

Analysis of Langmuir-Hinshelwood Kinetics Model for Photocatalytic Degradation of Aqueous Direct Blue 71 Through Analytical Expression

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Abstract: An analysis of the Langmuir-Hinshelwood expression is presented for the photocatalytic degradation of Aqueous Direct Blue 71. This analysis contains a nonlinear term that explains the kinetics of the heterogeneous catalytic processes. In this paper, we obtain approximate analytical solutions for the nonlinear equation by employing the Perturbation-Iteration Algorithms (PIA). The main objective is to propose an analytical method of solution, which do not require small parameters and avoid linearization and physically unrealistic assumptions. Furthermore, in this work decolorization efficiency (DE%) and the numerical solution to the problem is also reported using MATLAB program. The analytical results are compared with the numerical and limiting case result. The obtained results are valid for the whole solution domain. A good agreement between the theoretical predictions and numerical results is observed. Langmuir-Hinshelwood model is analyzed with the help of analytical result for the different values of H_2O_2 and SiO_2 -NP to describe photocatalytic degradation of the dye.

Keywords: Langmuir-Hinshelwood kinetics, First order catalytic kinetics, Perturbation-Iteration Algorithms, Photocatalysis, Degradation.

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1. Introduction

In the last few decades, dyestuffs and allied industries have become subject to stringent scanner of rules and regulation charted out to protect the human health and environment. As a consequence, the effective elimination of colored effluents originating from the textile and related industries has become an important problem to the textile dyer and finisher as to meet the new discharge limit values [1]. The most common methods employed to treat waste water containing organic dyes and pigments are classifiable into three main categories physical (adsorption, filtration, flotation), chemical (coagulation, oxidation, reduction, electrolysis) and biological (aerobic, anaerobic degradation) [2]. However, due to the complexity and variety of dyestuffs employed in the textile dyeing process, it has become rather difficult to find a unique treatment procedure that covers the effective elimination of all dye types and classes. Particularly, biochemical oxidation suffers from significant limitations since most dyestuffs found in the commercial market have been intentionally designed to resist aerobic microbial degradation.

Consequently, most dyestuffs are of a rather recalcitrant nature and have to be treated by alternative advanced physicochemical processes. Homogenous advanced oxidation via combinations of H_2O_2 , O_3 and UV light is one of the principal and most

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effective methods for decomposing water-soluble organic pollutants found in water and wastewater and their application to reactive dyestuffs has already been investigated by many researchers recently. Hydrogen peroxide alone does not oxidize more difficult to degrade dyestuffs, however, it can be activated to form highly reactive species, mainly hydroxyl radicals (OH) by means of adding soluble ferrous ion salt to an acidic solution of H_2O_2 producing the Fenton's reagent, ozone at high pH, or in the presence of UV-C ($300 \text{ nm} > \lambda > 200 \text{ nm}$) light irradiation.

The field of heterogeneous photocatalysis [3] has expanded rapidly within the last four decades, having undergone various developments especially in relation to energy and the environment. It can be defined as the acceleration of photoreaction in the presence of a catalyst. Heterogeneous photocatalysis is one of the advanced oxidation processes (AOP) that has proven to be a promising method for the elimination of toxic and bio-resistant organic and inorganic compounds in wastewater by transforming them into innocuous species. Advanced oxidation process (AOP) [4] is a chemical oxidative process, which can be applied to wastewater treatment to oxidize pollutants. It generates hydroxyl radicals which are considered as the second strongest known oxidant (2.8 V vs. standard hydrogen electrode). It is able to oxidize and mineralize almost every organic molecule, yielding CO_2 and inorganic ions. The principal advantage of the SiO_2/UV system over homogenous advanced oxidation processes (AOPs) is its relative robustness to reaction conditions. Homogeneous photochemical and SiO_2 -mediated heterogeneous photocatalytic treatment of various organic and inorganic model pollutants has been extensively reported in the recent scientific literature. However, the effectiveness of AOPs in decomposing commercial reactive azo dyes as well as their competitiveness in terms of operating costs needs still to be further questioned, in particular for the heterogeneous photocatalytic treatment process due to its outstandingly high operational cost and complexity [5].

