Mathematical model for steady state current at PPO-modified micro-cylinder biosensors

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ABSTRACT

A Mathematical model for a modified micro-cylinder electrode in which polyphenol oxidase (PPO) occurs for all values of the concentration of catechol and o-quinone is analysed. This model is based on system of reaction-diffusion equations containing a non-linear term related to Michaelis Menten kinetics of the enzymatic reaction. Here a new analytical technique Homotopy Perturbation Method is used to solve the system of non-linear differential equations, that describe the diffusion coupled with a Michaelis-Menten kinetics law. Here we report an analytical expressions pertaining to the concentration of catechol and o-quinone and corresponding current in terms of dimensionless reaction-diffusion parameters in closed form. An excellent agreement with available limiting case is noticed.

Keywords: Non-Linear Reaction/Diffusion Equation; Biosensors; Polymer-Modified Micro-Cylinder Electrode; Polyphenol Oxidase; Homotopy Perturbation Method

1. INTRODUCTION

Microelectrodes are increasingly being used in biosensors [1-3]. This is due to factors such as fast response times, high signal: noise ratios and the ability to operate in low conductivity media, sub-micro volume and in vivo [4]. The most commonly used microelectrode in bio-sensor is microcylinder such as carbon fibres. This is because they are cheap, readily available, their form is suited to implantation [5] and because much is known about their surface characteristics [6].

Immobilization of enzymes is used in biosensors to detect the concentration of a specific analyte as a result of the biological recognition between the analyte and the immobilized enzyme. Enzymes have been immobilized at carbon fibres by many methods. Among all the methods, layer-by-layer (LbL) self assembly process is a simple technique which may be applied to a wide range of enzymes and that it is one of the few immobilization procedures which allows control over the amount and spatial distribution of the enzyme [7]. This property is important both for constructing and modeling studies of biosensors. The layer-by-layer process was first introduced by Decher and Hong [7]. This method has been applied to planar electrodes of Au [8,9], carbon electrodes [10] and polystyrene latex [11-15].

To analyse the performance of biosensors of any kind, it would be useful to have a mathematical model of the electrode response. Theoretical models of enzyme electrodes give information about the mechanism and kinetics operating in the biosensor. Unlike experimental investigations of biosensors, where changing one parameter inevitably alters others, the influence of individual variables can be assessed in an idealized way. Thus, the information gained from modeling can be useful in sensor design, optimization and prediction of the electrodes response.

Recently Rijiravanich et al. [16] obtained the steady state concentration profile of o-quinone and dimensionless sensor response $j$ for the limiting cases of low substrate concentrations. To the best of our knowledge, no rigorous analytical solutions for the steady state concentrations for micro-cylinder biosensors for all values of the parameters have been published. In this communication, we have derived the new and simple analytical solutions of the concentration and the current for all values of parameters using the Homotopy Perturbation Method.

2. MATHEMATICAL FORMULATION OF THE PROBLEM AND ANALYSIS

The system presented here is a cylindrical electrode which is uniformly coated by an enzyme immobilized in non-conducting material which is porous to substrate.
The electrode is used in a stirred solution containing an excess of supporting electrolyte. The enzyme and electrode reaction are [16]:

\[
\begin{align*}
O_2 + 2\text{catechol} & \rightarrow 2o - \text{quinone} + 2\text{H}_2\text{O} \\
o - \text{quinone} + 2\text{H}^+ + 2e^- & \rightarrow \text{catechol}
\end{align*}
\]  
(1)  
(2)

Hence the catechol/quinone conversion forms an amplification cycle within the enzyme film. While it is possible in principle to solve for either phenol or catechol as substrate, solving for catechol is simpler, since it involves only one enzymic conversion. The actual mechanism of that conversion is complex, and involves three different states, oxy, met, deoxy [17] i.e. (where Ca is catechol, Q is quinone).

