Advection-diffusion-reaction in a porous catalyst

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Abstract

In the last eight years great progress has been made towards developing new analytical solutions that describe nonlinear reaction and diffusion in a porous slab. This is a classical engineering problem with many industrial applications. Historically it has been studied by means of numerical analysis due to the nonlinearity of the governing partial differential equation. Recently attention has been given to solution of this problem through the application of Adomian's decomposition method [1] and the Homotopy Analysis Method (HAM) [2]. The application of these methods led to the derivation of an analytical solution, formulated in terms of Gauss's hyper-geometric function by Magyari in 2008 [3]. However, the current solutions do not take advection into account. In this paper, we derive, by use of Adomians decomposition method, the Maclaurin series of the function in question.

1 Introduction and Formulation of Problem

An important problem in chemical engineering is to accurately predict reaction and diffusion rates in porous catalysts when the reaction rate is a nonlinear function of the concentration [4]. If the diffusion occurs in a porous slab that is infinite in two dimensions then the concentration function $C(x,t)$ is governed by [4]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - kC^n \tag{1}$$

Where D denotes the effective diffusion coefficient, k denotes the reaction rate, n denotes the order of the reaction and V is the advective velocity. This equation is subject to the boundary conditions:

$$\left.\frac{\partial C}{\partial x}\right|_{x=0} = 0$$
$$C(L,t) = C_s$$

Where C_s denotes some constant concentration at $x = L$. In particular, we are interested in determining the concentration profile once the system has reached equilibrium, in which case we can assume that the time derivative is zero.
Much study has been given to the specific case in which no advective transport is considered. An exact analytical solution to the linear form of this equation without the advection term was derived by Thiele in 1939 [4]. More recently, in the case where there is no advection (but the equation remains nonlinear) an exact analytical solution has been derived by E. Magyari [3]. However, no analytical solution is currently known for equation (1) in its general form, and so, as a result, engineers are forced to rely upon computationally expensive numerical methods of solution. The objective of this paper is to develop accurate series approximations for the equilibrium solution of $C(x,t)$ by use of Adomian's decomposition technique, and to further generalise the results given by past investigators [1] [2] [3] [4].

2 Adomian Decomposition

Adomian's decomposition method depends upon decomposing the nonlinear differential equation:

$$F[C(x,t)] = 0 \tag{2}$$

Into the three components:

$$L[C(x)] + R[C(x)] + N[C(x)] = 0 \tag{3}$$

Where $L[\cdot]$ represents the highest order linear component of the operator, $N[\cdot]$ represents the nonlinear component of the operator and $R[\cdot]$ represents the remainder of the linear operator. The operator $L[\cdot]$ is assumed to be easily invertible. In our particular case, we have to following definitions for L, R and N.

$$L[\cdot] = D\frac{d^2}{dx^2}[\cdot],\ R = -V\frac{d}{dx}[\cdot],\ N = -k[\cdot]^n \tag{4}$$

The inverse linear operator is thus:

$$L^{-1} = \frac{1}{D} \int \int dx dx \tag{5}$$

Applying the inverse linear operator to equation (3) gives us the following.

$$C(x) = -L^{-1}R[C(x)] - L^{-1}N[C(x)] \tag{6}$$

We now assume that $C(x)$ can be represented as an infinite series of the form:

$$C(x) = \sum_{m=0}^{\infty} c_m \tag{7}$$

And we assume furthermore that the nonlinear term can be represented as an infinite series of Adomian polynomials:

$$N[C(x)] = \sum_{m=0}^{\infty} A_m \tag{8}$$

The Adomian polynomials A_m are unique to the problem and are derived from Adomian's formulae [5]. It has been established that they converge very quickly [5]. By substituting equations (7) and (8) into (6) we can derive the following recurrence relationship:

$$c_m = -L^{-1}Rc_{m-1} - L^{-1}A_{m-1} \tag{9}$$

From this relationship, and Adomian's formulae for his polynomials [5], we can derive the following values for A_m and c_m:

