

On the effectiveness factor calculation for a reaction – diffusion process in an immobilized biocatalyst pellet

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Abstract

This contribution deals with effectiveness factor (η) and concentration profile of key component estimations when a single independent reaction takes place in a porous catalyst structure where enzymes are immobilized. The procedure is quite general since any kinetic expression can be handled and the case of catalytic activity distribution can also be taken into account. With the knowledge of kinetic parameters and effective diffusivity η and concentration profiles can be estimated through very simple algebraic equations. Thus, the numerical solution of a non linear second order boundary value differential equation, which usually needs some spline scheme, is avoided.

The obtained approximate results are compared with numerical findings for the case of slab geometry where a very simple numerical procedure can be used to solve the resulting differential non linear equation. Approximate results are shown very accurate in the whole range of kinetic parameters, even in those cases where the reaction kinetics shows an apparent negative order of reaction and η values can be above unity. Tables are used to better compare approximate and numerical values. Concentration profile predictions are also very accurate in the region nearby the external surface of the catalyst particle.

These approximate results are used to establish criteria to analyze experimental kinetic data in those cases where diffusional phenomena, that could affect chemical parameter estimations, must be avoided.

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1. Introduction

Mittal [1] pointed out the main advantages of enzyme immobilization in food processing. Usually, these techniques involve adsorption, covalent attachment, cross linking, entrapment and encapsulation. The support structure needs pore size of appropriate dimensions to ensure uniform enzyme concentration inside the resulting catalyst and a reasonable rate of diffusion of substrates and reaction products. When these conditions are not fully met non uniform enzyme concentration within the catalyst results and/or strong diffusional internal limitations with significant overall reaction decays. According to engineering purposes a number of experimental

reactors have been reported [1] to test this kind of biological catalysts.

In recent years, there is an increasing concern to estimate effectiveness factor (η) in bioengineering processes where immobilized enzymes are used as catalysts. Since the kinetic expression is usually non linear in term of concentration, numerical procedures are needed to solve the resulting governing differential equation for the concentration profile inside the pellets. These procedures are not straightforward as shown by Kubicek and Hvalacek [2] and Villadsen and Michelsen [3].

Recently Li et al. [4] presented an approximate procedure to estimate η when chemical kinetics are well represented by the Michaelis–Menten equation. They basically assumed that substrate concentration can be represented by a polynomial up to third degree in the dimensionless position (x) of

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Nomenclature

a	auxiliary parameter defined by Eq. (14)
A	auxiliary variable defined by Eq. (17a)
C	dimensional key component concentration (mol/l)
D	effective diffusivity of key component (cm^2/s)
E	percent deviation $ (\eta_N - \eta_A)/\eta_N \times 100$
$f(x)$	normalized spatial catalytic activity function (see Eq. (5))
$F(\gamma)$	variable defined by Eq. (21)
$g(x)$	auxiliary variable defined by Eq. (17c)
K_m	Michaelis–Menten dimensional kinetic parameter (mol/l)
L	dimensional characteristic catalyst dimension (cm)
m	geometrical parameter 0, 1, 2
n	reaction order
r	rate of reaction (mol/l s)
r_m	Michaelis–Menten dimensional kinetic parameter (mol/l s)
R	dimensionless rate of reaction, Eq. (2c)
$R'(1)$	first derivative of R with respect to γ evaluate at $\gamma = 1$
x	dimensionless spatial coordinate (x'/L)
x'	dimensional spatial coordinate (cm)
z	auxiliary function of γ and γ_c (Eq. (22))

Greek Letters

α	auxiliary parameter defined by Eq. (12)
β	dimensionless kinetic parameter (C_s/K_m)
γ	dimensionless concentration (C/C_s)
γ^*	value of γ that satisfy $R(\gamma^*) = 0$
$(\gamma_c)_{\text{lim}}$	value of γ given by Eq. (26)
ε	auxiliary parameter given by Eq. (24)
η	effectiveness factor
$(\eta_A)_{\text{max}}$	maximum value of η when $R'(1) < 0$ (see Eq. (28))
λ	auxiliary variable defined by Eq. (17b)
ρ	auxiliary parameter defined by Eq. (7)
σ	auxiliary parameter given by Eq. (11)
ϕ	Thiele modulus given by Eq. (2d)
ϕ^*	modified Thiele modulus (ϕ/ρ)

