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Sub-micrometric and nanometric solid phases obtained through reductive decomposition reaction of β-cyclodextrin

B-siklodekstrin indirgeyici bozunma reaksiyonu yoluya elde edilen alt mikrometrik ve nanometrik katı fazlar

Abstract: Objective: Cyclodextrins have been used to catalyze chemical reactions in the synthesis of different materials. The aim of this study is to produce nanoparticles using cyclodextrin as a nanoreactor.

Methods: In this study, nanoparticles from the solid phase of iron oxide (Fe3O4), copper oxide (CuO) and metallic silver (Ag0) were obtained through hydrothermal synthesis at 100 and 150°C for six hours. This was produced for cyclodextrin glycosyltransferase from Bacillus lehensis isolated from wastewater of a cassava flourmill. The nanoparticles were characterized through X-ray diffraction Fourier transform infrared spectroscopy and field emission gun scanning electron microscopy.

Results: The images demonstrated that the nanoparticles exhibited a polyhedral shape with a diameter of 100 nm for Fe3O4, an irregular oval shape with a diameter of 45 nm for CuO and a platelet shape with a diameter of 138 nm for Ag0.

Conclusion: Based on this characterization, the proposed technique proved to be an efficient, low-cost, convenient method for the production of sub-micrometric and nanometric solid phases and can likely be scaled up for industrial use. The results demonstrate the possibility of producing nanoparticles using cyclodextrin as a nanoreactor.

Keywords: Iron oxide, copper oxide, metallic silver, cyclodextrin

Özet: Amaç: Siklodekstrinler değişik materyallerin sentezindeki kimyasal reaksiyonlarının katalizasyonunda kullanılmaktadır. Bu çalışmanın amacı nanopartikül olarak siklodekstrin kullanıp bir nanoreaktör oluşturmaktır.

Metod: Bu çalışmada, katı fazdaki demir oksit (Fe3O4), bakır oksit (CuO) ve metalik gümüş (Ag0) nano partikülleri 6 saatlik 100 ve 150°C de hidrotermal sentezleme yol ile elde edilmiştir. Burada, siklodekstrin glikotransferaz üretimi, Tapyoka (Manyok) deşirmeni atık suyundan izole edilen Bacillus lehensis’den elde edilmiştir. Nanopartiküllerin karakterizasyonu ise x – ışını kırılımının Fourier dönü-

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Introduction

Cyclodextrin glycosyltransferase (CGTase, EC 2.4.1.19) is a bacterial enzyme capable of converting the starch in cyclodextrins (CDs) [1]. CDs are cyclic oligosaccharides and its cone structure has a hydrophobic cavity. CDs are externally soluble due to the presence of primary and secondary OH groups [2].

The use of CDs as chemical reactors is based on the hydrophobic cavity, which has the ability to recognize molecules and form inclusion complexes with a wide range of molecules and ions [3,4]. CDs can be used to encapsulate metal complexes in this hydrophobic cavity without the need for covalent bonds, thereby allowing the construction of supramolecular structures that can serve as precursors for condensed phases, such as oxides, metals, polymers and biomolecules [5]. The control of these properties on the sub-micrometric or nanometric scale allows the use of these systems in a wide range of applications in the field of nanotechnology, such as in the controlled release of pharmacological agents, electronic applications and catalytic processes [6,7].

The ability to employ organic and inorganic molecules and supramolecular aggregates for the formation of stable inclusion complexes in aqueous solutions allows the use of CDs as reactors for the formation of iron oxide ($Fe_3O_4$), copper oxide (CuO) and metallic silver (Ag) on the nanoscopic scale [8]. The advantages of the high surface/volume ratio of solid phases formed by reactions with CDs make these substances important in a number of technological applications, allowing greater surface sensitivity as well as a reduction in material costs [9].

Magnetite ($Fe_3O_4$) has been used in biotechnology and biomedicine for the separation of biological molecules as well as in magnetic resonance imaging, the controlled release of pharmacological agents and clinical diagnostic processes [8]. Tenorite (CuO) has been used as a catalyst for the conversion of carbon monoxide into carbon dioxide [10]. Ag nanoparticles have adequate optical, electrical and thermal properties for incorporation into products such as chemical and biological sensors and antimicrobial linings [11].