$$\begin{aligned}
A_0 &= -kc_0^n \\
c_1 &= \frac{1}{2!}\frac{kc_0^n x^2}{D} \\
A_1 &= -\frac{n}{2!}\frac{k^2 c_0^{2n-1} x^2}{D} \\
c_2 &= \frac{1}{3!}\frac{Vkc_0^n x^3}{D^2} + \frac{n}{4!}\frac{k^2 c_0^{2n-1} x^4}{D^2} \\
A_2 &= -\frac{1}{4!}\frac{k^2 n x^3 (4Vc_0^{2n} + 4kc_0^{3n-1}x - 3kxc_0^{3n-1})}{c_0 D^2} \\
c_3 &= \frac{1}{6!}\frac{kx^4(30V^2 c_o^{n+1} + 12knVc_0^{2n} + 4k^2n^2x^2c_0^{3n-1} - 3k^2nx^2c_0^{3n-1})}{c_0 D^3}
\end{aligned}$$

etc.

From the above, and formula (7), we can now determine our approximation of $C(x)$ to three terms as:

$$C(x) \approx c_0 + \frac{k}{D}c_0^n\frac{x^2}{2!} + \frac{kV}{D^2}c_0^n\frac{x^3}{3!} + \left(\frac{k^2}{D^2}nc_0^{2n-1} + \frac{kV^2}{D^3}c_0^n\right)\frac{x^4}{4!}$$
$$\frac{2nk^2Vc_0^{2n-1}}{D^3}\frac{x^5}{5!} + \frac{(4n^2-3n)k^3c_o^{3n-2}}{D^3}\frac{x^6}{6!} + \mathcal{O}(x^7)$$

As Adomian's polynomials converge very quickly, for most problems 3 or 4 terms are sufficient for approximating the function in question [5]. However, Sun et al. [1] have demonstrated that for equation (1) with $V = 0$ that is not always the case. Accordingly we approximated $C(x)$ to 8 terms by use of the symbolic algebra software package *Maple 13*. The constant c_0, which is the quantity of main interest from an engineering standpoint, can be derived from the above approximation for $C(x)$ by applying the boundary conditions for any choice of parameters, and then numerically solving the resulting polynomial.

3 Accuracy of the Adomian approximation

There are two special cases of equation (1) for which an analytical solution has been determined. The first is the case in which $n = 1$ in which case a closed form analytical solution can easily be derived. The second is the case in which $V = 0$ in which an analytical solution has recently been derived by Magyari [3] in terms of a transcendental function known as Gauss's Hypergeometric function. These two cases are:

$$D\frac{d^2C}{dx^2} - V\frac{dC}{dx} - kC = 0 \qquad (10)$$

$$D\frac{d^2C}{dx^2} - kC^n = 0 \qquad (11)$$

The solution to equation (10) is:

$$C(x) = q_1e^{\frac{1}{2}\frac{(V+\sqrt{V^2+4kD})x}{D}} + q_2e^{-\frac{1}{2}\frac{(-V+\sqrt{V^2+4kD})x}{D}} \qquad (12)$$

The constants q_1 and q_2 can easily be determined by the boundary conditions but have been omitted here due to their complexity and length. The full solution is included in appendix A. Magyari's solution [3] to the second case is:

$$x = \frac{1}{\phi}\left(\frac{2}{mc_0^{m-2}}\right)^{\frac{1}{2}}\left(\frac{c}{c_0}\right)^{1-m}\left[\left(\frac{c}{c_0}\right)^{m-1}\right]^{\frac{1}{2}} F\left(1, 1-\frac{1}{m}; \frac{3}{2}; 1-\frac{c}{c_0}^{-m}\right) \tag{13}$$

Where $m = n + 1$, F denotes Gauss's hyper-geometric function and ϕ denotes the Thiele modulus [4]. The Thiele modulus is defined as:

$$\phi = \sqrt{\frac{kL^2C_s^{n-1}}{D}} \tag{14}$$

And Gauss's hypergeometric function is defined as:

$$F(\alpha, \beta, \gamma; x) = 1 + \sum_{n=1}^{\infty} \frac{(\alpha)_n(\beta)_n}{n!(\gamma)_n} x^n \tag{15}$$

Where:

$$(t)_n = \frac{\Gamma(t+n)}{\Gamma(t)} \tag{16}$$

And Γ denotes the Gamma function.

