric network. Following elimination of the imprint molecule reveals the binding sites which are reciprocal in shape and size to the analyte. The polymeric material which is high specific and capable of rebinding with the analyte is introduced by molecular memory, in this way. There are two well defined points of view to molecularly imprinting as given in Fig. 4 [69]. A complicated compound is composed by polymerization through non-covalent interactions (self-assembly) which is lying in between functionalized monomeric molecule (heavy metals) and the imprint molecule (Fe₃O₄/SiO₂/Thermosensitive nanomaterials). On the other hand, the derivatives of the polymer are synthesized by the coupling of covalently bonded monomers with the imprint molecules [70]. Furthermore, the outcomes in binding sites are related to the concentration of imprint molecule consumed (imprinting efficiency), which should be greater than that of the non-covalent protocols. This perspective has been originated by Wulff and his subordinates [71].

2.4. **Applications how to eliminate the toxic metals from aqueous solution**

For metal removal applications, an adequate surface modification of the nanoparticles is a critical aspect regarding both selectivity and aqueous stability of these materials. A brief description of the most widely used applications for the removal of heavy metals from aqueous solution is discussed below.

2.4.1. Static adsorption experiments

In order to understand the rate and mechanism of the adsorption process, the adsorption kinetics was also reported with its relation to adsorption mechanism by various researchers [72].

Adsorption isotherm was carried by stirring fixed amount of nanocomposite as a nanosorbent (g) with a solution of a metal salt for few minutes at room temperature to attain equilibrium. The concentration of unadsorbed metal ions was found out with the help of calibration graph of the metal solution at a fixed wavelength with varying initial metal concentration. After the equilibration the pH of the reaction medium was changed prior to finding out the metal concentration of the filtrate, pH should be stabilized to neutral. It was reported by various researchers that the observed experimental data of adsorption would fit into different adsorption isotherms such as Langmuir and Freundlich isotherms.

2.4.2. Regeneration and reusability

In order to demonstrate the applicability and reliability of the method for factual samples, i.e. two samples – including tap water (ground water) and pharmaceutical manufacturing wastewater were prepared and analyzed simultaneously. Ground water samples were taken from our research laboratory (Nanochemistry Laboratory, Jamia Millia Islamia, New Delhi, India) and pharmaceutical manufacturing wastewater was collected in a 2.0 LPTFE bottle. All samples were filtered through a Whatmann filter paper (No. 40) to remove suspended particulate matter. The mechanism of the regeneration cycle and its relation to desorption process, researchers have shared their views [73], which specifies that the desorption of heavy metal ions, in the beginning, was found to be maximum, but later on, desorption capacity was decreased with increasing number of regeneration cycle. After complete elution, the adsorbent was separated and metal concentration in the supernatant was determined. The recovered adsorbent was reused till more recycling process happened. In addition
to this, these sorbents properties recycled in the environment for remediation of heavy metals on a world wide scale.

3. Results and discussion

The characterizations of the prepared magnetite (Fe₃O₄) nanoparticles and silica-coated magnetite nanoparticles were carried out by XRD, SEM, EDX, HR-TEM, FT-IR, VSM, adsorption and desorption studies have been discussed with reference to these techniques. Their surface morphology was studied by SEM which also showed nanoparticles had the mean diameter 18–20 nm. XRD results showed the prominent peak of Fe₃O₄ at 2θ = 35° and its cubic spinel structure.