The aim of the present study was to employ CDs produced through the treatment of CGTase from *Bacillus lehensis* isolated from the wastewater of a flourmill as nanoreactors for the synthesis of the solid phase of $Fe_3O_4$, CuO and Ag.

Materials and Methods

Bacteria and enzyme production

*Bacillus lehensis* was isolated from wastewater samples from a cassava flour mill in Brazil. The 16S rRNA sequence was deposited in the genetic sequence databank of the US National Center for Biotechnology Information (GenBank: HQ399547). For *Bacillus lehensis* grown and CGTase production was realized fermentation process. Was carried out in a 5-L stirring tank reactor (Bio-t-mini Zeta, Rapperswil, Switzerland) at 35°C, 150 rpm, initial pH of 9.2, containing 2 L production medium. For this was used nutrient medium containing 0.500% cassava starch (w/v), 0.374% yeast extract (w/v), 0.375% tryptone (w/v), 0.100% K$_2$HPO$_4$, 0.020% MgSO$_4.7$H$_2$O and 1.000% Na$_2$CO$_3$ (w/v). Fermentations were run for 72 h at 35±1°C. Enzymatic activity was measured based on the discoloration of phenolphthalein solutions, following the method of Makela et al. [12].

Purification of CGTase

CGTase was purified in a two-step process through precipitation with ammonium sulfate 80% and the dialyzed enzyme was chromatographed on a DEAE-Sepharose 6B column (Pharmacia Fine Chemical Inc.) containing immobilized β-CD.
Production of cyclodextrin

The enzyme reaction using CGTase from *Bacillus lehensis*, 1.0% potato starch (w/v) in Tris-HCl buffer, pH 8.0, was performed at 55°C for 35 h. Following centrifugation at 8.8000 g for 10 min, the supernatant was analyzed using high-performance liquid chromatography with UV detection at 210 nm of the 4.6x250 mm column (Phenomenex, Torrance, CA, USA) at 26°C. The samples were added to the column following membrane filtration (0.22 µm; Millipore). The mobile phase was acetonitrile/water (50:50) (v/v) with a flow of 0.7 mL.min⁻¹. The injection volume was 20 mL.

Synthesis of solid phase of magnetite, tenorite and metallic silver

Different proportions of FeCl₃·H₂O (Sigma Aldrich, 98%) and β-CD were mixed for the production of magnetite (Fe₃O₄); different proportions of CuSO₄·5H₂O (Sigma Aldrich, 98%) and β-CD were mixed for the production of tenorite (CuO); and different proportions of AgNO₃ (Sigma Aldrich, 99%) and β-CD were mixed for the production of Ag⁺. The working volume was 100 ml (volume of the stainless steel reactor is 150 ml) at 100°C (Fe₃O₄ and CuO) and at 150°C (Ag⁺) and 1907 atm (pressure calculated from general equation of gases) for 6 h. Whereas, the temperatures tested were 80, 90, 100, 110, 120, 130, 140 and 160°C. The following were the synthesis conditions: concentration (10:10, 20:10, 20:10 [M/M]) of CD, FeCl₃·H₂O, CuSO₄·5H₂O and AgNO₃; pH (6.7 and 8.0); ethylene glycol (25, 50 and 75%); and dextran (10 and 20 M). The reagents were mixed at 65°C for 30 minutes and the pH was adjusted with NH₄OH (25%). The solid phase formation reaction was performed through hydrothermal synthesis with a stainless steel reactor lined internally with polytetrafluoroethylene. The solid particles were washed six times with deionized water and dried at 100°C. Due to the difficulty in synthesizing silver particles, temperatures ranging from 70 to 150°C (at 10°C intervals) were also tested. The synthesis of the Fe₃O₄, CuO and Ag⁺ under the ideal reaction conditions (10 M of FeCl₃·H₂O and 20 M of β-CD at 150°C, pH 8.0; 10 M of CuSO₄·5H₂O and 20 M of β-CD at 150°C, pH 8.0; and 20 M of Ag⁺ and 10 M of β-CD at 100°C) was demonstrated by X-ray photoelectron spectroscopy (XPS).

Characterization of oxide and metallic phases

Fourier transform infrared (FT-IR) and XPS spectra have important characteristics to identify the structure of the sample.

X-ray photoelectron spectroscopy

XPS was performed with a SIEMENS D5000 (Kristallofle), using Cu Kα radiation and a wavelength of 1.5406 Å, with a current of 30 mA, voltage of 40 kV, scanning of 0.02° and time of 3 s.

