

Mathematical Models of the Infinite Porous Rotating Disk Electrode

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Received: 27 April 2018 / *Accepted:* 29 May 2018 / *Published:* 1 September 2018

An analytical expression of the current generated from the electrochemical reaction in a porous rotating disk electrode (PRDE) is derived when the reactant transport is dominated by advection and diffusion. Simple algebraic expressions for the concentration of reactant and the current response are obtained as a function of the rotation rate, reaction rate, permeability of the porous medium, diffusion coefficients, kinematic viscosity, and geometry of the porous film. Upon comparison, the analytical expression of current in this work coincides with the existing results for the limiting case of low rotation rates. Also the concentration/current expressions here derived are in satisfactory agreement with numerical results.

Keywords: Mathematical modelling, Porous rotating disk electrode, Non-linear convection diffusion equation, Homotopy perturbation method.

1. INTRODUCTION

Non-linear phenomena play a crucial role in physical chemistry and biology (heat and mass transfer, filtration of liquids, diffusion in chemical reactions, etc.). In the past several decades, many authors mainly paid attention to the resolution of non-linear equations by using various methods, such as the variational iteration method (VIM) [1-4], the homotopy perturbation method (HPM) [5-9] and the Adomian decomposition method (ADM) [10-13]. The homotopy perturbation method has been proved by many authors to be a powerful mathematical tool for various kinds of non-linear problems, being unique in its applicability, accuracy and efficiency. The conventional perturbation method is based on the existence of small/large parameters, the so-called perturbation quantities. However, many non-linear problems do not contain such kind of perturbation quantities. The perturbation theory leads

to an expression for the desired solution in terms of a formal power series in some "small" parameter – known as a perturbation series – that quantifies the deviation from the exactly solvable problem. Generally, the perturbation method is valid only for weakly non-linear problems. The combination of the perturbation and the homotopy methods eliminates the above drawbacks of the traditional perturbation method while keeping all the advantages.

In the present work, the HPM method is used to treat the problem of the uniformly-accessible porous rotating disc electrode (PRDE) under steady state conditions. The use of porous materials as electrodes are found in many electrochemical technologies and devices, including batteries [14,15], fuel cells [16] and capacitors[17], in electrolytic cells [18] as well as in electro analytical sensors [19-22]. In general, these systems allow for larger current densities than uniform flat electrodes, with benefits in terms of power output, electrolysis yield or sensitivity. The mass transport in the film, as a function of the porous morphology, and the electrochemical kinetics mostly determine the electrolysis efficiency. The mathematical modelling of these processes in the case of stationary porous electrodes was developed in the last decade[19,23,24]. In contrast, theoretical studies of hydrodynamic methods, such as the PRDE, which can be employed in the evaluation of materials electrocatalytic activity, are much more limited[25,27]likely due to the higher complexity of the advection-diffusion problem. Thus, the flow in a porous disc electrode was discussed by Joseph [27] for an infinite permeable disc steadily rotating in an unbounded fluid. Blaedel and Joseph [28] presented the electrochemical characterization and the analytical use of porous carbon rotating disc electrodes. More recently, Nam *et al.* [25] obtained expressions for the steady-state concentration of the reactant and the PRDE current using the conventional perturbation technique.

In this work, analytical expressions will be deduced for the concentration profile of the reactant and for the overall rate of transformation (the current generated) as a function of the reaction kinetics, the film permeability (k) and thickness, and the rotation rate, among other parameters. The closed-form solutions presented can assist the optimization of electrochemical devices and operating conditions, as well as the evaluation of the electrocatalytic activity of the film material.

2. MATHEMATICAL FORMULATION OF THE PROBLEM

The dimensionless form of the convection-diffusion transport problem of the reactant close to the PRDE surface can be expressed as follows after eliminating all radial dependence assuming that the depletion/boundary layer is very thin compared to the radius of the film [25]:

$$(-\alpha Z^2 - \beta) \frac{dc}{dz} = \frac{D_f}{\nu} \frac{d^2c}{dz^2} \quad (1)$$

$$(-\gamma Z - \beta) \frac{d\hat{c}}{dz} = \frac{D_p}{\nu} \frac{d^2\hat{c}}{dz^2} - \frac{k_r}{\Omega} \hat{c} \quad (2)$$

where $\alpha = 0.51$, $\beta = 2kh(\Omega/\nu)^{3/2}$, $\gamma = 2k\Omega/\nu$, D_f and D_p are the diffusion coefficients in the fluid phase and in the porous media, respectively. c and \hat{c} are the concentrations of the reactant in the solution phase and in the porous media, respectively. k_r is the first-order reaction rate constant, k the permeability, h the thickness of the film, Ω the rotation rate and ν the kinematic viscosity. The boundary conditions are,

$$c = I, \quad z \rightarrow \infty \tag{3}$$

$$\hat{c} = 0, \quad z \rightarrow -\infty \tag{4}$$

$$c = \hat{c}, \quad z = 0 \tag{5}$$

$$\frac{dc}{dz} = \frac{D_p}{D_f} \frac{d\hat{c}}{dz}, \quad z = 0 \tag{6}$$

Using the following dimensionless variables

$$y = \frac{z}{\lambda}$$

$$\lambda = \left(\frac{3D_f}{\alpha v} \right)^{1/3}$$

$$B = \frac{3\beta}{\alpha \lambda^2} = 2k h \left(\frac{9\Omega^9}{v^5 \alpha^2 D_f^4} \right)^{1/6} \tag{7}$$

$$D = \frac{D_p}{D_f}$$

$$G = \frac{3\gamma}{\alpha \lambda} = 2k\Omega \left(\frac{9}{\alpha^2 v^2 D_f} \right)^{1/3}$$

$$K = \frac{3k_r}{\alpha \lambda \Omega} = \frac{k_r}{\Omega} \left(\frac{9v}{\alpha^2 D_f} \right)^{1/3}$$

equations (1)-(6) become in dimensionless form as follows:

$$-(3y^2 + B) \frac{dc}{dy} = \frac{d^2c}{dy^2} \tag{8}$$

$$-(Gy + B) \frac{d\hat{c}}{dy} = D \frac{d^2\hat{c}}{dy^2} - K\hat{c} \tag{9}$$

Assuming that (i) the concentration of reactant in the fluid far from the interface is its bulk concentration, (ii) at deep inside the porous disk, the concentration of reactant in porous media is zero (since the reactant is completely consumed in the boundary layer), (iii) the concentrations and flux of reactant in the fluid and porous media are equal at the fluid-porous disk boundary(y=0), the boundary conditions are defined as follows:

$$c = I, \quad y \rightarrow \infty \tag{10}$$

$$\hat{c} = 0, \quad y = -\infty \tag{11}$$

$$c = \hat{c}, \quad y = 0 \tag{12}$$

$$\frac{dc}{dy} = D \frac{d\hat{c}}{dy}, \quad \text{at } y = 0 \tag{13}$$

From the concentration profile of the reactant inside the porous film where the first-order redox reaction takes place, the current response can be calculated as

$$I = \int_V k_r \hat{c} n F dV \tag{14}$$

where n is the number of electrons transferred in the reaction, F is the Faraday constant and V is the volume of the disk film. The dimensionless current is given by:

$$I_R = \frac{I}{I_M} = \left(\frac{V}{\Omega}\right)^{1/2} \frac{\lambda}{h} \int_{-\infty}^0 \hat{c} dy \tag{15}$$

where the maximum current I_M is defined as [25]

$$I_M = \pi k_r c_\infty n F R^2 h \tag{16}$$

3. ANALYTICAL RESOLUTION OF THE PRDE PROBLEM USING THE HOMOTOPY PERTURBATION METHOD (HPM)

By solving equations (8) and (9) using the homotopy perturbation method (Appendix A), the following expressions for the concentration of the reactant in the fluid phase and porous media are obtained:

$$c(y) = 1 + (m_1 + k_2) \Gamma\left(\frac{1}{3}, y^3\right) - B m_1 \Gamma\left(\frac{2}{3}, y^3\right) \tag{17}$$

$$\hat{c}(y) = e^{ay} \left[k_1 + l_0 + l_1 y + \frac{b}{4a} y^2 \right] \tag{18}$$

where,

$$m_1 = -\frac{D k_1 a}{3}, \quad k_1 = \frac{3}{3 + 2.6789 D a}, \quad k_2 = \frac{-D(l_1 + l_0 a)}{3} = \frac{l_0 + l_2}{2.6789}, \quad b = -\frac{G k_1 a}{D}, \tag{19}$$

$$l_0 = \frac{-3l_2 - 2.6789 D l_1}{2.6789 D a + 3}, \quad m = -\frac{B}{D} k_1 a, \quad l_1 = -\frac{b}{4a^2} + \frac{m}{2a}, \quad l_2 = 1.3541 B m_1, \quad a = \sqrt{\frac{K}{D}}$$