Subscripts

A	refers to approximate values
C	refers to value at $x = 0$
e	refers to exact value
L	refers to Li et al. [4] definitions
N	refers to numerical estimated value
s	refers to value at $x = 1$

a spherical particle. The polynomial coefficients are determined once the expression is introduced in the resulting differential equation and terms of like power are equated. They [4] also presented a comparison among approximate and numerical η predictions where is clearly shown that η behavior is not as expected and deviations becomes very large as Thiele modulus increases. A numerical “shooting” procedure is also mentioned but no details are given in the publication. However, it is well known that numerical procedure reported in the literature becomes unstable, unless some spline scheme is put forward (Villadsen and Michelsen [3]). On the other hand, plain shooting procedure can become non convergent when the Thiele modulus is greater than 2, approximately, depending upon the expression used to represent the chemical kinetics.

The aim of this contribution is to clearly show that an early procedure developed by Gottifredi and Gonzo [5] can be safely used to estimate η with great accuracy. The procedure is very simple and straightforward. η can be estimated through a unique algebraic equation and the parameters needed can be calculated analytically or, with very complex kinetic expressions, by direct quadrature.

It is further assumed that the enzyme concentration within the porous catalyst structure is not uniform. Nevertheless, as will be seen, the procedure is completely general instead of being restricted to a given kinetic expression and/or pellet geometry. In order to compare approximate η estimated values, a stable and simple numerical procedure is also shown that, unfortunately, is only applicable to slab geometry. Nevertheless, in this case, it is quite useful to show the accuracy of η approximate predictions and also, to test an approximate algebraic expression to predict concentration profiles inside the pellet. The effect of diffusional phenomena on kinetic data is also discussed.

2. Theory

Let us consider the case of a single independent reaction taking place inside the catalyst porous structure at steady state and where isothermal conditions prevail. With these assumptions the mass continuity equation can be written in dimensionless form as:

$$\frac{d}{dx} \left(x^m \frac{d\gamma}{dx} \right) = \phi^2 x^m f(x) R(\gamma) \quad (1)$$

where x denotes the spatial coordinate, γ the key component concentration, $f(x)$ the normalized catalytic activity distribution function, $R(\gamma)$ the rate of reaction and ϕ the Thiele modulus:

$$x = \frac{x'}{L}; \quad (2a)$$

$$\gamma = \frac{C}{C_s}; \quad (2b)$$

$$R(\gamma) = \frac{r(C)}{r(C_s)} \quad (2c)$$

$$\phi^2 = \frac{L^2 r(C_s)}{C_s D} \quad (2d)$$

L being the characteristic dimension length of the porous catalyst, C the dimensional concentration, $r(C)$ the rate of reaction and D the effective diffusivity of the key component within the porous catalyst. Subindex s denotes the corresponding value evaluated at the catalyst external surface conditions. Appropriate boundary conditions are:

$$\gamma = 1 \quad x = 1; \quad \frac{d\gamma}{dx} = 0 \quad x = 0 \quad (3)$$

The effectiveness factor (η) is defined as the mean rate of reaction divided by the same rate of reaction evaluated at external conditions:

$$\eta = (m + 1) \int_0^1 R(\gamma) f(x) x^m dx = \frac{m + 1}{\phi^2} \left[\frac{d\gamma}{dx} \right]_{x=1} \quad (4)$$

From Eq. (4) it should be noticed that $f(x)$ must be normalized so that:

$$(m + 1) \int_0^1 f(x) x^m dx = 1 \quad (5)$$

$f(x)$ plays a crucial role in supported biocatalysts. Enzymes, usually, are very complex molecular charged structures. They do not obey Fick diffusion model and the resulting pellet, or membrane, is not uniform regarding enzyme (catalyst) concentration. As a result, catalyst concentration decreases from the surface to the internal zone of the resulting catalyst. $f(x)$ is the mathematical description of this phenomena.

