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Approximate solution for the nonlinear model of diffusion and reaction in porous catalysts by the decomposition method

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Abstract

The problem of diffusion and reaction in catalyst pellets is considered for the case of *n*th order reactions. The Adomian decomposition method is used to solve the nonlinear model of diffusion and reaction and to obtain approximate solutions. The variation of reactant concentration in the catalyst pellet and the effectiveness factors are determined for second-, half- and first order reaction. The approximate analytical solutions obtained are compared with solutions obtained with a finite difference numerical method. In general, the Adomian polynomial method with three terms gives solutions comparable to the numerical procedure for Thiele modulus approximately up to 4.0.

Keywords: Catalyst pellet; Model; Diffusion and reaction; *n*th order reaction; Adomian polynomial; Effectiveness; Thiele modulus; Numerical solution

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1. Introduction

Nonlinear problems frequently arise in engineering, but many texts are oriented towards linear problems due to the difficulty of nonlinearity. Adomian [1] has developed the decomposition method to solve the deterministic or stochastic differential equations. The solutions obtained are approximate and fast to converge as shown by Cherrault [2]. In general, satisfactory results can be reached by using the first few terms of the approximate, series, solution. The Adomian method has been used to solve several mathematical problems in science and engineering, but there has been no reported application in chemical engineering to date.

The model for coupled diffusion and reaction in porous catalyst pellets generates a typical differential equation in chemical engineering. Thiele [3] obtained the analytical solution for the first order reaction in 1939, and then Wheeler [4] and Aris [5], etc. discussed this problem in details in their books. However, most of their conclusions were based on the analytical solution for the irreversible reaction with the first reaction order. Several researchers, such as Satterfild [6], have considered solutions for the nonlinear model with *n*th order reaction, but approximate solutions were not derived. Finlayson [7] has applied many numerical methods to solve nonlinear models of fluid flow, heat transfer and chemical reactor by using pre-programmed computer packages. The difficulty in the solution of such problems occurs when there is a large change in reaction rate, where the method does not always converge and convergence may depend critically on the initial guess. A disadvantage of numerical techniques is that they cannot give analytical expressions as solution.

In this paper, the Adomian decomposition method is introduced into chemical engineering, to solve the nonlinear model of diffusion and reaction in porous catalysts with *n*th order reaction and to obtain approximate analytical solutions. Such expressions are of immediate value to catalytic reactors as they enable rapid estimation of the effect of pore diffusion on reactions in porous catalysts via the well-known concept of effectiveness.

2. The model of diffusion and reaction

An important problem in chemical engineering is to predict diffusion and reaction rates in porous catalysts when the reaction rate can depend on concentration in a nonlinear way. In this heterogeneous system (solid material with pores through which the reactants and products diffuse), the system is modelled as simple diffusion using an effective diffusion coefficient. We assume for diffusion that all the microscopic details of the porous medium are lumped

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Nomenclature

A_m	Adomian polynomial
c	dimensionless concentration
c'	concentration
D_e	effective diffusion coefficient
k	reaction rate constant
l	catalyst pore length
L	linear operator
m	terms in the Adomian polynomial
n	order of reaction
N	nonlinear operator
r	reaction rate
R	remainder of linear operator
x	dimensionless co-ordinate dimension
x'	co-ordinate dimension

Subscripts

0	position $x = 0$
1	position $x = 1$

Greek letters

η	effectiveness
θ	approximate solution
ϕ	effectiveness factor

together into the effective diffusion coefficient D_e for reactant. With this approximation a mass balance on a volume of the porous medium gives

$$\frac{\partial c'}{\partial t} = \nabla \cdot D_e \nabla c' - r(c') \tag{1}$$

where t is the time, c' the chemical reactant concentration, and $r(c')$ the rate of reaction per unit volume.

Let us next assume that the diffusion occurs, at a steady state, in a porous slab that is infinite in two directions, giving a large plane sheet with diffusion through the thickness of the sheet. We thereby simplify Eq. (1) to one dimension by assuming negligible variation of the concentrations in the y and z directions, to give, when D_e is constant

$$\frac{d^2c'}{dx'^2} - \frac{r(c')}{D_e} = 0 \tag{2}$$

where x' is the diffusion distance.

Here, we consider one side (or the centre) of the slab as impermeable (no flux) and the concentration is held fixed at the other side. The two boundary conditions are

$$x'_0 = 0, \qquad -D_e\frac{dc'}{dx'} = 0 \tag{3}$$

$$x'_1 = l, \qquad c' = c'_s \tag{4}$$

The problem in Eqs. (2)–(4) is an ordinary differential equation and a boundary-value problem. This nature of boundary-value problems, i.e. having conditions at each end of the domain, complicates the solution techniques but is characteristic of diffusion, heat transfer and fluid flow problems.

We consider the reaction A → B, with the rate depending on the nth power of concentration of A, denoted by kc'^n, where the reaction constant k is a function of temperature. The goal is to predict the overall reaction rate, or the mass transfer in and out of the catalyst pellet.

For a suitable solution, dimensionless equation can be derived from Eqs. (2)–(4) by letting $x = x'/l$, $c = c'/c'_s$. For an isothermal reaction that is nth order and irreversible in planar geometry, we obtain

$$\frac{d^2c}{dx^2} - \phi^2 c^n = 0 \tag{5}$$

$$x = 0, \qquad \frac{dc}{dx} = 0 \tag{6}$$

$$x = 1, \qquad c = 1 \tag{7}$$

where the Thiele modulus, $\phi^2 = k_0 l^2 c_0^{n-1}/D_e$. The group $1/l(k_0 c_0^{n-1})$ is a characteristic property for reaction, while D_e/l is a characteristic property for diffusion. The Thiele modulus thus measures the relative importance of the diffusion and reaction phenomena.