These results (Eqns. (17) and (18)) can be re-written in terms of the important dimensionless quantities B, G, D and K as follows:

$$c(y) = 1 + \frac{1}{b_0} \left[-\sqrt{KD} + \left[\frac{0.373283}{b_0} \left\{ 4.0623 B \sqrt{KD} - 2.6789 D \left(\frac{3G}{4\sqrt{KD}} - \frac{3B}{2D} \right) \right\} - 0.505468 B \sqrt{KD} \right] \Gamma\left(\frac{1}{3}, y^3\right) - \frac{B\sqrt{KD}}{b_0} \Gamma\left(\frac{2}{3}, y^3\right) \right] \tag{20}$$

$$\hat{c}(y) = \frac{e^{\sqrt{K/D}y}}{b_0} \left[3 + \frac{1}{b_0} \left[4.0623 B \sqrt{KD} - 2.6789 D \left(\frac{3G}{4\sqrt{KD}} - \frac{3B}{2D} \right) \right] + \left(\frac{3G}{4\sqrt{KD}} - \frac{3B}{2D} \right) y - \frac{3G}{4D} y^2 \right] \tag{21}$$

where

$$b_0 = 3 + 2.6789 \sqrt{KD} \tag{22}$$

Using Eqns. (15) and (18), the following expressions are obtained for the current

$$I_R = \frac{I}{I_M} = \left(\frac{v}{\Omega}\right)^{1/2} \frac{\lambda}{h} \left[\frac{k_1 + l_0}{a} - \frac{l_1}{a^2} + \frac{b}{2a^4} \right] \tag{23}$$

$$I = I_R \left(\frac{v}{\Omega}\right)^{-1/2} \frac{h}{\lambda} = \left[\frac{k_1 + l_0}{a} - \frac{l_1}{a^2} + \frac{b}{2a^4} \right]$$

The above equation can be re-written in terms of the dimensionless parameters B, G, D , and K :

$$I \sqrt{\frac{K}{D}} = \frac{1 + 0.8930 \sqrt{KD} + 0.4514 B \sqrt{KD} - 0.8930 \frac{GD}{\sqrt{KD}} + 0.8930 B - 0.75 \frac{G}{K} + 0.5 \frac{B}{\sqrt{KD}}}{(1 + 0.8930 \sqrt{KD})^2} \tag{24}$$

The non-linear system of convection-diffusion equations (Eqs. (8) and (9)) with the corresponding boundary conditions (Eqs.(10–13)) has also been solved numerically via a finite-difference numerical method finding a reasonable agreement (less than 10 % error) for typical conditions ($G = 10^{-4} - 0.1$ [12]) when $K > 50$ for $B \approx 0.1$ and $K > 1000$ for $B \approx 1$.

4. PREVIOUS ANALYTICAL EXPRESSIONS

Nam *et al.* [25] developed a mathematical model for an infinite porous disk electrode with $G=0$ and small values of B , obtaining the following expressions for the concentration profile of the reactant inside and outside the porous medium:

$$c(y) = \frac{1 + \sqrt{KD} \int_0^y e^{-y^3} dy + B \left[\sqrt{KD} \int_y^\infty y e^{-y^3} dy - (KD b_2 - 1/2) \int_y^\infty e^{-y^3} dy \right]}{1 + \sqrt{KD} b_1} \tag{25}$$

$$\hat{c}(y) = \frac{e^{(K/D)^{1/2} y} \left\{ 1 + B \left[\sqrt{KD} b_2 + \sqrt{KD} \left(\frac{1}{2} - \frac{y}{2D} \right) b_1 - \frac{y}{2D} \right] \right\}}{1 + \sqrt{KD} b_1} \tag{26}$$

where

$$b_1 = \int_0^\infty \exp(-y^3) dy = \frac{2\pi\sqrt{3}}{9\Gamma(2/3)} = 0.8930$$

$$b_2 = \int_0^\infty y \exp(-y^3) dy = 0.4514$$
(27)

Note that Eqns. (25) and (26) derived by Nam *et al.* [25] do not satisfy the boundary condition $c = \hat{c}$ at $y = 0$.

Using Eqns. (26) and (15), the current becomes,

$$I = I_R \left(\frac{v}{\Omega} \right)^{-1/2} \frac{h}{\lambda} = \left[\hat{A} D \left[\frac{1}{(KD)^{1/2}} + B \left\{ \frac{b_1}{2(KD)^{1/2}} + \frac{1}{2(KD)} + b_2 + \frac{b_1}{2} \right\} \right] \right]$$

$$= \left[\hat{A} \sqrt{\frac{D}{K}} \left[1 + B \left\{ \frac{b_1}{2} + \frac{1}{2(KD)^{1/2}} + \sqrt{KD} \left(b_2 + \frac{b_1}{2} \right) \right\} \right] \right]$$

$$I \sqrt{\frac{K}{D}} = \left[\hat{A} \left[1 + B \left\{ \frac{b_1}{2} + \frac{1}{2(KD)^{1/2}} + \sqrt{KD} \left(b_2 + \frac{b_1}{2} \right) \right\} \right] \right] \tag{28}$$

where

$$\hat{A} = \frac{1}{\sqrt{KD} b_1 + 1} = \frac{1}{1 + 0.8930 \sqrt{KD}} \tag{29}$$

5. LIMITING CASES

1. Limiting Case

The parameters B and G are directly proportional to the rotation rate. When diffusion dominates or there is no convection within the porous medium, then $G = 0$ and $B = 0$ and equations (8) and (9) become into:

$$\frac{d^2c}{dy^2} + 3y^2 \frac{dc}{dy} = 0 \tag{30}$$

$$D \frac{d^2\hat{c}}{dy^2} - K \hat{c} = 0 \tag{31}$$

The exact solution of the above equation is given by:

$$c(y) = 1 - \frac{\sqrt{KD}}{3 + 2.6789\sqrt{KD}} \Gamma(1/3, y^3) \tag{32}$$

$$\hat{c}(y) = \frac{3e^{\sqrt{\frac{K}{D}}y}}{3 + 2.6789\sqrt{KD}} \tag{33}$$

which are identical to Eqns. (20) and (21) after making $G = 0$ and $B = 0$ (i.e. $k_2 = b = m = l_0 = l_1 = l_2 = 0$).

The current for $G = 0$ and $B = 0$ is given by,

$$I = I_R \left(\frac{v}{\Omega}\right)^{-1/2} \frac{h}{\lambda} = \int_{-\infty}^0 \hat{c} dy = \left[\frac{1}{1 + 0.8930\sqrt{KD}} \right] \sqrt{\frac{D}{K}} \tag{34}$$

which coincides with Eqn. (24), and also with the result derived by Nam *et al.* [25] (Eqn. (28)) for $B = 0$. Moreover, when the reaction is very fast ($K \gg 1$), Eqn. (34) reproduces the Levich equation for flat rotating disk electrodes since the reactant is consumed exhaustively on the surface of the disk [25]:

$$I \sqrt{\frac{K}{D}} = \frac{0.0867 \Omega^{1/2} D_f^{2/3}}{\gamma^{1/6} D_p^{1/2}} \tag{35}$$

2. Limiting case

When the G -term of the convection within the porous medium can be neglected [25], the concentration of reactant in the fluid phase (Eqn. (20) and porous media (Eqn. (21)) becomes as follows:

$$c(y) = 1 + \frac{1}{b_0} \left[-\sqrt{KD} + \left[\frac{0.373283}{b_0} \left\{ 4.0623B\sqrt{KD} + 2.6789 \left(\frac{3B}{2} \right) \right\} \right] - 0.505468B\sqrt{KD} \right] \Gamma\left(\frac{1}{3}, y^3\right) - \frac{B\sqrt{KD}}{b_0} \Gamma\left(\frac{2}{3}, y^3\right) \tag{36}$$

$$\hat{c}(y) = \frac{e^{\sqrt{K/D}y}}{b_0} \left[3 + \frac{1}{b_0} \left[4.0623B\sqrt{KD} + 2.6789 \left(\frac{3B}{2} \right) \right] - \left(\frac{3B}{2D} \right) y \right] \tag{37}$$

Eqns. (36) and (37) are compared with the previous results for this limiting case (Eqns. (25) and (26)) in Table.1. The average relative error between the present analytical results (Eqns. (36) and (37)) and those derived by Nam *et al.* [25] (Eqns. (25) and (26)) for the reactant concentration is ca. 2% in the solution phase and ca. 14% in the porous media.

