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Optimization of process parameters for the rapid biosynthesis of hematite nanoparticles

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ABSTRACT

Hematite (α-Fe_2O_3) nanoparticles are widely used in various applications including gas sensors, pigments owing to its low cost, environmental friendliness, non-toxicity and high resistance to corrosion. These nanoparticles were generally synthesized by different chemical methods. In the present study, nanoparticles were synthesized rapidly without heat treatment by biosynthesis approach using culture supernatant of *Bacillus cereus* SVK1. The physiochemical parameters for rapid synthesis were optimized by using UV–visible spectroscopy. The time taken for hematite nanoparticle synthesis was found to increase with the increasing concentration of the precursor. This might be due to the inadequate proportion of quantity of biomolecules present in the culture supernatant to the precursor which led to delayed bioreduction. Greater quantities of culture supernatant with respect to precursor lead to rapid synthesis of hematite nanoparticles. The nucleation of the hematite nucleus happens more easily when the solution pH was less than 10. The optimum parameters identified for the rapid biosynthesis of hematite nanoparticles were pH 9, 37 °C (temperature) and 1 mM ferric chloride as precursor. The particles were well crystallized hexagonal structured hematite nanoparticles and are predominantly (110)-oriented. The synthesized nanoparticles were found to contain predominantly iron (73.47%) and oxygen (22.58%) as evidenced by Energy Dispersive X-ray analysis. Hematite nanoparticles of 15–40 nm diameters were biosynthesized in 48 h under optimized conditions, compared to 21 days before optimization.

1. Introduction

Hematite (α-Fe_2O_3) is a naturally abundant versatile material which is used in a wide range of applications such as in lithium ion batteries, gas sensors, fine ceramics, pigments, photo anode in photoelectrochemical cells, field effect transistor, catalysts, and photoelectrolysis reactors [1,2]. The semiconductor properties of the hematite are highly beneficial in photocatalysis, solar energy conversion and water splitting. Hematite is exceptionally stable and is often the concluding stage of conversions of other iron oxides. Hematite nanoparticles are generally prepared by various chemical techniques such as hydrothermal treatment [3], electrospinning polyvinylpyrrolidone/ferric acetyl acetonate composite followed by annealing at 500 °C [4], sol–gel method [5], vapor–solid growth techniques [6], forced hydrolysis of Fe (III) solution [7], and calcination of γ-Fe_2O_3 [8]. Till date, the best method of nanoparticle synthesis developed for controlled size and morphology appears to be thermal decomposition. But thermal decomposition method is a complicated process requiring high temperature. These methods are not only expensive but also have a complex production process or require special equipment, large scale production of uniform-sized nanocrystals are critical and are not environment friendly. Use of biological organisms such as microorganisms or plant extract may be an efficient alternative to chemical and physical methods for the generation of metal or metal oxide nanoparticles in an eco-friendly manner. Till date, plant mediated synthesis is limited solely to metal nanoparticles, however bacteria assisted biosynthesis of metal oxide nanoparticles has been reported.

In our previous study, hematite nanoparticles were synthesized after 21 days by using culture supernatant of *Bacillus cereus* SVK1 (GENBANK Accession number: KF612021). Even though this biosynthesis process was easy and environmentally friendly, it was time-consuming [9]. Optimization of the reaction parameters and ingredients can result in rapid synthesis of nanoparticles with controlled sizes. In the present study, optimization of physiochemical parameters was carried out for the rapid biosynthesis of hematite nanoparticles. UV–visible spectrophotometry is one of the most frequently employed techniques in characterizing nanoparticle synthesis.

2. Materials and Methods

2.1. Materials

All chemicals (analytical grade) and media components were purchased from HiMedia (Mumbai, India).

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2.2. Rapid Biosynthesis of Hematite Nanoparticles

2.2.1. Preparation of Culture Supernatant

The optimized media containing sucrose, beef extract, sodium chloride, ferrous sulfate, magnesium chloride and potassium dihydrogen phosphate in the concentration of (g/L) 8.6473, 8.2926, 5.0, 0.0053, 0.05 and 0.04 respectively (reported elsewhere) was used for culturing *B. cereus* SVK1. A loop full of *B. cereus* SVK1 bacterial colony was inoculated in 100 mL of sterile optimized media (pH 6.5) and it was incubated at 37 °C for 48 h on a shaker (100 rpm). The culture was centrifuged at 10,000 *g* for 10 min to obtain supernatant.

2.2.2. Effect of Precursor

Various precursors *viz.* ferric citrate, ammonium ferric citrate, ferric nitrate, ferric chloride, ferrous sulfate, mixture of ferric chloride + ferrous sulfate, mixture of potassium ferrocyanide + potassium ferricyanide were used to study the effect on the synthesis of hematite nanoparticles. Culture supernatant was mixed with equal volume of 1 mM different precursor solution and incubated at 35 °C at 100 rpm in a rotary shaker until formation of hematite nanoparticles in the solution which can be identified by visible color change of the solution from golden yellow to black [10,11].

2.2.3. Effect of Concentration of Precursor

Equal volumes of cell-free supernatant and precursor (ferric chloride) of different concentration was mixed and incubated at 35 °C at 100 rpm in a rotary shaker to study the effect of concentration of precursor on the synthesis of hematite nanoparticles.