In catalytic reactors, the effectiveness factor is defined as the average reaction rate, i.e. with diffusion, divided by the reaction rate if the rate of reaction is evaluated at the boundary condition value at $x = 1$. The last quantity is the average reaction rate if diffusion is very fast, presenting no limitation to the mass transfer. The effectiveness factor is generally given by

$$\eta = \frac{\int_0^1 r_1(c(x))x^{a-1}\,dx}{\int_0^1 r_1(1)x^{a-1}\,dx} \tag{8}$$

The parameter $a = 1$, 2 and 3, respectively, for flat plate, cylindrical or spherical geometry. We can integrate Eq. (8) over the domain $x = 0$–1 and rewrite Eq. (8) as

$$\eta = \frac{a}{\phi^2}\frac{(dc/dx)(1)}{r(1)} \tag{9}$$

At small ϕ, the effectiveness factor is close to 1, meaning that the rate of reaction is relatively uninfluenced by diffusion. For large ϕ, the effectiveness factor is smaller than 1, meaning the average reaction rate is lower than that without diffusion limitations. This effect must be correctly modelled by the chemical engineer in the design and operation of catalytic reactors.

3. The solution with decomposition

In general, a differential equation can be expressed by an operator equation. With the first decomposition, the original deterministic nonlinear differential equation can be written into Adomian's general form as

$$Fy = g(x) \tag{10}$$

$$\tilde{F}y = Ly + Ry + Ny = g(x) \tag{11}$$

where L is a linear operator and is the highest order differential, R the remainder of the linear operator, N the nonlinear operator of an analytic nonlinearity, and $g(x)$ an inhomogeneous or forcing term. Eq. (11) can be solved by applying the inverse operator L^{-1}

$$L^{-1}Ly = L^{-1}g(x) - L^{-1}Ry - L^{-1}Ny \tag{12}$$

where L^{-1} simply symbolises n-fold integrations for an nth order L.

In the case of Eq. (5), for an isothermal nth order reaction in a slab of porous catalyst

$$L = \frac{\mathrm{d}^2}{\mathrm{d}x^2}, \quad L^{-1} = \int\int_0^x [\cdot]\,\mathrm{d}x\,\mathrm{d}x, \quad y = c,\ R = 0,\ g = 0$$

The solution of equation Eq. (5) can thus be described as

$$Lc = \phi^2 Nc \tag{13}$$

Processing the inverse operation, we have

$$L^{-1}Lc = L^{-1}\phi^2 Nc \tag{14}$$

$$c = \phi^2 L^{-1}Nc + \phi \tag{15}$$

Secondly, the solution process is assumed to be given by decomposition, i.e.

$$c = \sum_{m=0}^{\infty} c_m \tag{16}$$

$$Nc = f(c) = \sum_{m=0}^{\infty} A_m \tag{17}$$

where A_m is called the Adomian polynomial.

Collecting terms, Eqs. (16) and (17) can be parameterised as

$$c = \sum_{m=0}^{\infty} \lambda^m c_m = c_0 + \lambda c_1 + \lambda^2 c_2 + \cdots \tag{18}$$

Consequently,

$$Nc = f(c) = f[c(\lambda)] = \sum_{m=0}^{\infty} \lambda^m A_m \tag{19}$$

where $f(c)$ is to be specified and assumed analytical in λ.

Substituting Eqs. (16) and (17) into Eq. (15), we obtain

$$\sum_{m=0}^{\infty} \lambda^m c_m = \phi^2 L^{-1} \sum_{m=0}^{\infty} \lambda^m A_m \tag{20}$$

According to Adomian's work [1], the expressions for $A_0, A_1, A_2, \ldots, A_m$, can be written as

$$\begin{aligned}
A_0 &= h_0(c_0) = f(c_0)\\
A_1 &= h_1(c_0)c_1\\
A_2 &= \tfrac{1}{2}[h_2(c_0)c_1^2 + 2h_1(c_0)c_2]\\
A_3 &= \tfrac{1}{6}[h_3(c_0)c_1^3 + 6h_2(c_0)c_1c_2 + 6h_1(c_0)c_3]\\
A_4 &= \tfrac{1}{24}[h_4(c_0)c_1^4 + 12h_3(c_0)c_1^2c_2 + h_2(c_0)(12c_2^2\\
&\quad + 24c_1c_3) + 24h_1(c_0)c_4]\\
&\vdots\\
A_m &= \frac{1}{m!}[h_v(c_0)]\\
h_v(c_0) &= \left(\frac{\mathrm{d}^v}{\mathrm{d}c^v}\right) f[c(\lambda)]_{\lambda=0} = \left(\frac{\mathrm{d}^v}{\mathrm{d}c^v}\right) f(c_0)\\
&\vdots
\end{aligned} \tag{21}$$

where

$$\begin{aligned}
c_0 &= \text{constant}\\
c_1 &= \phi^2 L^{-1} A_0\\
c_2 &= \phi^2 L^{-1} A_1\\
&\vdots\\
c_m &= \phi^2 L^{-1} A_m\\
&\vdots
\end{aligned} \tag{22}$$

