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Facile one-step fabrication of magnetite particles under mild hydrothermal conditions

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ABSTRACT

Hydrophilic magnetite particles for biological applications were synthesized by hydrothermal method in the presence of D-Glucose as both reducing and capping agent in a facile, one-step, low energy and environmentally friendly route. The role of D-Glucose as a reducing agent in the formation of magnetite particles under mild hydrothermal conditions has been investigated. The absence of D-Glucose results in the formation of hematite. The magnetite particles synthesized were characterized using powder X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) Spectroscopy, High Resolution Scanning Electron Microscopy (HR-SEM), Dynamic Light Scattering (DLS) and Vibrating Sample Magnetometery (VSM). The influence of the quantity of D-Glucose used and the reaction duration on the formation of magnetite were studied. DLS and HR-SEM results show that the size of the particles was in nano- to micron range. The antioxidant potency of the particles was confirmed using DPPH assay, where 2,2- Diphenyl-1-picrylhydrazyl was used as a source of free radicals. Hence the magnetite particles obtained could be considered for the use in various biological applications.

1. Introduction

Magnetic particles ranging from the nanometer to micrometer scale are being used in an increasing number of medical applications. The important properties of magnetic particles suitable for medical applications are their biocompatiblilty, nontoxicity, injectability and high-level accumulation in the target tissue or organ [1]. Magnetite presents the most interesting properties among all other iron oxides because of the presence of iron cations in two valence states, Fe^{2+} and Fe^{3+} in the inverse spinel crystal structure [2,3]. They are used for biomedical applications such as magnetic resonance imaging [4,5], magnetic hyperthermia [6,7], cancer therapy [8–10], drug targeting and delivery [11,12], tissue engineering [13], biological fluids detoxification and cell separation [14], due to their favorable magnetic properties and high biocompatibility [1,15,16].

Although there are various synthesis methods for preparing magnetite (Fe_3O_4) particles employing solid, liquid and gaseous phase reactions [17–19], several of them are relatively complicated and organic solvents that are unsuitable for biomedical applications is often used. Hence, hydrothermal synthesis of Fe_3O_4 nanoparticles in organic solvent-free system is useful because the process is simple and has very low environmental load [20]. In this study, hydrothermal method was chosen to synthesize Fe_3O_4 particles due to its advantages: the use of organic reagents is waived, the process is relatively cost-effective, gives high yield of products with excellent particle crystallinity, controllable size and good morphology. In addition, no post-heat treatment is required for the particles synthesized which makes this method highly desirable as heat treatment might result in secondary agglomeration [21].

The present authors report the preparation of hydrophilic magnetite particles by mild hydrothermal method. The reducing sugar, D-Glucose which is a nontoxic and renewable biochemical [22], is used as the reducing and capping agent. Hydrated ferric salt was employed as a single iron precursor and water as the solvent to synthesize Fe_3O_4 particles, in a facile one step route. The effects of varying concentrations of D-Glucose and the duration of reaction on the particle synthesis were also studied and optimized thoroughly.

The particles were also tested for their free radical scavenging ability in DPPH assay to establish their antioxidant potency since antioxidants have an important role in the functioning of biological systems. Antioxidants are widely distributed in the bio-systems and they scavenge harmful free radicals generated as by-products during biochemical phenomena occurring inside living cells. A fair understanding of the interaction of magnetic particles with the biological systems would be incomplete without the

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study of antioxidant property of these particles. The antioxidant property of the magnetic material has been investigated by following the standard protocol [23,24]. It might be of interest to know the performance of iron oxide particles as potential antioxidants.

2. Experiments

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) (Molychem), sodium hydroxide (NaOH) (Ranbaxy) and D-Glucose (Dextrose) (Rankem) were used for the preparation of magnetite particles. On the other hand, for testing the antioxidant potency of the synthesized particles, DPPH (2,2- Diphenyl-1-picrylhydrazyl) (HiMedia) was used as a source of free radicals. The water used in all experiments was ultrapure water with a resistivity of 18.2 MΩ cm purified by PURELAB Option Q7, ELGA, UK.

2.2. Methods

2.2.1. Synthesis of magnetite

The fabrication of magnetite was carried out using General Purpose autoclave made of stainless steel (SS 316), provided with Teflon liner of 30 ml capacity. The synthesis of magnetite particles was carried out according to the procedure reported earlier [25], involving a single step hydrothermal fabrication with D-Glucose as a reducing agent. Aqueous solution of $FeCl_3 \cdot 6H_2O$ (0.5 M) was prepared to which sodium hydroxide was added in drops until *pH* 9 was reached and was then stirred for 10 min. The resulting $Fe(OH)_3$ which appears as a reddish brown precipitate was then washed in deionised water repeatedly to remove excess ions and till *pH* 7 is reached. Then D-Glucose solution (0.5 M) was added to the precipitate obtained.