\[
\begin{align*}
\left[\text{Cu} (I) - \text{Cu} (I)\right]_{\text{deoxy}} + O_2 + 2\text{H}_2\text{O} & \rightarrow \left[H_2\text{O} - \text{Cu} (II) - O - \text{Cu} (II) - H_2\text{O}\right]_{\text{oxy}} \\
\left[H_2\text{O} - \text{Cu} (II) - O - O - \text{Cu} (II) - H_2\text{O}\right]_{\text{oxy}} & \rightarrow \left[\text{Cu} (II) - \text{Cu} - \text{Cu} (II)\right]_{\text{met}} + 2\text{H}_2\text{O} + 2\text{H}^+ \\
\left[\text{Cu} (II) - \text{Cu} - \text{Cu} (II)\right]_{\text{met}} & \rightarrow \left[\text{Cu} (I) - \text{Cu} (I)\right]_{\text{deoxy}} + Q
\end{align*}
\]  
(3)  
(4)  
(5)

The steady-state current can be given as [16]:

\[
I = \frac{nF}{\pi L r_0 D_r \left( \frac{dc_r}{dr} \right)_{r = 0}}
\]  
(6)

We introduce the following set of dimensionless variables:

\[
\begin{align*}
C &= \frac{c_C}{c_C^*}, & Q &= \frac{c_Q}{c_Q^*}, & R &= \frac{r}{r_0}, & \alpha &= \frac{\gamma_E}{\gamma_M}, & \gamma_S &= \frac{k_{out} c_r r_0^2}{D_r K_M}, \\
\gamma_Y &= \frac{\gamma_E}{\gamma_M}, & \gamma_S &= \frac{D_r}{D_C} \gamma_S
\end{align*}
\]  
(7)  
(8)  
(9)

where \(C\) and \(Q\) are the dimensionless concentration of the catechol and o-quinone. \(R\) is the dimensionless distance parameter. \(\gamma_E, \gamma_M\) and \(\alpha\) are the dimensionless reaction-diffusion parameters and saturation parameter [16].

\[
\begin{align*}
\frac{d^2 C}{dR^2} + \frac{1}{R} \frac{dC}{dR} - \gamma_Y C &= 0 \\
\frac{d^2 Q}{dR^2} + \frac{1}{R} \frac{dQ}{dR} + \gamma_Y C &= 0
\end{align*}
\]  
(10)  
(11)

The boundary conditions are represented as follows:

\[
\begin{align*}
C &= 1, & Q &= 0 & \text{when } R = 1 \\
C &= 1, & Q &= 0 & \text{when } R = r/r_0
\end{align*}
\]  
(12)  
(13)

The dimensionless current at the micro-cylinder electrode can be given as follows:

\[
\psi = I/\pi F L D_r c_C^* = 2\pi (dQ/dR)_{R=1}
\]  
(14)

3. ANALYTICAL SOLUTIONS OF THE CONCENTRATIONS AND THE CURRENT USING THE HOMOTOPY PERTURBATION METHOD

Nonlinear phenomena play a crucial role in applied
mathematics and chemistry. Construction of particular exact solutions for these equations remains an important problem. Finding exact solutions that have a physical, chemical or biological interpretation is of fundamental importance. This model is based on steady-state system of diffusion equations containing a non-linear reaction term related to Michaelis-Menten kinetics of the enzymatic reactions. It is not possible to solve these equations using standard analytical technique. In the past, many authors mainly had paid attention to study solution of nonlinear equations by using various methods, such as Backlund transformation [19], Darboux transformation [20], Inverse scattering method [21], Bilinear method [22], The tanh method [23], Variational iteration method [24] and Homotopy Perturbation Method [25-28] etc. The Homotopy Perturbation Method was first proposed by He [24-26] and was successfully applied to autonomous ordinary differential equations to nonlinear polycrystalline solids and other fields.

