Mathematical Model for Potassium Release from Polymer-coated Fertiliser

C. Du¹; J. Zhou¹; A. Shaviv²; H. Wang¹

¹Institute of Soil Science, Chinese Academy of Sciences, Beijing Street East, Nanjing, 210008, China; e-mail of corresponding author: jmzhou@ns.issas.ac.cn
²Faculty of Civil and Environmental Engineering, IIT-Israel Institute of Technology, Haifa, 32000, Israel

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An exact mathematical model based on Fick’s Second Diffusion Law was developed to predict the release rate of polymer-coated fertiliser using a numerical solution and Fourier series expansion. From the explicit mathematical model, an approximate solution for the nutrient release was obtained. The model showed that the nutrients release was mainly controlled by the diffusion coefficient, membrane thickness and granule radius. This model was simpler compared with the original numerical solution, and different radii of polymer-coated controlled-release fertiliser was used to verify the approximate release model. The nutrient was mainly released in the linear stage, and the cumulative percentage of nutrient release decreased when the granule radius increased. The cumulative release profile of potassium from the polymer-coated fertiliser into water agreed with the prediction of the model on the whole.

1. Introduction

Polymer-coated controlled-release fertilisers are used to overcome and improve current low nutrient use efficiency, and the potential economic and environmental benefits have been reported (Shaviv, 1999, 2000, 2001). The release of nutrients should coincide with the requirement of plants and the objective for the modelling work is designed to ensure that products are manufactured that meet crop requirement.

Baker (2000) developed a model to predict the release of drug from a sphere:

\[
\frac{M_t}{M_0} = 4 \left( \frac{D t}{\pi l^2} \right)^{0.5} \quad \text{for } 0 \leq \frac{M_t}{M_0} \leq 0.4
\]

\[
\frac{M_t}{M_0} = 1 - \left( \frac{8}{\pi} \right) \exp \left( -\frac{\pi^2 D t}{l^2} \right) \quad \text{for } 0.4 \leq \frac{M_t}{M_0} \leq 1.0
\]

where: \( D \) is the diffusion coefficient for the polymer in \( \text{mm}^2 \text{d}^{-1} \); \( l \) is the thickness of the polymer membrane in \( \text{mm} \); \( M_t \) is the mass diffusion in kg up to time \( t \) in d, and \( M_0 \) is total mass in kg. The model does not contain the parameter of sphere radius. Al-Zahrani (1999) developed a mathematical model for the nutrient release from polymer-coated controlled-release fertiliser, and an approximate solution was deduced as follows:

\[
\frac{M_t}{M_0} = 6(1 + z) \left( \frac{t D^{0.5}}{\pi b^{0.5}} \right)
\]

where: \( D \) is the diffusion coefficient for the polymer in \( \text{mm}^2 \text{d}^{-1} \); \( b \) is radius of the fertiliser granule in \( \text{mm} \); and \( z \) is a constant. This model is simple, but the parameter \( z \) is difficult to obtain. Some other models were investigated (Abdekhodaie & Cheng, 1996; Abdekhodaie, 2002; Arnoldus & Andries, 2002), but were found to be too complex for the polymer-coated fertiliser application.

Shaviv (2000) divided the release course into three stage: (1) the initial stage during which almost no release is observed (lag period), (2) the constant-release stage, and (3) the stage where there is a gradual decay of release rate. This three stage approach gives a good description of the release course for polymer-coated fertiliser. Adopting this three stage of release, the purpose of the paper is to develop a model that can adequately represent K release from polymer-coated fertilisers.
2. Mathematical modelling

The diffusional release of solute from a polymer-coated fertiliser granule of spherical geometry into water with a certain external volume is considered. The diffusion coefficient is assumed to be independent of concentration, and solute diffusion is assumed to be rate controlling step rather than polymer swelling or nutrient dissolution. A fertiliser granule consists of a core containing fertiliser nutrients and a polymer coat, which is the rate-limiting element in the release process. For the granule of core radius $a$ in mm and coated sphere radius $b$ in mm, the thickness of the coating $l$ in mm is given as the difference $(b-a)$. A schematic diagram of cross-sectional view of fertiliser granule is illustrated in Fig. 1.

The first stage of release according to Zaidel (1996) and Shaviv (2000) is a lag period, in which water diffuses into the granule through the polymer membrane, and the lag period time $t'$ in day is deduced as following:

$$t' = \frac{\gamma l}{3 p_h \Delta P}$$

where: $\gamma$ is total granule porosity including also voids between the nutrient core and the membrane, and has a value of between 5 and 10%; $p_h$ is water permeability of the membrane in $\text{mm}^2 \text{Pa}^{-1} \text{d}^{-1}$, $\Delta P$ is the vapour pressure difference between water and saturated nutrient solution in Pa; and $r$ is radius of diffusion in mm in the coated granule. According Eqn (4) the nutrient release is almost zero during the lag period. Therefore, the cumulative percentage of nutrient release $g_t$ is

$$g_t = \frac{Q_t}{M_0} = 0 \quad \text{for} \quad t \leq t'$$

where $Q_t$ is the quantity of diffusion in kg up to time $t$.  