The calculation of the mean particle size (D in nm) was estimated by Scherer’s formula from the strongest peak in their XRD patterns. SEM study was done to find out the surface and textural morphology of magnetite and surface functionalized magnetite nanoparticles. EDX study was done by using Philips XL 30 ESEM-PEG equipped with a Phoenix energy dispersive X-ray analysis system (EDX) to examine the chemical composition. The chemical composition was determined by EDX and the relative ratio of O, Fe, Si and C elements clearly indicated the successful preparation of surface functionalized magnetite nanoparticles. HR-TEM were determined the size and morphology of bare magnetite nanoparticles and silica-coated-magnetite nanoparticles. FT-IR spectra were obtained for the analysis of attached functional groups on the surface of magnetite nanoparticles by milling with KBr and pressing into a disc. FT-IR spectra revealed that functionalization of ethylene-diammine tetra acetic acid on the surface of Si-coated Fe₃O₄ was successfully done as characteristics peaks of –COOH was depicted clearly. Their magnetic property was determined by VSM and result showed that the nanoparticles were super paramagnetic and inert silica coating and functionalization did not reduce the magnetic property markedly. VSM study was shown for the measurement of magnetic properties at room temperature. Super paramagnetic behaviour of synthesized magnetite nanoparticles was also confirmed. The relation between the applied magnetic field (H) and saturation magnetization (Mₛ) of the prepared magnetite (Fe₃O₄), silica-coated magnetite nanoparticles functionalized by EDTA were measured and compared by the vibrating sample magnetometer at room temperature.

3.1. XRD analysis

XRD of the magnetite (Fe₃O₄) nanoparticles and silica-coated magnetite nano-particles were done on XRD Phillips Xpert PRO diffractometer over the 2 theta range from 10 to 90° at rate of 25°/min, using Cu-Kα radiation (λ = 1.54060 Å). XRD pattern of magnetite and silica-coated magnetite nanoparticles are shown in Figs. 5(a) and 4(b). The synthesized magnetite nanoparticles were quite identical to pure magnetite when compared with the JCPDS s patterns (Joint Committee on
Powder Diffraction Standards) of magnetite nanoparticles. The synthesized sample was crystalline in nature and has an inverse cubic spinal structure. The broad peak in the XRD pattern indicates the ultra fine nature and small crystallite size of nanoparticles.

The characteristic peak of magnetite (Fe_3O_4) nanoparticles was clearly identified at around 2θ = 35° and the particles size calculated by the Debye–Scherer formula came out to be 20 nm which is approximately the size determined by SEM. The broad peak at around 2θ = 20° are due to the amorphous silica shell on the surface of the magnetite nanoparticles as shown in Fig. 5(b). It is concluded from both the graphs that the magnetite nanoparticles surface were coated with silica but shows very distinguishable Fcc peaks (Face centred cubic) of magnetite crystal were observed, which means that they have the phase stability. The different functional groups Si-OH, –COOH, do not affect on crystallinity and morphology in this study.

3.2. Surface morphology and elemental analysis

(a) SEM analysis: The surface and textural morphology of magnetite and silica-coated magnetite nanoparticles were studied by their SEM images which are illustrated in Fig. 6. The synthesized magnetite nanoparticles are homogenized and spherical in shape with average diameter of core size is 18 nm is shown in Fig. 6(a). The spherical in shape of silica-coated magnetite nanoparticles with average diameter in the range of 16–20 nm are shown in Fig. 6(b). The thickness of silica shell is 1–2 nm and can be adjusted easily by controlling the ratio of TEOS to Fe_3O_4. After functionalization with EDTA on the surface of silica-coated magnetite nanoparticles, average diameter of magnetite core size becomes 20 nm as shown in Fig. 6(c). The average core size of Fe_3O_4 by SEM has in excellent agreement with core size determined by XRD. These results clearly indicate that the magnetite nanoparticles were coated with silica and EDTA.

(b) EDX analysis: EDX spectra for the Fe_3O_4 and silica-coated Fe_3O_4 are shown in Fig. 7. The intensity of peaks corresponding to iron (Fe) and oxygen (O) elements are shown in Fig. 7(a), and 3:4 elemental ratios was here excellent agreement with the molecular composition of Fe_3O_4 nanoparticles. This clearly indicates that Fe_3O_4 nanoparticles have been successfully synthesized. The additional peak of silica element alongside peaks of iron and oxygen are shown in Fig. 7(b). The intensity of oxygen peak is relatively high due to the contribution of oxygen from TEOS used in coating of silica on the surface of Fe_3O_4 nanoparticles. Further functionalization with EDTA is shown in Fig. 7(c). The intensity of oxygen peak is dramatically increased due to contribution of oxygen from four carboxyl groups from EDTA.