Table 1. Comparison of the analytical expression for the concentration of reactant in the fluid phase c and the porous media \hat{c} with previous results. The numerical values of parameters are $B=0.1$, $K=75$, $D=0.1$, and $G=0$,

$y = z / \lambda$	Concentration of the reactant in the fluid phase c			$y = z / \lambda$	Concentration of the reactant in the porous media \hat{c}		
	This work Eqn. (36)	Nam <i>et al.</i> [25] Eqn. (25)	Error %		This work Eqn. (37)	Nam <i>et al.</i> [25] Eqn. (26)	Error %
0	0.30440	0.31925	4.87	0	0.30441	0.36159	18.78
0.01	0.31259	0.32720	4.67	-0.01	0.23259	0.27877	19.85
0.08	0.36967	0.38283	3.55	-0.08	0.03534	0.04491	27.08
0.1	0.38589	0.39871	3.32	-0.1	0.02062	0.02661	29.05
0.2	0.46632	0.47790	2.48	-0.2	0.00139	0.00193	38.84
0.3	0.54496	0.55610	2.04	-0.3	0.00009	0.00014	55.55
0.5	0.69216	0.70467	1.80	-0.5	0.00000	0.00000	0
0.7	0.81602	0.83224	1.98	-0.7	0.00000	0.00000	0
1	0.93805	0.96107	2.45	-1	0.00000	0.00000	0
2	0.99998	1	0	-2	0.00000	0.00000	0
3	1	1	0	-3	0.00000	0.00000	0
10	1	1	0	-10	0.00000	0.00000	0
∞	1	1	0	$-\infty$	0.00000	0.00000	0
	Average error %		2.09		Average error %		14.55

It is noted that in Nam *et al.* [25] $c \neq \hat{c}$ at $y=0$ while the present solutions for the concentration profiles of the reactant satisfy all the boundary conditions. Using Eqns. (23) and (24), the current becomes,

$$\begin{aligned}
 I &= I_R \left(\frac{v}{\Omega} \right)^{-1/2} \frac{h}{\lambda} = \left[\frac{k_1 + l_0}{a} - \frac{l_1}{a^2} \right] \\
 &= \frac{1 + 0.8930 D \sqrt{\frac{K}{D}} + 0.4514 B \sqrt{KD} + 0.8930 B + \frac{B}{2\sqrt{KD}}}{\sqrt{\frac{K}{D}} \left(1 + 0.8930 D \sqrt{\frac{K}{D}} \right)^2} \\
 I \sqrt{\frac{K}{D}} &= \frac{1 + 0.8930 D \sqrt{\frac{K}{D}} + 0.4514 B \sqrt{KD} + 0.8930 B + \frac{B}{2\sqrt{KD}}}{\left(1 + 0.8930 D \sqrt{\frac{K}{D}} \right)^2} \tag{38}
 \end{aligned}$$

Equation (38) is compared with Eqn. (28) for various values of the parameters *B*, *K*, and *D* in Table (2A) - (2D) and reasonable agreement is found (differences smaller than 7%).

Table 2A. Comparison of the expression for the current (Eqn. (38)) with previous solution for *G*=0 (Eqn. (28)) for various values of *K* when *D*=0.1, and *B*=0.01.

Numerical Value of <i>K</i>	Our solution Eqn.(38)	Nam et.al [25] Eqn.(28)	Error%
5	0.62016	0.61908	0.17
10	0.53341	0.53354	0.03
50	0.33606	0.33703	0.29
60	0.31590	0.31687	0.31
70	0.29940	0.30036	0.32
80	0.28551	0.28646	0.33
90	0.27360	0.27453	0.34
100	0.26321	0.26413	0.35
	Average error %		0.27

Table 2B. Comparison of the expression for the current (Eqn.(38))with a previous solution for *G*=0 (Eqn.(28)) for various values of *K* when *D*=0.1, and *B*=0.1.

Numerical Value of <i>K</i>	Our solution Eqn.(38)	Nam et.al [25] Eqn.(28)	Error%
5	0.68506	0.67425	1.58
10	0.57973	0.58109	0.23
50	0.35736	0.36706	2.71
60	0.33542	0.34511	2.89
70	0.31751	0.32712	3.03
80	0.30250	0.31199	3.14
90	0.28965	0.29899	3.22
100	0.27846	0.28766	3.30
	Average error %		2.51

Table 2C. Comparison of the expression for the current (Eqn. (38)) with a previous solution for $G=0$ (Eqn. (28)) for various values of D when $K=60$, and $B=0.1$.

Numerical Value of D	Our solution (Eqn.(38))	Nam et.al [25] (Eqn.(28))	Error%
0.01	0.65709	0.65023	1.04
0.1	0.33542	0.34511	2.88
0.2	0.25982	0.26872	3.42
0.3	0.22159	0.22971	3.66
0.4	0.19715	0.20466	3.80
0.5	0.17971	0.18672	3.90
0.8	0.14707	0.15306	4.07
0.9	0.13972	0.14546	4.11
1	0.13341	0.13894	4.14
2	0.09781	0.10202	4.30
5	0.06395	0.06680	4.45
	Average error %		3.61

Table 2D. Comparison of the expression for the current (Eqn. (38)) with a previous solution for $G=0$ (Eqn. (28)) for various values of B when $K=60$, and $D=0.1$.

Numerical Value of B	Our solution (Eqn.(38))	Nam et.al [25] (Eqn.(28))	Error%
0.001	0.31395	0.31405	0.03
0.01	0.31590	0.31687	0.30
0.03	0.32024	0.32315	0.90
0.05	0.32458	0.32942	1.49
0.07	0.32891	0.33570	2.06
0.09	0.33325	0.34197	2.61
0.1	0.33542	0.34511	2.88
0.2	0.35710	0.37648	5.42
0.3	0.37878	0.40786	7.67
0.5	0.42215	0.47060	11.47
0.7	0.46551	0.53335	14.57
0.8	0.48720	0.56472	15.91
0.9	0.50888	0.59610	17.13
1	0.53056	0.62747	18.26
	Average error %		7.19

From Tables (2A) – (2D), it is inferred that the error of Eqn. (28) decreases as B is smaller. Equation (28) is valid for small values of B whereas the present solution (Eqn.38) is valid for any B -value.

6. DISCUSSION

Equations (20) and (21) are the new analytical expressions of the concentration of reactant in the fluid phase and porous media. The analytical expression for the steady state current at porous rotating disc electrodes is given by equation (24). The concentration of the reactant and current depends on the kinetic parameters K , B , ratio of *diffusion coefficient* D , and convection term in the

porous media G . The parameters B and G (convection term) are directly proportional to the rotation rate whereas the parameter K is inversely proportional to it. When the rotation rate is large, the transport of fluid to and through the porous disc is dominated by advection. However, when the rotation rate is small, diffusion becomes significant and in some cases it is the dominant mass transport mechanism.

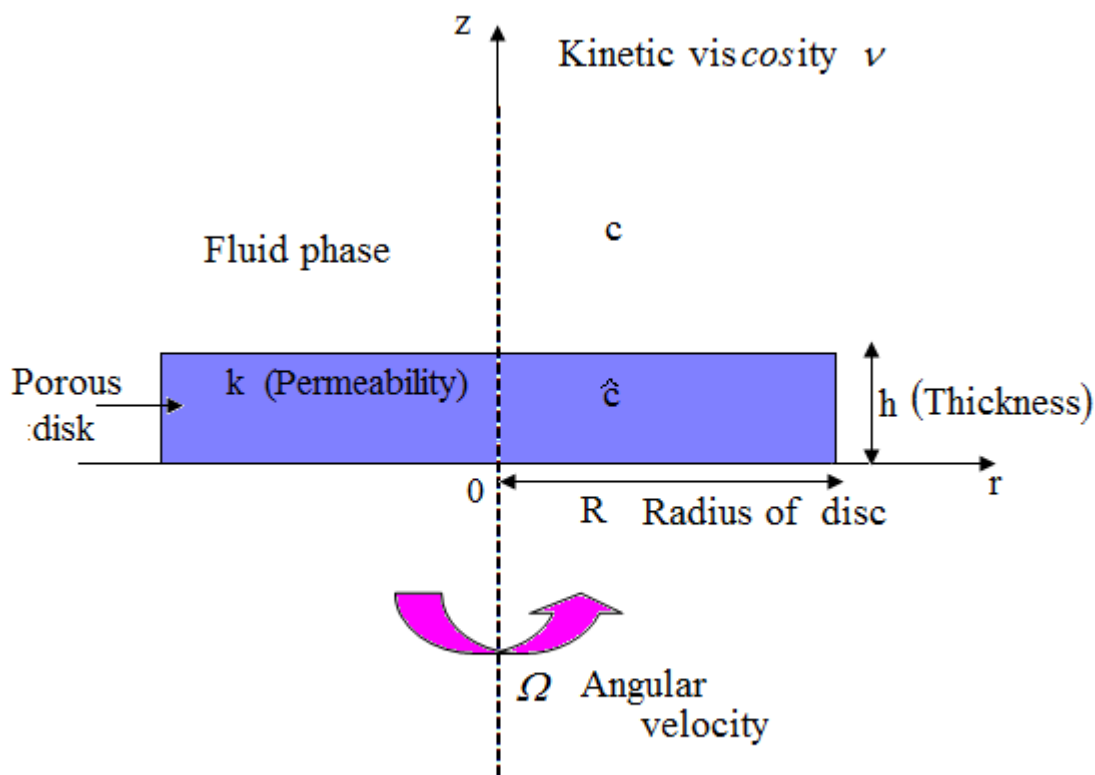


Figure 1. Schematic of a porous rotating disk electrode.