Then the particular solutions of $c(x)$ can be written directly as

$$\begin{aligned}
A_0 &= c_0^n\\
c_1 &= \frac{1}{2!}\phi^2 c_0^n x^2\\
A_1 &= \frac{1}{2!}\phi^2 c_0^{2n-1} x^2\\
c_2 &= \frac{n}{4!}\phi^4 c_0^{2n-1} x^4\\
A_2 &= \frac{4n^2 - 3n}{4!}\phi^4 c_0^{3n-2} x^4\\
c_3 &= \frac{4n^2 - 3n}{6!}\phi^6 c_0^{3n-2} x^6\\
A_3 &= \frac{34n^3 - 63n^2 + 30n}{6!}\phi^6 c_0^{4n-3} x^6\\
c_4 &= \frac{34n^3 - 63n^2 + 30n}{8!}\phi^8 c_0^{4n-3} x^8\\
A_4 &= \frac{496n^4 - 1554n^3 + 1689n^2 - 630n}{8!}\phi^8 c_0^{5n-4} x^8\\
c_5 &= \frac{496n^4 - 1554n^3 + 1689n^2 - 630n}{10!}\phi^{10} c_0^{5n-4} x^{10}\\
&\vdots
\end{aligned} \tag{23}$$

4. Analytical approximate solutions with three terms

Let the approximate solution $\theta_{m+1}(x) = \sum_{m=0}^{m} c_m$, $\theta_{m+1} \to c$ as $m \to \infty$ ($0 \le \theta_{m+1} \le 1$). We will first derive the approximate solution for a first reaction order to compare to its analytical solution, and then the approximate solutions with common nonlinear reaction orders—second and half.

4.1. The linear case

For the first order reaction $n = 1$, the $f(c)$ is linear. Hence, we have

$$c_m = \frac{1}{(2m)!}\phi^{2m} c_0 x^{2m},$$

$$\sum_{m=1}^{\infty} c_m = c_0 \left[1 + \sum_{m=1}^{\infty} \left[\frac{1}{(2m)!}\phi^{2m} c_0 x^{2m} \right] \right] = c_0 \cosh(\phi x) \tag{24}$$

Substitution of the boundary conditions Eqs. (6) and (7), the analytical can be obtained

$$c = \frac{\cosh(\phi x)}{\cosh(\phi)} \tag{25}$$

4.2. The nonlinear case

The approximate solution can be described

$$\begin{aligned} \theta_{m+1} &= c_0 + c_1 + c_2 + \cdots + c_m \\ &= c_0 + \frac{1}{2!}\phi^2 c_0^n x^2 + \frac{n}{4!}\phi^4 c_0^{2n-1} x^4 \\ &\quad + \frac{34n^3 - 63n^2 - 30n}{6!}\phi^6 c_0^{3n-2} x^6 \\ &\quad + \frac{34n^3 - 63n^2 + 30n^2}{8!}\phi^8 c_0^{4n-3} x^8 \\ &\quad + \frac{496n^4 - 1554n^3 + 1689n^2 - 630n}{10!}\phi^{10} c_0^{5n-4} x^{10} \\ &\quad + \cdots + c_m \end{aligned} \tag{26}$$

Taking the first three terms of Eq. (26) and using the boundary condition

$$x = 1, \qquad c = 1$$

Eq. (26) becomes

$$\theta_{m+1} = c_0 + c_1 + c_2 = c_0 + \frac{1}{2!}\phi^2 c_0^n x^2 + \frac{n}{4!}\phi^4 c_0^{2n-1} x^4,$$

$$1 = c_0 + \frac{1}{2!}\phi^2 c_0^n + \frac{n}{4!}\phi^4 c_0^{2n-1} \tag{27}$$

For the reaction order $n = 1$, we have

$$1 = c_0 + \frac{1}{2!}\phi^2 c_0 + \frac{1}{4!}\phi^4 c_0, \quad c_0 = \left(1 + \frac{1}{2!}\phi^2 + \frac{1}{4!}\phi^4 \right)^{-1}$$

An expression of the approximate solution for $n = 1$, $\theta_{3,1}$ denoted, can be written

$$\theta_{3,1} = c_0 \left(1 + \frac{1}{2!}\phi^2 x^2 + \frac{1}{4!}\phi^4 x^4 \right) \tag{28}$$

For the reaction order $n = 2$, we have

$$1 = c_0 + \frac{1}{2!}\phi^2 c_0^2 + \frac{2}{4!}\phi^4 c_0^3$$

Solving the algebraic equation of the third degree, the root can be obtained

$$c_0 = \sqrt[3]{\frac{8}{\phi^6} + \frac{12}{\phi^4}} - \frac{2}{\phi^2}$$

An expression of the approximate solution for $n = 2$, $\theta_{3,2}$ denoted, can be written

$$\theta_{3,2} = c_0 + \frac{1}{2!}\phi^2 c_0^2 x^2 + \frac{2}{4!}\phi^4 c_0^3 x^4 \tag{29}$$

For the reaction order $n = 0.5$, we have

$$1 = c_0 + \frac{1}{2!}\phi^2 c_0^{0.5} + \frac{0.5}{4!}\phi^4 c_0^0$$

Let $\alpha = c_0^{0.5}$, then

$$\theta_3 = -1 + \alpha^2 + \frac{1}{2!}\phi^2 \alpha + \frac{2}{4!}\phi^4$$

Solving the algebraic equation of the second degree, the root can be obtained

$$\alpha = \tfrac{1}{4}\left(\sqrt{\tfrac{2}{3}\phi^4 + 16} - \phi^2 \right), \qquad c_0 = \alpha^2$$

An expression of the approximate solution for $n = 0.5$, $\theta_{3,0.5}$ denoted, can be written

$$\theta_{3,0.5} = c_0 + \frac{1}{2!}\phi^2 c_0^{0.5} x^2 + \frac{2}{4!}\phi^4 x^4 \tag{30}$$

5. The approximate solution with more than three terms

To obtain the value of root c_0 from Eq. (26), we have to use a numerical method, for example, the Newton's approximation, except in the case of a first reaction order. For example, we consider the expressions with six terms are as follows.