Silica is basically inert for many reactions, but it shows noticeable activities towards some catalytic reactions [6]. Silica is proven to remote photocatalytic reactions, e.g. photocatalytic degradation of methyl red by silica nanoparticles doped with Ag^+ or Au^{3+} . In the present work, the photocatalytic effect of SiO_2 -NPs in an irradiation photocatalytic process (UV intensity from 28 to $167 \mu W/cm_2$) is studied for the discoloration of Direct Blue 71 (DB71) [7] solution. The influencing factors investigated were the H_2O_2 and SiO_2 -NP initial concentrations and the irradiation time duration. The kinetic experiments were also conducted with different values of H_2O_2 and SiO_2 -NP to describe photocatalytic degradation of the dye. Moreover, the photodegradation of Aqueous Direct Blue 71 in aqueous solution satisfactorily was described by the Langmuir-Hinshelwood model. Kinetics expression, based on Langmuir-Hinshelwood model has been experimentally studied [8, 9]. Vasanth Kumar et.al reported that it was impossible and inappropriate to approximate the Langmuir-Hinshelwood kinetics [10] to zero order $KC_0 \gg 1$. Most of researchers approximated Langmuir-Hinshelwood kinetics to first order kinetics for the condition $KC \ll 1$ [11, 12]. The analytical solutions were obtained for limiting cases by linearizing the nonlinear term. To the best of our knowledge, no general analytical expression for the nonlinear Langmuir-Hinshelwood model that describes the concentration of the dye has so far been reported. The purpose of this paper is to derive an analytical expression for the concentration of the dye for all values of the rate constants using the Perturbation-Iteration Algorithms (PIA) [13-15]. The discoloration rate of DB71 was calculated to all possible values of the parameters k_r , KC_0 and t .

2. Mathematical Formulation of the Problem and Analysis

The Langmuir-Hinshelwood model (LHM) includes the sorption effect in their kinetic model. The main idea of LHM is that all the reactants are adsorbed on the active sites of the catalyst surface before the reaction starts [16]. The Langmuir-Hinshelwood expression explains the kinetics of heterogeneous catalytic processes and it is given below [17]:

$$r = -\frac{dC}{dt} = \frac{k_r KC}{1 + KC} \quad (1)$$

where C is the dye concentration at any time t , the initial dye concentration is C_0 , K is the adsorption coefficient of the dye, k_r is the reaction rate constant, r represents the rate of reaction that changes with time t . The term r in Equation (1) is represented in terms of initial reaction rate, r_0 , as a function of the initial dye concentration C_0 ,

$$r_0 = \frac{k_r K C_0}{1 + K C_0} \quad (2)$$

An appropriate set of initial condition is given as follows:

$$C(0) = C_0 \quad (3)$$

3. Solution of Boundary Value Problem Using Perturbation-Iteration Algorithm (PIA)

Numerous methods [18–22] have been introduced by researchers in their recent literature to attain admissible solutions which eschew the requirement of a small parameter. Lately, a class of alternative Perturbation-Iteration Algorithms (see Appendix A) had been proposed, the fundamentals of which were outlined for the first-order differential equations by Pakdemirli et al. [15]. One of the best advantages of the new method is that it does not require initial transformation of the equations to another form. In fact, the technique was first developed for algebraic equations and then tweaked to adapt to ordinary differential equations [14, 15]. In this paper, the PIA is aptly and tactfully employed to obtain the approximate solution of Langmuir-Hinshelwood model. Using PIA method, we can obtain,

$$C = C_0 e^{-k_r K t} \left[(1 + \varepsilon C_0 K (1 - e^{-k_r K t})) \right] \quad (4)$$

$$C = C_0 e^{-k_r K t} \left[1 - \frac{C_0 K \varepsilon (2(e^{-k_r K t} - 1) + \varepsilon C_0 K (e^{-2k_r K t} - 1))}{2(1 + \varepsilon C_0 K e^{-k_r K t} (2 + \varepsilon C_0 K e^{-k_r K t}))} \right] \quad (5)$$

Equations (4) and (5) represent the dye concentration which are derived using PIA(1,1) (see Appendix B) and PIA(1,2) (see Appendix C) respectively.