Figs.2-6 show the reactant concentration in the fluid phase c and in the porous media \hat{c} using Eqns.(20) and (21) and the influence of parameters K , D , B and G . In Fig.2, it is observed that at the vicinity of the interface of the porous disk, the concentrations(c and \hat{c}) change abruptly. It can be seen that the sharp change in concentration takes place within a boundary layer of thickness $-0.225 \leq \delta' \leq 0$ and $0 \leq \delta \leq 1.5$. The normalized concentration of reactant in the fluid phase is 1 when $y \geq 1.5$ and the concentration of the reactant in the porous media is zero when $y \leq -0.225$, since the reactant is completely consumed in the boundary layer (Figs.2B & 2C). From Fig.3, it can be inferred that the concentration in the fluid phase and porous media increases as K decreases.

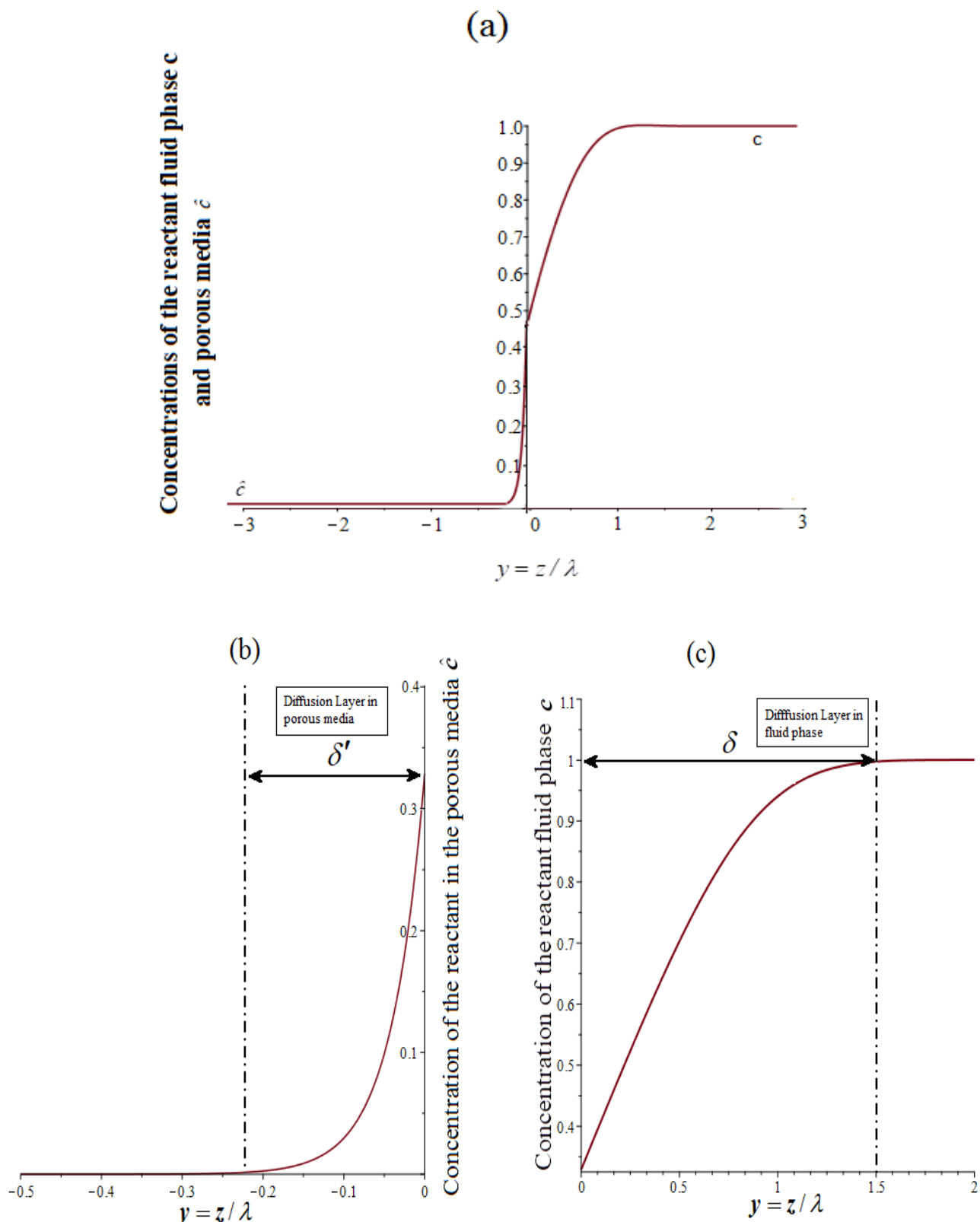


Figure 2. (a)-(c). Concentrations in the fluid phase c and in the porous media \hat{c} using Eqns. (20) and (21).

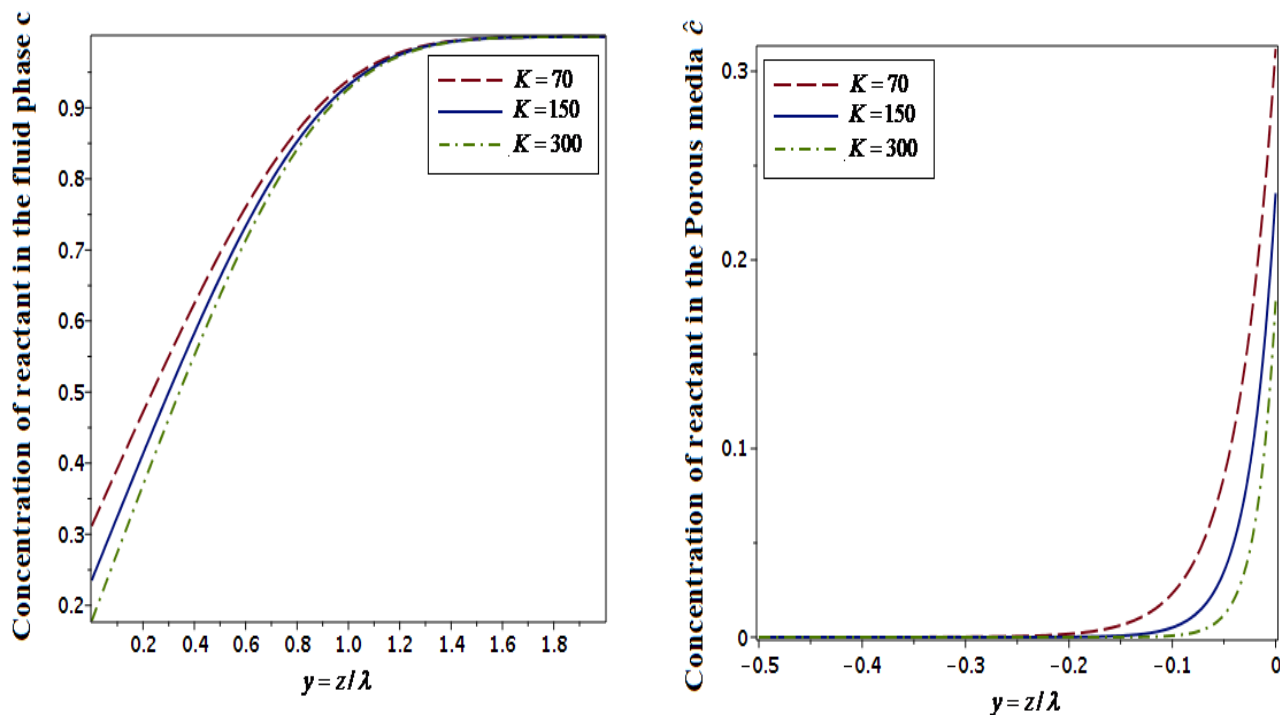


Figure 3. Effect of parameter K on the concentration profiles (a) in the fluid phase c and (b) in the porous media \hat{c} using Eqns. (20) and (21). $D=0.1$, $B=0.1$, $G=0.01$