Taking the first six terms of Eq. (26) and using the boundary condition

$$x = 1, \qquad c = 1$$

Eq. (26) becomes

$$\begin{aligned} 1 &= c_0 + \frac{1}{2!}\phi^2 c_0^n + \frac{n}{4!}\phi^4 c_0^{2n-1} + \frac{4n^2 - 3n}{6!}\phi^6 c_0^{3n-2} \\ &\quad + \frac{19n^3 - 18n^2}{8!}\phi^8 c_0^{4n-3} \\ &\quad + \frac{481n^4 - 1509n^3 + 1659n^2 - 630n}{10!}\phi^{10} c_0^{5n-4} \end{aligned} \tag{31}$$

Table 1
The values of root c_0 for $n = 2$ at various values of parameter ϕ

ϕ	Four terms	Five terms	Six terms
0.5	0.8959	0.8959	0.8959
1	0.7125	0.7123	0.7123
2	0.4467	0.4444	0.4439
4	0.2232	0.2176	0.2144
10	0.0716	0.0635	0.0621

Then we can determine the meaningful real root of the polynomial, $0 \le c_0 \le 1$.

(1) For the reaction order $n = 1$

$$\begin{aligned}
1 &= c_0\left(1+\frac{1}{2!}\phi^2+\frac{1}{4!}\phi^4+\frac{1}{6!}\phi^6+\frac{1}{8!}\phi^8+\frac{1}{10!}\phi^{10}\right),\\
c_0 &= \left(1+\frac{1}{2!}\phi^2+\frac{1}{4!}\phi^4+\frac{1}{6!}\phi^6+\frac{1}{8!}\phi^8+\frac{1}{10!}\phi^{10}\right)^{-1},\\
\theta_{6,1} &= c_0\left(1+\frac{1}{2!}\phi^2x^2+\frac{1}{4!}\phi^4x^4+\frac{1}{6!}\phi^6x^6\right.\\
&\quad\left.+\frac{1}{8!}\phi^8x^8+\frac{1}{10!}\phi^{10}x^{10}\right)
\end{aligned} \tag{32}$$

(2) For the reaction $n = 2$

$$\begin{aligned}
1 &= c_0+\frac{1}{2!}\phi^2c_0^2+\frac{2}{4!}\phi^4c_0^3+\frac{10}{6!}\phi^6c_0^4+\frac{80}{8!}\phi^8c_0^5\\
&\quad+\frac{1000}{10!}\phi^{10}c_0^6,\\
\theta_{6,2} &= c_0+\frac{1}{2!}\phi^2c_0^2x^2+\frac{2}{4!}\phi^4c_0^3x^4+\frac{10}{6!}\phi^6c_0^4x^6\\
&\quad+\frac{80}{8!}\phi^8c_0^5x^8+\frac{1000}{10!}\phi^{10}c_0^6x^{10}
\end{aligned} \tag{33}$$

The values for the roots of c_0 are given in Table 1.

(3) For the reaction order $n = 0.5$

$$\begin{aligned}
1 &= c_0+\frac{1}{2!}\phi^2c_0^{0.5}+\frac{0.5}{4!}\phi^4c_0^0+\frac{-0.5}{6!}\phi^6c_0^{-0.5}\\
&\quad+\frac{-2.125}{8!}\phi^8c_0^{-1}+\frac{-58.8125}{10!}\phi^{10}c_0^{-1.5}
\end{aligned}$$

The roots of the polynomial can be calculated for different values of Thiele moduli, as shown in Table 2. We have for the solution

$$\begin{aligned}
\theta_{6,2} &= c_0+\frac{1}{2!}\phi^2c_0^{0.5}x^2+\frac{2}{4!}\phi^4c_0^0x^4+\frac{10}{6!}\phi^6c_0^{-0.5}x^6\\
&\quad+\frac{80}{8!}\phi^8c_0^{-1}x^8+\frac{1000}{10!}\phi^{10}c_0^{-1.5}x^{10}
\end{aligned} \tag{34}$$

Table 2
The values of root c_0 for $n = 0.5$ at various values of parameter

ϕ	Four terms	Five terms	Six terms
0.5	0.8813	0.8813	0.8813
1	0.5946	0.5946	0.5946
1.5	0.2965	0.2987	0.2959
2	0.1160	0.2176	0.2144
2.5	0.0642	0.0635	0.0621

6. The effectiveness factor of the catalyst

By using the Eq. (9), the analytical expressions for the effectiveness factor can be obtained from Eqs. (27), (29) and (30) with three terms

$$\begin{aligned}
\eta_3 &= \frac{a}{\phi^2}\frac{(\mathrm{d}c/\mathrm{d}x)(1)}{c^n(1)} = \frac{1}{\phi^2}\frac{(\mathrm{d}c/\mathrm{d}x)(1)}{1}\\
&= c_0^n+\frac{n}{3!}\phi^2c_0^{2n-1}
\end{aligned} \tag{35}$$

For the reaction order $n = 2$, the effectiveness factor

$$\eta_{3,2} = \left(\sqrt[3]{\frac{8}{\phi^6}+\frac{12}{\phi^4}}-\frac{2}{\phi^2}\right)^2+\frac{\phi^2}{3}\left(\sqrt[3]{\frac{8}{\phi^6}+\frac{12}{\phi^4}}-\frac{2}{\phi^2}\right)^3 \tag{36}$$

For the reaction order $n = 0.5$, the effectiveness factor

$$\eta_{3,0.5} = \frac{1}{4}\left(\sqrt{\frac{2\phi^4}{3}+16}-\phi^2\right)+\frac{\phi^4}{12} \tag{37}$$

