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Development of advanced biorefinery concepts using magnetically responsive materials

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ABSTRACT

Utilization of magnetic materials and particles brings a considerable simplification into biorefinery technologies, based on their fast, simple and selective separation even from various difficult-to-handle environments and conditions. Additionally, application of magnetically responsive (bio)catalysts can significantly improve the productivity, economic feasibility, sustainability and product quality during the biorefinery processes. This review is focused on the presentation of typical examples of magnetic materials applicable in biorefinery, especially for the preparation of magnetically responsive enzymatic and whole-cell biocatalysts, as well as solid acid/base catalysts, magnetically responsive adsorbents or magnetically separable materials with suitable properties for isolation and purification of target compounds from complex mixtures. This brief overview emphasises remarkable possibilities of magnetic materials and magnetic techniques and their application potential in biorefinery technologies.

1. Introduction

Biological materials of different origin are very important sources of biologically active compounds and other biomaterials-derived molecules and products. A new biorefinery paradigm enabling conversion of almost all the types of biomass feedstocks to different types of biochemicals, biofuels and energy through jointly applied conversion technologies has been developed recently. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic bio-based industry [1].

Various standard fermentation, separation and catalytic processes and technologies, developed several decades ago, are routinely used in biorefinery; substantial improvement of technologies is necessary in all stages of biorefinery processing. In this review paper, we will pay our attention to the possible applications of magnetically responsive nano- and microparticles and composites containing them [2]. These materials exhibit several types of responses to external magnetic field. The most important one enables efficient separation of ferro- and ferrimagnetic particles and composites containing them using an appropriate magnetic separator, permanent magnet or electromagnet. Due to the fact that majority of biological materials exhibit diamagnetic (i.e., “nonmagnetic”) properties, magnetic separation enables selective separation of magnetically responsive materials from biological mixtures. Magnetic particles have already been employed in many applications in various areas of biosciences, medicine, biotechnology and environmental technology; enormous amount of laboratory scale experiments has confirmed the usefulness of these materials [3]. However, there are not so many examples of successful applications of magnetically responsive materials in large scale processes in biotechnology and biorefinery. Large scale biotechnology, fermentation and biorefinery processes require the availability of low-cost, but still efficient magnetically responsive materials, and large scale magnetic separators enabling efficient removal of magnetic materials from biological suspensions. Implementation of magnetic particles can significantly improve the productivity, economic feasibility, sustainability and product quality during the biorefinery processes and considerably simplify many separation techniques.

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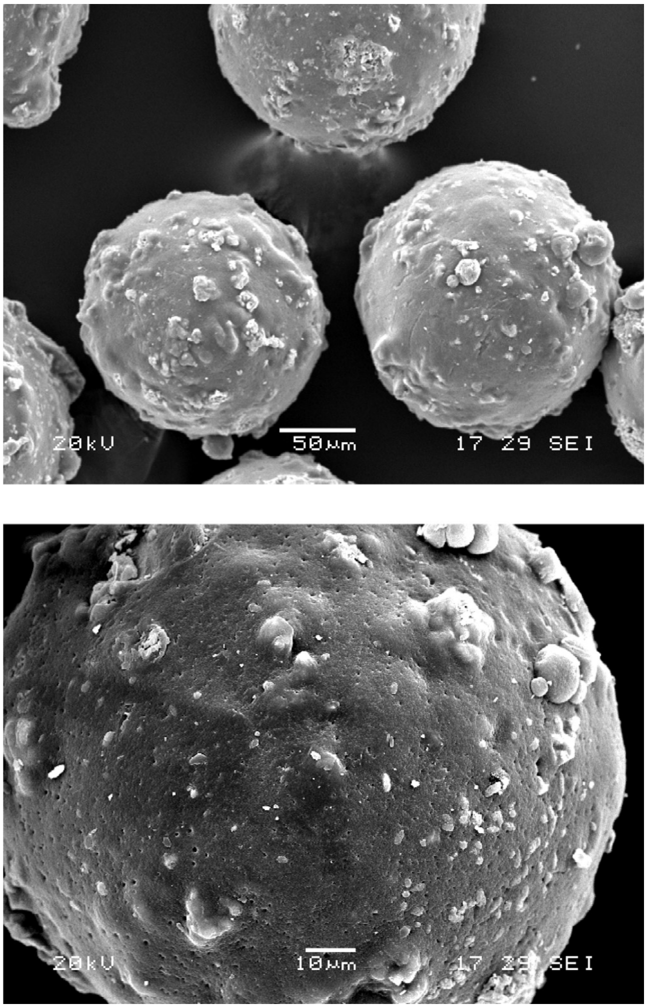

Fig. 1. Scanning electron microscopy of magnetic macroporous bead cellulose. Magnification: 300 × (top), 1000 × (bottom). Reproduced, with permissions from Ref. [13].