Recently Meena and Rajendran [29], Anitha et al. [30] and Manimozhi et al. [31] implemented Homotopy perturbation method to give approximate and analytical solutions of nonlinear reaction-diffusion equations containing a nonlinear term related to Michaelis-Menten kinetic of the enzymatic reaction. Esvari et al. in series [32,33] solved the coupled non linear diffusion equations analytically for the microdisk and micro-cylinder enzyme electrode when a product from an immobilized enzyme reacts with the electrode. Using Homotopy Perturbation Method (see Appendix B), we can obtain the following solutions to the Eqs.14 to 15.

\[
C(R) = 1 + \left[ \frac{\gamma_E R^2 - \gamma_S \left(1 + \frac{r_i}{r_0}\right) R + \gamma_S \left(\frac{r_i}{r_0}\right)}{2(1 + \alpha)} \right] \tag{19}
\]

\[
Q(R) = \left[ \frac{-\gamma_S R^2 + \gamma_S \left(1 + \frac{r_i}{r_0}\right) R - \gamma_S \left(\frac{r_i}{r_0}\right)}{2(1 + \alpha)} \right] \tag{20}
\]

The Eqs.19-20 satisfies the boundary conditions (16) to (17). These equations represent the new and simple analytical expression of the concentration of catechol and o-quinone for all possible values of the parameters \(\gamma_E\), \(\gamma_S\), \(\alpha\) and \(\frac{r_i}{r_0}\). The Eqs.19 and 20 also satisfy the relation

\[
C(R) + \left(\frac{\gamma_S}{\gamma_E}\right) Q(R) = 1. \text{ From Eqs.19 and 20, we can obtain the dimensionless current, which is as follows:}
\]

\[
\psi = I/nFLDc_0^* = 2\pi \frac{\gamma_S \left(1 + \frac{r_i}{r_0}\right) - 2\gamma_S}{2(1 + \alpha)} \tag{21}
\]

Eq. (21) represents the new and closed form of an analytical expression for the current for all possible values of parameters.

3.1. Limiting Cases for Unsaturated (First Order) Catalytic Kinetics

In this case, the catechol concentration \(c_c\) is less than Michaelis constant \(K_M\). Now the Eqs.8 and 9 reduce to the following forms:

\[
\frac{D_c}{r} \frac{dc_c}{dr} - \frac{k_{cat} c_E c_c}{K_M} = 0 \tag{22}
\]

\[
\frac{D_Q}{r} \frac{dc_Q}{dr} + \frac{k_{cat} c_E c_c}{K_M} = 0 \tag{23}
\]

By solving the Eq.22 using the boundary condition (Eq.10), the concentration of catechol \(c_c\) can be obtained in the form of modified Bessel functions of zeroth order \(I_0(\chi r)\) and \(K_0(\chi r)\).

\[
\frac{c_c(r)}{c_c^0} = \frac{[I_0(\chi r) - K_0(\chi r_0)] + K_0(\chi r) I_0(\chi r_0) - K_0(\chi r) I_0(\chi r_0)]}{K_0(\chi r_0) I_0(\chi r_0) - K_0(\chi r) I_0(\chi r_0)} \tag{24}
\]

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where
\[ \chi^2 = k_{\text{cat}} c_c / D_c K_M \] (25)

Inserting Eqs. 24 into Eqs. 11, we can obtain the concentration \( c_0 \)

\[ \frac{D_o c_0(r)}{D_c c_c} = 1 - \left[ \frac{I_o(\chi r) [K_o(\chi r_i) - K_o(\chi r)] + K_o(\chi r) [I_o(\chi r_i) - I_o(\chi r_i)]}{K_o(\chi r_i) I_o(\chi r_i) - K_o(\chi r_i) I_o(\chi r)} \right] \] (26)

The sensor response \( j \) in terms of modified Bessel function of zeroth order can be obtained as follows:

\[ j = \frac{I}{nFLD_c c_c} = \frac{2\pi \chi r_0}{[K_o(\chi r_i) I_o(\chi r_i) - K_o(\chi r_i) I_o(\chi r)]} \left[ K_i(\chi r_i) [I_o(\chi r_i) - I_o(\chi r_0)] - I_i(\chi r_0) [K_o(\chi r_i) - K_o(\chi r_i)] \right] \] (27)