The general expression for the effectiveness factor for nth reaction order can be derived from Eq. (26) as

$$\begin{aligned}
\eta_{m+1,n} &= \frac{(\mathrm{d}\theta_{m+1,n}/\mathrm{d}x)(1)}{\phi^2} = c_0^n+\frac{n}{3!}\phi^2c_0^{2n-1}\\
&\quad+\frac{4n^2-3n}{5!}\phi^4c_0^{3n-2}+\frac{19n^3-18n^2}{7!}\phi^6c_0^{4n-3}\\
&\quad+\frac{481n^4-1509n^3+1659n^2-630n}{9!}\phi^8c_0^{5n-4}\\
&\quad+\cdots+\frac{1}{\phi^2}\frac{\mathrm{d}c_m}{\mathrm{d}x}(1)
\end{aligned} \tag{38}$$

The effectiveness factor calculated by Eq. (8) or (9) may be different for numerical and decomposition methods.

7. Discussion

For this problem, c_0, the root of the polynomial, is the value of c at $x = 0$, where the boundary condition is $\mathrm{d}c/\mathrm{d}x = 0$. We can only obtain all of the forms of partial solutions if the c_0 is known. It is obvious that, the stronger the nonlinearity of the problem, the more terms will be required in the approximate solution. The nonlinearity depends on both the function and the value of parameter ϕ.

In this work, we obtain typical variations of reactant concentrations in the catalyst pellet and effectiveness factors using the decomposition method and compare them against

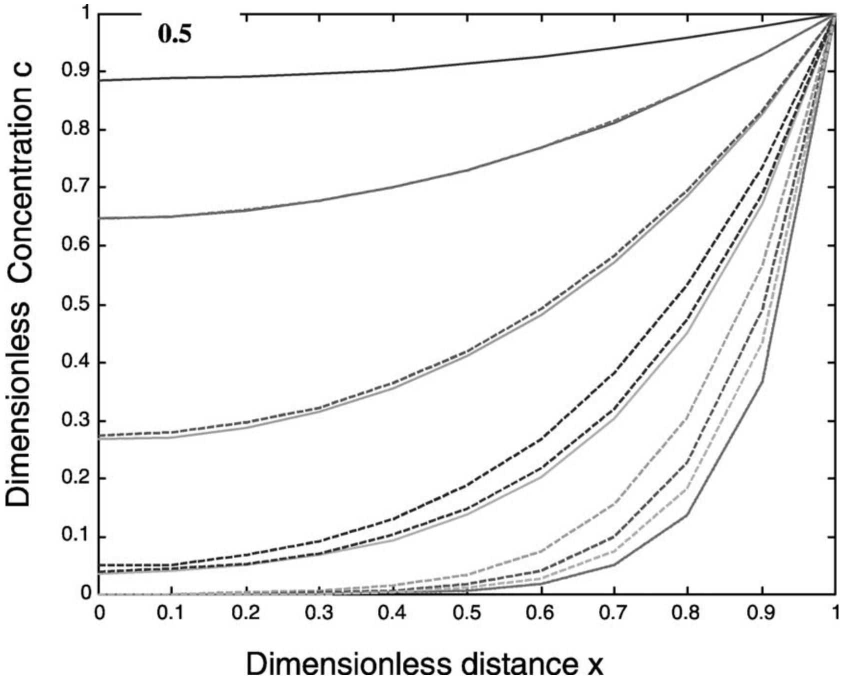

Fig. 1. Variation of concentration in porous catalyst as a function of Thiele modulus for a first order reaction. Values of ϕ on figure. Numerical/analytical solution overlap as solid lines. Values of Thiele modulus increase from top to bottom as 1, 2, 5, 10. Adomiam decomposition three, four, five and six terms increase from top to bottom of associated curves.

values obtained by a numerical solution. The numerical solution method is a finite difference procedure based on Newman's BAND method [8]. The BAND method has proven to be very effective for solution of nonlinear problems of diffusion and reaction in electrochemical systems [9].

7.1. Concentration profiles

Figs. 1–5 show the variation in dimensionless concentration in the catalyst slab as a function of Thiele modulus.

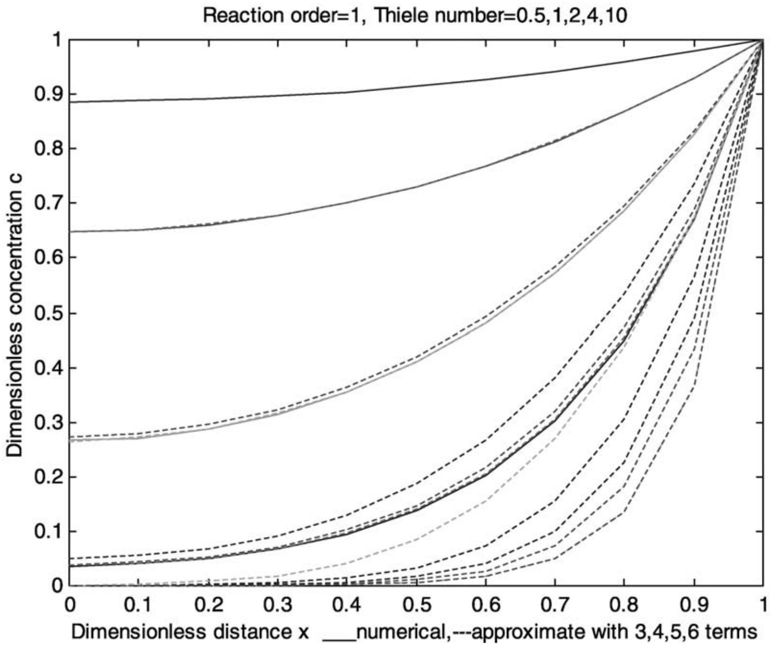

Fig. 2. Variation of concentration in porous catalyst as a function of Thiele modulus for a second order reaction. Values of Thiele modulus increase from top to bottom. Numerical solution (- - -). Adomiam decomposition three, four, five and six terms increase from top to bottom of associated curves.