Reactants (mg/L)	Langmuir-Hinshel wood model		First-order model
	k_r	K	k_1
$H_2O_2 = 100, SiO_2 = 200$	8.04	0.0198	0.17586
$H_2O_2 = 100, SiO_2 = 0$	4.89	0.0275	0.1239
$H_2O_2 = 250, SiO_2 = 200$	13.23	0.0130	0.21771
$H_2O_2 = 250, SiO_2 = 0$	7.56	0.0194	0.16195

Table 1. The rate constants of DB71 degradation [17]

Limiting Case: First order reaction kinetics

The rate of photodegradation of organic compounds follows the first order reaction kinetics. For pseudo first order reaction KC is very small as compared to 1 (i.e) when $KC \ll 1$. Equation (1) reduces to

$$\frac{dC}{dt} = -k_r K C \quad (6)$$

$k_1 = k_r K$ is the apparent first-order reaction rate constant

$$\frac{dC}{dt} = -k_1 C \quad (7)$$

$$C(t) = C_0 e^{-k_1 t} \quad (8)$$

In order to make the concentration-time relationship linear, the equation can be rewritten as per the integrated rate law, as follows

$$\ln(C(t)/C_0) = -k_1 t \quad (9)$$

When the natural log of the normalized concentration of $C(t)/C_0$ is plotted as a function of time, the constant k_1 can be easily determined from the slope of linear best fit.

Decolorization efficiency: The decolorization efficiency (DE%) was calculated as below [8]:

$$DE\% = \frac{C_0 - C_t}{C_0} \times 100\% \quad (10)$$

where C_0 and C_t are the concentration of dye at time 0 and t , respectively; and t is the irradiation time. Using Equations (5) and (10) we obtain,

$$DE\% = \frac{50KC_0 e^{-k_r K t} [(2 - KC_0) + 2(KC_0 - 1)e^{-k_r K t} - KC_0 e^{-2k_r K t}] + 100(1 - e^{-k_r K t})}{1 + KC_0 e^{-k_r K t} (2 + KC_0 e^{-k_r K t})} \quad (11)$$

4. Results and Discussion

Langmuir-Hinshelwood kinetics model describes that photocatalytic degradation of dye cannot be solved using rigorous standard analytical methods because of their nonlinearity. In this paper the nonlinear differential Equation (1) is solved both analytically and numerically. Perturbation-Iteration Algorithm (PIA) is used to solve the equation analytically for all values of the rate constants k_r , K and the initial concentration C_0 . Here the initial concentration of the dye is taken as 30mg/L [17]. The function ode45 in MATLAB software has several different functions (built-ins) for the numerical solution of ordinary differential equations (ODEs). The MATLAB program is also given in Appendix D.

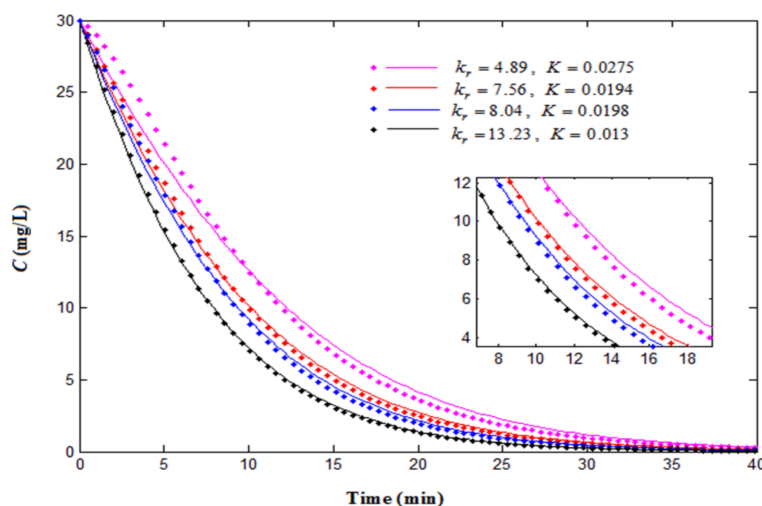


Figure 1: Plot of two-dimensional comparative diagram between analytical solution obtained using Perturbation-Iteration Algorithm PIA(1,1) and numerical solution of the concentrations of dye $C(mg/L)$ Equation (4) versus the time t (min) for the initial concentration of the dye $C_0 = 30 mg/L$ and various values of k_r (mg/L.min) and K (L/mg). Dotted lines represent analytical solution obtained in this work whereas solid lines represent numerical solution.