3. Effectiveness factor estimation

Petersen [6], has shown that when $\phi^2 \gg 1$ the concentration at $x=0$ can be assumed negligible and:

$$\eta = \frac{\rho}{\phi} = \frac{1}{\phi^*} \quad (6)$$

where ρ is given by:

$$\rho = (m + 1) \left[2f(1) \int_0^1 R(\gamma) d\gamma \right]^{1/2} \quad (7)$$

The integral given in Eq. (7) can be usually solved analytically for most kinetic expressions used to describe chemical reaction transformations. If not, it can be calculated by very simple numerical procedures.

For the particular case of Michaelis–Menten model:

$$R(\gamma) = \frac{r(C)}{r(C_s)} = \frac{(1 + \beta)\gamma}{1 + \beta\gamma} \quad \text{with} \quad \beta = \frac{C_s}{K_m} \quad (8)$$

and

$$\rho = \frac{(m + 1)\sqrt{2f(1)(1 + \beta)}}{\beta} [\beta - \ln(1 + \beta)]^{(1/2)} \quad (9)$$

On the other hand, when $\phi^2 \gg 1$ the following asymptotic solution can be found [5]:

$$\eta = 1 - \sigma\phi^2 + O(\phi^4) \approx 1 - \sigma\rho^2\phi^{*2} \quad (10)$$

where:

$$\sigma = \alpha R'(1) \quad (11)$$

$R'(1)$ being the derivative of $R(\gamma)$ calculated at $\gamma=1$ and

$$\alpha = (m + 1) \int_0^1 x^{-m} \left[\int_0^x x^m f(x) dx \right]^2 dx \quad (12)$$

Gottifredi et al. [7] proposed the following expression to match Eqs. (6) and (10) when ϕ^2 is very large or very small, respectively:

$$\eta = [\phi^{*2} + \exp(-a\phi^{*2})]^{-(1/2)} \quad (13)$$

“ a ” can be found by expanding Eq. (13) when $\phi^2 \gg 1$ and by comparing the resulting expression with Eq. (10):

$$a = 1 - 2\sigma\rho^2 \quad (14)$$

Eq. (13) needs “ a ” to be positive. When the calculation has given a negative “ a ” value, it should be taken equal to zero ($a=0$) and our Eq. (13) reduces to Churchill and Usagi [8] proposal. It should also be noticed that when $a > 1$, η could be larger than one. Clearly $a > 1$ means that $R'(1) < 0$ which implies an apparent negative order of reaction.

Notice that Li et al. [4] introduced a particular definition of the dimensionless rate of reaction and Thiele modulus. A comparison shows:

$$\phi_L^2 = \frac{1 + \beta}{9} \phi^2 \quad (15)$$

where the subscript L denotes Li et al. [4] definition for the specific case of a Michaelis and Menten kinetic expression.

4. Substrate concentration profile inside the pellet

Gottifredi and Gonzo [9] have shown, that once η is known, the profile inside the pellet can be predicted using an expression that match the asymptotic solutions for the profile at low and high values of ϕ . This equation is:

$$A = \exp \left[\frac{-\lambda(1 - x^2)}{\{2 - ([1 - xg(x)]/([1 + (2/\lambda)])\}} \right] \quad (16)$$

where

$$A = \frac{\gamma - \gamma^*}{1 - \gamma^*} \quad (17a)$$

$$\lambda = \frac{\phi^2 \eta}{(m+1)(1-\gamma^*)} \quad (17b)$$

$$g(x) = \frac{1 - \exp(-\lambda x)}{1 - \exp(-\lambda)} \quad (17c)$$

γ^* being the dimensionless concentration that satisfies $R(\gamma^*)=0$

5. Numerical method

When $m=0$ (slab geometry) and uniform activity distribution, Eq. (1) can be rewritten as:

$$2 \left(\frac{d\gamma}{dx} \right) \frac{d}{dx} \left(\frac{d\gamma}{dx} \right) = 2\phi^2 R(\gamma) \frac{d\gamma}{dx} = \frac{d}{dx} \left[\left(\frac{d\gamma}{dx} \right)^2 \right] \quad (18)$$

which can be integrated once:

$$\frac{d\gamma}{dx} = \left(2\phi^2 \int_{\gamma_c}^{\gamma} R(\gamma') d\gamma' \right)^{1/2} \quad (19)$$

γ_c being γ value at $x=0$.

