멤브레인(Membrane Journal)
Vol. 19, No. 1 March, 2009, 72-82

Bio-degradation of Phenol in Wastewater by Enzyme-loaded Membrane Reactor: Numerical Approach

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(Received February 24, 2009, Revised March 3, 2009, Accepted March 24, 2009)

Abstract: A mathematical model was written for simulating the removal of phenol from wastewater in enzyme-loaded membrane reactor (EMR). The numerical simulation program was developed so as to predict the degradation of phenol through an EMR. Numerical model proves to be effective in searching for optimal operating conditions and creating an optimal microenvironment for the biocatalyst in order to optimize productivity. In this study, several dimensionless parameters such as Thiele Modulus (Φ^2), dimensionless Michaelis-Menten constant (ξ), Peclet number (Pe) were introduced to simplify their effects on system efficiency. In particular, the study of phenol conversion at different feed compositions shows that low phenol concentrations and high Thiele Modulus values lead to higher reactant degradation.

Keywords: *wastewater treatment, numerical simulation, membrane reactor, bio-degradation*

1. Introduction

Phenol is not only an important raw material in petrochemical, pharmaceutical, plastic and pesticide industry but also one of the major components concerning the industrial wastewater [1]. During the phenol production, depending on the process, up to 0.6 ton of wastewater, containing 2~3% phenol and other 5~10% of organic pollutant like an acetone, sodium salt and aromatic hydrocarbons, is produced per ton of phenol [2]. Wastewater containing phenol is produced by different type of industries, such as plastics and resins, coal refining and steel industries etc. The major sources of phenols and related aromatics from various industrial effluents are given in Table 1.

Among these pollutants, the phenol is one of the most common representatives of toxic organic compounds, harmful to human health, and causing an increase in the demand of oxygen in water even at low levels. Furthermore, phenol is persistent in the environment when released in large quantities, or if it is continuously released from a source. Therefore, the development of an effective technology for the removal of phenol from wastewater is important.

These effluents can be treated by physicochemical methods such as adsorption [4,5], oxidation [6,7], biological (enzymatic) treatments [8-10], membrane treatment [1,2,11,12], and combined techniques [13,14]; however, they often suffer from serious drawbacks in-

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Table 1. Sources of Phenols and Other Related Aromatic Compounds in Wastewater [3]

Source	Significant phenolic compounds
Petroleum refining	Hydrocarbones, benzenes, substituted benzene, toluenes, n-octanes, n-decanes, naphthalenes, biphenyl, phenol, cyanide, sulphide and ammonia
Petrochemicals	Naphthalene, heptanes, benzenes, butadiene, C-4, phenol and resorcinol
Basic organic chemical manufacturing	m-amino phenol, resorcinol, dinitrophenol, p-nitrophenol, trinitrophenol, benzene sulphonic acids, aniline, chlorobenzenes and toluenes
Coal refining	Phenol, catechol, o-, m-, p-cresol, resorcinol, hydroquinone, pyridines, xylene, toluene, benzoic acid, pycolines and lutidines
Pharmaceuticals	Toluene, benzyl alcohol, phenyl acetic acid, chlorinated products of benzene, chloroform, ether and ethyl alcohol
Tannery	Tannin, catechin, phenol, chlorophenol and nitrophenols
Pulp and paper mills	Lignin, vanilline, vanillic acid, ferulic acid, cinnamic acid, benzoic acid, guadiachols, catechol, phenyl propionic acid, phenols and chlorophenols

cluding high cost and the formation of hazardous byproducts. The validity of each of these methods will depend on a combination of factors, the most important of which are the phenol concentration and any other chemical pollutants eventually present in the wastewater. Among these methods, enzymatic technology offers several advantages compared to other techniques, such as: 1) low energy requirement, 2) easy to control, 3) operate over a wide range of conditions and 4) minimal environmental impact, etc. [15-19].

