



Facile green synthesis of L-methionine capped magnetite nanoparticles for adsorption of pollutant Rhodamine B



Neway Belachew^a, D. Rama Devi^b, K. Basavaiah^{a,*}

^a Department of Inorganic & Analytical Chemistry, Andhra University, Vishakapatnam 530003, India

^b A.U. College of Pharmaceutical Sciences, Andhra University, Visakhapatnam -530003, India

ARTICLE INFO

Article history:

Received 28 June 2016

Received in revised form 29 September 2016

Accepted 17 October 2016

Available online 19 October 2016

Keywords:

Green synthesis

Magnetite nanoparticles

Amino acid

Capping agents

Co-precipitation

Dye adsorption

ABSTRACT

Surface modified magnetite nanoparticles (Fe_3O_4 NPs) were synthesized by the one pot co-precipitation method using L-methionine (L-Met) as a capping agent. As synthesized Fe_3O_4 NPs have been characterized by using UV-Visible spectroscopy, FTIR spectroscopy, powder XRD, SEM-EDX and TEM. Magnetic property of L-Met capped Fe_3O_4 NPs was investigated by vibrating sample magnetometer (VSM). The XRD results indicated that formation of pure phase Fe_3O_4 NPs. The spectroscopic (FTIR and UV-Vis spectroscopy) results further confirm the effective capping of Fe_3O_4 NPs using L-Met. The VSM curve clearly depicts the superparamagnetic behavior of L-Met capped Fe_3O_4 NPs with saturation magnetization value of 65 emu/g. The kinetic studies for Rhodamine B (RhB) adsorption showed rapid adsorption within the first 40 min and sorption process best linear fitted to second-order kinetic model, suggesting chemisorption mechanism. Dye adsorption equilibrium data were fitted well to the Langmuir isotherm.

© 2016 Published by Elsevier B.V.

1. Introduction

During the past decade, magnetic nanoparticles have attracted much attention beyond to basic scientific interest due to many technological applications such as magnetic fluids, data storage, catalysis, waste water treatment and bio-medical applications [1–6]. More recently, there have been an increased investigations based on iron oxide nanoparticles in particularly magnetite nanoparticles (Fe_3O_4 NPs), maghemite ($\gamma\text{-Fe}_2\text{O}_3$ NPs), etc. Among all iron oxide nanoparticles, Fe_3O_4 NPs emerged as a potential candidate for advanced technological applications due to their biocompatibility, low toxicity and high magnetic saturations as well as potential applications [7–9]. All these applications requires Fe_3O_4 NPs to be superparamagnetism with particle size less than the critical particle size (20 nm), well dispersed in aqueous solution without any aggregation [10]. However, Fe_3O_4 NPs can be easily aggregated because of their large specific surface area, strong magnetic dipole–dipole interaction and Van der Waals forces between the nanoparticles and hence change in magnetic properties and low dispersibility in aqueous solution, which restricts the application of Fe_3O_4 NPs [11]. In order to overcome these limitations, Fe_3O_4 NPs should be capped with capping materials such as polymers [12], surfactants [13], inorganic metal or metal oxides [14], silica [15], polyaniline [16], dodecyl amine [17], etc. The protective capping materials not

only arrest aggregation of Fe_3O_4 NPs but also act as a platform for functionalization to enhance their surface properties for technological applications. However, to exploit the potential application of Fe_3O_4 NPs especially in biomedical application, it is essential for synthesis of a Fe_3O_4 NPs through facile and green synthesis approaches. It has been reported that several papers on the synthesis of capped Fe_3O_4 NPs using biocompatible capping agents, such as dextran [18, 19], polyvinyl alcohol [20,21], poly (ethylene-glycol) [22], pullulan [11], dimercaptosuccinic acid [23], ascorbic acid [24] and proteins, like albumin [25] and transferrin [26]. Recently, among all biocompatible capping agents for Fe_3O_4 NPs, amino acids besides to biocompatibility and physiological importance, in the synthesis point of view have greater potential as a capping of Fe_3O_4 NPs. The amino ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) groups are the most common surface capping agents frequently used for capping of Fe_3O_4 NPs [24, 27]. However, synthesis of Fe_3O_4 NPs by using common capping materials such as polymers [12] and silica [15] showed significantly increased the particle size, no uniform particle size distribution and reduce the magnetic saturation value.