2.2.4. Effect of Ratio of Culture Supernatant and Precursor

To study the effect of ratio of culture supernatant and precursor on the synthesis of hematite nanoparticles, cell-free supernatant and precursor (ferric chloride) were mixed in different proportions and incubated at 35 °C at 100 rpm in a rotary shaker.

2.2.5. Effect of pH

For studying the influence of pH value of the reaction system (culture supernatant and precursor mixture) on the synthesis of hematite nanoparticles, equal volumes of cell-free supernatant and 2 mM precursor (ferric chloride) was mixed. The pH of solution was adjusted with 0.1 M hydrochloric acid/0.1 M sodium hydroxide and incubated at 35 °C at 100 rpm in a rotary shaker.

2.2.6. Effect of Temperature

To study the effect of temperature on the synthesis of hematite nanoparticles, equal volumes of cell-free supernatant and 2 mM precursor (ferric chloride) were mixed and incubated at different temperatures.

2.3. Synthesis of Hematite Nanoparticles Under Optimized Conditions

Supernatant was mixed with equal volume of 1 mM ferric chloride solution and the pH was adjusted to 8 with sodium hydroxide solution. This mixture was incubated at 35 °C until the color of the solution changes to black. The solution was centrifuged at 10,000 *g* for 15 min to collect the nanoparticles as pellet. The nanoparticles were washed twice with Milli Q water and dried at room temperature. Dried nanoparticles were used for characterization and application studies.

2.4. Characterization of Nanoparticles

UV–visible spectroscopy (Schimadzu UV spectrophotometer, model UV-1800) helps in characterizing optical properties of metal nanoparticles. Particle shape and size was characterized by using a field emission scanning electron microscope (FE-SEM) (Model: SIGMA VP, make: Carl Zeiss Microscopy GmbH, Germany) equipped with X-ray energy-dispersive spectrometry system and atomic force microscopy (AFM) (NanoSurf Easy Scan2, Switzerland). Crystalline structure was identified by X-ray Electron Diffraction analysis using D8 Advance Powder X-ray diffractometer (Bruker, Germany). Chemical composition was identified by IR Affinity-1 FTIR (Shimadzu, Japan). Particle size distribution and stability of the nanoparticles were studied using Nanopartica SZ-100 nanoparticle analyzer (Horiba Ltd., Kyoto, Japan).

3. Results and Discussion

3.1. Optimization of Physiochemical Parameters

3.1.1. Effect of Precursor

Hematite nanoparticles of different structures have been prepared by chemical method using different precursors such as ferric chloride [12–16], ferric nitrate [15,17,18], potassium ferrocyanide [19], iron (II) acetate [20], ferrous sulfate [21–22]. In the present study, the effect of various precursors which aid in rapid synthesis of hematite nanoparticles was studied. SVKI culture supernatant reduced all the precursors (except mixture of potassium ferrocyanide + potassium ferricyanide) within 45 days (Fig. 1a). Initial color change was observed with ferric chloride treated with SVKI culture supernatant (21 days). Flasks containing other precursor *viz.* ammonium ferric citrate, ferric citrate and mixture of ferric chloride + ferrous sulfate produced color change in 35 days. Whereas those containing ferric nitrate and ferrous sulfate produced hematite nanoparticles in 45 days. The solubility of precursors specifically in water affected the kinetics of the reaction [23]. Less soluble precursors led to the formation of mixed phases of hydroxides. The inorganic anions from the precursor got selectively adsorbed on some of facets during the crystallization and directed the final morphology of the nanoparticle. Further, along with the different morphologies the starting precursor material also affected the phases of the material

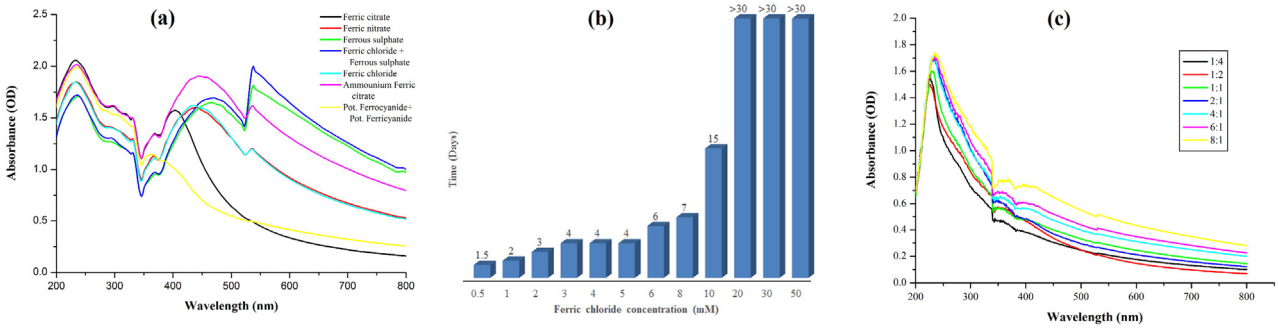

Fig. 1. (a) UV–visible spectra of hematite nanoparticles synthesized using different precursor, (b) time taken for hematite nanoparticle synthesis with different precursor concentration and (c) UV–visible spectra of hematite nanoparticles (diluted) synthesized with different ratio of precursor and culture supernatant.