Comparison of analytical with numerical results: Concentration of the dye depends upon the rate constants k_r and K . Equations (4) and (5) are the new and simple analytical expressions of concentration profiles obtained using PIA(1,1)

and PIA(1,2) respectively. Figures 1 and 2 represent the concentration of C against the time t for various values of the rate constants which is given in Table 1. These figures also illustrate the comparison of analytical results obtained in this work with the numerical result. In comparison, it is evident that faster convergence is achieved with PIA(1,2) compared to PIA(1,1). Analytical expression obtained through PIA(1,2) gives excellent agreement with the numerical result. These figures show that the concentration of the dye follow a first-order exponential decay and it is always a decreasing function from the initial value C_0 .

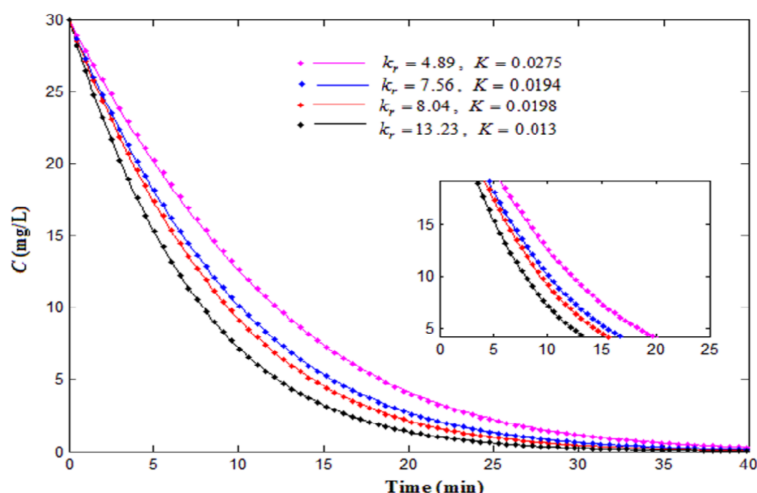


Figure 2: Plot of two-dimensional comparative diagram between analytical solution obtained using Perturbation-Iteration Algorithm PIA(1,2) and numerical solution of the concentrations of dye $C(mg/L)$ Equation (5) versus the time t (min) for the initial concentration of the dye $C_0 = 30mg/L$ and various values of $k_r(mg/L.min)$ and K (L/mg). Dotted lines represent analytical solution obtained in this work whereas solid lines represent numerical solution.

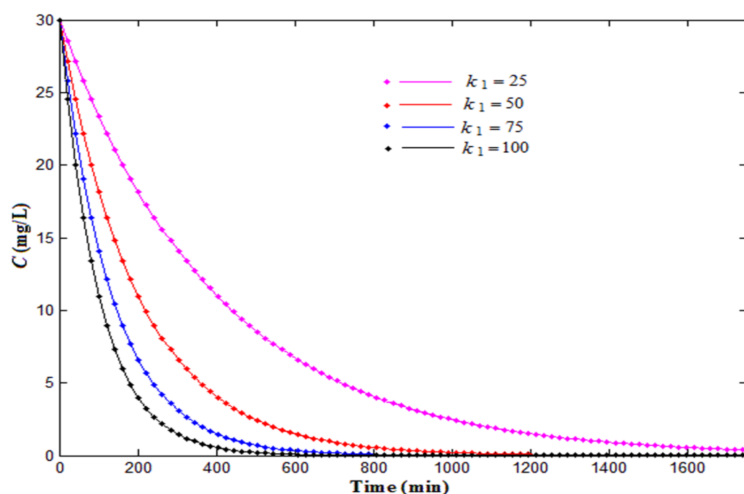


Figure 3: Plot of the two-dimensional comparative case diagram of the concentrations of dye $C(mg/L)$ versus time t (min) when $KC \ll 1$ for $C_0 = 30mg/L$ and $K = 10^{-4}$ (L/mg) and various values of $k_1(mg/L.min)$. Dotted lines are plotted according to Equation (5), and solid lines are plotted according to Equation (8).