(c) FT-IR spectral analysis: The unmodified magnetite nanoparticles and silica-coated magnetite are analyzed by FT-IR are shown in Fig. 8. The characteristic peak of magnetite nano particles is found nearly 595 cm\(^{-1}\) which is assigned to the stretching vibration of Fe–O bond is shown in Fig. 8(a). The spectra of Si-coated Fe_3O_4 nanoparticles, in which a new peak at 1095.9 cm\(^{-1}\)is observed for Si-OH bond indicating that silane polymer adsorbed on the surface of magnetite nanoparticles but peak for Fe–O–Si bond could not be seen because of
overlapping with peak Fe–O bond is shown in Fig. 8(b). All curves show the peaks of stretching vibrations of –CH₂ at 2825 cm⁻¹ to 2855 cm⁻¹ range. The peak at 1680 cm⁻¹ is due to –COOH is shown in Fig. 8(c). This clearly indicates that EDTA is attached to the surface of silica coated Fe₂O₃ nanoparticles by making bond with silanol groups which are exposed on the surface of magnetite nanoparticles. EDTA is a hexadentate ligand and has six available sites to form chelae with toxic metals efficiently by a variety of physico-chemical interaction with metals [37].

(d) HR-TEM analysis: The size and morphology of bare magnetite nano-particles and Silica-coated magnetite nano-particles were determined by HR-TEM images as shown in Fig. 9(a) and (b). It reveals that the nano-particles both have been spherical in shape and structure at different range 100–200 nm.

3.3. VSM (Vibrating Sample Magnetometer)

The magnetization curve of Fe₂O₃, Si–Fe₂O₃ and EDTA-functionalized Si–Fe₂O₃ nanoparticles at room temperature are shown in Fig. 8. Their saturation magnetization (Mₛ) values are found at 51 emu/g, 46 emu/g and 44 emu/g respectively. All the curves in Fig. 10 exhibits super paramagnetic behaviour as no hysteresis; coercivity (Hₓ) and remanence (Mᵣ) are found. It also shows that magnetization increases with increasing strength of applied magnetic field until it attains saturation point. The super paramagnetic property of Fe₂O₃ nano-particles are shown in Fig. 10(I) at room temperature and attributed to their size. It has been found that when the size is less than 20 nm thermal fluctuations can change the direction of magnetization of the entire crystal. Fe₂O₃ nanoparticles become disorder and lose their magnetization beyond Curie temperature. The coating of SiO₂ shell on the surface of Fe₂O₃ nanoparticles causes to decrease the magnetization due to the contribution of weight by non magnetic SiO₂ as shown in Fig. 10(II) when it is compared with the graph of Fe₂O₃ nanoparticles. Further functionalization with EDTA as shown in Fig. 10(III) causes further decrease in magnetization but their super magnetic properties are retained and enough to carry out an efficient magnetic separation of toxic metals by applying external magnetic field [74].
4. Applications for removal of heavy metals from aqueous solution

A brief description of the most widely used applications for the removal of heavy metals from aqueous solution is discussed below.

4.1. Adsorption process

In order to understand the rate and mechanism of the adsorption process, the adsorption kinetics was also reported with its relation to adsorption mechanism by various researchers [75]. Adsorption isotherm was carried by stirring fixed amount of a nano-composite as a nanosorbent (g) with a solution of a metal salt for 15 min at room temperature to attain equilibrium [76]. The concentration of unabsorbed metal ions was found out with the help of calibration graph of the metal solution at a fixed wavelength with varying initial metal concentration. After the equilibration the pH of the reaction medium was changed prior to finding out the metal concentration of the filtrate, pH should be stabilized to 6–7 [77]. The amount of adsorbed metal (Ca) was then found out by applying the formula:

\[ Ca = Ci – Cf \]

where \( Ci \) is the initial concentration, \( Cf \) is the final concentration.