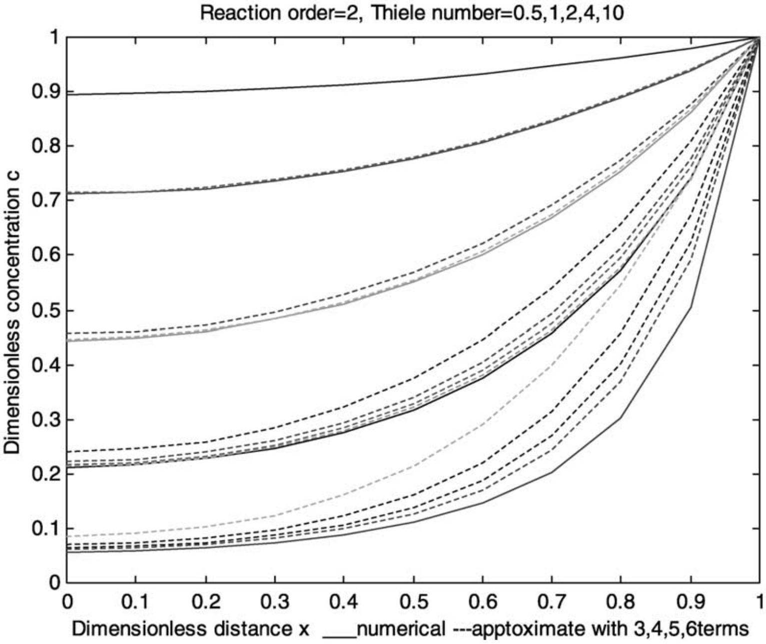

Fig. 3. Variation of concentration in porous catalyst as a function of Thiele modulus for a half order reaction. Values of ϕ (0.5, 1.0, 1.5, 2.0) increase from top to bottom. Numerical solution (- - -). Adomiam decomposition three and four terms.

For a first order reaction (Fig. 1), the classic trend of a greater nonlinear variation in concentration profile with increase in Thiele modulus is seen. The numerical method gives agreement with the analytical solution to within 0.00001 for all data. In the case of the Adomian decomposition at values of very high Thiele modulus (>5), the three-term approximation does not yield satisfactory agreement with the numerical solution. However, on increasing the terms to six in the decomposition method, a reasonable agreement with the numerical solution is achieved.

Figs. 2 and 3 show the equivalent concentration profiles for second and half order reactions, respectively. In the case

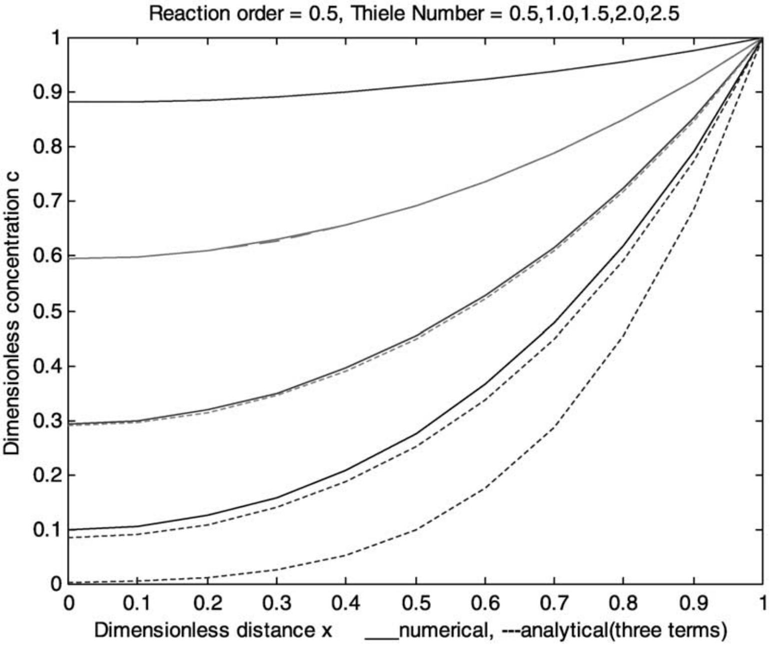

Fig. 4. Variation of concentration in porous catalyst as a function of Thiele modulus for a 1.73th order reaction. Values of ϕ (0.5, 1.0, 1.5, 2.0) increase from top to bottom. Numerical solution (- - -). Adomiam decomposition four, five and six terms increase from top to bottom of associated curves.

