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Nanoscale tuning of enzyme localization for enhanced reactor performance in a novel magnetic-responsive biocatalytic membrane reactor



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ABSTRACT

The synergistic magnetic interaction between biofunctionalized magnetic nanoparticles and a hybrid membrane is exploited to develop a nano-inspired, magnetic-responsive enzyme membrane (micro) reactor. The novelty of the process lies in the use of superparamagnetic nanoparticles both as enzyme carrier to form bionanocomposites and as nanofiller to form organic–inorganic (O/I) hybrid membrane to render both reversibly magnetizable. This reversible magnetic force facilitates dispersion of the enzymatically active magnetic nanoparticles (bionanocomposites) over the membrane surface, allows retention of the enzyme by a large pore, i.e., high-flux membrane and renders enzyme recovery after use is very easy. The feasibility and versatility of the concept is demonstrated through 2 case studies, i.e., a pectin/polygalacturonase and an arabinoxylan/xylanase system, for membrane fouling prevention through in-situ enzymatic membrane cleaning. This robust multidisciplinary approach resulted in a 75% reduction in filtration resistance, thus realizing significant energy savings and high reactor productivity. The advantages of the novel approach include: (i) absence of need for neither functionalized nor retentive membrane surfaces, (ii) no leakage of nanosized, high surface area immobilized enzymes through microporous membranes, (iii) full recovery and re-usability of the enzymes, (iv) possibility to apply enzyme cocktails to achieve optimal conversions and (v) use of the membrane beyond the enzyme life cycle.

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Abbreviations: BCA, bicichronic acid; BMR, biocatalytic membrane reactor; BMR^{SP}, superparamagnetic biocatalytic membrane reactor; BSA, bovin serum albumin; DMF, dimethylfomamide; EDX, dispersive X-ray spectroscopy; Enz^{SP}, superparamagnetic immobilized enzymes; GalA, galacturonic acid; M^{SP}, superparamagnetic mixed matrix membrane; NP^{SP}, superparamagnetic nanoparticles; Pect^{SP}, superparamagnetic immobilized pectinase; PVDF, polyvinylidene fluoride; SEM, scanning electron microscopy; TMP, transmembrane pressure; Xyl^{SP}, superparamagnetic immobilized xylanase; O/I, organic–inorganic; NP, nanoparticle

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1. Introduction

Superparamagnetic ferric oxide based nanoparticles (NP^{SP}) represent a versatile biocompatible nano-platform. Hence, colloidal dispersions of NP^{SP} surrounded by biocompatible coatings have attracted much interest for use in smart devices, sensors, catalysis, bio-separation, magnetic guidance, and targeted drug delivery [1–4]. When used for bio-magnetic separation after functionalization with for instance enzymes, they are often associated with long-term stability over multiple cycles and during storage, in addition to easy recovery from reaction mixtures [5].

The research on hybrid membranes, consisting of a polymeric matrix with incorporated NP^{SP}, holds many unexplored interesting avenues [6]. Their incorporation leads to stimuli-responsive “smart” polymeric membrane with magnetic properties that can be modulated in a reversible manner.

This study presents an innovative combination of these two NP^{SP} application fields to create a new type of efficient, magnetic-responsive enzyme membrane reactor. The NP^{SP} serves a dual purpose in the biocatalytic membrane (micro) reactors (BMRs) where superparamagnetism is employed to tailor physical confinement of enzymes at the membrane surface, thus combining biocatalysis, superparamagnetic nanoparticles and superparamagnetic membranes during reaction.

Immobilization of enzymes on membranes to form BMRs is a typical example of process intensification which aims at hybridizing two or more traditional operations to make industrial production more efficient [7], since the coupling lowers chemicals and energy consumption, while increasing reaction yields and minimizing waste [8–10]. BMRs have been applied in different sectors, e.g., in the pharmaceutical industry [11,12], in the production of bio-renewables [13] and in waste valorization [14].

However, in a prolonged run, membrane fouling and enzyme activity loss demand chemical cleaning of the membrane and enzyme replenishment, respectively. Since enzymes are loaded in conventional BMRs either by simple adsorption on the membrane or by covalent binding to the membrane, they are highly sensitive to chemical cleanings. In addition, when membrane immobilized enzymes get denatured or oversaturated, it is very difficult (if not impossible) to replenish with fresh enzymes. Consequently, the ultimate fate of biocatalytic membranes is only disposal. Hence, a novel immobilization technique that fulfils the conditions of the BMRs, but still facilitates membrane chemical cleaning and enzyme renewal is urgently needed.