Comparison of analytical result obtained using PIA with Limiting case: The analytical result Equation (5) obtained for nonlinear model Equation (1) is also compared with the limiting case result Equation (8) in Figure 3. This figure shows that the concentration of the dye is inversely proportional to the apparent first-order reaction rate constant ($k_1 = k_r K$). From the limiting case (First order reaction kinetics), it has been confirmed that the plot of the logarithmic

value of $\frac{C(t)}{C_0}$ vs t should be a straight line whose slope is $k_1 = k_r K$ which is coincident with result presented in Figure 4.

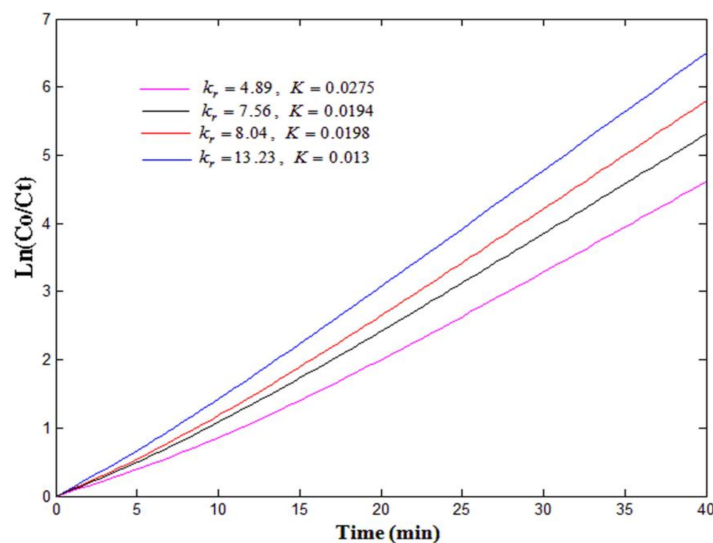


Figure 4: Plots of $\ln(C_0/C_t)$ versus time t (min) for the initial concentration of the dye $C_0 = 30 \text{ mg/L}$ and various values of k_r (mg/L.min) and K (L/mg).

Kinetic data of photodecolorization: An azo-dye Direct Blue 71 is chosen as a model pollutant for study the photocatalytic behavior of SiO_2 nanoparticles. The removal of DB71 dye is investigated at different concentrations of dye solutions. Fig. 5 demonstrates the photodegradation of DB71 in the certain irradiation time intervals. Decolorization efficiency was high when the amounts of H_2O_2 and SiO_2 -NP were 250 and 200 mg/L respectively. The slowest reaction rate was found when only H_2O_2 was present in the system (Figure 5). It is observed from the Figure 6a that there is a decrease in the DE% with increasing initial dye concentration it may be due to two reasons [23]. (i). More dye molecules were adsorbed on the surface of the catalyst as the initial concentration of dye increased, and thus the generation of hydroxyl radicals at the catalyst surface was reduced since the active sites were occupied by dye molecules. (ii). An increase in the light absorbed by the dye molecules leads to a reduction in the number of photons that reach the catalyst surface [24]. The maximum value of discoloration under the optimum operating conditions was determined to be greater 99% at 15 minutes irradiation time (Figure 6b).