Thus according to Eq. (4):

$$\eta = \frac{\left(2 \int_{\gamma_c}^1 R(\gamma') d\gamma' \right)^{1/2}}{\phi} \quad (20)$$

which allows the numerical calculation of η as a function of ϕ , provided γ_c is known. To find the corresponding γ_c value for the given ϕ , Eq. (19) can be integrated once again:

$$\int_{\gamma_c}^1 \left(\int_{\gamma_c}^{\gamma} R(\gamma') d\gamma' \right)^{-1/2} d\gamma = \sqrt{2}\phi = F(\gamma_c) \quad (21)$$

Since in most cases

$$\int_{\gamma_c}^{\gamma} R(\gamma') d\gamma' = z(\gamma, \gamma_c) \quad (22)$$

can be found analytically:

$$\int_{\gamma_c}^1 (z(\gamma_c, \gamma))^{-1/2} d\gamma = \int_{\gamma_c}^{\gamma_c+\varepsilon} (z(\gamma_c, \gamma))^{-1/2} d\gamma + \int_1^{\gamma_c+\varepsilon} (z(\gamma_c, \gamma))^{-1/2} d\gamma \quad (23)$$

which is equivalent to a spline orthogonal collocation procedure to carry out η calculations. In facts, both integrals were calculated with six points collocations as given by Table 25.8 of Abramowitz and Stegun [10]. The criterion used to establish ε values was:

$$\frac{1 - \gamma_c}{10} = \varepsilon \quad (24)$$

There are two possible procedures. The first one is to fix γ_c value and then find ϕ that satisfies Eq. (21). The second procedure is to fix ϕ value and by some numerical procedure find γ_c that satisfies Eq. (21). In our case Polymath [11] non

linear algebraic equation routine was used to calculate γ_c in each case.

Once the pair ϕ and γ_c is determined, concentration profile can be easily calculated by changing the integration limits of Eq. (21):

$$\int_{\gamma_c}^{\gamma_c+\varepsilon} (z(\gamma_c, \gamma))^{-1/2} d\gamma + \int_{\gamma_c+\varepsilon}^{\gamma_A} (z(\gamma_c, \gamma))^{-1/2} d\gamma = \sqrt{2}\phi x \quad (25)$$

Thus for a fixed value of γ_A , x is straightforwardly calculated and the concentration profile is known by applying repeatedly this routine. In this case the same criterion given by Eq. (24) is applied but with γ_A replacing 1.

6. Results and discussion

6.1. Effectiveness factor predictions

To better show the agreement between approximate (η_A) and numerical (η_N) (eventually exact η_e) values of the effectiveness factor the produced results will be tabulated. In some cases the percent deviation (E) is reported in an additional column.

Comparison among numerical, exact and approximate η values for the linear case ($n=1$) show an extremely good agreement (maximum deviations are below 0.3%). Tables 1 and 2 present η values for n th order irreversible kinetic expression ($n=0.5, 2$) in a slab pellet. It should be

Table 1

Approximate and numerical effectiveness factor values for a power law kinetic

ϕ	γ_c	η_N	η_A
0.30	0.955003	0.993956	0.984997
0.60	0.825258	0.962836	0.940426
1.00	0.561278	0.879014	0.842379
1.50	0.241401	0.722708	0.693524
2.00	0.055594	0.573554	0.559991
2.30	0.011926	0.501717	0.495205
2.40	0.003490	0.481155	0.476152

$n=0.5$, slab geometry.