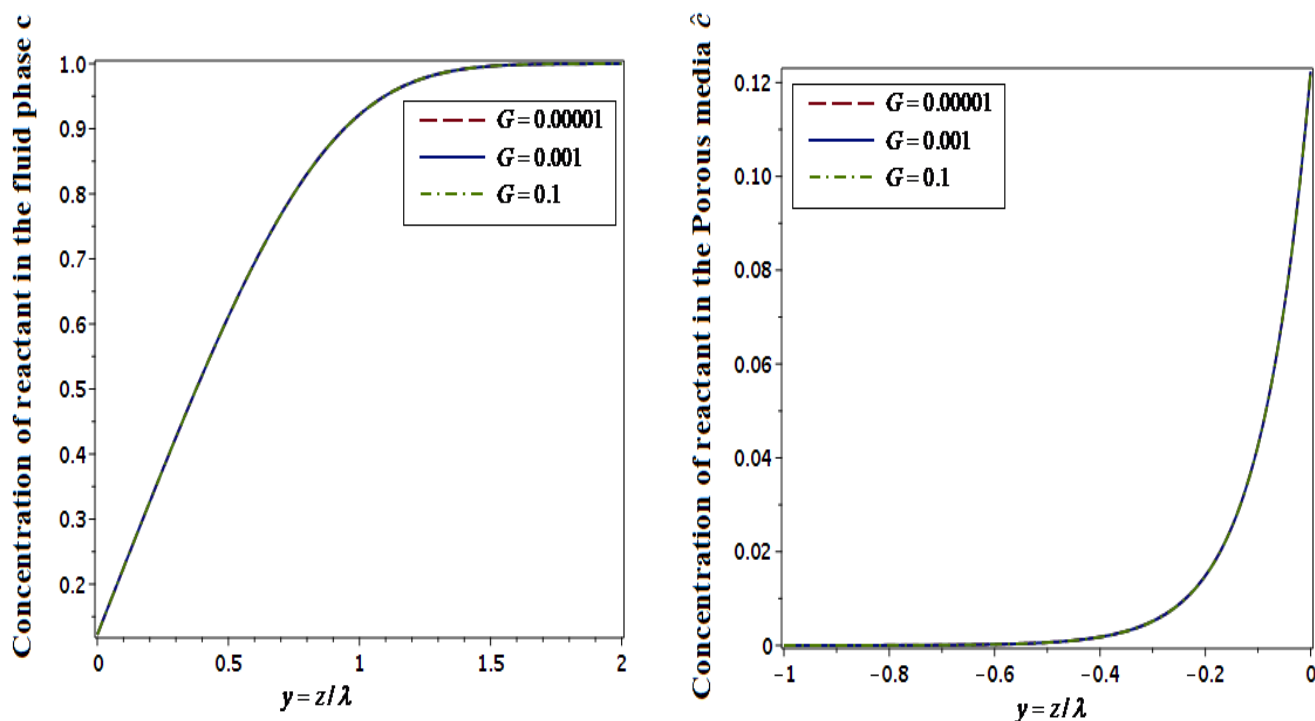


Figure 4. Effect of parameter G on the concentration profiles (a) in the fluid phase c and (b) in the porous media \hat{c} using Eqns. (20) and (21). $K=90$, $D=0.8$, $B=0.1$

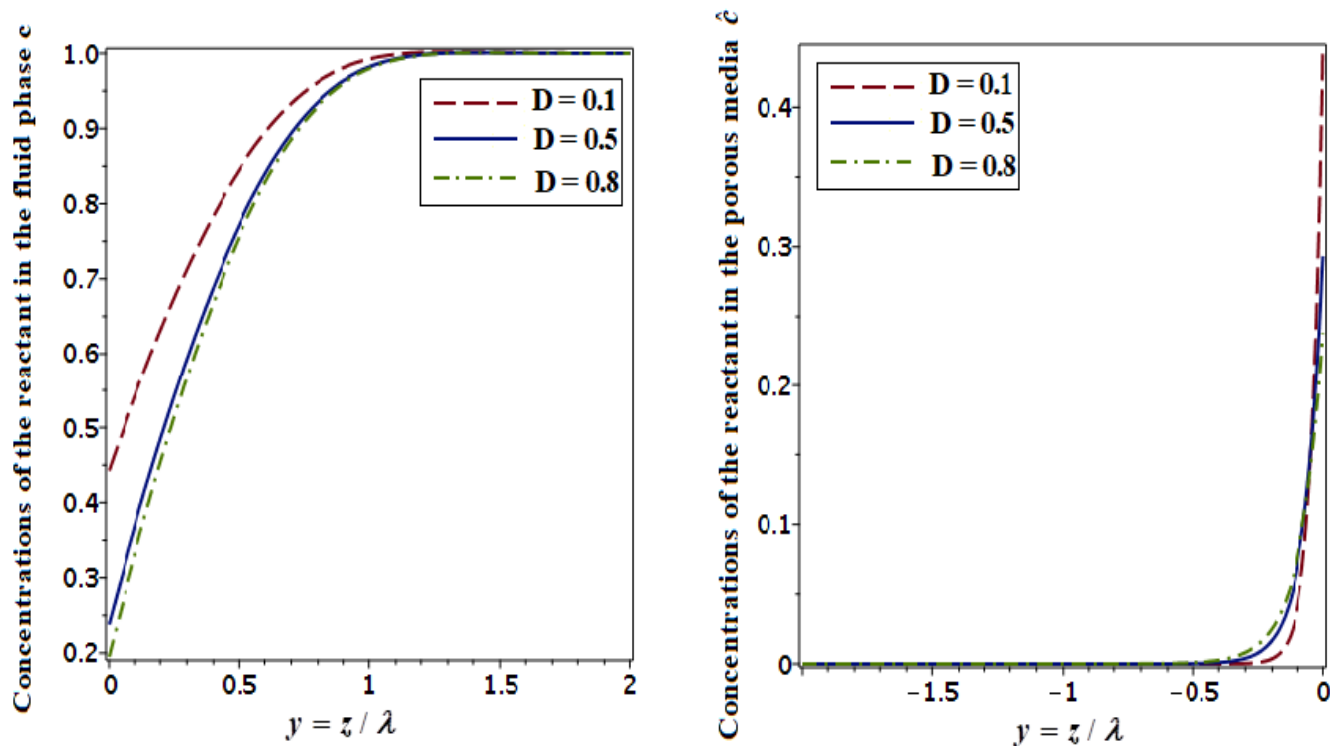


Figure 5. Effect of parameter D on the concentration profiles (a) in the fluid phase c and (b) in the porous media \hat{c} using Eqns. (20) and (21). $K=70$, $B=1$, $G=0.01$

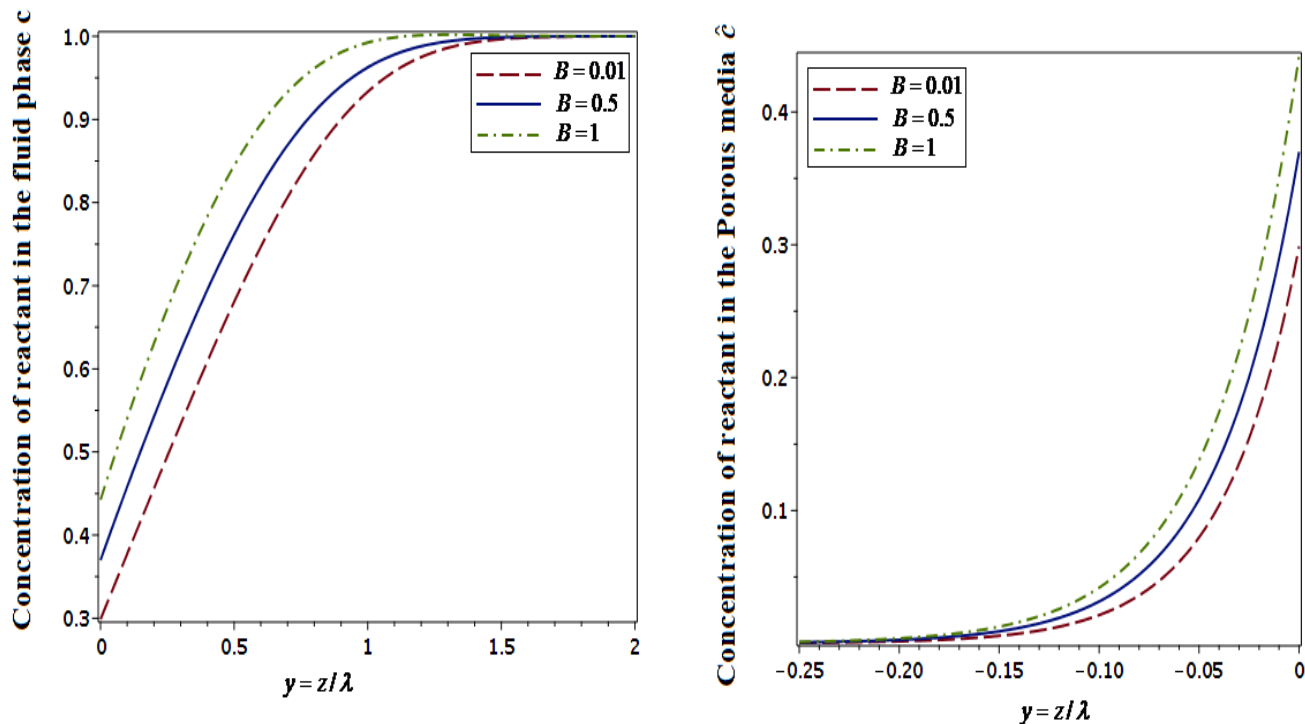


Figure 6. Effect of parameter B on the concentration profiles (a) in the fluid phase c and (b) in the porous media \hat{c} using Eqns. (20) and (21). $K=70$, $D=0.1$, $G=0.01$

Table 3. Comparison of the concentration of the reactant in the fluid phase c and the porous media \hat{c} between the present analytical results and previous results. $B=0.1, K=60, D=0.1,$ and $G=0.01$