4. COMPARISON WITH LIMITING CASE WORK OF RIJIRAVANICH ET AL. [16]

Recently, they [16] have derived the analytical expression of the steady-state concentration \( Q_c \) (Eq. 28 and 29) in integral form for the limiting case \( c_c < K_M \).

\[ \frac{D_o c_0(r)}{D_c c_c} = g \chi \left\{ -f \int_0^{\chi r} I_i(\chi r) dr + \int_0^{\chi r} K_i(\chi r) dr + \frac{\ln(r/r_0)}{\ln(r_i/r_0)} \left[ f \int_0^{\chi r} I_i(\chi r) dr - \int_0^{\chi r} K_i(\chi r) dr \right] \right\} \] (28)

\[ j = \frac{I}{nFLD_c c_c} = 2\pi \chi g \times \left\{ f \left[ -f l_i(\chi r_0) + K_i(\chi r_i) \right] + \frac{1}{\ln(r_i/r_0)} \left[ f \int_0^{\chi r} I_i(\chi r) dr - \int_0^{\chi r} K_i(\chi r) dr \right] \right\} \] (29)

where
\[ g = \frac{1}{[f l_i(\chi r_0) + K_i(\chi r_i)]}, \quad f = [K_o(\chi r_i) - K_o(\chi r_i)]/[I_o(\chi r_i) - I_o(\chi r_0)] \]

Rijiravanich et al. [16] obtained the empirical expression of the current

\[ j = 2\pi x^p \tanh((x / 2)(\alpha_1 - 1))^q \] (30)

where \( p \) and \( q \) are empirical constants and \( \alpha_1 = r_1/r_0 \). The value of \( p \) and \( q \) are given for various values of \( x = \chi r_i \) in the Tables 1-3. This empirical expression is compared our simple closed analytical expression Eq. 27, in Tables 2-3. The average relative difference between our Eq. 27 and the empirical expression Eq. 30 is 0.71% when \( \alpha_1 = 1.5 \) and 0.59% when \( \alpha_1 = 5 \).

6. DISCUSSION

Figures 2 and 3 shows the dimensionless concentration profile of catechol \( C(R) \) using Eq. 19 for all various values of the parameters \( \gamma_s, \gamma_e, r_i/r_0 \) and \( \alpha \).

Thus it is concluded that there is a simultaneous increase in the values of the concentration of catechol as well as in saturated parameter \( \alpha \) for small values of \( \gamma_e \). Also the value of catechol concentration \( C \) is approximately equal to 1 when \( R = 1 \) and \( R = r_i/r_0 \) for all values of \( \alpha \) and \( \gamma_e \).

Figures 4 and 5 show the concentration profile of \( \gamma \)-quinone \( Q(R) \) in R space for various values of \( \alpha \) and \( \gamma_s \) calculated using Eq. 20. The plot was constructed for \( r_i/r_0 = 1.5 \) and 5. From these figures, it is confirmed that the value of the concentration of \( \gamma \)-quinone increases when \( \gamma_s \geq 0.1 \) for small values of \( \alpha \). From the Figures 2-5, we can observed that the dimensionless concentration of catechol should vary between 0 and 1. Because catechol is converted to \( \gamma \)-quinone, the \( \gamma \)-quinone concentration should be the inverse of catechol. The substrate catechol \( C \) is minimum and product \( \gamma \)-quinone \( Q \) is maximum when \( \alpha = 1.5 \) and \( \gamma_s = 0.5 \).

The minimum value of concentration profile of catechol is
\[ C_{\text{min}} = \frac{8 + 8\alpha - \gamma_e + 2\gamma_s \alpha_1 - \gamma_e \alpha_1^2}{8(1 + \alpha)} \] (31)
Table 2. Comparison of dimensionless sensor response \( j \) for various values of \( \chi r_0 \) using Eqs. 27 and 30 when thickness of the film \( (a_l = r_i/r_0 = 5) \).