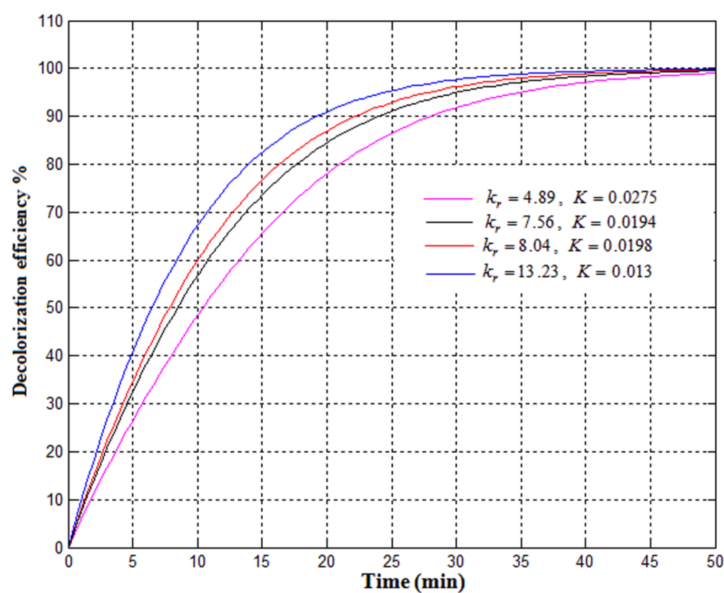


Figure 5: Decolorization efficiency % of the concentration of the dye C Equation (11) versus time t (min) for the initial

concentration of the dye $C_0 = 30 \text{ mg/L}$ and various values of k_r (mg/L.min) and K (L/mg).

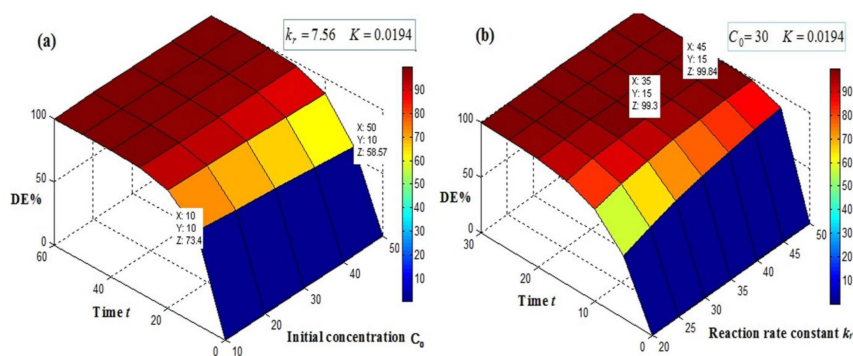


Figure 6: Plot of the three dimensional Decolorization efficiency (DE%) versus time t (a) Initial concentration C_0 (b) Reaction rate constant k_r obtained via Equation (11).

5. Conclusion

In this study, a theoretical model of Langmuir–Hinshelwood kinetics for the photocatalytic degradation of Aqueous Direct Blue 71 is presented. We successfully applied Perturbation Iteration Algorithm (PIA) to obtain approximate analytical solutions to a time-dependent nonlinear reaction equation. The solutions obtained by the Perturbation Iteration Algorithm (PIA) seem to match well when compared with those obtained from the numerical and limiting case results. We have shown that the proposed algorithm is very accurate and efficient method compared with other methods for Langmuir Hinshelwood kinetics model. The results revealed that kinetic rate constants of decolorization were decreased by the increasing of initial concentration of dye. Theoretical analysis is found to be substantiating the experimental results and thereby enhanced value of discoloration is achieved to be greater than 99% at 15 minutes irradiation time. The information gained from this theoretical model can be useful for the kinetic analysis of the experimental results.

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Appendix A

Basic concepts of the PIA: The perturbation iteration algorithm is represented by $PIA(n, m)$ where n embodies the correction terms in the perturbation expansion and m is the highest order derivative term in the Taylor series. Multiple iteration algorithms can be equated by taking various numbers of terms in the perturbation expansions and different order of correction terms in the Taylor series expansions. In this section, a perturbation-iteration algorithm $PIA(1, m)$ is constructed by taking one correction term in the perturbation expansion and correction terms of m^{th} -order derivatives in the Taylor series expansion. Consider the following system of first-order differential equations.