The Adomian approximation to $C(x)$ and the analytical solutions were visually indistinguishable when graphed.

It is also possible to derive a numerical solution by discretising the problem. Using second order finite differences on equation (1) and the regular lattice spacing Δx, such that $x = i\Delta x$ gives us the following stencil for $2 \geq i \geq n-1$:

$$\frac{D}{(\Delta x)^2}[c_{i-1} - 2c_i + c_{i+1}] - \frac{V}{2(\Delta x)}[c_{i+1} - c_{i-1}] - kc_i^1 c_i^{n-1} = 0 \tag{17}$$

And the boundary conditions for $i = 1$ and $i = n$:

$$\begin{aligned} c_1 &= c_2 \\ c_n &= 1 \end{aligned} \tag{18}$$

The stencil (17) results in a tridiagonal matrix of the form:

$$U = \frac{D}{(\Delta x)^2} - \frac{V}{2\Delta x} \tag{19}$$

$$D = -\frac{2D}{(\Delta x)^2} - kc_i^{n-1} \tag{20}$$

$$L = \frac{D}{(\Delta x)^2} + \frac{V}{2(\Delta x)} \tag{21}$$

(Where D denotes the diagonal, U denotes the superdiagonal, L denotes the subdiagonal and the right hand side vector is zero). The term kc_i^{n-1} was approximated via the Picard method.

The Adomian polynomial taken to eight terms and the numerical approximation were visually indistinguishable. Figures 1 to 4 show the effect of changes in the parameters k, V, D and reaction order n.

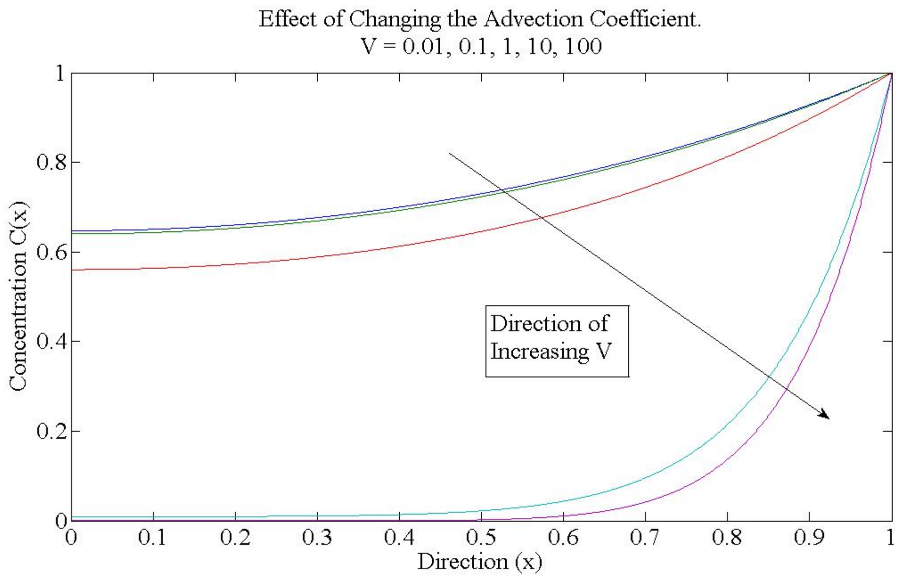

Figure 1: Our Adomian approximation of $C(x)$ taken to 8 terms when n = 1, k = 1 and D = 1.