The aforementioned combination of enzyme functionalized superparamagnetic nanoparticles (bionanocomposites) and stimuli-responsive “smart” polymeric membrane is now suggested as the key to solve this bottleneck issue. Particularly, the appearance of the magnetic properties of the NP^{SP} only in presence of an external magnetic field gives a high degree of freedom for reversible enzyme immobilization [15]. They can first be dispersed easily in a reactor in the absence of the magnetic field and readily moved to a desired location by switching the magnetic field on, while being removed later by switching it off again [16,17].

Therefore, in this study, NP^{SP} are used as (1) support material for enzyme immobilization to form an enzyme immobilized superparamagnetic particles (Enz^{SP}) and (2) as fillers in an organic-inorganic (O/I) hybrid membrane to form a superparamagnetic membrane (M^{SP}). Both the Enz^{SP} and the M^{SP} thus exhibit superparamagnetism which allows the Enz^{SP}, initially homogeneously dispersed in the bulk reaction mixture, to be attracted onto the M^{SP} surface. The synergies of the magnetic-responsive M^{SP} and the Enz^{SP} enhance the formation of a dynamic layer of Enz^{SP} on the M^{SP} surface. More specifically, by applying an external magnetic field parallel to the surface of the M^{SP}, the particles dispersed in the bulk stream will align parallel to the

applied magnetic field [18–20]. The relatively stronger magnetic force at the surface of the membrane due to the presence of M^{SP}, creates a magnetic field gradient that helps in relocating the NP^{SP} in the liquid to the surface of the membrane. Since the north and south poles of the NP^{SP} attract each other, they align the NP^{SP} and form chains. On the contrary, particles coming close to each other with the magnetization direction parallel will repel each other, thus leaving spaces between the aligned nanobiocatalysts. The dynamic layer of Enz^{SP} can thus be considered as a specific reactor resulting from an array of microreactors formed by the voids between the NPs connected by magnetic forces. The M^{SP} thus serves as a magnetic field actuator, i.e. create a localized magnetic field, while also helping in a magnetophoretic dispersion of the NP^{SP} on and near the membrane surface.

Their superparamagnetic properties can again be employed later on to recover the Enz^{SP} from the M^{SP} surface whenever the M^{SP} has for instance been severely fouled and needs chemical cleaning, or when the Enz^{SP} has been denatured, by simply switching off the external magnetic field and a subsequent mechanical stirring. This novel approach, further referred as a superparamagnetic BMR (BMR^{SP}), offers a paradigm shift in addressing two of the most critical bottlenecks of BMRs currently hindering their widespread use: easy recycling of the enzyme and extending the membrane working life cycle beyond the enzyme's active period. Similar to direct onto membrane immobilization, the enzyme immobilized on NP^{SP} will indeed be denatured in time. The novelty of the current system however is the ease to remove the denatured Enz^{SP} and re-supply with fresh Enz^{SP}, while direct onto membrane immobilization forces one to dispose a full membrane module.

As a proof-of-concept, the BMR^{SP} is applied in an in-situ enzymatic membrane cleaning for a pectin/polygalacturonase system, as encountered in a typical vegetation wastewater. The optimization of pectinase immobilization and the characterization of the M^{SP} were first carried out. The effectiveness of the BMR^{SP} system is then evaluated, including the effect of Enz^{SP} loading, reaction temperature, self-cleaning capacity, and Enz^{SP} reusability. In a second example, the BMR^{SP} is tested in an arabinoxylan/xylanase system, as typically used in bio-ethanol production or present in brewery and bakery wastewaters [21]. Ultimately, the effect of using a superparamagnetic enzyme mixture is also evaluated.

2. Materials and methods

2.1. Materials

Dimethylformamide (DMF) was acquired from Arcos. Polyvinylidene fluoride (PVDF, 534 kDa), 2-cyanoacetamide, citrus fruit pectin (25–35% degree of esterification), polygalacturonase, galacturonic acid, sulfuric acid, sodium tetraborate, *m*-hydroxybiphenyl and glycine were obtained from Sigma-Aldrich (Belgium); borate buffer solution (pH 9.2) from Fisher scientific; water extractable arabinoxylan (Mw = 300 kDa) and xylazyme AX tablets from Megazyme (Bray, Ireland), *Bacillus subtilis* XynA xylanase (Grindamyl H640) from Danisco (Copenhagen, Denmark), methoxy(polyethyleneoxy)-propyltrimethoxysilane (PEG Silane), (3-aminopropyl) trimethoxysilane (APTMS) from ABCR chemicals.

2.2. NP^{SP} synthesis

The NP^{SP} used as nanofillers during membrane preparation were polyethylene glycol (PEG) coated iron oxide nanoparticles with an average particle size of 8 nm. Analytical grade ferric chloride ferric trichloride (FeCl₃) was used as salt precursor, ethylene glycol as both

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