Generally, the enzymatic bioconversion processes are operated in batch operation and at the end of the reaction the enzyme is inactivated before recovering the final products. The reactors used in this system are relatively simple and easy to operate but when these systems must treat large quantities of wastewater such as industrial applications, there are a certain number of disadvantages: low productivity, high operating costs, loss of catalytic activity due to inactivation and great variability of the quality of the products, etc. [20]. These problems were solved by introducing immobilization of enzyme in certain support, especially by combining the membrane technologies with immobilization technique. Immobilization of enzyme means that the enzymes have been localized in certain support (usually solid support) so that it can be reused continuously [21]. Many studies have been carried out with different biological media to biodegrade organic compounds (especially, phenolic compounds) present in wastewater [22-31]. Among the various biocatalysts, tyrosinase is a copper-containing protein that catalyses the phenolic compounds to o-diphenols and the oxidation of o-diphenols to o-quinones [24,32-36]. It is widely distributed in microorganism, animals and plants. Much of the current interest in the development of biotechnological applications has been focused on the use of mushroom tyrosinase [37]. A major drawback of phenol biotransformation in wastewater using tyrosinase is the inactivation of enzyme due to the interaction of quinone with its amino groups [15,38].

In this study, a numerical simulation program was developed to predict the degradation of phenol through an enzyme-loaded membrane reactor. Numerical models prove to be effective in searching for optimal operating conditions and creating an optimal microenvironment for the biocatalyst to optimize the productivity [39,40]. In order to design and optimize the process, it is important to understand the enzyme kinetic properties and the effects of operating conditions on reactor performances. In this report an approach for the development of the enzyme-loaded membrane reactor was made, accounting for the following steps:

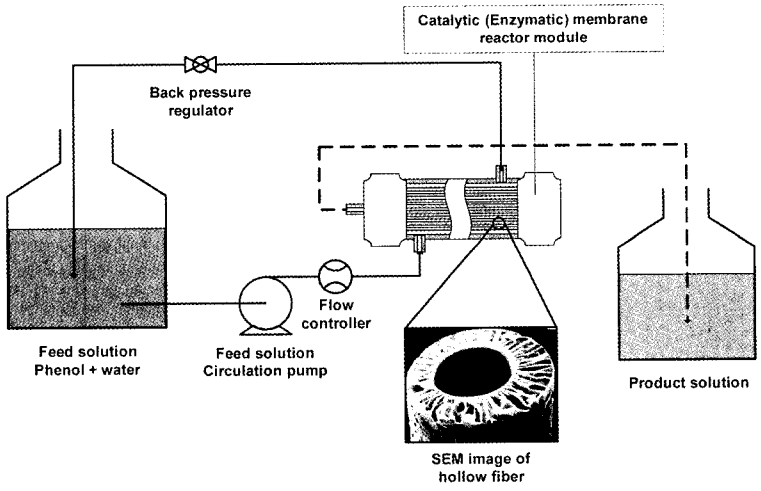

Fig. 1. Schematic drawing for phenol wastewater treatment with catalytic membrane reactor.

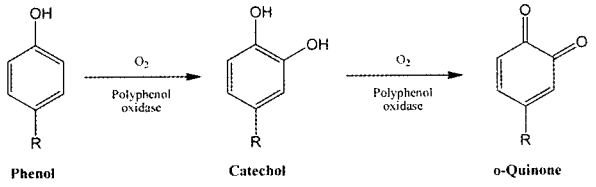

Fig. 2. Hydroxylation of phenols and oxidation of catechols catalyzed by polyphenol oxidase [15].

1) Assumptions for chemical reactions and reactors.

2) Identification of parameters.

3) Mathematical formulation of mass balance and reactions.

4) Coding the model equations in the solving program (COMSOL Multiphysics® 3.4).

5) Model validation.

6) If necessary, modification and revise the assumptions and/or parameters, etc.

7) Calculation and analysis of the results.

8) Optimization and suggestions.