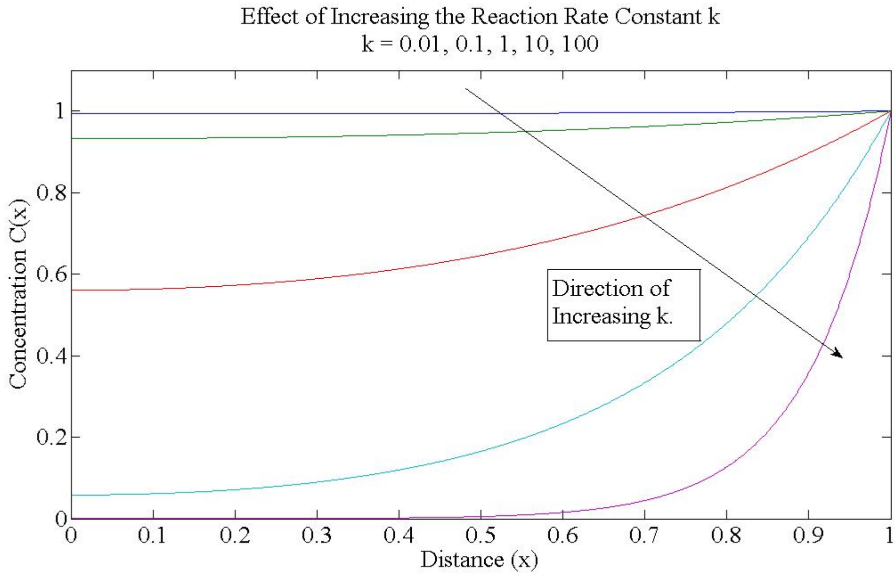

Figure 2: Our Adomian approximation of $C(x)$ taken to 8 terms when n = 1, V = 1, and D = 1.

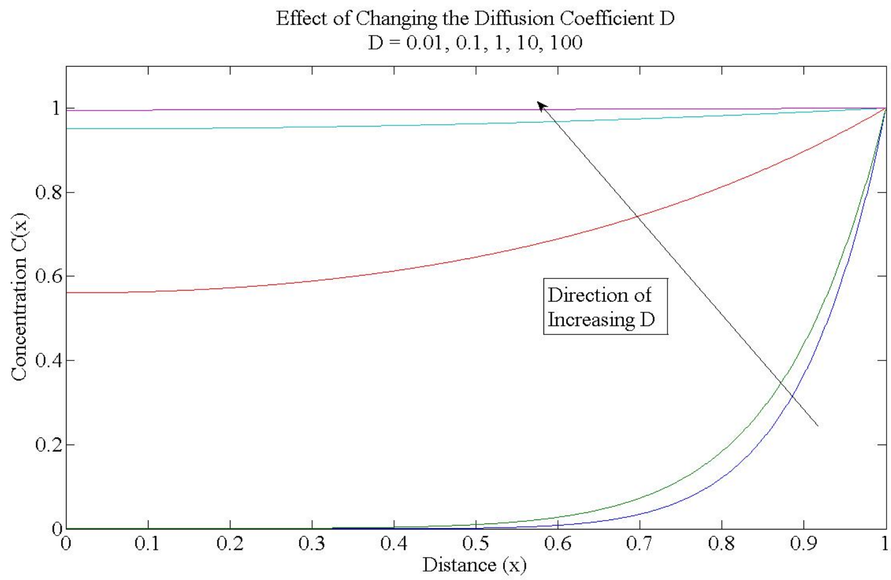

Figure 3: Our Adomian approximation of $C(x)$ taken to 8 terms when n = 1, k = 1 and V = 1.

