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Mechanochemical synthesis of magnetically responsive materials from non-magnetic precursors

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ABSTRACT

Mechanochemical synthesis of various types of magnetically responsive materials from non-magnetic powdered precursors has been developed. The preparation is based on the mechanochemical conversion of ferrous and ferric ions at the presence of alkaline hydroxide into magnetic iron oxides nanoparticles (maghemite identified by XRD measurements). The presence of powdered nonmagnetic materials during the mechanochemical process led to the efficient deposition of magnetic nanoparticles on the surface of the treated materials in the form of individual nanoparticles and their aggregates. The prepared magnetically responsive materials have been used as adsorbents for xenobiotics removal and as a carrier for enzymes immobilization.

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1. Introduction

Magnetic nano- and microparticles have attracted an increasing interest in various fields including nanoscience, nanotechnology, biosciences, biotechnology and environmental technology. Many chemical procedures have been used to synthesize magnetic particles, such as classical co-precipitation, reactions in constrained environments (e.g. microemulsions), sol-gel syntheses, sonochemical reactions, hydrothermal reactions, hydrolysis and thermolysis of precursors, flow injection syntheses, electrospray synthesis and microwave synthesis [1,2].

Recently mechanochemical procedures have been used to synthesize magnetic iron oxides and ferrites nanoparticles [3–5]. Mechanochemistry represents one of several ways of chemical activation. In solid-state mechanochemistry, nonthermal chemical reactions occur because of the deformation and fracture of solids, which are technically induced by milling or grinding of the materials. During this process the mechanical energy induces chemical reactions and phase transformations [6].

Up to now, mechanochemical synthesis has been employed mainly for the production of individual iron oxides and ferrites. However, mechanochemistry can be successfully used also for the preparation of magnetically responsive materials from originally

nonmagnetic powdered precursors. In this paper we present a very simple, generally applicable procedure for the preparation of magnetic materials from variety of inorganic, organic and biological precursors, together with the illustration of their possible applications as adsorbents and enzyme carriers. Mechanochemical postmagnetization can be very useful for smart magnetic modification of diverse non-magnetic materials.

2. Materials and methods

Materials: FeCl₃·6H₂O, FeCl₂·4H₂O, montmorillonite, halloysite, *Candida rugosa* lipase (EC 3.1.1.3), 1,4-butanediol diglycidyl ether (BDDE), sodium (meta)periodate, 1,1'-carbonyldiimidazole (CDI), 4-nitrophenyl butyrate, dimethyl sulfoxide, Bismarck brown Y and sodium acetate were purchased from Sigma-Aldrich, USA. Microcrystalline cellulose, safranin O and 4-nitrophenol were from Lachema, Czech Republic, while the common chemicals were from Lach-Ner, Czech Republic. Finally powdered biological materials with diameters below 1 mm (spruce sawdust, scales from grass carp (*Ctenopharyngodon idella*), wheat straw, pistachio nut shells, peanut husks, oak acorns, spent coffee grounds), as well as potato starch and pine pollen were obtained locally.

The natural ochreous sediment containing biogenic iron oxides was collected using glass vessels from a water stream in Ceske Budejovice (Czech Republic); it was sieved through a 1 mm sieve to remove larger detrital fraction, then repeatedly washed with deionized water and air dried at a temperature not exceeding 50 °C.

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Mechanochemical synthesis of magnetically responsive materials: In the standard procedure a mixture of 1.35 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.005 mol), 0.50 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.0025 mol) and 4 g of sodium chloride (inert material used to avoid particles agglomeration) was grounded in a mortar at room temperature for 10 min. Then, appropriate amount of target nonmagnetic powdered material (usually 1–2 g) was added and after thorough mixing the process continued for another 10 min. As the last step, powdered potassium hydroxide (1.22 g) was added and after mixing the grinding continued for 10 min. After KOH addition the mixture became brown. During the grinding process the material was scraped from the mortar wall occasionally. After finishing the mechanochemical process, the magnetically modified material was thoroughly washed with water (to remove soluble impurities and free iron oxides particles) and stored in a suspension, or it was air dried.

Structural characterization of iron oxide nanoparticles prepared by mechanochemical procedure: X-ray powder diffraction (XRD) patterns of selected samples were recorded on PANalytical X'Pert PRO instrument in Bragg–Brentano geometry with Fe-filtered $\text{CuK}\alpha$ radiation (40 kV, 30 mA). The samples were inserted into conventional front-loading cavity sample holder and scanned in the 2θ range of $10\text{--}90^\circ$ (step size 0.017°). The commercial standards SRM640 (Si) and SRM660 (LaB_6) from NIST were used for the evaluation of the line positions and instrumental line broadening, respectively. The acquired patterns were evaluated using the X'Pert HighScore Plus software (PANalytical) together with PDF-4+ database.