2. Materials and Methods: Description of System

Fig. 1 shows a schematic diagram of the system considered for the simulation of the degradation of phenol contained in wastewater. Fig. 2 shows the mechanism of reaction taking place in the membrane pores, where polyphenol oxidase converts phenol to catechol and finally to o-quinone.

In this study an enzyme-loaded capillary membrane (a hollow fiber membrane configuration) has been used with polyphenol oxidase homogeneously immobilized in the asymmetric porous fibers. The feed solution (water + phenol), continuously re-circulated by means of a pump, is fed to the shell side of the membrane module. Depending on operating trans-membrane pressure difference (see the Darcy law, eq. 10), a part of the feed stream flows, in radial direction, through the membrane pores and herein the phenol is converted into its degradation products by means of the enzyme immobilized in the porous walls. By controlling the trans-membrane pressure, the residence time and, then, the contact time between substrate and enzyme can be easily controlled. The permeate stream (water + products of phenol degradation + unconverted phenol) is the final product of the process. The development of a mathematical method for this process aims to describe the species concentration profiles inside the membrane module and, then, the catalytic membrane reactor performance at different operating conditions.

Since the reactions take place only inside the membrane pores, no concentration profiles can arise in the bulk of liquid feed/retentate phase, also because the high trans-membrane convective flux through the porous membrane prevents any counter-diffusion of reactions products from the membrane pores to the feed

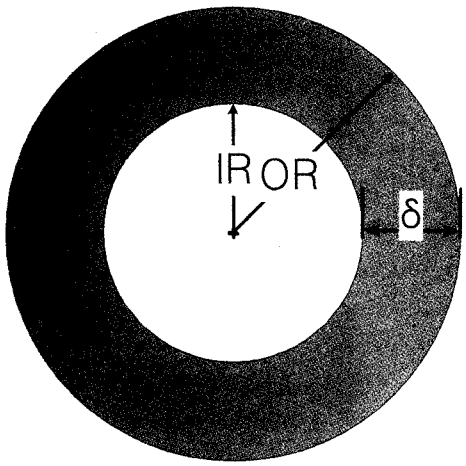

Fig. 3. Enzymatic capillary membrane cross section. Schematic coordinates of simulated dominium [41].

side bulk. Therefore, in the shell of the membrane module (feed side) there will be no variation of species concentration during the membrane module operation and, thus, it can be considered as a lumped parameter system, whose composition depends only on feed conditions. This composition can be assumed as the concentration value at the interface on the outer capillary surface.

Moreover, owing to the cylindrical symmetry of the capillaries, the species concentration inside the membrane pore changes only along the radial direction. Hence, this is that is a 1D (one dimensional) problem (Fig. 3).

The mathematical model for this system consists of the mass balances for the three species involved, accounting for the convection, diffusion and reaction along the radial direction inside the membrane pores. The partial differential equations constituting the model equations will introduced in the next paragraph.

3. Modeling and Kinetics

The model is based on the following assumptions [42,43]:

(1) Cylindrical symmetry of the EMR.

(2) Feed concentration is constant at feed side.

(3) Homogeneous enzyme distribution in the porous capillary support.

(4) *Michaelis-Menten* kinetics was considered for the both reactions.

(5) Effective diffusion coefficients for phenol, catechol and o-quinone were assumed to be the same.

The governing mass balance partial differential equations for phenol (A), catechol (B), and o-quinone (C) can be described for the radial coordinate accounting for convection-diffusion-reaction:

$$\frac{\partial C_A}{\partial t}+v_r\frac{\partial C_A}{\partial r}=D_A\left(\frac{1}{r}\frac{\partial C_A}{\partial r}+\frac{\partial^2 C_A}{\partial r^2}\right)+R_A \tag{1}$$

$$\frac{\partial C_B}{\partial t}+v_r\frac{\partial C_B}{\partial r}=D_B\left(\frac{1}{r}\frac{\partial C_B}{\partial r}+\frac{\partial^2 C_B}{\partial r^2}\right)+R_B \tag{2}$$

$$\frac{\partial C_C}{\partial t}+v_r\frac{\partial C_C}{\partial r}=D_C\left(\frac{1}{r}\frac{\partial C_C}{\partial r}+\frac{\partial^2 C_C}{\partial r^2}\right)+R_C \tag{3}$$

