Chemical Engineering Journal 308 (2017) 853–862

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Effect of operational parameters on the performance of a magnetic responsive biocatalytic membrane reactor

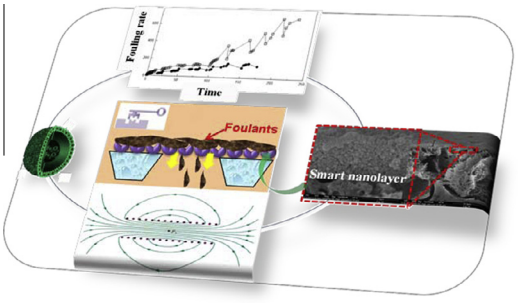
Abaynesh Yihdego Gebreyohannes [a,b,e], Lidietta Giorno [c], Ivo F.J. Vankelecom [a], Thierry Verbiest [d], Pierre Aimar [e,*]

[a] Centrum voor Oppervlaktechemie en Katalyse Dept. M²S, Faculteit Bio-ingenieurswetenschappen, KU Leuven, Leuven Chem&Tech, Postbus 2461, Celestijnenlaan 200F, 3001 Leuven, Belgium
[b] Department of Environmental and Chemical Engineering, University of Calabria (DIATIC-UNICAL), via P. Bucci CUBO 45ª, 87036 Rende (CS), Italy
[c] Institute on Membrane Technology, National Research Council of Italy, ITM-CNR, Via P. Bucci Cubo 17C, 87036 Rende (CS), Italy
[d] Molecular Imaging and Photonics, Faculty of Bioengineering Sciences, KU Leuven, Celestijnenlaan 200d - box 2425, 3001 Leuven, Belgium
[e] Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France

## HIGHLIGHTS

- Magnetic stimuli-responsive biocatalytic membrane reactor was optimized.
- It was stable over a broad range of various operating parameters.
- Flux and feed concentration, related by reactor productivity were crucial parameters.
- Productivity increased with increased enzyme amount, despite the universal trend.
- There was no enzyme leakage, activity decay or TMP rise continuously over 240 h.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 10 May 2016
Received in revised form 8 September 2016
Accepted 12 September 2016
Available online 28 September 2016

*Keywords:*
Biocatalysis
Membrane fouling
Nanocomposite
Magnetic nanoparticle
Packed bed reactor
Stimuli-responsive membrane

## ABSTRACT

In this work, the performance of an innovative magnetic responsive biocatalytic membrane reactor ($BMR^{SP}$) has been investigated under various operational parameters. In particular, feed concentrations, flow rates across the bed, temperature and amount of biocatalytic bead were varied to probe the flow-dependent transport and kinetic properties of the reaction and the subsequent hydrolytic performance of the $BMR^{SP}$. The rate of fouling for the $BMR^{SP}$ was always lower than a corresponding control system. For a given enzymatic concentration, a constant foulant hydrolyzing capacity is identified. At 3 g/m$^2$ pectinase containing bionanocomposites, the $BMR^{SP}$ hydrolytic efficiency was 1.5 g/m$^2$ h. This efficiency was further increased by increasing the amount of bionanocomposites per membrane area. This further allowed the $BMR^{SP}$ to hydrolyze higher loads of foulants while keeping a low if not zero increase in TMP over time at constant flux.

Identification of an optimal operating condition laid the platform for continuous operation of the $BMR^{SP}$ over 200 h, without visible transmembrane pressure drift while maintaining constant flux. Product assay in the permeate gave constant value in the entire duration, i.e., no enzymatic activity decay owing to

*Abbreviations:* $Enz^{SP}$,, enzyme functionalized superparamagnetic nanoparticles; $M^{SP}$,, superparamagnetic membrane; TMP,, transmembrane pressure; $BMR^{SP}$,, superparamagnetic biocatalytic membrane reactor; $NP^{SP}$,, superparamagnetic nanoparticles; DMF,, dimethylformamide; PVDF,, polyvinylidene fluoride; GalA,, galacturonic acid; APTMS,, 3-aminopropyl) trimethoxysilane; PEG,, polyethylene glycol; BCA,, bicinchoninic Acid; Pe,, Peclet number; $J_{opt}$,, optimum flux (L/m$^2$ h); SEM,, scanning electron microscopy.

* Corresponding author.
*E-mail addresses:* abayneshy@yahoo.com (A.Y. Gebreyohannes), l.giorno@itm.cnr.it (L. Giorno), ivo.vankelecom@biw.kuleuven.be (I.F.J. Vankelecom), thierry.verbiest@fys.kuleuven.be (T. Verbiest), Pierre.Aimar@univ-toulouse.fr (P. Aimar).

http://dx.doi.org/10.1016/j.cej.2016.09.057

stable enzyme immobilization and no leakage through the pores of the membrane owing to the synergistic magnetic interaction between the magnetic membrane and magnetic bionanocomposites.

The obtained stability over a broad range of operational parameters and sustainable performance over long period gives a high prospect to the newly developed $BMR^{SP}$ to be utilized in continuous biocatalysis and separation, thereby significantly improved process efficiency.