Fourier transform infrared spectroscopy

The particles were prepared with a mixture of 5 mg and 150 mg of KBr pressed at 40 KN for 5 min and identified using FT-IR spectroscopy (Shimadzu). Analysis was performed in the range of 4500 to 500 cm⁻¹, with a resolution of 4 cm⁻¹ and 16 cm⁻¹.

Scanning electron microscopy

Field emission gun scanning electron microscopy (FEG-SEM; JEOL, model 7500 F) was used for the analysis of the size and shape of the particles. Secondary electron and backscattered electron detectors were used for the analysis.

Results

The present study describes the development of a method for synthesizing nanoparticles of magnetite, tenorite and silver. The XPS, FT-IR and FEG-SEM findings confirm and characterize the synthesis of these nanoparticles.

Synthesis of oxide phase of copper and iron and metallic phase of silver

After losing their cyclic structure in the presence of H⁺ ions, CDs become non-cyclic oligosaccharides. FeCl₃·H₂O at 1907 atm and 150°C, CuSO₄·5H₂O at 1907 atm and 150°C AgNO₃ at 1907 atm and 100°C added to the non-cyclic oligosaccharide in the redox reaction respectively form Fe(OH)₃, Cu(OH)₂ and Ag₂O and carboxylic acid. The addition of NH₄OH induces the acid-base reaction to form ammonium carboxylate salt [13]. The terminal amide contained in the salt impedes the growth of the nanoparticles, thereby stabilizing the shape of the nano-phase (Figure 1).

The first indication of the formation of nanoparticles is a change in color [14]. In the formation of the magnetite, tenorite and silver nanoparticles, the reagents in the solution exhibited a reddish brown, blue and transparent col-
oration, respectively, prior to hydrothermal synthesis and dark red, black and dark green coloration, respectively, following hydrothermal synthesis.

Characterization of oxide phase of copper and iron and metallic phase of silver

XPS revealed the structure of the Fe₃O₄ (Fig. 2 a), CuO (Fig. 2 d) and Ag⁺ (Fig. 2 g) nanoparticles under the ideal reaction conditions: 10 M of FeCl₃.H₂O and 20 M of β-CD at 150°C, pH 8; 10 M of CuSO₄.5H₂O and 20 M of β-CD at 150°C, pH 8; and 20 M of Ag⁺ and 10 M of β-CD at 100°C. Figure 2 a, d and g show the crystalline planes of the particles synthesized from the use of CDs as nanoreactors in comparison to the diffraction standards with PDF No. 19–629 (Fe₃O₄), 3–884 (CuO) and 4–783 (Ag). The diffraction peaks of the nanoparticles were 4.85, 2.96, 2.53, 2.09, 1.61, 1.48 and 1.28 for magnetite, 2.48, 2.32, 1.87, 1.58, 1.51, 1.41, 1.38 and 1.23 for tenorite and 2.35, 2.04, 1.44, 1.23 for silver. These peaks are consistent with the standard structures. The results indicate that the products are made up of pure phases.

The Figure 2 b, e and h displays the FT-IR spectra of the synthesized Fe₄O₆, CuO and Ag⁺ nanoparticles, respectively. The signal at 574 cm⁻¹ [15] is an absorption band characteristic of Fe-O from Fe₃O₄ (Fig. 2 b). In a study involving the synthesis of Fe₃O₄ nanoparticles, Hong et al. (2007) [16] demonstrated FT-IR spectra with 586.8 cm⁻¹ vibration bands in the bonding of Fe-O to Fe₃O₄. The presence of NH, NH₂ and CN is demonstrated by the acute absorption bands at 3323 cm⁻¹ [17], 1619 cm⁻¹ [18] and 1016 cm⁻¹ [19], respectively. The formation of terminal amide stabilizes the phase of magnetite formed, impeding the growth of the particles. Absorption peaks at 1067, 1104 and 1162 cm⁻¹, 1339 and 1404 cm⁻¹ and 2347, 2376 and 2929 cm⁻¹ are attributed to C-N [20], C-O-H [21], and C-H bonds [22], which characterize the formation of organic molecules with terminal amide illustrated in Figure 1.