<table>
<thead>
<tr>
<th>( x(=\chi r_0) )</th>
<th>( a_l = r_i/r_0 )</th>
<th>( p )</th>
<th>( q )</th>
<th>Eq. (30) [16]</th>
<th>Eq. (27) This work</th>
<th>Error %</th>
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<tr>
<td>9</td>
<td>5</td>
<td>1</td>
<td>1.01</td>
<td>57.78</td>
<td>57.78</td>
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<tr>
<td>8</td>
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<td>1.01</td>
<td>51.30</td>
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<tr>
<td>7</td>
<td>5</td>
<td>1.03</td>
<td>1.05</td>
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<td></td>
<td></td>
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<td>0.59</td>
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Table 3. Comparison of dimensionless sensor response \( j \) for various values of \( \chi r_0 \) using Eqs.27 and 30 when thickness of the film \( (a_l = r_i/r_0 = 1.5) \).

<table>
<thead>
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<th>( p )</th>
<th>( q )</th>
<th>Eq. (30) [16]</th>
<th>Eq. (27) This work</th>
<th>Error %</th>
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Figure 2. Typical normalized steady-state concentration profile of catechol \( C(R) \) plotted from Eq.19 for different values of parameters \( \gamma_E \) and \( \alpha \) when \( r_i/r_0 = 1.5 \).
Figure 3. Typical normalized steady-state concentration profile of $C(R)$ plotted from Eq.19 for different values of parameters $\gamma_E$ and $\alpha$ when $r_i/r_0 = 2.5$. 

(a) $r_i/r_0 = 2.5$
(b) $r_i/r_0 = 2.5$
(c) $r_i/r_0 = 2.5$
(d) $r_i/r_0 = 2.5$

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Figure 4. Typical normalized steady-state concentration profile of $Q(R)$ plotted from Eq.20 for different values of parameters $\gamma_E$ and $\alpha$ when $r_1/r_0 = 1.5$.

Figure 5. Typical normalized steady-state concentration profile of $Q(R)$ plotted from Eq.20 for different values of parameters $\gamma_E$ and $\alpha$ when $r_1/r_0 = 2.5$. 
and the maximum value of concentration profile of quinone is

$$Q_{\text{max}} = \frac{\gamma_d(1 - 2\alpha_1 + \alpha_1^2)}{8(1 + \alpha)}$$

(32)

where \( r_l/r_0 = \alpha_1 \). The dimensionless current \( \psi \) versus \( r_l/r_0 \) using Eq.21 is plotted in Figure 6. The value of current \( \psi \) increases when thickness of the film \( r_l/r_0 \) and dimensionless reaction-diffusion parameter \( \gamma_d \) is increases or decreases.

7. CONCLUSIONS

A non-linear time independent ordinary differential equation has been formulated and solved analytically. Analytical expression for the concentration of catechol and o-quinone and steady state current are derived by contains significant non-linear contributions using the Homotopy Perturbation Method. The primary result of this work is simple approximate calculation of concentration of catechol, o-quinone and current for all values of \( \gamma_c, \gamma_d, \alpha \) and \( r_l/r_0 \) and \( \chi_d \). Formerly in polyphenol oxidase micro-cylinder biosensor models are [16] have only considered the first order kinetics of the enzyme and therefore could only be applied to the sensor’s linear range. However, in this paper, calibration curves of many of the catechol/phenol biosensors contain most important non-linear contributions are reported. Also, the length of the linear range is an important analytical parameter. In developing a sensor, experimental scientists would like this range to cover all concentrations expected in actual samples, as this makes calibration of the sensor in the field much easier. In Tables 2-3, our analytical results are compared with limiting case of first order catalytic kinetics [16] results, which yield a good agreement with the previous limiting case results.