$y = z/\lambda$	Concentration of the reactant in the fluid phase c			$y = z/\lambda$	Concentration of the reactant in the porous media \hat{c}		
	This work Eqn. (20)	Numerical Solution	Error%		This work Eqn. (21)	Numerical Solution	Error%
0	0.32900	0.32140	2.36	0	0.32901	0.32140	2.37
0.01	0.33690	0.32948	2.28	-0.01	0.25876	0.25032	3.37
0.08	0.39197	0.38545	1.72	-0.08	0.04812	0.04481	7.39
0.1	0.40763	0.40138	1.58	-0.1	0.02975	0.02770	7.40
0.2	0.48521	0.48003	1.08	-0.2	0.00268	2.65410e-3	0.98
0.3	0.56107	0.55695	0.74	-0.3	0.00024	2.82900e-4	-
0.5	0.70307	0.70052	0.36	-0.5	0.00000	0	-
0.7	0.82255	0.82208	0.069	-0.7	0.00000	0	-
1	0.94026	0.93820	0.22	-1	0.00000	0	-
2	0.99998	0.99985	0.013	-2	0.00000	0	-
3	1	1	0	-3	0.00000	0	-
10	1	1	0	-10	0.00000	0	-
∞	1	1	0	$-\infty$	0.00000	0	-

Table 4: Effect of the parameter G on the concentration of the reactant in the porous media \hat{c} and the current I using Eqns. (21) and (24). $B = 0.1, K = 60$ and $D = 0.1$.

G	Concentration of reactant \hat{c} at $y=0$ Eqn.(21)	Current I for porous media Eqn.(24)
0	0.3290220758	0.01369372328
0.0001	0.3290219859	0.01369370360
0.001	0.3290211786	0.01369352654
0.01	0.3290131044	0.01369175596
0.1	0.3289322637	0.01367405012
1	0.3281249563	0.01349699175
2	0.3272278367	0.01330026022
3	0.3263307173	0.01310352870
5	0.3245364783	0.02171006564
7	0.3227422393	0.01231660259
10	0.3200508808	0.01172640801
25	0.3065940887	0.008775435104
50	0.2841661018	0.003857146937
60	0.2751949069	0.001889831668

Table 5. Numerical value of $k_1, m_1, b, m, l_1, l_2, k_2, l_0$ for various values of parameters B, G, K, D and a

Parameters of Equation	$k_1 = \frac{3}{3 + 2.6789 Da}$	$m_1 = -\frac{Dk_1 a}{3}$	$b = -\frac{Gk_1 a}{D}$	$m = -\frac{B}{D} k_1 a$	$l_1 = -\frac{b}{4a^2} + \frac{m}{2a}$	$l_2 = 1.3541 B m_1$	$k_2 = \frac{-D[l_1 + l_0 a]}{3} = \frac{l_0 + l_2}{2.6789}$	$l_0 = \frac{-3l_2 - 2.6789 D l_1}{2.6789 D a + 3}$
B=0.1 G=0.01 K=1 D=0.1 $a = \sqrt{\frac{K}{D}}$	0.7798	-0.0822	-0.2466	-2.4659	-0.3283	-0.0111	0.0070	0.0315
B=0.1 G=0 K=1 D=0.1 $a = \sqrt{\frac{K}{D}}$	0.7798	-0.0822	0	-0.2466	-0.0390	-0.0111	0.0001	0.0114
B=0.1 G=1 K=1 D=0.1 $a = \sqrt{\frac{K}{D}}$	0.7798	-0.0822	24.6588	2.4659	-5.7748	-0.0111	0.1492	0.4108

Fig.4 shows that the convection parameter G has no significant effect on the concentration profiles for typical conditions ($G \leq 0.1$). The effect of parameter G on the reactant concentration in the porous media \hat{c} and on the current I using Eqns.(21) and (24) is quantified in Table 4 where significant influence is only observed when $G \geq 10$ and $G \geq 5$, respectively.

Hence, B and D are the most determining parameters of the concentrations and current values. As can be observed in Figs. 5 and 6, the decrease of the species diffusivity inside the porous media (*i.e.*, smaller D in Fig. 5) or of the rotation rate (*i.e.*, smaller B in Fig. 6) gives rise to the increase of the reactant concentration at the interface between the fluid phase and the porous media. Also, from the data included in Tables 2c and 2d, it is inferred that decrease of the species diffusivity inside the porous media or the increase of rotation rate gives rise to larger values of the dimensionless current.

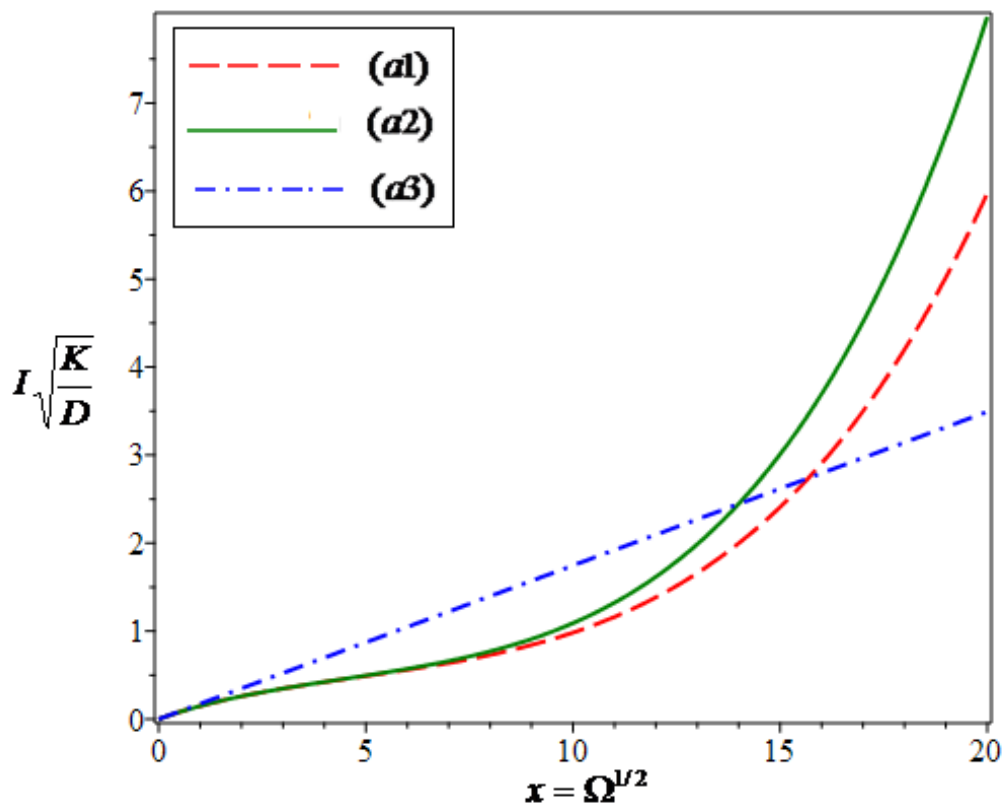


Figure 7. Variation of current $I\sqrt{K/D}$ with square root of rotation rate $\Omega^{1/2}$. Eqn. (35) represents the Levich equation. The typical values of parameters are taken as follows:

$$\alpha = 0.51, \Omega = x^2, k_r = 1 s^{-1}, k = 0.00001 mm^2, \nu = 1 mm^2 s^{-1}, h = 0.1 mm, D_p = D_f = 0.0005 mm^2 s^{-1}$$

$$\text{or } B = 0.005731043246 h x^3, G = 0.0008211214172 x^2, K = 41.05607086 / x^2, D = 1$$

- (a1) Eqn. (24).
- (a2) Eqn. (38) (Where G is a neglected).
- (a3) Eqn. (35) (Levich equation).

Fig.7 includes the results obtained with the new analytical solution for the PRDE current versus the square root of the rotation rate. Deviations from linearity suggest that a kinetic limitation is involved in the electron-transfer reaction. Equation (35) corresponds to the Levich equation, which is the expression of the current on a flat rotating disk electrode for a mass transfer limited reaction. From this plot it can be concluded that the behaviour of the PRDE current (Eq. (24) with respect to the rotation rate can differ greatly from the Levich current (Eq. (34) or (35)) when $\Omega^{1/2} \geq 15$.

Also when the rotation rate is small ($\Omega^{1/2} \leq 10$), the current recorded with by a flat rotating disc electrode (RDE) is qualitatively similar to that of a porous rotating disc electrode (PRDE), with the current increasing with the square root of the rotation rate. When $\Omega^{1/2} \geq 15$ the current at the porous rotating disc electrode (PRDE) rises more abruptly than predicted by the Levich theory.