The absorption peak at 480-585 cm⁻¹ is characteristic of Cu-O. Figure 2 e shows an absorption peak at 530 cm⁻¹. The signals at 1637, 2374, 2932 and 3460 are vibrations in the molecular bonds of C=O, CO₂, CH and NH in the formation of tenorite nanoparticles [23].

Silver nanoparticles are demonstrated by an intense band centered at 410 nm (Fig. 2 h), as suggested by Suresh (2012). The FEG-SEM images (Fig. 2 c, f, i) reveal the shape and size of the particles obtained through hydrothermal synthesis under optimized experimental conditions. Magnetite exhibited a polyhedral shape measuring 100 nm in diameter, with particles dispersed on the surface (Fig. 2 c). Tenorite exhibited an irregular shape and size measuring 45 nm in diameter, with particles dispersed on the surface (Fig. 2 f). The silver particles were uniformly dispersed, measuring 138 nm in diameter (Fig. 2 i).
The ability of CDs to form stable inclusion complexes in aqueous solutions allowed the hydrothermal synthesis of precursors for the formation and stabilization of nanometric particles of Fe$_3$O$_4$ [24], CuO [25] and Ag$^+$ [26] in the present study. The dispersed Fe$_3$O$_4$ nanocrystals were synthesized by hydrothermal method.

**Figure 2:** XPS of standard Fe$_3$O$_4$ and particles obtained (a); FT-IR spectrum of Fe$_3$O$_4$ particles (b); High-resolution micrographs (MEV-FEG) of Fe$_3$O$_4$ particles (c); XPS of standard CuO and particles obtained (d); FT-IR spectrum of CuO particles (e); High-resolution micrographs (MEV-FEG) of CuO particles (f).

**Discussion**
The green hydrothermal synthesis route was reported for dispersed TiO2 nanoparticles with particle sizes of 9–16 nm of β-CD (11)

This Simple hydrothermal synthesis technique presents well dispersed pure nanoparticles with high yield and uniform particle size. Nano-compounds produced by thermal decomposition present stable features of size, shape, and structure. Nanoparticle of MgO produced for hydrothermal reaction exhibited a high surface area with stable features of structure. The particle size distribution of magnetite particles were restricted by the use of the b-CD [27]. This novel technique is efficient, with high reactivity of reactants, low air pollution and energy consumption, with b-CD renewable after the extraction process.

The production of sub-micrometric and nanometric solid phases can likely be scaled up for industrial use [28]. Further studies on the applications of these promising nanoparticles from CD are needed and could offer benefits to the field of biotechnology.

The nanoparticle synthesis process involves the chemical catalysis of metal ions Ronald Breslow [29]. CDs have widely been used as reactors that can bond to substrates and catalyze chemical reactions [30]. CDs cooperate in the cleavage of ester [31]. The CDs catalyzes the debromination and bromination of bromocyclohexadienones and aromatic rings, respectively. The CDs also catalyzes the reaction of formic acid with bromine [32]. The CD catalyze the isomerization of vitamin D3 by thermal reaction [30].

Figure 1 illustrates the synthesis of the solid phases of magnetite, tenorite and silver from the reductive decomposition reaction of β-CD. This synthesis is possible due to the oxide-reduction mechanism of metal ions stemming from the CD. The decomposition of b-CD under the reaction conditions reduces Fe3+ ions for final formation of Fe3O4. The particles of superparamagnetic magnetite were synthesized by cyclodextrin [9]. Uniform copper oxide nanoparticles are prepared via thermal decomposition using CD [11]. The Shape- silver nanoparticles were synthesized by seed-mediated techniques in the presence of β-cyclodextrin [33]. CDs promote the deoxygenation of allylic alcohols formation by effective mass transfer [34], and a,b-unsaturated acids, α-keto esters and conjugated dienes by reduction [35]. The conversion of metal ions into nanoparticles was stabilized using NH4OH for the formation of terminal amide, impeding an increase in the size of the particles [36]. The properties of synthesized particles vary when in the form of nanostructures due to the greater surface area per unit in comparison to larger particles [37]. Magnetite has potential use in biomedicine and biotechnology, such as the separation of a number of biomolecules, as well as in magnetic resonance imaging,
the controlled release of pharmacological agents and clinical diagnostic methods. Copper oxide nanoparticles have applications in gas sensors and superconductors [38]. Evenly dispersed silver nanoparticles have applications in biological and chemical detection methods as well as in electronic devices.

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