Table 2

Approximate and numerical effectiveness factor values for a power law kinetic

ϕ	γ_c	η_N	η_A
0.30	0.956191	0.965146	0.944864
0.60	0.848380	0.849162	0.821505
0.80	0.765435	0.733347	0.757971
1.00	0.685360	0.672346	0.652817
1.50	0.519498	0.504733	0.496152
2.00	0.401616	0.394804	0.391828
3.00	0.247755	0.270088	0.269944
4.00	0.137781	0.203857	0.203829

$n=2$, slab geometry.

Table 3

Estimated and numerical values of the effectiveness factor for $R(\gamma) = \frac{(1+\beta)\gamma}{(1+\beta\gamma)}$

ϕ	γ_c	η_N	η_A	E
0.6	0.9410	0.9865	0.9860	0.05
1	0.8414	0.9615	0.9586	0.29
2	0.4755	0.8343	0.8198	1.74
4	0.0659	0.5014	0.4995	0.38
5	0.0234	0.4027	0.4024	0.08
6	0.0084	0.3357	0.3356	0.03

$\beta=2$, slab geometry.

noticed that ϕ values cover the asymptotic region for large values of the Thiele modulus where Eq. (6) produces very accurate η predictions.

In actual facts Eq. (6) is strictly valid when $\gamma_c = 0$. However, tabulated values of γ_c clearly show that numerical (η_N) and approximate (η_A) predictions are very close (less than 1% deviation) even when γ_c is far away from being zero. Moreover, the limiting value of γ_c below which Eq. (6) can be safely used is strongly dependent on reaction order. A very simple criterion can be established requiring Eq. (6) to predict η values with maximum deviation below 1%:

$$(\gamma_c)_{\text{lim}} \leq (0.02)^{(1/n+1)} \tag{26}$$

In all cases investigated, this limiting value was overcome while showing that the numerical procedure is stable and accurate although double precision routines were never used.

Tables 3 and 4 show the results obtained with a Michaelis–Menten kinetic expression (Eq. (8)) with $\beta = 2$ and $\beta = 10$ (almost zero order), in a slab pellet. It can be seen that, again, the agreement between η_N and η_A values is extremely good in most cases and maximum deviation is around 6% for large values of β ($\beta = 10$).

Tables 5 and 6 show the particular case of apparent negative reaction order which can produce η values greater than one. The kinetic expression tested was:

$$R(\gamma) = \frac{(1 + \beta)^2 \gamma}{(1 + \beta\gamma)^2} \tag{27}$$

β values in each table were varied from 1.5 to 2. It must be noticed that $R'(1)$ can be negative when $\beta > 1$.

In these cases, it can be expected that the rate of reaction inside the particle will be greater than its corresponding value at the surface ($R(1) = 1$). Provided $R'(1) < 1$, ($a > 1$) from Eq.

Table 4

Estimated and numerical values of the effectiveness factor for $R(\gamma) = \frac{(1+\beta)\gamma}{(1+\beta\gamma)}$

ϕ	γ_c	η_N	η_A	E
0.6	0.9837	0.9991	0.9989	0.02
1	0.9547	0.9972	0.9967	0.05
2	0.8210	0.9876	0.9806	0.71
4	0.3496	0.9211	0.8680	5.76
4.23	0.2917	0.9046	0.8482	6.23
6	0.0423	0.7124	0.6854	3.79
8	0.0044	0.5373	0.5328	0.84

$\beta = 10$, slab geometry.

Table 5

Estimated and exact values of the effectiveness factor for $R(\gamma) = \frac{(1+\beta)^2 \gamma}{(1+\beta\gamma)^2}$

ϕ	γ_c	η_N	η_A	E
0.141	0.99	1.0023	1.0013	0.10
0.443	0.90	1.0135	1.0086	0.48
0.623	0.80	1.0240	1.0090	1.46
0.877	0.60	1.0340	0.9900	4.25
1.215	0.30	0.9800	0.9150	6.63
1.361	0.20	0.9240	0.8680	6.06
1.660	0.10	0.7870	0.7640	2.92
1.870	0.05	0.7060	0.6940	1.70
2.111	0.02	0.6275	0.6230	0.72

$\beta = 1.5$, slab geometry.