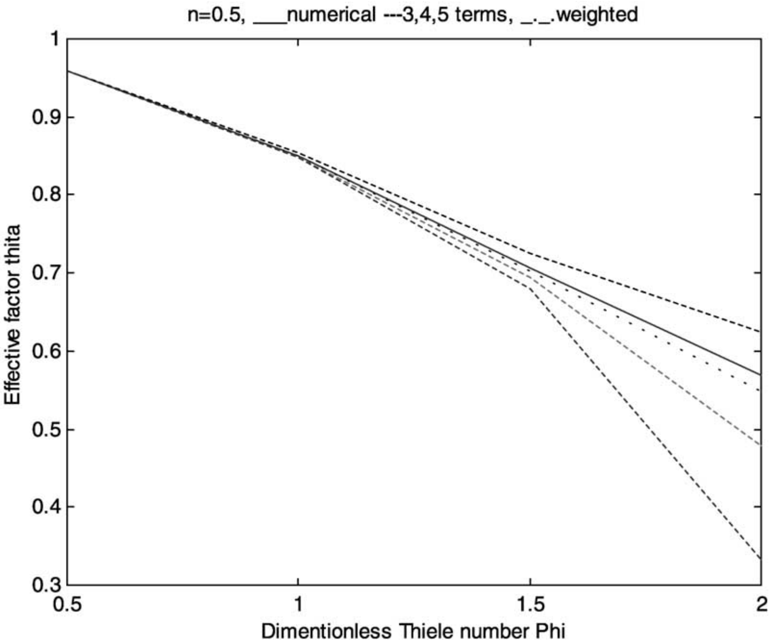

Fig. 5. Variation of concentration in porous catalyst as a function of Thiele modulus for a 0.67th order reaction. Values of ϕ (0.5, 1.0, 1.5, 2.0, 2.5, 3.0) increase from top to bottom. Numerical solution (- - -). Adomiam decomposition four and five terms increase from top to bottom of associated curves.

of these reaction orders, there is no analytical solution to the problem and thus comparisons with a numerical method can only be made. For the second order reaction, there is good agreement between the decomposition method with three terms and numerical solution for a Thiele modulus of 1.0. As the Thiele modulus increases the accuracy (agreement with the numerical solution) decreases with a three-term decomposition solution. In the case of Thiele moduli >5, a six-term decomposition is required to achieve reasonable agreement.

With an half order reaction, the decomposition method gives again good agreement with the numerical solution at lower values of Thiele modulus. At higher values of Thiele modulus either the three- or four-term decomposition method give acceptable agreement with the numerical method.

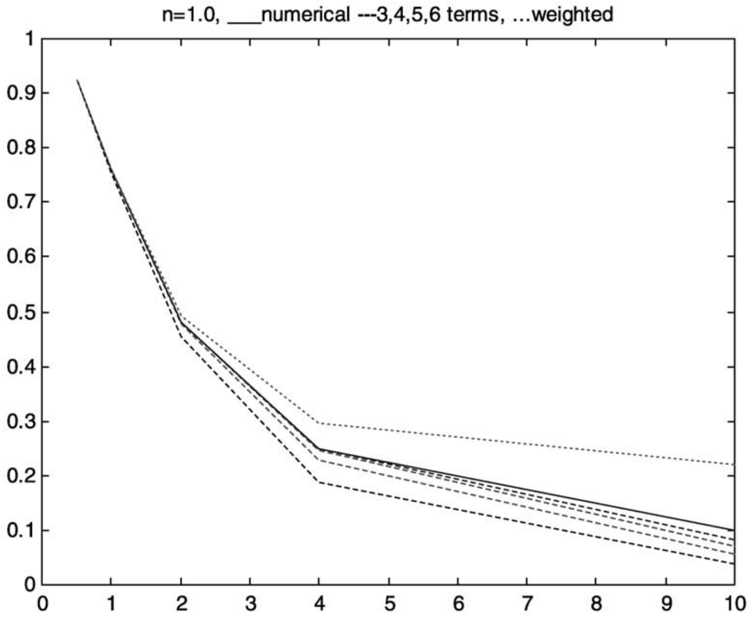

Fig. 6. Variation of concentration in porous catalyst as a function of Thiele modulus for negative order reaction. Values of ϕ increase from top to bottom. Numerical solution (- - -). Adomiam decomposition four terms (—).

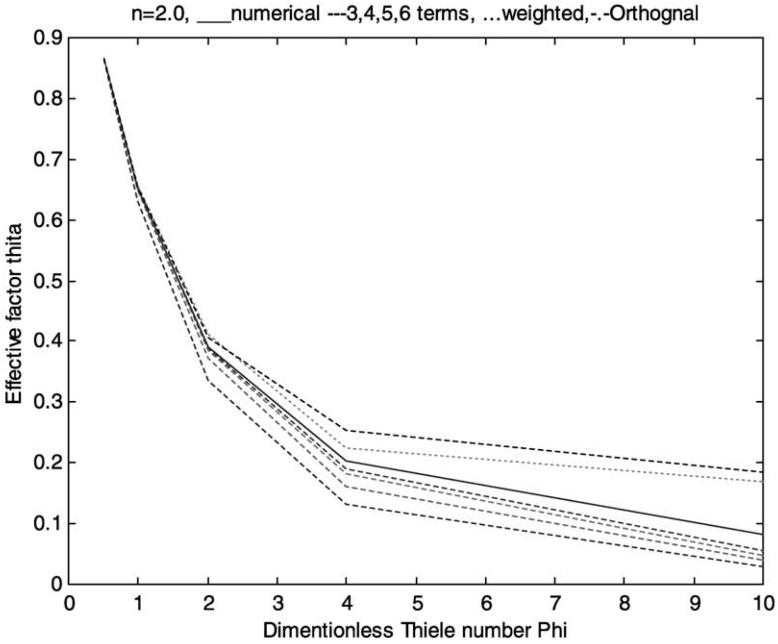

Fig. 7. Variation in effectiveness factor with Thiele modulus for first and second order reactions. Upper set: first order reaction; lower set: second order reaction. Numerical solution (- - -). Adomiam decomposition four, five and six terms increase from bottom to top. O.C: solution by orthogonal collocation (—).