To optimize the concentration of D-Glucose (0.5 M), different quantities (0.25, 0.5, 1, 2, 4 and 8 ml) were added to the reddish brown precipitate (10 ml) and their total volumes were made up to 18 ml with deionised water. A control experiment was carried out by taking only deionised water in the place of D-Glucose to establish its role as a reducing agent. The mixtures were stirred well and then transferred into teflon-lined autoclaves. The autoclaves were kept at 160 °C in a hot air oven for 16 h and then allowed to cool down to room temperature. The products were washed with deionised water followed by ethanol via magnetic decantation several times and then freeze dried to get the product.

To investigate the effects of reaction time on the structure and phase formation of iron oxide particles, samples with the optimum concentration of D-Glucose (0.5 ml) were synthesized at 160 °C and reaction durations from 2 to 22 h.

2.2.2. Characterization

Powder X-ray diffraction (XRD) technique is an effective tool to ascertain crystal structure of Fe_3O_4 particles. CuKα radiation was used to investigate the purity of Fe_3O_4 powder in the range of 2θ from 6° to 70°. The crystal structure of Fe_3O_4 nanoparticles was confirmed using a Rigaku MiniFlex II X-ray diffractometer, Japan, at room temperature. Typically, 0.2 g of the sample was used for XRD scanning. The pattern obtained was then compared with the standard peaks provided by JCDPS 00-019-0629 of International Center for Diffraction Data.

The adsorption of certain functional groups on the Fe_3O_4 nanoparticles surface as a result of D-Glucose coating can be determined with a Fourier transform infrared (FT-IR) spectrometer. Samples were prepared by diluting the particles in KBr at 1% by weight and made into pellets. Infrared (IR) spectra were recorded in the wave numbers ranging 4000–400 cm^{-1}, with a Jasco FTIR-460 plus spectrophotometer, Japan, using KBr wafers.

Colloidal properties (mean hydrodynamic size and zeta potential) of the aqueous suspensions were obtained by Dynamic Light Scattering (DLS) using Nanotrac wave particle analyzer, USA. The diluted samples dispersed in deionized distilled water at 1 mg/ml and sonicated for 3 min were used in this study. The hydrodynamic size was measured at *pH* 7.

The morphology of the particles was observed by a using a High Resolution Scanning electron microscope, FEI Quanta FEG 200, USA, operating at 30 kV. A drop of the particle suspension was deposited on a carbon coated copper grid and left to dry at room temperature and the images were recorded.

Magnetization studies were performed at room temperature using a Lake Shore-7404 Vibrating Sample Magnetometer, USA, operating at a vibration frequency of 82.5 Hz and maximum field of 15 kG.

2.3. Antioxidant activity

Antioxidant activity of the synthesized particles was also measured by using the modified DPPH method as reported previously [23,24]. Antioxidant activity of the samples synthesized with varying D-Glucose concentration was tested by mixing 6 mg/ml of particles suspended in deionised water with 1 mL of 100 μM DPPH solutions. The samples were vortexed and allowed to scavenge DPPH in dark for 30 min. The absorbance of the supernatants after centrifugation at 14,000 rpm for 5 min was measured at 517 nm by using ELICO SA 165 Array spectrophotometer, India. The measurements were done in triplicates and the scavenging percentages were calculated using the formula:

$$\text{DPPH Scavenging \%} = (Ac - As)100/Ac$$

where, *Ac* and *As* are absorption of blank DPPH and DPPH subjected to interact with the sample at 517 nm respectively. The effect of varying the quantity of the particles on the scavenging ability was also studied with different concentrations of magnetite particles from 6 mg/ml to 0.18 mg/ml, synthesized using 0.5 ml of D-Glucose.

3. Results and discussion

Magnetite particles were synthesized by a facile hydrothermal route employing D-Glucose as a reducing agent as depicted in Fig. 1. In the present work, the nitrogen purging is not required in order to obtain pure magnetite phase, which makes this method simple and efficient to obtain hydrophilic magnetite particles in one step suitable for biological applications. The fabrication of Fe_3O_4 nanoparticles follows the two steps, i.e., precipitation of $Fe(OH)_3$ and hydrothermal treatment. The products after the reaction of $Fe(OH)_3$ with D-Glucose, appear as black precipitate showing the characteristic color of magnetite and were strongly attracted to external magnetic field which ensures efficient washing by repeated magnetic decantation. Reactions carried out at different soaking times showed that samples synthesized at 16 h duration showed good crystallinity with prominent peaks in XRD patterns and strong absorption bands in FT-IR spectra.

3.1. Physical properties – structural, microstructural and magnetic properties

XRD pattern of the particles synthesized is shown in Fig. 2. It can be seen that all the main peaks on the XRD pattern of the sample are related to hematite for the sample synthesized in the