(13) it can be shown that η_A is expected to reach a maximum value:

$$\eta_{A \text{ max}} = \frac{1 + \ln a}{a} \tag{28}$$

when

$$\phi^2 = \frac{\rho^2 \ln a}{a} \tag{29}$$

Numerical predictions for smaller β values ($\beta = 0.5$) are in close agreement with approximate results and η always decreases as ϕ increases. However in Tables 5 and 6 ($\beta = 1.5$ and 2, respectively) η first increases and then decreases as ϕ increases passing through a maximum value. Although deviations among numerical and approximate η values could be above 10% and the location of the maximum is not well predicted by simple Eq. (13), η_A values are still acceptable for engineering purposes. Moreover Eq. (13) clearly show its capacity to predict η values greater than one.

Li et al. [4] predictions are strictly valid for a spherical pellet ($m = 2$). In facts their procedure can only be valid when $\phi^2 < 1$, since, otherwise, γ_c would become negative. Moreover by revising the algebra it can be shown that all coefficients of odd power terms of their polynomial vanish. Nevertheless, the overall results would have been similar even if the correct fourth power coefficient of the polynomial had been properly deduced.

Table 7 presents a comparison between our predictions (η_A) and those obtained by applying Li et al. [4] (η_L) procedure for the particular case of Michaelis–Menten kinetics in a spherical pellet.

Table 6

Estimated and numerical values of the effectiveness factor for $R(\gamma) = \frac{(1+\beta)^2 \gamma}{(1+\beta\gamma)^2}$

ϕ	γ_c	η_N	η_A	E
0.20	0.979	1.0265	1.0014	2.45
0.40	0.914	1.0410	1.0038	3.57
0.60	0.802	1.0658	1.0029	5.90
1.00	0.427	1.1129	0.9669	13.12
1.40	0.111	0.9740	0.8690	10.78
2.00	0.013	0.6968	0.6815	2.19
3.00	3.47E-04	0.4647	0.4645	0.04

$\beta = 2$, slab pellet.

Table 7
Comparison between the effectiveness factor predictions with our procedure and that of Li et al. [4]

$\beta = 2$			
ϕ_L	15	20	30
ϕ^*	7.4479	9.9305	14.8957
η_A (this work)	0.1343	0.1007	0.0671
η_L [4]	0.5053	0.5030	0.5014
$\beta = 6$			
ϕ_L	10	20	30
ϕ^*	3.0102	6.0204	9.0306
η_A (this work)	0.3322	0.1661	0.1108
η_L [4]	0.5250	0.5063	0.5027
$\beta = 10$			
ϕ_L	10	20	30
ϕ^*	2.3315	4.6629	6.9944
η_A (this work)	0.4289	0.2144	0.1430
η_L [4]	0.5383	0.5096	0.5043

From these results is clearly seen that Li et al. [4] procedure is not useful when $\phi^2 > 1$, since η_L reach a constant value, around 0.5, almost independently of ϕ and β values. As known most biocatalyst system operate in range of diffusion control. Under these conditions Li et al. [4] procedure is not applicable at all.

6.2. Internal pellet concentration profile

Comparison among analytical and approximate concentration profiles given by Eq. (16) for the particular case of first order reaction show a fair agreement and are not shown here.

Tables 8 and 9 show the values of the dimensionless concentration as function of distance from the center of the pellet for a reaction kinetics given by Eq. (27), for $\beta = 2$ and two values of the Thiele modulus.

Table 8
Concentration profile for $R(C) = \frac{(1+\beta)^2 C}{(1+\beta C)^2}$

x	γ_N	γ_A	$R(\gamma_N)$
0.2360	0.46	0.584	1.123
0.3396	0.50	0.609	1.125
0.5341	0.60	0.679	1.1157
0.7949	0.80	0.829	1.065
0.8987	0.90	0.909	1.0332
0.9467	0.95	0.9504	1.0166

$\beta = 2$, $\gamma_c = 0.427$, $\phi = 1.0$; slab pellet.