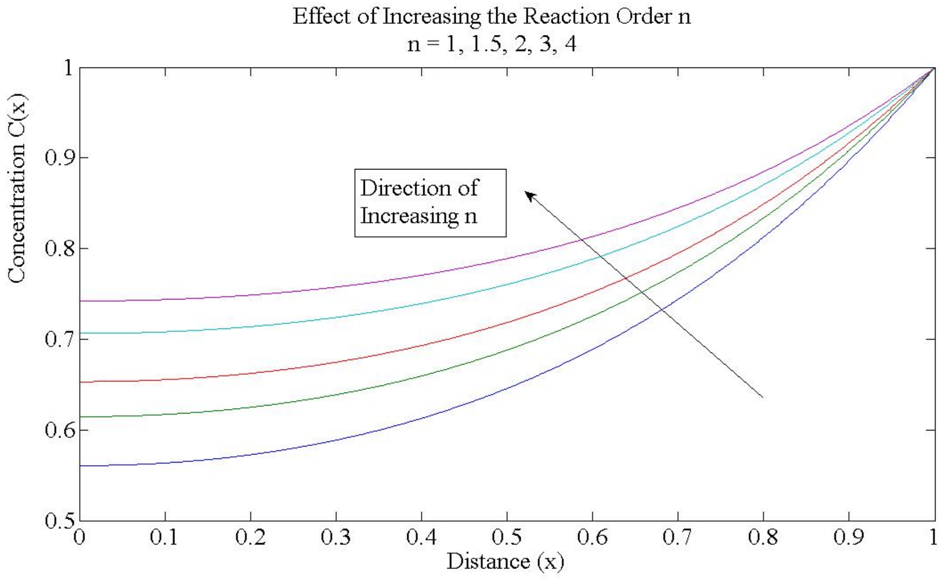

Figure 4: Our Adomian approximation of $C(x)$ taken to 8 terms when k = 1, V = 1 and D = 1.

4 Comparison with Maclaurin series

Examination of the Maclaurin series for $C(x)$ developed by the decomposition technique led me to a different method for deriving the Maclaurin series for $C(x)$ from equation (1), which does not rely upon any specialised technique. We begin by assuming that it is possible to write down the Maclaurin series for $C(x)$. If we are solving for equilibrium solutions then it is possible to rearrange equation (1) into the form:

$$\frac{d^2C}{dx^2} = \frac{k}{D}C(x)^n + \frac{V}{D} \cdot \frac{dC}{dx} \tag{22}$$

If we abide by the notation given earlier in this paper, then we also have that:

$$\begin{aligned} C(0) &= c_0 \\ \left.\frac{dC}{dx}\right|_{x=0} &= 0 \end{aligned} \tag{23}$$

We can evaluate equation (22) at $x = 0$ by use of equations (23). Doing so gives us:

$$\left.\frac{d^2C}{dx^2}\right|_{x=0} = \frac{k}{D} \cdot c_0^n \tag{24}$$

We can now differentiate equation (22) with respect to x to get an expression for $C'''(x)$.

$$\frac{d^3C}{dx^3} = \frac{k}{D} nC(x)^{n-1} \frac{dC}{dx} + \frac{V}{D} \frac{d^2C}{dx^2} \tag{25}$$

As we already know expressions for all the terms on the right hand side of the above equation at $x = 0$, we can derive an expression for $C'''(0)$.

We can continue this process ad infinitum. By differentiating equation (22) a sufficient number of times we can find an analytical expression for any derivative of $C(x)$ with respect to x. As each derivative is defined in terms of derivatives of lower degree, we can recursively derive the value of any derivative of $C(x)$ at $x = 0$.
Given the values for each of the derivatives of $C(x)$ by this process at $x = 0$, we can now immediately write down the Maclaurin series for $C(x)$:

$$C(x) \approx c_0 + \frac{k}{D} c_0^n \frac{x^2}{2!} + \frac{kV}{D^2} c_0^n \frac{x^3}{3!} + \left(\frac{k^2}{D^2} n c_0^{2n-1} + \frac{kV^2}{D^3} c_0^n \right) \frac{x^4}{4!} + \mathcal{O}(x^5) \tag{26}$$