To assess the generality of the decomposition solution method, we have applied it to several arbitrary reaction orders. In the case of reaction orders greater than 1.0, e.g. 1.73 (Fig. 4) the trends in the solution with the decomposition method are as seen earlier (Figs. 2 and 3). However, for reaction orders less than 1.0, e.g. 0.67, the decomposition method appears to be the preferred method (see Fig. 5). With the finite difference method, attempts at solution with Thiele moduli of 2.5 and greater resulted in divergence whereas the four-term decomposition method always gave a solution. Furthermore, in analysing systems where high concentration impedes reaction, apparent negative reaction orders, the decomposition method proved to be the preferred method in solution (see Fig. 6). For a reaction order of −1.0,

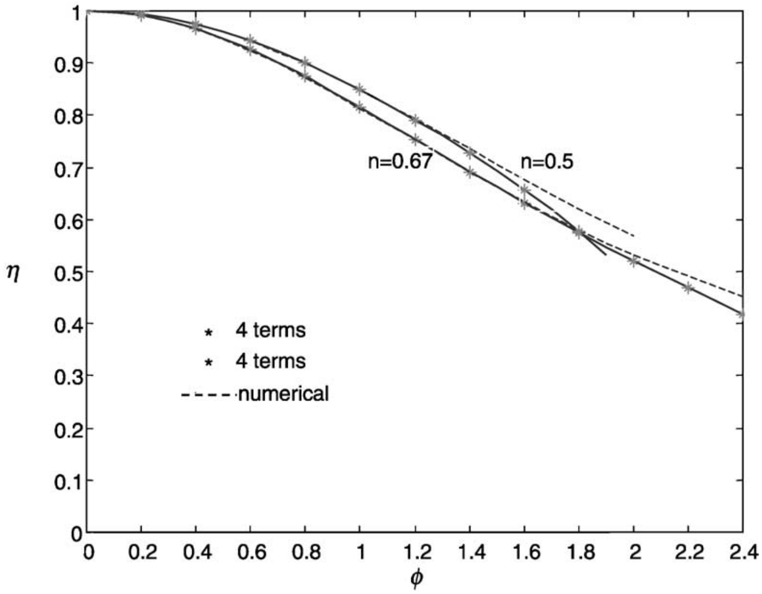

Fig. 8. Variation in effectiveness factor with Thiele modulus for a half and 0.67th order reaction. Upper set: first order reaction; lower set: second order reaction. Numerical solution (—). Adomiam decomposition four terms (- - -).

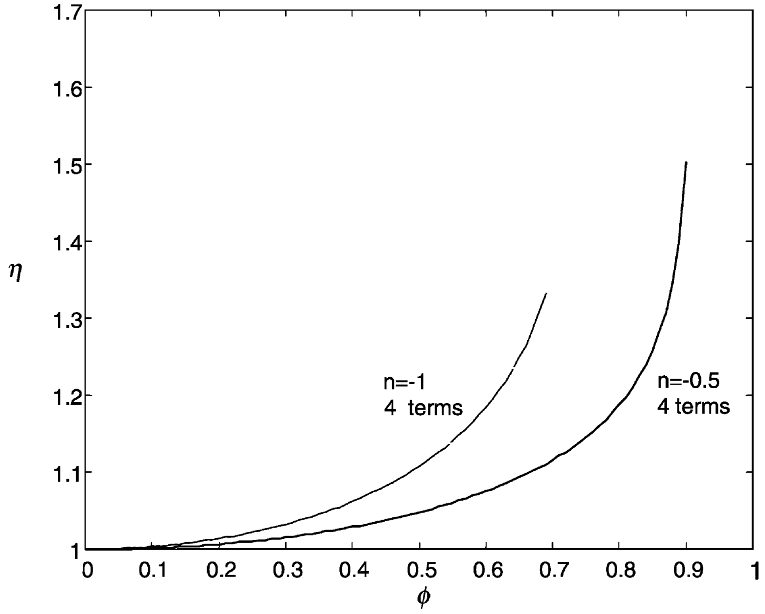

Fig. 9. Variation in effectiveness factor with Thiele modulus for a negative order reaction.

solution by finite difference was not achieved whereas the four-term decomposition gave convergent solutions. With an apparent reaction order of -0.5, finite difference could only be used for Thiele moduli of 0.3–0.5 and the solution was in good agreement with the four-term decomposition method.

7.2. *Effectiveness*

Effectiveness is an important concept in catalytic reactor analysis. Calculated values of effectiveness for the reaction orders discussed in Section 7.1 are described here. Clearly all of the data show the expected trend of a decrease in effectiveness with increase in Thiele modulus. For the first order reaction, numerical and analytical solution agree as expected (see Fig. 7). The agreement between the numerical method and decomposition improves as the number of terms in the decomposition method increase; again as expected. Also shown in Fig. 7 are values effectiveness, obtained using an analytical solution obtained with one-point orthogonal collocation, for a second order reaction [7]. This is the only known approximate analytical solution obtained prior to this work. As can be seen agreement with solutions by finite difference or decomposition methods is poor.

Fig. 8 shows effectiveness values determined for reaction orders less than 1.0, i.e. 0.5 and 0.67. Agreement between finite difference and the four-term decomposition is generally good up to Thiele moduli of 2.0.

Fig. 9 shows typical values of effectiveness for apparent reaction order less than 0, i.e. $n = -0.5$. As expected effectiveness increases with Thiele modulus as at lower concentrations in the pores the reaction rate is suppressed less.

8. Conclusions

The Adomian decomposition method for solution of nonlinear boundary-value problems has been successfully applied to the case of diffusion and reaction in a porous catalyst. An approximate form of solution is obtained which can continuously give the value of the function y for any value of variable x. A three-term solution for effectiveness is often quite accurate and easy to derive. It is possible to obtain an analytical expression of approximate when the nonlinear term is simple.

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