In this study, we report a simple and environmentally friendly method for the preparation of L-Met capped Fe_3O_4 NPs through a one pot synthesis approach using L-Met as a capping agent. L-Met capped Fe_3O_4 NPs was synthesized in the presence of different molar concentration of L-Met. Finally, the optimum adsorption conditions of L-Met capped Fe_3O_4 NPs for removal of RhB dye, adsorption isotherms and kinetic studies were extensively studied.

* Corresponding author.

E-mail address: klbasu@gmail.com (K. Basavaiah).

2. Experimental

2.1. Materials

Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and Iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) used for synthesis of Fe_3O_4 NPs were purchased from Merck used as without further purification. L-Met was purchased from HiMedia, India. NH_3 (25%) and other reagents were analytical grade and used without further purification. Milli-Q water was used throughout the whole synthesis process.

2.2. Synthesis of L-methionine capped Fe_3O_4 nanoparticles

The synthesis scheme of Fe_3O_4 NPs was followed single pot coprecipitation reaction under the presence of L-Met as a capping agent. Typically, 2:1 M ratio of metal salts Fe^{+3} (0.54 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and Fe^{+2} (0.278 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was added in a 250 mL round bottomed flask respectively. Allow the reaction under nitrogen atmosphere at 80 °C for 1 h at a continuous constant string. Then 5 mL of 2 mol L^{-1} L-Met was added to the reaction mixture and after 30 min 5 mL ammonia solution (25%) was rapidly injected into a reaction mixture. The reaction was preceded for 2 h at 80 °C under constant string. Then finally the black precipitate was obtained and magnetically separated, washed several times with Milli-Q water, and then dried vacuum at room temperature. In the same analogy uncapped Fe_3O_4 NPs was synthesized in the absence of L-Met. The same procedure was adopted for preparation of L-Met capped Fe_3O_4 NPs by varying the concentration of L-Met while all other reaction parameters were kept constant and their detailed preparation conditions were shown in Table 1.

2.3. Characterization

The UV–Visible absorption spectra were recorded using a Shimadzu 2450 – SHIMADZU spectrometer. Fourier transform-infrared (FTIR) spectra were recorded over the range of 400–4000 cm^{-1} using a SHIMADZU-IR PRESTIGE-2 Spectrometer. Powder samples were mixed thoroughly with KBr and pressed into thin pellets. X-ray diffraction (XRD) patterns were recorded by PANalytical X'pert pro diffractometer at 0.02 °/s scan rate using $\text{Cu-K}\alpha_1$ radiation (1.5406 Å, 45 kV, 40 mA). Transmission electron microscopy images were obtained (TEM model FEI TECNAI G2 S-Twin) at an accelerating voltages of 120 and 200 kV. Surface morphology was examined by scanning electron microscopy (SEM) using JEOL-JSM6610 LV equipped with an electron probe-micro analyzer. Thermogravimetric analysis (TGA) curves were obtained using a Shimadzu thermogravimetric analyzer (DTG-60H) with the temperature ranging from 25 to 800 °C under a stable N_2 flow (50 mL/min) and with a heating rate set at 10 °C min^{-1} . Room temperature magnetization measurements versus applied magnetic field were carried out using vibrating sample magnetometer (VSM), Lakeshore 665, USA.