Reaction term in equations (1)~(3) can be expressed by using Michaelis-Menten kinetics as follows,

$$R_A=-\frac{v_{max}\cdot C_A}{K_M+C_A} \tag{4}$$

$$R_B=\frac{v_{max}\cdot C_A}{K_M+C_A}-\frac{v'_{max}\cdot C_B}{K'_M+C_B} \tag{5}$$

$$R_C=\frac{v'_{max}\cdot C_B}{K'_M+C_B} \tag{6}$$

By replacing the reaction term with eqs. (4)~(6) in eqs. (1)~(3):

$$\frac{\partial C_A}{\partial t}+v_r\frac{\partial C_A}{\partial r}=D_A\left(\frac{1}{r}\frac{\partial C_A}{\partial r}+\frac{\partial^2 C_A}{\partial r^2}\right)-\frac{v_{max}\cdot C_A}{K_M+C_A} \tag{7}$$

$$\frac{\partial C_B}{\partial t}+v_r\frac{\partial C_B}{\partial r}=D_B\left(\frac{1}{r}\frac{\partial C_B}{\partial r}+\frac{\partial^2 C_B}{\partial r^2}\right)+\left(\frac{v_{max}\cdot C_A}{K_M+C_A}-\frac{v'_{max}\cdot C_B}{K'_M+C_B}\right) \tag{8}$$

$$\frac{\partial C_C}{\partial t}+v_r\frac{\partial C_C}{\partial r}=D_C\left(\frac{1}{r}\frac{\partial C_C}{\partial r}+\frac{\partial^2 C_C}{\partial r^2}\right)+\frac{v_{max}\cdot C_B}{K'_M+C_B} \quad (9)$$

Boundary conditions and initial conditions are expressed as follow:

$$r=\frac{OD}{2}=OR\rightarrow[A]=C_A^{feed},\quad [B]=C_B^{feed}=0,$$
$$[C]=C_C^{feed}=0$$

$$r=\frac{ID}{2}IR\rightarrow \text{ convective flux}$$

Velocity of substrate in porous membrane can be predicted by Darcy's law or Brinkman equation

$$Q = k\frac{1}{\mu}\frac{S}{\theta}(\triangle p) \quad (10)$$

According to the eq. (10), the residence time can be easily controlled by pressure differences through the membrane with certain membrane substrate.

Introducing dimensionless group in equations (7~9)

$$r^*=\frac{r}{IR} \quad (11)$$
$$IR\le r\le OR\rightarrow 1\le r^*\le\frac{OR}{IR}$$

$$C_A^*=\frac{C_A}{C_A^{feed}} \quad (12)$$

$$C_A^{feed}\ge C_A\ge 0\rightarrow 1\ge C_A^*\ge 0 \text{ (reactant)}$$
$$C_B^*=\frac{C_B}{C_A^{feed}},\ 0\le C_B\le C_B^{feed}\rightarrow 0\le C_B^*\le 1$$
(product)
$$C_C^*=\frac{C_C}{C_A^{feed}},\ 0\le C_C\le C_C^{feed}\rightarrow 0\le C_C^*\le 1$$
(by-product)

$$t^*=\frac{t}{\tau} \quad (13)$$

where residence time (τ) can be defined as $\tau\frac{\delta}{v_r}$

The governing equations (7~9) then become:

$$\frac{IR^2}{D_A\tau}\frac{\partial C_A^*}{\partial t^*}+Pe_A\cdot\beta\frac{\partial C_A^*}{\partial r^*} \quad (14)$$
$$=\left(\frac{1}{r^*}\frac{\partial C_A^*}{\partial r^*}+\frac{\partial^2 C_A^*}{\partial r^{*2}}\right)-\Phi^2\beta^2\frac{C_A^*}{1+\xi\cdot C_A^*}$$