Adsorption of organic dyes on magnetically responsive composites: 30 mg of selected magnetically modified adsorbents were mixed with 7.0 mL of water in a test tube. Then, 0.1–3 mL of stock water solution of a tested dye (1 mg/mL) was added and the total volume of the solution was made up to 10.0 mL with water. The suspension was mixed on a rotary mixer (Dyna, Norway) for 3 h at room temperature. The magnetic adsorbent was then separated from the suspension using a magnetic separator (MPC-1 or MPC-6, Dynal, Norway) and the clear supernatant was used for the spectrophotometric measurement. The concentration of free (unbound) dye in the supernatant (C_{eq}) was determined from the calibration curve. The amount of dye bound to the unit mass of the adsorbent (q_{eq}) was calculated using the following formula:

$$q_{eq} = (C_{tot} - C_{eq})/3 \quad (\text{mg/g}) \quad (1)$$

where C_{tot} is the total (initial) concentration of dye ($\mu\text{g/mL}$) used in the experiment. The value q_{eq} was expressed in mg of adsorbed dye per 1 g of adsorbent. Equilibrium adsorption data were fit to Langmuir adsorption isotherms using SigmaPlot software.

Immobilization of lipase on magnetic cellulose particles: *C. rugosa* lipase was immobilized on magnetically modified cellulose particles. Three various agents were used for activation of hydroxyl groups present in the cellulose structure, namely sodium periodate, butanediol diglycidyl ether and carbonyldiimidazole. To prepare samples, 30 mg of prepared magnetic cellulose particles were washed with water and magnetically separated by NdFeB magnet. In the next step, particles were treated by the activating agent. Using 1,1'-carbonyldiimidazole (CDI), 1.5 mL of 0.5% (w/v) solution in dimethyl sulfoxide was added to particles. For the periodate method, 1.5 mL of 1% (w/v) solution of sodium (meta)periodate (NaO_4) in 0.1 M sodium acetate buffer pH 4 was utilized. During activation by the epoxide method, 1.5 mL of 3% (v/v) solution of 1,4-butanediol diglycidyl ether (BDDE) in 0.25 M NaOH was used. Particles were shaken with these activating agents on an automatic rotator (20 rpm) for 24 h at room temperature in the dark. After the modification procedure, particles were magnetically separated, supernatants were poured off and particles were repeatedly washed with distilled water. Subsequently, 1.5 mL of lipase solution (1 mg/mL) in 50 mM potassium phosphate buffer,

pH 7.5, was added to the activated particles and shaken on automatic rotator (20 rpm) for 24 h at 4°C . After the immobilization procedure, particles were magnetically separated, supernatant containing unbound enzyme was removed and particles with bound enzyme were repeatedly washed with buffer until no enzyme activity in the supernatant was detected. Magnetic cellulose particles with immobilized lipase were stored in buffer at 4°C .

Lipase assay: Activity of lipase immobilized on magnetic cellulose particles was determined spectrophotometrically using 0.5 mM 4-nitrophenyl butyrate (dissolved in ethanol) in 50 mM potassium phosphate buffer, pH 7.5. Particles of magnetic cellulose with attached lipase were stirred during the reaction in buffer containing the substrate, then magnetically separated to the bottom of the cuvette to stop the reaction and increasing amount of yellow-colored 4-nitrophenol was measured at 405 nm.

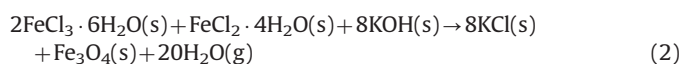
Molar absorption (extinction) coefficient (ϵ) of the reaction product was determined spectrophotometrically for the specific medium conditions used in this enzyme assay. Coefficient for 4-nitrophenol in 50 mM potassium phosphate buffer, pH 7.5 at 405 nm was 13815 L/mol cm.

Operational stability of immobilized lipase: Reusability of lipase immobilized on magnetic cellulose particles was tested as its operational stability; it was repeatedly used for 7 reaction cycles. Particles with attached lipase were washed with buffer between each cycle. Activity of lipase was measured spectrophotometrically as described previously. Residual activities of lipase after each cycle were determined and compared taking the initial activity in the first cycle as 100%.

Time stability of immobilized lipase: Particles of magnetic cellulose with immobilized lipase were stored in the reaction buffer at 4°C for 30 days and percentage of residual enzyme activity on the carrier was determined. Possible presence of lipase released from the support was tested during this time period by measuring the activity of free lipase in the supernatant.

3. Results and discussion

Mechanochemical synthesis of magnetic composite materials: In mechanochemical synthesis, hydrated solid reactants, namely ferrous and ferric chlorides reacted with KOH during grinding in a mortar to form magnetite nanoparticles. To avoid agglomeration, the excess of sodium chloride was added to the precursors before grinding. The following reaction takes place [7]:



Magnetite nanoparticles as the primary product are stable only in inert atmosphere [5]. However, in the described process which

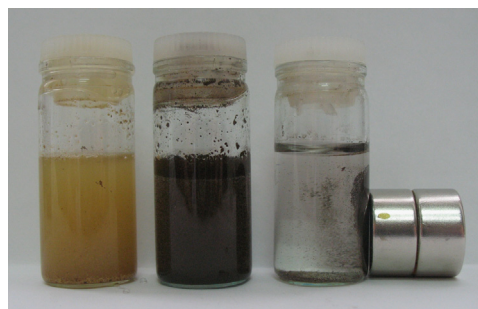


Fig. 1. Appearance of original powdered oak acorns suspension (left), suspension of oak acorns powder after magnetic modification (middle) and demonstration of magnetic separation of magnetically modified oak acorns powder (right).

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