$$F_k(\dot{u}_k, u_j, \varepsilon, t) = 0, \quad k = 1, 2, \dots, N; \quad j = 1, 2, \dots, N \quad (A.1)$$

where N represents the number of differential equations in the system and the number of dependent variables. $N = 1$ for a single equation. In the open form, the system of equations is

$$\begin{aligned} F_1 &= F_1(\dot{u}_1, u_1, u_2, \dots, u_k, \varepsilon, t) = 0, \\ F_2 &= F_2(\dot{u}_2, u_1, u_2, \dots, u_k, \varepsilon, t) = 0, \\ &\vdots \\ F_k &= F_k(\dot{u}_k, u_1, u_2, \dots, u_k, \varepsilon, t) = 0. \end{aligned} \quad (A.2)$$

Assume an approximate solution of the system with one correction term in the perturbation expansion.

$$u_{k,n+1} = u_{k,n} + \varepsilon u_{k,n}^c \quad (A.3)$$

The subscript n represents the n^{th} iteration over this approximate solution. The system can be approximated with a Taylor series expansion in the neighbourhood of $\varepsilon = 0$ as

$$F_k = \sum_{i=0}^m \frac{1}{i!} \left[\left(\frac{d}{d\varepsilon} \right)^i F_k \right]_{\varepsilon=0} \varepsilon^i, \quad k = 1, 2, \dots, N \quad (A.4)$$

where

$$\frac{d}{d\varepsilon} = \frac{\partial \dot{u}_{k,n+1}}{\partial \varepsilon} \frac{\partial}{\partial \dot{u}_{k,n+1}} + \sum_{j=1}^N \left(\frac{\partial u_{j,n+1}}{\partial \varepsilon} \frac{\partial}{\partial u_{j,n+1}} \right) + \frac{\partial}{\partial \varepsilon} \quad (A.5)$$

is defined for the $(n + 1)^{th}$ iterative equation

$$F_k(\dot{u}_{k,n+1}, u_{j,n+1}, \varepsilon, t) = 0. \quad (A.6)$$

Substituting Equation (A.5) into Equation (A.4), one can obtain an iteration equation

$$F_k = \sum_{i=0}^m \frac{1}{i!} \left[\dot{u}_{k,n}^c \left(\frac{\partial}{\partial \dot{u}_{k,n+1}} + \sum_{j=1}^N u_{j,n}^c \frac{\partial}{\partial u_{j,n+1}} + \frac{\partial}{\partial \varepsilon} \right)^i F_k \right]_{\varepsilon=0} \times \varepsilon^i = 0, \quad k = 1, 2, \dots, N \quad (A.7)$$

which is a first-order differential equation and can be solved for the correction terms $u_{k,n}^c$. Then using Equation (A.3), the $(n + 1)^{th}$ iteration solution can be found. Iterations are terminated after a successful approximation is obtained.

Note that for a more general algorithm, n correction terms instead of one can be taken in expansion Equation (A.3) which would then be a $PIA(n, m)$ algorithm. The algorithm can also be generalized to a differential equation system having arbitrary order of derivatives.

Appendix B

Perturbation-Iteration Algorithm PIA(1,1): In this section, a perturbation-iteration algorithm is developed by taking one correction term in the perturbation expansion and correction terms of only first derivatives in the Taylor Series expansion, i.e. $n = 1, m = 1$. The algorithm is named as *PIA(1,1)*. An artificial perturbation parameter is inserted as follows:

$$F = (1 + \varepsilon KC) \frac{dC}{dt} + k_r KC = 0 \quad (\text{B.1})$$

For the equation considered, taking $m = 1$ and $N = 1$, Equation (A.7) reduces to

$$\dot{C}_{1,n}^c + k_r KC_{1,n}^c = -\frac{\dot{C}_{1,n} + k_r KC_{1,n}}{\varepsilon} - K \dot{C}_{1,n} C_{1,n} \quad (\text{B.2})$$

where ε is an artificially introduced small parameter, and setting $\varepsilon = 1$, Equation (B.2) reduces to

$$\dot{C}_{1,n}^c + k_r KC_{1,n}^c = -(\dot{C}_{1,n} + k_r KC_{1,n}) - K \dot{C}_{1,n} C_{1,n} \quad (\text{B.3})$$

which is the determining iteration equation for the perturbation correction term. Assuming an initial solution, using Equations (A.3) and (B.3), successive iteration function can be determined. An initial trial function

$$C_{1,0} = C_0 e^{-k_r K t} \quad (\text{B.4})$$

which satisfies the initial condition is selected. Put $n = 0$ in Equation (B.3)

$$\dot{C}_{1,0}^c + k_r KC_{1,0}^c = -(\dot{C}_{1,0} + k_r KC_{1,0}) - K \dot{C}_{1,0} C_{1,0} \quad (\text{B.5})$$