2.4. Batch mode adsorption studies

Batch adsorption efficiency of L-Met capped Fe_3O_4 NPs experiments were carried out at room temperature (300 K) using RhB as a model dye. Typically, 50 mg of L-Met capped Fe_3O_4 NPs was mixed with 50 mL of known concentration of dye solution. The solution pH was adjusted by NaOH (0.1 M) or HCl (0.1 M). The flasks were stirred for the specified time period and sample from each flask were withdrawn at the desired time of reaction. The L-Met capped Fe_3O_4 NPs were collected by an external magnet. The residual dye concentration was determined by UV – Visible spectrophotometer by measuring the absorbance at a wavelength of maximum ($\lambda_{\text{max}} = 554 \text{ nm}$) absorbance of RhB. The amount of adsorbed RhB (q) was expressed in mg of dye per gram of L-Met capped Fe_3O_4 NPs, as shown by the Eq. (1):

$$q = (C_0 - C)V/m \quad (1)$$

where C_0 (mg/L) represents the initial RhB concentration, C (mg/L) is the RhB concentration in solution after adsorption, V (L) is the volume of the aqueous solution and m (g) is the mass of L-Met capped Fe_3O_4 NPs. The mechanism of adsorption and kinetics were correlated by common adsorption isotherms and kinetic models respectively.

2.5. Recyclability experiment

To test the recyclability or reusability of the L-Met capped Fe_3O_4 NPs for removal of RhB from water, 50 mg of the L-Met capped Fe_3O_4 NPs was added to 50 mL of RhB dye solution (5 ppm) and the mixture was stirred for 180 min at room temperature. After the separation of the L-Met capped Fe_3O_4 NPs via an external magnet, the supernatant dye solution was measured by UV–Visible spectrophotometer. Then the RhB adsorbed on L-Met capped Fe_3O_4 NPs was washed with 25 mL of ethanol several times at room temperature. The L-Met capped Fe_3O_4 NPs was collected by an external magnet and reused for the second RhB adsorption experiment. The reusability experiments were performed 5 times.

3. Result and discussion

Fig. 1 shows UV–Visible spectra of uncapped Fe_3O_4 NPs and L-Met capped Fe_3O_4 NPs. Fig. 1(a) shows two absorption bands at 251 and 351 nm for uncapped Fe_3O_4 NPs. The band at 250 nm is attributed to the absorption and scattering of light by magnetic NPs while the peak at 351 nm is due to the aggregation of fine Fe_3O_4 NPs [28]. The absorption spectrum of L-Met capped Fe_3O_4 NPs [Fig. 1(b)] reveals the strong absorption band at 200 nm is ascribed to the charge transfer between ligand (L-Met) to the unsaturated Fe atom in Fe_3O_4 NPs. The absence of the band at 351 nm in L-Met capped Fe_3O_4 NPs confirms the successful synthesis of aggregate free Fe_3O_4 NPs [29]. The UV–Vis spectra of capped Fe_3O_4 NPs with different concentration of L-Met were shown in Fig. S1. The blue shift of Fe_3O_4 NPs peak with increasing molar ratio of L-Met probably attributed to the decreasing size of the Fe_3O_4 NPs.

The crystalline structures of L-Met capped Fe_3O_4 NPs were characterized by XRD diffraction.

Table 1
Synthesis conditions of L-Met capped Fe_3O_4 NPs.

Sample	Precursor solution	Temperature (°C)	Total reaction time
2:1:2 M ratio M-1	$\text{Fe}^{3+}:\text{Fe}^{2+}:\text{L-Met}$ molar ratio 2:1:2	80	3 h
2:1:4 M ratio M-2	$\text{Fe}^{3+}:\text{Fe}^{2+}:\text{L-Met}$ molar ratio 2:1:4	80	3 h
2:1:8 M ratio M-3	$\text{Fe}^{3+}:\text{Fe}^{2+}:\text{L-Met}$ molar ratio 2:1:8	80	3 h
Uncapped Fe_3O_4	$\text{Fe}^{3+}:\text{Fe}^{2+}$ molar ratio 2:1	80	3 h

Download English Version:

<https://daneshyari.com/en/article/5409385>

Download Persian Version:

<https://daneshyari.com/article/5409385>

[Daneshyari.com](https://daneshyari.com)