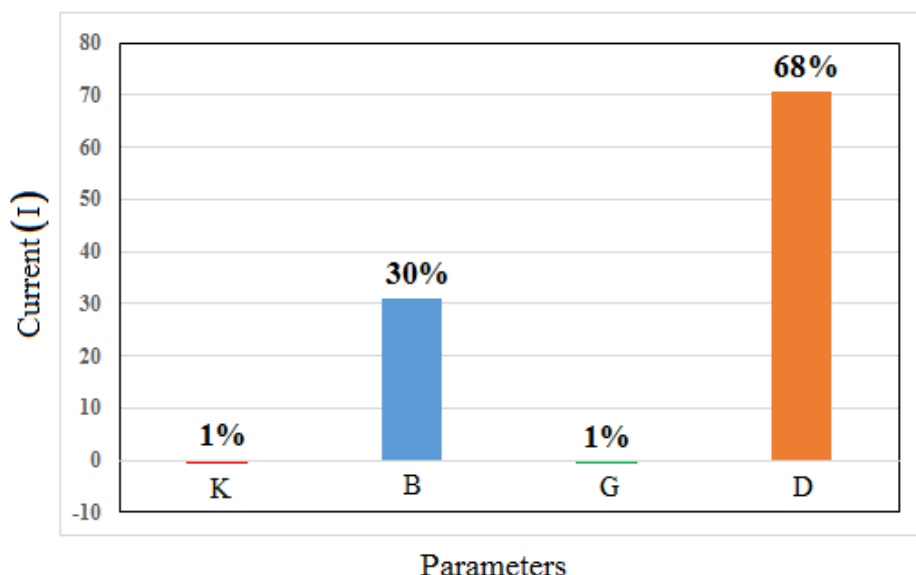


Figure 8. Sensitivity of parameters: Percentage change in dimensionless current I when $K = 60$, $D = 0.1$, $B = 0.1$ and $G = 0.1$

6.1 Sensitivity

The current on porous rotating disc electrodes depends on the parameters K , D , B and G . A sensitivity analysis is performed based on the differentiation of the aggregated model [29]. Thus, the partial derivative of current (dependent variable) with respect to parameters K , D , B and G (independent variables) is studied at typical values of these parameters ($K = 60$, $D = 0.1$, $B = 0.1$ and $G = 0.1$), obtaining the percentage of change of the current. The results are shown in Fig.8 and they point out that parameters D and B have more impact than K and G . These results are consistent with those observed in Figures 3-6.

7. CONCLUSIONS

We have derived new analytic expressions for (i) the concentration of reactant in the fluid phase, (ii) the concentration of reactant in porous media and (iii) the current at a porous rotating disc electrode (PRDE). These expressions have been derived using the homotopy perturbation method and they provide a complete delineation of the role played by kinetics and mass transport. The new analytical results are compared with available solutions for limiting cases as well as with numerical simulations, finding a satisfactory agreement. The theory presented provides a tool for suitable and rapid evaluation of the activity of porous materials via PRDE.

ACKNOWLEDGEMENT

This work was supported by the Department of Science and Technology, SERB-DST (EMR/2015/002279) Government of India. The Authors are also thankful to Shri J. Ramachandran, Chancellor, Col. Dr. G. Thiruvassagam, Vice-Chancellor, Academy of Maritime Education and Training (AMET), Deemed to be University, for their constant encouragement.

Nomenclature

S.NO	SYMBOL	UNIT	NUMERICAL VALUES
1	c (concentration of reactant in the fluid)	mol/cm ³	0 to 1
2	\hat{c} (concentration of the reactant in the porous media)	mol/cm ³	-1 to 0
3	α	Constant	0.51
4	k	mm ²	$O(10^{-5})$
5	k_r	S ⁻¹	O(1)
6	ν	mm ² S ⁻¹	$O(10^{-2})$
7	D_f	mm ² S ⁻¹	$O(10^{-3})$
8	D_p	mm ² S ⁻¹	$O(10^{-4})$
9	h	mm	$O(10^{-1})$
10	Ω	rpm	(10^3) (Since, $\Omega \leq 10^3$ rpm)
11	G/B	Dimensionless parameter	$10^{-2} - 10^{-1}$
12	B	None	$10^{-2} - 1$
13	T^∞	None	7.018×10^{-3}
14	$k_r k / \nu$	None	8×10^{-6}
15	k/R^2	None	2×10^{-6}
16	h/R	None	0.125
17	D_f / ν	None	2×10^{-3}
18	D_p / ν	None	4.4×10^{-4}
19	$D = D_p / D_f$	None	$O(10^{-1})$
20	$\beta = 2kh(\Omega/\nu)^{3/2}$	None	$2 \times O(10^2)$
21	$\gamma = 2k\Omega/\nu$	None	2
21	$\lambda = \left(\frac{3D_f}{\alpha\nu}\right)^{1/3}$		$1.9610 \times O(10^{-1})$
23	$y = z/\lambda$	Dimensionless height	-
24	Z	height	-

25	$G = 3\gamma / \alpha\lambda = 2k\Omega(9 / \alpha^2 v^2 D_f)^{1/3}$	None	$15.9946 \times O(10^5)$
26	$B = 3\beta / \alpha\lambda^2 = 2kh(9\Omega^9 / v^5 \alpha^2 D_f^4)^{1/6}$	None	$3.3826 \times O(10^2)$
27	$K = 3k_r / \alpha\lambda\Omega = (k_r / \Omega) \times (9v / \alpha^2 D_f)^{1/3}$	None	$0.0151 \times O(10^3)$
28	$b = -\frac{Gk_1 a}{D}$	None	-
29	$m = -\frac{B}{D} k_1 a$	None	-
30	$m_1 = -\frac{Dk_1 a}{3}$	None	-
31	$k_1 = \frac{3}{3 + 2.6789Da}$	None	-
32	$k_2 = \frac{-D[l_1 + l_o a]}{3} = \frac{l_0 + l_2}{2.6789}$	None	-
33	$l_0 = \frac{-3l_2 - 2.6789 D l_1}{2.6789 D a + 3}$	None	-
34	$a^2 = \frac{K}{D}, a = \sqrt{\frac{K}{D}}$	None	-
35	$l_1 = -\frac{b}{4a^2} + \frac{m}{2a}$	None	-
36	$l_2 = 1.3541 B m_1$	None	-

Notation:

- c - Concentration of the reactant in the fluid phase
- \hat{c} - Concentration of the reactant in the porous media
- D - Diffusion coefficient
- D_f - Diffusion coefficient in the fluid phase
- D_p - Diffusion coefficient in the porous media
- k_r - First-order reaction rate constant
- k - Permeability of the porous media
- h - Thickness of the film
- r - Radius
- Ω - Rotation rate (angular velocity)
- v - Kinematic viscosity
- n - Number of electrons in the reaction
- F - Faraday constant
- V - Volume of the disk film
- R - Radius of disc

APPENDIX A:

Analytical solution of equations (8) and (9) using HPM.

The homotopy for the equations (8) and (9) can be constructed as follows:

$$(1-p) \left[\frac{d^2c}{dy^2} + 3y^2 \frac{dc}{dy} \right] + p \left[\frac{d^2c}{dy^2} + 3y^2 \frac{dc}{dy} + B \frac{dc}{dy} \right] = 0 \tag{A1}$$

$$(1-p) \left[D \frac{d^2\hat{c}}{dy^2} - K\hat{c} \right] + p \left[D \frac{d^2\hat{c}}{dy^2} - K\hat{c} + Gy \frac{d\hat{c}}{dy} + B \frac{d\hat{c}}{dy} \right] = 0 \tag{A2}$$

The approximate solution of the equations (8) and (9) are:

$$c = c_0 + c_1p + c_2p^2 + \dots \tag{A3}$$

$$\hat{c} = \hat{c}_0 + \hat{c}_1p + \hat{c}_2p^2 + \dots \tag{A4}$$

where p is the embedding parameter and $p = [0,1]$ Substituting (A3) and (A4) in (A1) and (A2) and equating the like coefficients of p on both sides we get,

$$p^0 : \frac{d^2c_0}{dy^2} + 3y^2 \frac{dc_0}{dy} = 0 \tag{A5}$$

$$p^0 : \frac{d^2\hat{c}_0}{dy^2} - \frac{K\hat{c}_0}{D} = 0 \tag{A6}$$

$$p^1 : \frac{d^2c_1}{dy^2} + 3y^2 \frac{dc_1}{dy} + B \frac{dc_0}{dy} = 0 \tag{A7}$$

$$p^1 : D \frac{d^2\hat{c}_1}{dy^2} - K\hat{c}_1 + Gy \frac{d\hat{c}_0}{dy} + B \frac{d\hat{c}_0}{dy} = 0 \tag{A8}$$

The boundary condition for the equations (A5) and (A6) are as follows:

$$c_0 = 1, \quad y \rightarrow \infty \tag{A9}$$

$$\hat{c}_0 = 0, \quad y = -\infty \tag{A10}$$

$$c_0 = \hat{c}_0, \quad y = 0 \tag{A11}$$

$$\frac{dc_0}{dy} = D \frac{d\hat{c}_0}{dy}, \quad \text{at } y = 0 \tag{A12}$$

Solving the equation (A5), using the boundary condition (A9),

$$c_0(y) = 1 + m_1 \Gamma\left(\frac{1}{3}, y^3\right) \tag{A13}$$

where m_1 is a constant that is determined using the matching boundary condition (A11) and (A12).