Percentage recovery factor (\( \%R \)) was calculated by the following equation:

\[ \%R = \frac{Ca}{Co} \times 100 \]

where \( Ca \) and \( Co \) are adsorbed and initial concentration of metal ions.

The graph plotted by diluting the concentration of the standard solution in a fixed ratio and Corresponding absorption is measured with the help of UV–Vis spectrophotometer at a fixed wavelength (\( \lambda_{\text{max}} \)) [78]. The concentration of adsorbed metal ions was calculated as a difference between the initial concentration of the solution and the final concentration after the equilibration. A number of metal ions adsorbed at time \( t \), \( qt \) in mg/g were calculated as a mass balance equation

\[ qt = \frac{(Co – Ct)v}{m} \]

where \( Co, Ct, v, m \) are initial concentration of metal ions, the concentration of metal ions after time \( t \), the volume of the solution and the mass of the adsorbent. It was reported by various researchers that the observed experimental data of adsorption should fit to the different adsorption isotherms such as Langmuir, Freundlich, etc. [79].

4.2. Effect of adsorbent dose, pH and time intervals

In order to understand the effect of adsorbent dose, pH and time intervals it was pragmatic that the effect of adsorbent dosage on the adsorption capacity, different metal solutions were taken and pH of the solutions were adjusted accordingly. Then the various amounts of adsorbents were added to the solutions on stirrer at room temperature for 20 min time intervals [80]. As shown in Fig. 11(a), the percentage of the removal metals increased with the increase in the adsorbent dose, and reached a maximum level at a dose of 0.01 g. This observation can be explained by the increase in the surface area of the adsorbent and availability of more active sites for adsorption [81]. This phenomenon is attributed to the fact that a large number of vacant surface sites are available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to occupy due to the repulsive forces between the solute molecules adsorbed on the solid surface and the bulk phases [82].

The effect of pH on adsorption capacity (surface adsorption phenomenon) of metal ions (such as Cu\(^{2+}\)) was considered at room temperature by varying the pH of reaction medium ranges from 2 to 10 while keeping other parameters constant [83]. After the reaction, metal concentrations were calculated with the help of UV–Vis spectrophotometer. To study the effect of time on adsorption capacity, adsorbent was to be mixed with metal solutions at room temperature for various time intervals ranging from 5 to 25 min as reported by various authors [84].

As the pH rises, the aggregation becomes significant, for the size of the aggregate becomes larger and the maximum and after which the aggregation decreases as the pH value continues to rise. For the polymer-modified Fe\(_2\)O\(_4\) nanoparticles, however, the slope of the aggregation curve is much more flat.
which means that polymer modified on the surface of Fe$_3$O$_4$ nanoparticles can effectively decrease their sensitivity to pH [85].

The initial pH of aqueous solution plays an important role in the adsorption process and particularly affects the adsorption capacity by controlling the surface charge of the adsorbent. The effect of the pH on the adsorption of heavy metals was studied in the pH range of 4.0–9.0 for initial metal concentration of 20 mg/L. As shown in Fig. 11(b), the maximum adsorption was obtained at pH of 8.0. As it can be seen the adsorption curve of metal onto Fe$_3$O$_4$/SiO$_2$/Thermo sensitive/PAMAM-CS nanomaterials can be divided into three regions. In the first region (pH = 4.0–6.0), the adsorption of TMX sharply increases when the pH increases from 4.0 to 6.0. In the second region, when the pH values increase from 6.0 to 8.0, the adsorption reaches the maximum level. When the pH is above 8.0, the adsorption of TMX gradually decreases along with the increase in the pH values (the third region). Such variations in adsorption can be attributed to the different interactions between the Fe$_3$O$_4$/SiO$_2$/Thermo sensitive/PAMAM-CS nanomaterials and the TMX.