$$\frac{IR^2}{D_B\tau}\frac{\partial C_B^*}{\partial t^*}+Pe_B\cdot\beta\frac{\partial C_B^*}{\partial r^*} \quad (15)$$
$$=\left(\frac{1}{r^*}\frac{\partial C_B^*}{\partial r^*}+\frac{\partial^2 C_B^*}{\partial r^{*2}}\right)+\Phi^2\beta^2\frac{C_A^*}{1+\xi\cdot C_A^*}$$
$$-\Phi^2\frac{v'_{max}}{v_{max}}\frac{K_M}{K'_M}\beta^2\frac{C_B^*}{1+\xi\cdot\frac{K_M}{K'_M}C_B^*}$$

$$\frac{IR^2}{D_C\tau}\frac{\partial C_C^*}{\partial t^*}+Pe_C\cdot\beta\frac{\partial C_C^*}{\partial r^*} \quad (16)$$
$$=\left(\frac{1}{r^*}\frac{\partial C_C^*}{\partial r^*}+\frac{\partial^2 C_C^*}{\partial r^{*2}}\right)+\Phi^2\frac{v'_{max}}{v_{max}}\frac{K_M}{K'_M}\beta^2\frac{C_B^*}{1+\xi\cdot\frac{K_M}{K'_M}C_B^*}$$

where $\Phi^2=\frac{v_{max}\cdot\delta^2}{D_A K_M}$, $\xi=\frac{C_A^{feed}}{K_M}$, $\beta=\frac{IR}{\delta}$, $Pe=\frac{v_r\cdot\delta}{D_A}$

To solve the equations (14~16), the parameters were coded in COMSOL Multiphysics® 3.4. The kinetic constants and operating parameters used in the simulation work are listed in Table 2.

4. Results and Discussions

In this study, the steady state phenol degradation in an enzyme-loaded membrane reactor operated through the membrane pores was simulated. In particular, the effect of several dimensionless parameters such as Thiele Modulus (Φ^2), Michaelis-Menten constant (ξ), Peclet number (Pe) and the species concentration profiles along the radial coordinate inside the membrane was studied. One of the main advantages in using di-

Table 2. Kinetic Constants and Parameters used in the Simulation

Parameters	Values	Descriptions	References
OR	1.2 [mm]	Membrane outer radius	present work
IR	0.6 [mm]	Membrane inner radius	present work
δ	OR-IR [mm]	Catalytic membrane thickness	
L	14	Effective membrane length	present work
NF	4	Number of fiber charged in module	present work
ε	0.35	Porosity of membrane	present work
$A_{membrane}$	Π*OD*L*NF* ε	Effective membrane area	
c_{Afeed}	0.01 [mmol/l]	Concentration of phenol in feed stream	[34]
c_{Bfeed}	0.0 [mmol/l]	Concentration of catechol in feed stream	
c_{Cfeed}	0.0 [mmol/l]	Concentration of o-quinone in feed stream	
D_{Aeff}	0.89e-5 [cm^2/sec]	Effective diffusivity of phenol in water	[44]
D_{Beff}	0.89e-5 [cm^2/sec]	Effective diffusivity of catechol in water	
D_{Ceff}	0.89e-5 [cm^2/sec]	Effective diffusivity of o-quinone in water	
F	0.4 [cm^3/min]	Feed flow rate	present work
Vr	$F/A_{membrane}$	Velocity of feed solution	
Km1	0.7 [mmol/l]	Michaelis-Menten constant for 1st reaction	[34,45]
Km2	0.3 [mmol/l]	Michaelis-Menten constant for 2nd reaction	[34,45]
Vmax1	0.0029 [mmol/l/min]	Maximum reaction rate of 1st reaction	[34,46]
Vmax2	0.2 [mmol/l/min]	Maximum reaction rate of 2nd reaction	[34,46]
τ	δ/Vr	Dimensionless time	
Φ^2	Vamx1* δ^2/(D_{Aeff}*Km1)	Thiele Modulus	
ξ	C_{Afeed}/Km1	Dimensionless Michaelis constant	
β	IR/δ	Inner radius divided by thickness	
PeA	Vr* δ/D_{Aeff}	Peclet number for phenol	
PeB	PeA*(D_{Aeff}/D_{Beff})	Peclet number for catechol	
PeC	PeA*(D_{Aeff}/D_{Ceff})	Peclet number for o-quinone	