Substituting Equation (B.4) in Equation (B.5) and solving for the correction term, we get

$$C_{1,0}^c = C_0^2 K e^{-k_r K t} - C_0^2 K e^{-2k_r K t} \quad (\text{B.6})$$

Adding Equations (B.4) and (B.6) we get

$$C = C_{1,1} = C_0 e^{-k_r K t} \left[(1 + C_0 K (1 - e^{-k_r K t})) \right] \quad (\text{B.7})$$

Appendix C

Perturbation-Iteration Algorithm PIA(1,2): In this section, a perturbation-iteration algorithm is obtained by taking one correction term in the perturbation expansion and correction terms up to second derivatives in the Taylor Series expansion, i.e. $n = 1, m = 2$. The algorithm is called *PIA(1,2)*. For this choice, Equation (A.7) reduces to

$$(1 + \varepsilon KC_{1,n}) \dot{C}_{1,n}^c + (k_r K + \varepsilon K \dot{C}_{1,n}) C_{1,n}^c = -\frac{\dot{C}_{1,n} + k_r KC_{1,n}}{\varepsilon} - K \dot{C}_{1,n} C_{1,n} \quad (\text{C.1})$$

where ε is an artificially introduced small parameter, and setting $\varepsilon = 1$, Equation (C.1) reduces to

$$(1 + KC_{1,n}) \dot{C}_{1,n}^c + (k_r K + K \dot{C}_{1,n}) C_{1,n}^c = -(\dot{C}_{1,n} + k_r KC_{1,n}) - K \dot{C}_{1,n} C_{1,n} \quad (\text{C.2})$$

which is the determining iteration equation for the perturbation correction term. Taking the same initial trial function as given in Equation (B.4), Put $n = 0$ in Equation (C.2)

$$(1 + KC_{1,0})\dot{C}_{1,0}^c + (k_r K + K\dot{C}_{1,0})C_{1,0}^c = -(\dot{C}_{1,0} + k_r KC_{1,0}) - K\dot{C}_{1,0}C_{1,0} \quad (C.3)$$

Substituting Equation (B.4) in Equation (C.3) and solving for the correction term,

$$C_{1,0}^c = -\frac{1}{2} \frac{e^{-k_r Kt} (2C_0^2 K e^{-k_r Kt} + C_0^3 K^2 e^{-2k_r Kt} - C_0^2 K (2 + C_0 K))}{1 + 2C_0 K e^{-k_r Kt} + C_0^2 K^2 e^{-2k_r Kt}} \quad (C.4)$$

Adding Equations (B.4) and (C.4) we get

$$C = C_{1,1} = C_0 e^{-k_r Kt} \left[1 - \frac{C_0 K (2(e^{-k_r Kt} - 1) + C_0 K (e^{-2k_r Kt} - 1))}{2(1 + C_0 K e^{-k_r Kt} (2 + C_0 K e^{-k_r Kt}))} \right] \quad (C.5)$$

Appendix D

Numerical simulation: MATLAB program to find the solutions of the Equation (1)

function photo

```
options= odeset('RelTol',1e-6,'Stats','on');
```

```
Xo =30;
```

```
tspan = [0,50];
```

```
tic
```

```
[t,X] = ode45(@TestFunction,tspan,Xo,options);
```

```
toc
```

```
figure
```

```
hold on
```

```
plot(t, X(:,1),'m')
```

```
return
```

```
function [dx_dt]= TestFunction(t,x)
```

```
b1=0.0275;
```

```
a1=4.89;
```

```
dx_dt(1)=-(a1*b1*x(1)./(1+b1.*x(1)));
```

```
dx_dt = dx_dt';
```