Table 9
Concentration profile for $R(C) = \frac{(1+\beta)^2 C}{(1+\beta C)^2}$

x	γ_N	γ_A	$R(\gamma_N)$
0.334	0.05	0.208	0.3710
0.511	0.15	0.298	0.7990
0.659	0.30	0.417	1.0540
0.786	0.50	0.569	1.1250
0.882	0.70	0.729	1.0937
0.963	0.90	0.905	1.0331

$\beta = 2$, $\gamma_c = 0.0131$, $\phi = 2.0$; slab pellet.

The comparison between approximate and numerical predictions shows a fair agreement, although the deviation increases as $x \rightarrow 0$ and ϕ takes larger values. It should be stressed that in this particular case the apparent reaction order is negative and the rate of reaction inside the pellet is larger than the corresponding surface value as shown in Tables 8 and 9.

6.3. Diffusion phenomena on kinetic data analysis

Let us consider, for simplicity, the effect of diffusion in catalytic membrane of variable width ($2L$) assuming that chemical kinetics is well described by a Michaelis–Menten expression. A so called Lineweaver–Burk plots is presented in Fig. 1. The values of the parameters used were:

$$r_{\max} = 2.10^{-4} \text{ (mol/l s)} \quad K_m = 2.10^{-3} \text{ (mol/l)}$$

$$D = 10^{-6} \text{ (cm}^2/\text{s)}$$

Which are within the order of magnitude of most reported process.

With our method, η_A is accurate and rapidly calculated and the value of $(1/r_{\text{exp}})$ is easily simulated for each value of concentration and width. As can be seen the effect of intraparticle diffusion does not modify the expected linear plot although the slope is substantially affected as ϕ is increased. It can be concluded that a linear Lineweaver–Burk plot does not preclude the existence of internal diffusion resistance. Parametric results varying L are needed to empirically establish the effect of diffusional phenomena. To better understand the slope behavior shown in Fig. 1, η as function of C_s for

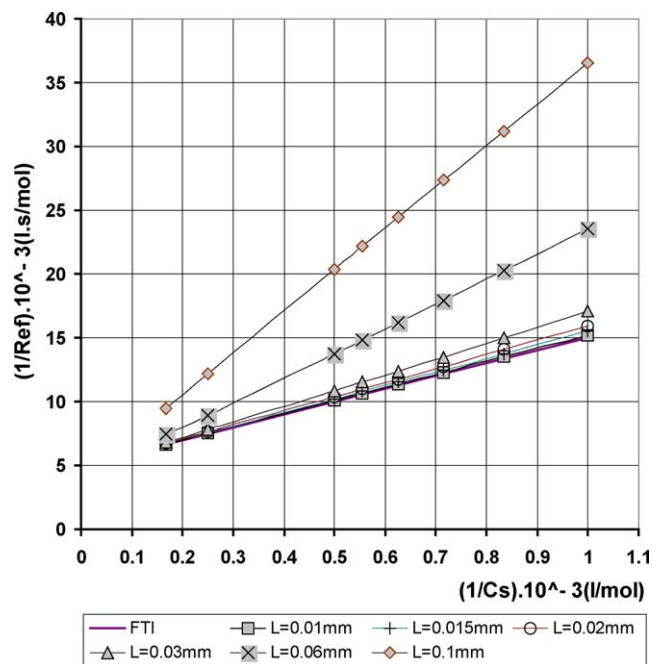


Fig. 1. Lineweaver–Burk plots for various width of membrane with immobilized enzyme that obey a Michaelis–Menten kinetic. FTI: free of transport influence.