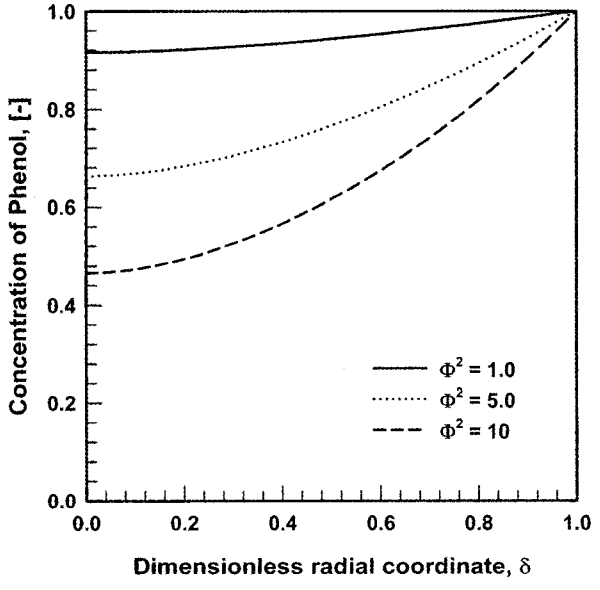

Fig. 4. Effect of Thiele Modulus (Φ^2) on concentration profile of phenol (ξ =0.014, $\Phi^2_{standard}$=0.0279).

mensionless equations is that dimensionless number values allow the rate determining step of the process and the relative weight of different mechanisms to be more easily individuated.

4.1. The Effects of Thiele Modulus

Thiele Modulus (Φ^2) has the physical meaning of a first order reaction rate divided by a diffusion rate [42]. A large value of Φ^2 indicates that the process is diffusion-limited whilst its small value means limitation by reaction kinetics. Fig. 4 shows the predicted phenol concentration profile along the radial coordinate inside the porous catalytic membrane, at different Thiele Modulus.

In particular, the phenol concentration reduces monotonically from its maximum value (the feed concentration) at the outer membrane surface. A large value

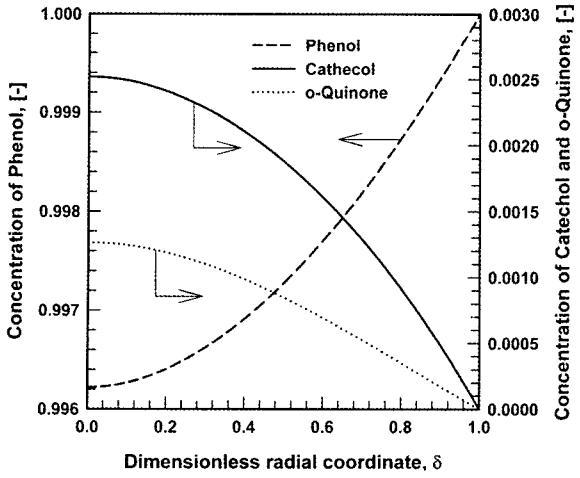

Fig. 5. Concentration profiles of three species in original operating conditions (operating conditions: Table 2).