This result exactly coincides with the Maclaurin series we derived using Adomian's decomposition method. Generally the expression for the m$^{\text{th}}$ coefficient of this series is given by:

$$\begin{aligned} C(x)|_{x=0} &= c_0 \\ \left.\frac{dC}{dx}\right|_{x=0} &= 0 \\ \left.\left(\frac{d^mC}{dx^m}\right)\right|_{x=0} &= \left.\left(\frac{d^{m-2}}{dx^{m-2}} \left[\frac{k}{D} C^n + \frac{V}{D} \cdot \frac{dC}{dx} \right]\right)\right|_{x=0} \text{; for } m \geq 2 \end{aligned} \tag{27}$$

At this point it is worthwhile considering a number of properties of $C(x)$. Equation (1) satisfies a maximum principle implying that the maximum value of the solution $C(x)$ necessarily lies on one of the boundaries. As $C'(0) = 0$ we are guaranteed a stationary point at $x = 0$. As $C''(0) > 0$, the minimum of the solution is c_0 and the maximum is $C(1) = 1$. This gives the result that $0 < c_0 < 1$.
Also, application of the ratio test on equation (27) demonstrates that the Maclaurin series for $C(x)$ is always convergent.

5 Summary and Conclusions

We determined the Maclaurin series of $C(x)$ to be:

$$C(x) \approx c_0 + \frac{k}{D}c_0^n\frac{x^2}{2!} + \frac{kV}{D^2}c_0^n\frac{x^3}{3!} + \left(\frac{k^2}{D^2}nc_0^{2n-1} + \frac{kV^2}{D^3}c_0^n\right)\frac{x^4}{4!} + \mathcal{O}(x^5) \quad (28)$$

When taken to more than four terms, this approximation was visually indistinguishable from our numerical approximation. When the right parameters are substituted into equation (28) it collapses down and coincides with other reported solutions [1] [2] [4].

The method of derivation which we used to arrive at this result can be further generalised to derive the Maclaurins series for any ODE of the form:

$$\frac{d^2c}{dx^2} = q_1\frac{dc}{dx} + q_2R(x) \quad (29)$$

Where q_1 and q_2 are constants, and $R(x)$ represents any function whose derivatives are bounded. This method is far more general that that used in previous studies [1] [2] [3] and can be expanded to include other reaction terms such as the Michaelis-Menten biochemical reaction model. It also has the advantage of being simple, and does not rely upon any specialised technique such as the Adomian decomposition technique [1] or the HAM technique [2], and is far more general as it incorporates the effects of advection. By adding on a sufficient number of terms to the series any desired level of accuracy can be attained.

We have also demonstrated that $C(x)$ converges and that there exists a real value of c_0 between 0 and 1.

6 Acknowledgments

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A Analytical solution to Linear Equation

The exact equilibrium solution to the linear form of equation (1):

$$D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - kC = 0 \quad (30)$$

Is:

$$C(x)=\frac{(-V+\sqrt{V^2+4kD})\cdot C_s\cdot e^{\frac{1}{2}\frac{(V+\sqrt{V^2+4kD})x}{D}}+(V+\sqrt{V^2+4kD})\cdot C_s\cdot e^{-\frac{1}{2}\frac{(-V+\sqrt{V^2+4kD})x}{D}}}{-V\cdot e^{\frac{1}{2}\frac{(V+\sqrt{V^2+4kD})L}{D}}+\sqrt{V^2+4kD}\cdot e^{\frac{1}{2}\frac{(V+\sqrt{V^2+4kD})L}{D}}+V\cdot e^{-\frac{1}{2}\frac{(-V+\sqrt{V^2+4kD})L}{D}}+\sqrt{V^2+4kD}\cdot e^{-\frac{1}{2}\frac{(-V+\sqrt{V^2+4kD})L}{D}}}$$

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