4.3. Desorption and regeneration study

In order to understand the mechanism of the regeneration cycle and its relation to desorption process throughout the cycle various researchers have shared their views, which specifies that the desorption of heavy metal ions in the beginning was found to be maximum, but later on desorption capacity was decreased with increasing number of regeneration cycle [86]. Study of desorption was conducted by mixing 10 ml of 0.1 M HNO$_3$ with 0.2 g adsorbent in a beaker, after which stirring was done by an ultrasonic stirrer for 15 min at normal temperature. Then nanosorbent was separated by applying external magnetic field and the concentration of the eluted metal ions in the filtrate are measured with the help of calibration graph of heavy metal ions (such as Cu$^{2+}$) by measuring the absorbance using UV-Visible Spectrophotometer. It was accounted that the desorption of heavy metal ions in the beginning could be almost (95–98%). Although the desorption capacity was decreased with increasing number of regeneration cycle but remained adequately till more cycles were accomplished [87]. As per Fig. 12, the elution of metal ions was quite significant until more cycles were shown.

5. Conclusions

A novel type of EDTA functionalized silica coated magnetite nanomaterials with the diameter of 20 nm was also synthesized. Silica coating (1–2 nm) was done on the surface of magnetite nanomaterials provides stability in acidic and basic medium as well as exposed silanol groups give tremendous opportunity for further functionalization with multi functional groups like EDTA. The functionalization of EDTA on the surface of silica coated magnetite nanoparticles provides –COOH group and –NH$_2$ group to be bonded with toxic metal ions from contaminated water by physico-chemical interaction process (physisorption and chemisorptions). It was pragmatic that adsorption was pH dependent and adsorption mechanism shows an ion exchange as well as electrostatic binding. Desorption investigations that acidic solution was an efficient eluent with maximum percentage of heavy metal ions released by the nanosorbent from the regeneration cycle. Due to superparamagnetic nature the EDTA-functionalized silica coated magnetite nanoparticles loaded with toxic heavy metals can be efficiently separated by applying external magnetic field. These nano-particles also have tremendous potential in the field of biomedical applications, primarily on account of their similar size to biological molecules. A silica coating on the surface of nano-particles decreases the aggregation, oxidation, and toxicity of these particles. The shielding of magnetic dipole interaction and enhancement of repulsion due to the negatively charged silica coating stabilizes the magnetic nanoparticles. So, it has great potential application in easy and fast separation of toxic heavy metals from waste water and controlling from the industrial effluents. In addition to this, these sorbents properties recycled in the environment for remediation of heavy metals on a world wide scale. Hence these nanocomposites has been shown best adsorbents would be a better option in remediation technology of waste water especially contaminated heavy metals due to its high adsorption capacity and easy separation ability.

Conflict of interests

The authors declare no conflict of interest.

Acknowledgements

The author is thankful to the Jamia Millia Islamia University; Central Instrumentation Facility (CIF) for providing instruments to conduct and characterizes the research work with overcomes with this study. The authors express their sincere gratitude to University Grants Commission, India for providing financial assistance in the form of research fellowships. Further persons from IIT Delhi and AIIMS (Science and Research Branch) are also highly acknowledged for their cooperation for
providing instruments to characterize the samples and comprehensive the study.

REFERENCES


[34] Lai L, Xie Q, Chi L, Gu W, Wu D. Adsorption of phosphate from water by easily separable Fe3O4@SiO2 core/shell magnetic nanoparticles functionalized with hydroxyl lanthanum oxide. J Colloid Interf Sci 2016;465:76–82 [Google Scholar] [CrossRef].