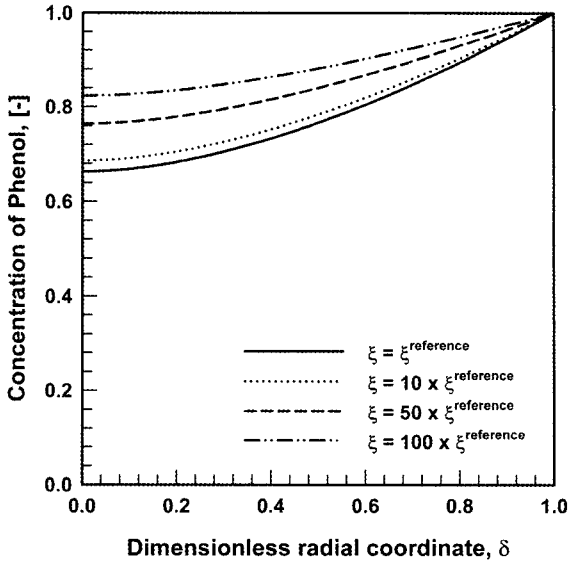

Fig. 6. Effect of dimensionless Michaelis-Menten constant (ξ) on concentration profile of phenol (at $\Phi^2=5$).

of this parameter (Φ^2) indicates a fast kinetics. The higher the Thiele Modulus, the higher the phenol conversion (that is, the lower the phenol concentration at the inner membrane surface). Based on these results, much more enzyme should be loaded in unit membrane area to accelerate biotransformation of phenol.

Considering the overall reaction mechanism shown in Fig. 2, the catechol produced by the phenol degradation is converted into o-quinone by the second reaction; the concentration profiles for all the three different species are reported in Fig. 5 at the following operating conditions of experimental data [32,34,45-47]: Thiele Modulus = 0.0279, Peclet = 3.0413 and ξ = 0.0143 (Table 2). As the intermediate product (catechol) concentration increases, the second reaction takes place and the o-quinone (third species) production starts to be produced appreciably.

As shown in Fig. 5, Thiele Modulus is too low and the reaction rate is not sufficient to appreciably convert phenol to other components. In order to improve the conversion rate of phenol, there are two options. One is increasing as much as possible either the amount of enzyme immobilized in capillaries or the enzyme activity [48]. However, there is a physical limit in the enzyme loading on the membrane and, thus, not high conversion enhancement can be achieved. The other possibility is to recycle the product stream to the feed solution tank. In this case the overall system becomes a batch process with an increase of phenol conversion to other component.

4.2. Dimensionless Michaelis-menten Constant Effect

The effect of feed phenol concentration on the biotransformation efficiency can be measured by changing the dimensionless Michaelis-Menten constant (ξ), which is a measure of the coupling effect K_M of and C_{Afeed}. Practically, the K_M value is fixed for certain enzyme-substrate pair. Therefore, in this work only the phenol concentration in feed stream is studied, making it vary from 0.01 mM ($\xi = \xi^{reference}$) to 1 mM ($\xi = 100 \times \xi^{reference}$) at fixed other constants. The results of this investigation are plotted in Fig. 6. Increasing the ξ parameter means to reduce the reaction rate for the phenol degradation.

4.3. Effect of Peclet Number

The Peclet number (Pe) is a dimensionless number relating the rate of a flow advection to the diffusion [49]. High values of number correspond to a slightly dispersed reactor which operates in plug flow conditions, whereas a close to zero means that the reactor

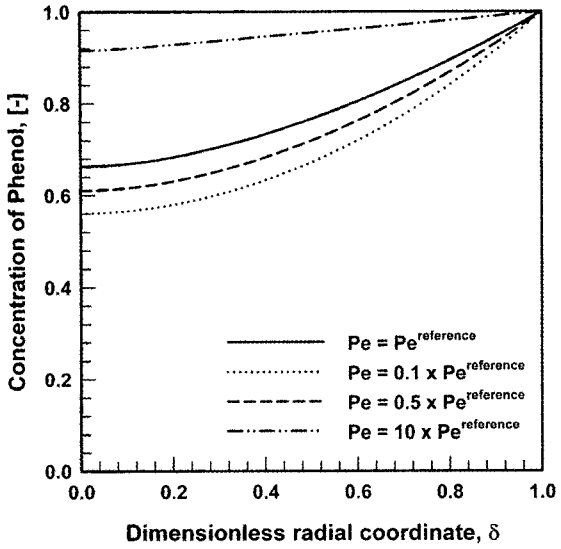

Fig. 7. Effect of Peclet number (Pe) on concentration profile of phenol ($\xi = 0.014$, $\Phi^2 = 5$).