## 1. Introduction

An immobilized enzyme membrane reactor provides the platform for a continuous reactor operation without the need for an additional step to recover the enzyme [1–3]. The average residence time within the reactor is far shorter for the substrate than for the immobilized enzyme, resulting in a high productivity compared to a batch operation in similar conditions [4].

Immobilized enzymes cannot however be replaced with fresh enzyme neither can the membrane be easily cleaned when the whole structure gets oversaturated with substrate or the enzyme is deactivated.

To surmount these major challenges, the concept of a magnetic stimuli-responsive biocatalytic membrane reactor has been investigated, that can reversibly immobilize enzymes on a membrane by effectively switching on or off an external magnetic field [5].

The system contains enzyme functionalized superparamagnetic nanoparticles (bionanocomposites; $Enz^{SP}$) and a "smart" paramagnetic polymeric membrane ($M^{SP}$). The application of an external magnetic field parallel to the surface of the $M^{SP}$ induces the $Enz^{SP}$ which are initially dispersed in the bulk stream to align along the applied magnetic field and to be attracted towards the $M^{SP}$ to form a biocatalytic layer [6–8]. The voids between the $Enz^{SP}$s connected head-to-tail by magnetic forces form as many micro-reactors. The system applied to the in-situ degradation of pectins and arabinoxylans showed an interesting performance. Moreover, thanks to its magnetic responsiveness and absence of residual magnetic memory in the absence of an external magnetic field, it was possible to easily recover the $Enz^{SP}$ and use both the enzyme and membrane over many cycles.

The accumulation of particles or solutes rejected by the so formed composite membrane can however lead to less flux at fixed transmembrane pressure (TMP) or a higher TMP for a given constant flux [9]. This eventually would result in a short operational period, frequent cleaning and premature replacement of the biocatalyst.

An increase in mass transfer resistance or an enzyme activity loss have a similar effect on the biocatalytic membrane reactor performance. The mechanisms to control them however are very different [10] and require a fine control of process parameters such as feed flowrate, feed and enzyme concentration and reaction temperature [11].

Thus, the main objective of this paper is the detailed investigation of the effect of different operational parameters on the efficiency and stability of the $BMR^{SP}$. The different operational parameters considered include: flux to control the mass transfer rate, temperature, feed concentration and enzyme concentration to control the reaction rate. The design of a continuous flow immobilized enzyme membrane reactor requires the knowledge of the enzyme kinetic parameters which have been assessed for the $Enz^{SP}$ in a flow-through continuous flow biocatalytic membrane reactor.

### 1.1. Background

Due to simultaneous reaction and separations, absence of enzyme-product inhibition can be assumed [1–3]. Therefore, the initial reaction rate ($v_r$) in a continuous flow reactor can be calculated based on the following mass balance equation [4,12]:

$$\frac{d(VC)}{dt} = (FC)_{in} - (FC)_{out} + v_r V_a \tag{1}$$

where $F$ is the feed flowrate (L/s), $C$ is the concentration (g/L), $v_r$ is the volumetric reaction rate (g/L s) and $V_a$ is the reactor volume (L). At steady state the accumulation term is zero and the reaction rate is:

$$v_r = \frac{F(C_f - C_p)}{V_a} \tag{2}$$

where $C_f$ and $C_p$ are substrate concentration in the feed and in the permeate (g/L) respectively. The $BMR^{SP}$ is made of bed of catalytic beads supported by a flat sheet membrane. The actual reactor volume ($V_a$) is the void volume, i.e. the fraction of the bed volume that is not filled with catalyst:

$$V_a = V_T - V_p \tag{3}$$

where $V_p$ is the volume of the $Enz^{SP}$ beads present on the surface of the membrane and $V_T$ is the total bed volume ($dm^3$) given by the $BMR^{SP}$'s geometric dimensions as:

$$V_T = L * A_m \tag{4}$$

where L is the catalytic bed thickness in dm (e.g. obtained from SEM micrographs in Fig. 2), while $A_m$ is the membrane area (0.16 $dm^2$ in the present work).

$V_p$ can be calculated as:

$$V_p = \frac{m_p}{\rho_p} \tag{5}$$

where $m_p$ is the total mass of $Enz^{SP}$ ($4.8 * 10^{-3}$ g) deposited on the membrane and $\rho_p$ is the density of ferrous particles (5150 g/L).

By combining Eqs. (3)–(5), the volume of the reactor is then:

$$V_a = LA_m - \frac{m_p}{\rho_p} \tag{6}$$

By combining Eqs. (2) and (6), the following equation is obtained for the volumetric reaction rate, $v_r$ (mol/L h):

$$v_r = \left\{ \frac{F\rho_p}{L\rho_p A_m - m_p} * (C_f - C_p) \right\} / M_{wt} \tag{7}$$

where $M_{wt}$ is the molecular weight of the hydrolysis product.

## 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 (GalA; $M_{wt}$: 212 g/mol) and glycine were obtained from Sigma-Aldrich (France). Borate buffer solution (pH 9.2) was supplied by Fisher scientific and methoxy(polyethyle