### Notation

- $A_1, A_2$: constants
- $A_3$: total mass of nutrient, kg
- $a$: radius of fertiliser granule, mm
- $a_1, a_2$: constants
- $B_1, B_2$: constants
- $B_3, B_4$: constants
- $b$: radius of coated fertiliser granule, mm
- $C$: diffusion concentration in the granule, $\text{kg m}^{-3}$
- $c_1$: nutrient concentration inside the granule, $\text{kg m}^{-3}$
- $c_2$: nutrient concentration outside the granule, $\text{kg m}^{-3}$
- $c_s$: saturated concentration of nutrients, $\text{kg m}^{-3}$
- $c_t$: nutrient concentration inside the granule (function of diffusion time), $\text{kg m}^{-3}$
- $D$: diffusion coefficient, $\text{mm}^2 \text{d}^{-1}$
- $g_t$: cumulative percentage of nutrient release up to time $t$, $\%$
- $g'_t$: cumulative percentage of nutrient release up to time $t'$, $\%$
- $g_Y$: cumulative percentage of nutrient release up to time $Y$, $\%$
- $J_0$: diffusion rate, $\text{kg d}^{-1}$
- $l$: thickness of membrane, mm
- $M_0$: total mass of nutrient, kg
- $M_t$: mass diffusion up to time $t$, $\text{kg d}^{-1}$
- $n$: natural number
- $p_h$: water permeability of coated membrane, $\text{mm}^2 \text{Pa}^{-1} \text{d}^{-1}$
- $Q_t$: quantity of diffusion up to time $t$, kg
- $r$: radius of diffusion in coated granule, mm
- $r'$: lag period, d
- $r_1$: lag period after diffusion of nutrient starts, d
- $t$: time, d
- $t_0$: lag period, d
- $t_1$: lag period after diffusion of nutrient starts, d
- $T$: function of diffusion time
- $v$: function of diffusion distance and time, kg mm$^{-1}$ d$^{-1}$
- $V$: granule volume, $\text{m}^3$
- $X$: function of diffusion distance
- $x_0$: diffusion distance in membrane, mm
- $Y$: time to dissolve all the solid nutrients in the granule, d
- $\alpha$: constant
- $\beta$: total granule porosity, $\%$
- $\gamma$: function of diffusion distance
- $\gamma_t$: nutrient concentration inside the granule (function of diffusion time), $\text{kg m}^{-3}$
- $\Delta P$: vapour pressure difference, Pa
- $\lambda$: constant
- $\rho_s$: nutrient density, $\text{kg m}^{-3}$

![Fig. 1. Schematic diagram of a cross-section view of a fertiliser granule: $a$, radius of granule; $b$, radius of coated granule; $l$, thickness of membrane](image-url)
After the lag period, the release of nutrient begins. The nutrient concentration inside and outside the granule is maintained at constant concentrations \(c_1\) and \(c_2\), respectively, in kg m\(^{-3}\). The concentration in the polymeric membrane \(C\) in kg m\(^{-3}\) is a function of both time \(t\) in d and the position variable \(r\) in mm, and is determined by transient diffusion according to Fick’s second law

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{2 \partial C}{r \partial r} \right)
\]

(6)

Substitution \(u\) for \(C\ r\), Eqn (6) becomes

\[
\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial r^2}
\]

(7)

Eqn (7) defines linear flow in one dimension.

The diffusion distance \(x\) in mm in the membrane is defined as

\[x = r - a\]

(8)

In the region \(0 < x < l\), the boundary conditions are

\[u(0, t) = c_1 a \quad t > 0\]

(9)

\[u(l, t) = c_2 b \quad t > 0\]

(10)

and the initial condition is

\[u(x, 0) = 0\]

(11)

The method of separation of variables is applied to solve Eqn (7), subject to the above boundary and initial conditions. Assuming that

\[u(x, t) = X(x)T(t)\]

(12)

where: \(X(x)\) is function of \(x\), and \(T(t)\) is function of \(t\), then by substitution into Eqn (7) and rearranging

\[
\frac{1}{DT} \frac{dT}{dt} = \frac{1}{X} \frac{d^2X}{dx^2} = -\lambda^2
\]

(13)

where \(\lambda\) is a constant.