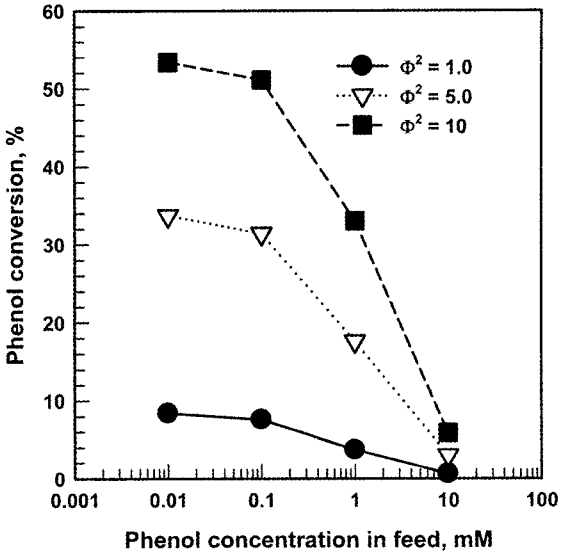

Fig. 8. Phenol conversion for different feed concentration at different Thiele modulus.

operates in perfect mixing. Fig. 7 shows the phenol concentration along the membrane radius for different Peclet numbers. Whenever Peclet number is high, a high fluid velocity is found (short residence time in membrane) and there is no chance to react with enzyme. Therefore, only a low phenol degradation degree is reached.

The last part of the phenol degradation simulation was carried out with the aim of studying the effect of feed composition on the enzyme-loaded membrane reactor. In particular, in Fig. 8 the conversion was evaluated as a function of phenol feed concentration for three different Thiele Modulus values (= 1, 5 and 10). Any change of the reactant feed concentration means a variation of the dimensionless Michaelis-Menten parameter. As expected, the higher feed concentration, the lower the phenol conversion, owing to the fact that, at a fixed Thiele Modulus, the loading of biocatalyst is also fixed. At higher Φ^2, the phenol conversion shows always the same trend, but the curves are shifted toward higher conversions.

The membrane reactor is able to process a higher amount of phenol for a concentrated feed with respect to a diluted one, in a given operation time. Considering for instance the case of $\Phi^2 = 10$, passing from 0.1 to 1 mM of phenol feed concentration, the conversion reduces from 51 to 33%. However, in the second case (1 mM) the overall amount of converted reactant is about 6 times the one converted when the feed composition is 10 folds lower.

5. Conclusions

A numerical analysis was performed to describe the preliminary study to develop an enzyme-loaded membrane reactor for the degradation of phenol in wastewater. In such a system, the enzyme (catalyst) immobilized in porous capillary media converts phenol to catechol and o-quinone. A mathematical model, consisting of 1D dimensionless mass balance equations for phenol, catechol and o-quinone, was developed in order to describe the species concentration profiles along the enzyme-loaded membrane thickness. The Michaelis-Menten kinetics was considered in the model. In the numerical simulation, Thiele Modulus, dimensionless Michaelis-Menten constant and Peclet number were introduced, investigating their effects on degradation efficiency. The performance of an enzymatic membrane reactor can be predicted by simulation, and optimal values of the dimensionless parameters can lead to an

improved design of experimental reactors.

Acknowledgements

The *Italian Ministry of Education, University and Research*, Progetto "FIRB-CAMERE RBNE03JCR5-Nuove membrane catalitiche e reattori catalitici a membrana per reazioni selettive come sistemi avanzati per uno sviluppo sostenibile" is gratefully acknoledged for co-funding this work.

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