In this review paper, we will focus on three specific areas of complex biorefinery processes where magnetically responsive materials can be used efficiently, namely:

- Application of magnetically responsive (bio)catalysts.
- Application of magnetically responsive microbial cells.
- Application of magnetic separation processes for the isolation of target compounds.

We hope that this short review paper will stimulate the biorefinery research community to pay more attention to the application of these progressive materials and technologies.

2. Preparation of magnetic materials

Both basic ferro- and ferrimagnetic materials (e.g., magnetite, maghemite, different types of ferrites) and magnetically responsive composite materials formed by magnetically labelled diamagnetic materials are of great importance. Various procedures have been used to synthesize magnetic nano- and microparticles, such as classical coprecipitation, reactions in constrained environments (e.g., microemulsions), sol-gel syntheses, hydrolysis and thermolysis of precursors, sonochemical and microwave reactions, hydrothermal reactions, flow injection syntheses, electrospray syntheses and mechanochemical processes [4–8].

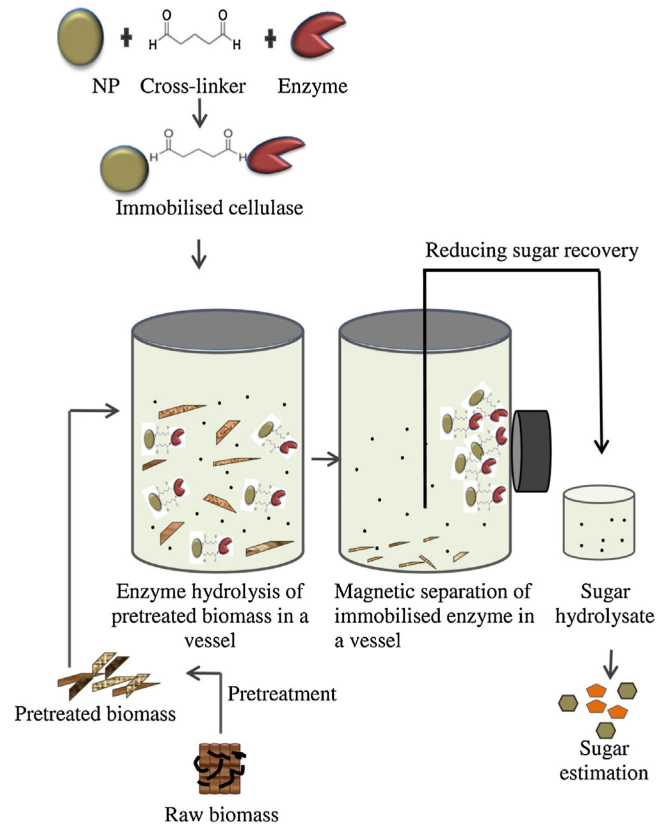

Fig. 2. A typical flowchart illustrating the hydrolysis of plant biomass using cellulose immobilised on magnetic particles [17].

Coprecipitation technique (aging stoichiometric mixture of ferrous and ferric salts in aqueous alkaline medium) is the simplest procedure to synthesize large amount of iron oxide nanoparticles, either in the form of magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3). The addition of chelating organic anions (e.g., citric, gluconic, or oleic acids) or polymer surface complexing agents (dextran, carboxydextran, starch, or polyvinyl alcohol) during the formation of magnetic iron oxides enables to prepare surface stabilized, biocompatible nanoparticles. Alternatively, synthesis of uniform iron oxide nanoparticles can be performed in synthetic and biological nanoreactors, such as water-swollen reversed micellar structures in non-polar solvents, apoferritin protein cages, dendrimers, cyclodextrins, and liposomes. Hydrothermal syntheses of magnetite nanoparticles are carried out in aqueous media in reactors or autoclaves at high pressure and temperature. The sol-gel process is based on the hydroxylation and condensation of molecular precursors in solution, originating a "sol" of nanometric particles; further condensation and inorganic polymerization followed by heat treatments are needed to acquire the final crystalline state. The polyol process utilizes e.g. polyethylene glycol as a solvent exhibiting high dielectric constants, which can dissolve inorganic compounds; polyols also serve as reducing agents as well as stabilizers to control particle growth and prevent interparticle aggregation [4].

The flow injection synthesis employs continuous or segmented mixing of reagents under laminar flow regime in a capillary reactor which enables precise external control of the process; magnetite nanoparticles with the diameters 2–7 nm can be prepared. In spray pyrolysis, a solution of ferric salts and a reducing agent in organic solvent is sprayed into a series of reactors, where the aerosol solute condenses and the solvent evaporates; maghemite particles with