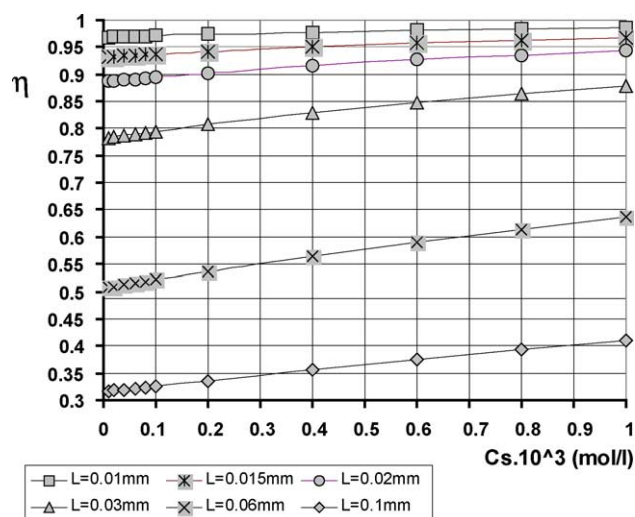


Fig. 2. Effectiveness factor as a function of external surface concentration for different values of the membrane width.

different values of L is presented in Fig. 2. Although η varies significantly with L nevertheless a linear relation between η and C_s is established explaining the observations discussed from Fig. 1. It must be stressed that for this particular case the resulting limiting value of half thickness (L_{\max}) is very small ($L_{\max} < 0.013$ mm).

The other possible way to tackle this problem is to establish a reasonable criterion. The authors [12] assumed that:

$$|1 - \eta| \leq 0.05 \quad (30)$$

would be a safe limiting condition to neglect diffusional phenomena when kinetic data treatment is needed.

In this particular case Eq. (30) can be rewritten in the following fashion:

$$L_{\max} = \sqrt{\frac{0.15(1 + \beta)C_s D}{r_{\text{exp}}}} \quad (31)$$

where r_{exp} will be the measured value in a given experiment.

Some knowledge is needed to estimate D while β must be assumed and finally checked from experimental data. Fig. 2 is useful to illustrate the application of Eq. (31) in this case.

7. Conclusions

An approximate method is presented to estimate effectiveness factor for a porous catalytic structure with the only limitation that a single independent reaction takes place at steady state conditions. It can be used with any kinetic expression (even for non isothermal system) and also in those cases where a non uniform catalytic activity must be considered inside the pellet.

The results produced in terms of effectiveness factor have been tested against numerical accurate results for the specific

case of slab geometry. Approximate results are always in fair agreement with corresponding numerical findings for all kinetic expressions tested in the whole range of ϕ values even in those cases where the apparent reaction orders is negative and $\eta > 1$. The results are very accurate for the particular case of the popular Michaelis–Menten kinetic expression. Maximum deviations are always less than 7% in this particular case.

It is also shown the application of this simple algebraic procedure to estimate η values for other geometrical shapes. The specific case recently analyzed by Li et al. [4] was revised showing that could lead to unacceptable predictions for large ϕ values.

Another interesting feature is the capability of applying this simple method when a catalytic activity distribution inside the porous resulting structure must be taken into account. Provided this spatial function is known (i.e. enzyme concentration distribution inside the pellet) it can be easily used to estimate η values.

The very simple algebraic expression proposed to calculate η is shown to be able to predict η values higher than one whenever the derivative of the dimensionless rate of reaction evaluated at the pellet external surface is negative (which implies an apparent negative reaction order).

An attempt is also presented to predict the concentration profile inside the catalyst pellet without solving the non linear second order boundary value differential equation. Approximate concentration profiles are in fair agreement with numerical calculations at least in a great region of the particle. However, the fitness is poor as the spatial coordinate approaches the center of the particle and when ϕ is very large. More precise calculations are needed to better predict concentration profiles.

In this work some general non linear kinetic expressions were tested. It is well known that the true kinetics on enzyme catalyzed reaction, taking into account multiple reaction sites, can be extremely complex. Nevertheless, provided the reaction system can be described by a single reaction our procedure is still applicable.

Finally, a criterion is proposed to preclude the existence of diffusional phenomena when kinetics data analysis is faced in the presence of immobilized enzymes. The proposed criterion is discussed for the particular case of a Michaelis–Menten kinetics model. It is clearly shown that a linear Lineweaver–Burk plot is not a safe criterion to neglect the existence of diffusional parallel controlled phenomena in the catalytic particle.

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