8. ACKNOWLEDGEMENTS

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REFERENCES


## APPENDIX A
### SYMBOLS USED

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<tr>
<th>Symbol</th>
<th>Definitions</th>
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<td>$D_C$</td>
<td>Diffusion coefficient of catechol</td>
<td>cm$^2$/s</td>
</tr>
<tr>
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<td>mole/cm$^3$</td>
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<td>Concentration profile of enzyme</td>
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</tr>
<tr>
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<td>Michaelis Menten constant</td>
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<td>$K_{cat}$</td>
<td>Catalytic rate constant</td>
<td>sec$^{-1}$</td>
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<tr>
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</tr>
<tr>
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<td>Diffusion coefficient of quinone</td>
<td>cm$^2$/s</td>
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<td>$c_C^*$</td>
<td>Bulk concentration of $C$</td>
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</tr>
<tr>
<td>$r$</td>
<td>Radius of the cylinder</td>
<td>cm</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
<td>ampere</td>
</tr>
<tr>
<td>$r_0$</td>
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<td>$L$</td>
<td>Length of the electrode</td>
<td>cm</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
<td>c·mole$^{-1}$</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons</td>
<td>none</td>
</tr>
</tbody>
</table>

## APPENDIX B

Solution of the Eqs.14 and 15 using Homotopy perturbation method. In this appendix, we indicate how Eqs.19 and 20 in this paper are derived. Furthermore, a Homotopy was constructed to determine the solution of Eqs.14 and 15.

\[
(1 - p) \left[ \frac{d^2 C}{dR^2} \right] + p \left[ \frac{d^2 C}{dR^2} + \frac{1}{R} \frac{dC}{dR} - \frac{\gamma_E C}{1 + \alpha C} \right] = 0 \tag{B1}
\]

\[
(1 - p) \left[ \frac{d^2 Q}{dR^2} \right] + p \left[ \frac{d^2 Q}{dR^2} + \frac{1}{R} \frac{dQ}{dR} + \frac{\gamma_S C}{1 + \alpha C} \right] = 0 \tag{B2}
\]

and the initial approximations are as follows:

\[
R = 0, \quad C = 1, \quad Q = 0 \tag{B3}
\]

\[
R = \frac{r_1}{r_0}, \quad C = 1, \quad Q = 0 \tag{B4}
\]
The approximate solutions of (B1) and (B2) are
\[ C = C_o + pC_i + p^2C_2 + p^3C_3 + \cdots \] (B5)
and
\[ Q = Q_o + pQ_i + p^2Q_2 + p^3Q_3 + \cdots \] (B6)
Substituting Eqs.B5 and B6 into Eqs.B1 and B2 and comparing the coefficients of like powers of \( p \)
\[ p^0 : \quad \frac{dC_o}{dR^2} = 0 \] (B7)
\[ p^1 : \quad \frac{d^2C_i}{dR^2} + \frac{1}{R} \frac{dC_o}{dR} - \frac{\gamma_s C_o}{1 + \alpha C_o} = 0 \] (B8)
and
\[ p^0 : \quad \frac{dQ_o}{dR^2} = 0 \] (B9)
\[ p^1 : \quad \frac{d^2Q_i}{dR^2} + \frac{1}{R} \frac{dQ_o}{dR} + \frac{\gamma_s C_o}{1 + \alpha C_o} = 0 \] (B10)
Solving the Eqs.B7 to B10, and using the boundary conditions (B3) and (B4), we can find the following results
\[ C_i(R) = 1 \] (B11)
\[ C_i(R) = \frac{\gamma_s R^2 + \gamma_s \left( \frac{r_i}{r_o} \right) - \gamma_s \left( 1 + \frac{r_i}{r_o} \right) R}{2(1 + \alpha)} \] (B12)
and
\[ Q_o(R) = 0 \] (B13)
\[ Q_i(R) = \frac{\gamma_s \left( 1 + \frac{r_i}{r_o} \right) R - \gamma_s \left( \frac{r_i}{r_o} \right) - \gamma_s R^2}{2(1 + \alpha)} \] (B14)
According to the HPM, we can conclude that
\[ C(R) = \lim_{p \to 0} C(R) = C_o + C_i + C_2 + \cdots \] (B15)
\[ Q(R) = \lim_{p \to 0} Q(R) = Q_o + Q_i + Q_2 + \cdots \] (B16)
Using Eqs.B11 and (B12) in Eq.B15 and Eqs.B13 and B14 in Eq.B16, we obtain the final results as described in Eqs.19 and 20.