Solving equation (A6) using the boundary condition (A10),

$$\hat{c}_0(y) = k_1 \exp(ay) \tag{A14}$$

where, $a = \sqrt{\frac{K}{D}}$ and k_1 is constant. (A15)

Also, using the boundary conditions, $c_0 = \hat{c}_0$, at $y = 0$ and $\frac{dc_0}{dy} = D \frac{d\hat{c}_0}{dy}$ at $y = 0$,

$$1 + m_1 \Gamma\left(\frac{1}{3}, 0\right) = k_1 \tag{A16}$$

$$-3m_1 = Dk_1 a \tag{A17}$$

The numerical value $\Gamma\left(\frac{1}{3}, 0\right) = 2.6789$. Solving equations (A16) and (A17),

$$k_1 = \frac{3}{3 + 2.6789 D a}, m_1 = -\frac{Dk_1 a}{3} \tag{A18}$$

Now equation (A7) becomes,

$$\frac{d^2 c_1}{dy^2} + 3y^2 \frac{dc_1}{dy} + Bm_1 \frac{d}{dy} \Gamma\left(\frac{1}{3}, y^3\right) = 0 \tag{A19}$$

such that

$$c_1(y) = -B m_1 \Gamma\left(\frac{2}{3}, y^3\right) + k_2 \Gamma\left(\frac{1}{3}, y^3\right) + k_3 \tag{A20}$$

Using the boundary condition $c_1 = 0$ at $y = \infty$, the constant $k_3 = 0$.

$$c_1(y) = -B m_1 \Gamma\left(\frac{2}{3}, y^3\right) + k_2 \Gamma\left(\frac{1}{3}, y^3\right) \tag{A21}$$

where, k_2 is constant. Also,

$$\frac{dc_1}{dy} = 3 \exp(-y^3)(B m_1 y) - 3k_2 e^{-y^3} \tag{A22}$$

$$\left. \frac{dc_1}{dy} \right|_{y=0} = -3 k_2 \tag{A23}$$

Equation (A8) can be written as,

$$\frac{d^2 \hat{c}_1}{dy^2} - \frac{K}{D} \hat{c}_1 + \frac{G}{D} y \frac{d\hat{c}_0}{dy} + \frac{B}{D} \frac{d\hat{c}_0}{dy} = 0 \tag{A24}$$

Using equation (A14),

$$\frac{d^2 \hat{c}_1}{dy^2} - a^2 \hat{c}_1 - e^{ay} [b y + m] = 0 \tag{A25}$$

$$\text{where, } b = -\frac{G}{D} k_1 a, \quad m = -\frac{B}{D} k_1 a, \quad a = \sqrt{\frac{K}{D}}. \tag{A26}$$

Solving the equation (25),

$$\hat{c}_1(y) = -\frac{b y e^{ay}}{4a^2} + \frac{b y^2 e^{ay}}{4a} + l_0 e^{ay} + m y \frac{e^{ay}}{2a} + p_1 e^{-ay} \tag{A27}$$

Using the boundary condition, $c_I(y) = 0$ at $y = -\infty$, we get, $p_1 = 0$,

$$\hat{c}_1(y) = y e^{ay} \left(-\frac{b}{4a^2} + \frac{m}{2a} \right) + \frac{b y^2 e^{ay}}{4a} + l_0 e^{ay} \tag{A28}$$

The derivative of $\hat{c}_1(y)$ becomes,

$$\frac{d\hat{c}_1}{dy} = \left(-\frac{b}{4a^2} + \frac{m}{2a} \right) (y a e^{ay} + e^{ay}) + \frac{b}{4a} (y^2 a e^{ay} + 2y e^{ay}) + l_0 (a e^{ay}) \tag{A29}$$

From the above equation,

$$\left. \frac{d\hat{c}_1}{dy} \right|_{y=0} = \left(-\frac{b}{4a^2} + \frac{m}{2a} \right) + l_0 a \tag{A30}$$

And applying the boundary condition, $c_I = \hat{c}_1$, at $y = 0$ and $\frac{dc_I}{dy} = D \frac{d\hat{c}_1}{dy}$, at $y = 0$

we obtain the following equations,

$$-B m_1 \Gamma\left(\frac{2}{3}, 0\right) + k_2 \Gamma\left(\frac{1}{3}, 0\right) = l_0 \quad (or) \quad -B m_1 (1.3541) + k_2 (2.6789) = l_0 \tag{A31}$$

$$-3k_2 = D \left(\left(-\frac{b}{4a^2} + \frac{m}{2a} \right) + l_0 a \right) \tag{A32}$$

Solving the equations (A31) and (A32), we can obtain constants l_0 and k_2 (Eqn. (A35)). The expression for the concentration of the reactant in the fluid phase and porous media becomes as follows:

$$\begin{aligned} c(y) &= c_0(y) + c_I(y) \\ &= l + (m_1 + k_2) \Gamma\left(\frac{1}{3}, y^3\right) - B m_1 \Gamma\left(\frac{2}{3}, y^3\right) \end{aligned} \tag{A33}$$

$$\begin{aligned} \hat{c}(y) &= \hat{c}_0(y) + \hat{c}_1(y) \\ &= k_1 e^{ay} + y e^{ay} \left(-\frac{b}{4a^2} + \frac{m}{2a} \right) + \frac{b}{4a} y^2 e^{ay} + l_0 e^{ay} \end{aligned} \tag{A34}$$

where the dimensionless constants are

$$\begin{aligned} m_1 &= -\frac{D k_1 a}{3}, \quad k_1 = \frac{3}{3 + 2.6789 D a}, \quad k_2 = \frac{-D(l_1 + l_0 a)}{3} = \frac{l_0 + l_2}{2.6789}, \quad b = -\frac{G k_1 a}{D}, \\ l_0 &= \frac{-3l_2 - 2.6789 D l_1}{2.6789 D a + 3}, \quad m = -\frac{B}{D} k_1 a, \quad l_1 = -\frac{b}{4a^2} + \frac{m}{2a}, \quad l_2 = 1.3541 B m_1, \quad a = \sqrt{\frac{K}{D}} \end{aligned} \tag{A35}$$

APPENDIX B:

The exact solution of Eqns. (30) and (31).

Let $G = 0, B = 0$ the equations (8) and (9) becomes,

$$\frac{d^2c}{dy^2} + 3y^2 \frac{dc}{dy} = 0 \tag{B1}$$

$$D \frac{d^2\hat{c}}{dy^2} - K \hat{c} = 0 \tag{B2}$$

The exact solution of equation (B1) is,

$$c(y) = \frac{\alpha_1 y \Gamma(1/3, y^3)}{\sqrt{y^3}} + \alpha_2 \tag{B3}$$

Using the boundary condition, $c = 1, y \rightarrow \infty$ we get $\alpha_2 = 1$,

$$c(y) = \alpha_1 \Gamma(1/3, y^3) + 1 \tag{B4}$$

$$\frac{dc}{dy} = -3 \alpha_1 \exp(-y^3), \left. \frac{dc}{dy} \right|_{y=0} = -3 \alpha_1 \tag{B5}$$

The solution of the equation (B2) is,

$$\hat{c}(y) = \beta_1 e^{-\frac{\sqrt{K} y}{\sqrt{D}}} + \beta_2 e^{\frac{\sqrt{K} y}{\sqrt{D}}} \tag{B6}$$

From the boundary condition, $c = 1, y \rightarrow \infty$ we get, $\beta_2 = 0$,

$$\hat{c}(y) = \beta_1 e^{-\frac{\sqrt{K} y}{\sqrt{D}}} \tag{B7}$$

$$\frac{d\hat{c}}{dy} = \frac{\beta_1 \sqrt{K} e^{-\frac{\sqrt{K} y}{\sqrt{D}}}}{\sqrt{D}}, \left. \frac{d\hat{c}}{dy} \right|_{y=0} = \frac{\beta_1 \sqrt{K}}{\sqrt{D}} \tag{B8}$$

Applying the boundary condition, $\frac{dc}{dy} = D \frac{d\hat{c}}{dy}$ at $y = 0$, from (B5) and (B8),

$$-3 \alpha_1 = D \frac{\beta_1 \sqrt{K}}{\sqrt{D}} \tag{B9}$$

$$-3 \alpha_1 = \beta_1 \sqrt{KD} \tag{B10}$$

and from the boundary condition, $c = \hat{c}$, at $y = 0$ we get,

$$\alpha_1 \Gamma(1/3, 0) + 1 = \beta_1, \alpha_1 (2.6789) + 1 = \beta_1 \tag{B11}$$

Solving the equation (B10) and (B11),

$$\alpha_1 = -\frac{\sqrt{KD}}{3 + 2.6789 \sqrt{KD}}, \beta_1 = -\frac{3 \alpha_1}{\sqrt{KD}} \tag{B12}$$

Substituting this value in (B3) and (B6), equations (29) and (30) in the main text are obtained.

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