From Eqn (12)

\[
\frac{dT}{dt} = -\lambda^2 DT
\]

(14)

\[
\frac{d^2X}{dx^2} = -\lambda^2 X
\]

(15)

Solving Eqns (14) and (15) gives

\[X = \begin{cases} A_1 x + A_2 & \text{for } \lambda = 0 \\ B_1 \sin \lambda x + B_2 \cos \lambda x & \text{for } \lambda \neq 0 \end{cases}\]

(16)

where \(A_1, A_2, B_1, B_2\) are constants, and

\[T = \begin{cases} \text{const} & \text{for } \lambda = 0 \\ B_3 \exp(-\lambda^2 Dt) & \text{for } \lambda \neq 0 \end{cases}\]

(17)

where \(B_3\) is a constant.

Therefore

\[u(x, t) = \begin{cases} a_1 x + a_2 & \text{for } \lambda = 0 \\ (A_3 \sin \lambda x + B_4 \cos \lambda x) \exp(-\lambda^2 Dt) & \text{for } \lambda \neq 0 \end{cases}\]

(18)

where \(a_1, a_2, A_3, B_4\) are constants.

Applying the boundary conditions, Eqns (9) and (10), to the solution for \(\lambda = 0\), and using the principle of superposition:

\[u(x, t) = c_1 a + \frac{(c_2 b - c_1 a)}{l} x + (A_3 \sin \lambda x + B_4 \cos \lambda x) \exp(-\lambda^2 Dt)\]

(19)

Applying the boundary conditions to the above expression implied that the value for \(B_4\) is zero, and that

\[\lambda = \frac{n\pi}{l}, \quad n = 1, 2, 3 \ldots\]

(20)

Therefore

\[u(x, t) = c_1 a + \frac{(c_2 b - c_1 a)}{l} x + \sum_{n=1}^{\infty} A_n \sin \frac{n\pi x}{l} \exp(-\lambda^2 Dt)\]

(21)

The initial condition, Eqn (11), requires that

\[-c_1 a - \frac{(c_2 b - c_1 a)}{l} x = \sum_{n=1}^{\infty} A_n \sin \frac{n\pi x}{l}\]

(22)

Using the Fourier series expansion yields

\[A_n = \frac{2}{l} \int_0^l \left[ -c_1 a - \frac{(c_2 b - c_1 a)}{l} x \right] \sin \frac{n\pi x}{l} \ dx\]

(23)

Thus the final solution is

\[u(x, t) = c_1 a + \frac{(c_2 b - c_1 a)}{l} x + \sum_{n=1}^{\infty} \frac{1}{n} \left[ (-1)^n c_2 b - c_1 a \right] \sin \frac{n\pi x}{l} \exp(-\lambda^2 Dt)\]

(24)

From Eqns (8) and (24)

\[c(r, t) = \frac{ac_1}{r} + \frac{(c_2 b - c_1 a)}{rl} (r - a) + \sum_{n=1}^{\infty} \frac{1}{n} \left[ (-1)^n c_2 b - c_1 a \right] \sin \frac{n\pi (r - a)}{l} \exp(-\lambda^2 Dt/l^2)\]

(25)
From this expression, \( D(\frac{\partial c}{\partial r})|_{r=a} \) which is the current volume flux \( J_0 \) in kg d\(^{-1}\) (rate at which the diffusing substance emerges at the interface) is readily calculated

\[
J_0 = \frac{D}{lr} (c_2 b - c_1 a) + \frac{2D}{\pi r} \sum_{n=1}^{\infty} \frac{1}{n} \left((-1)^n c_2 b - c_1 a\right) \times \exp \left(-n^2 \pi D t / l^2\right)
\]

(26)

and

\[
Q_t = J_0 4\pi a b t
\]

(27)

From Eqns (26) and (27)

\[
Q_t = 4\pi a b \left[\frac{D}{lr} (c_2 b - c_1 a) + \frac{2D}{\pi r} \sum_{n=1}^{\infty} \frac{1}{n} \left((-1)^n c_2 b - c_1 a\right) \exp \left(-n^2 \pi D t / l^2\right)\right]
\]

(28)

As the exponential coefficient appearing in the Eqn (28) is proportional to \( n^2 \), the term in the series with a large value for \( n \) or larger value for \( D t / l^2 \) decay very quickly with time. Thus, as a good approximation, only the first and the second terms may be retained. The nutrient concentration \( c_1 \) is very small when the water volume outside the granule is large enough, and it can be regarded as \( c_1 \approx 0 \).

As \( t \to \infty \), approaches the line:

\[
Q_t = 4\pi a b \left[\frac{D}{lr} (c_2 b - c_1 a) + \frac{1}{l^2 / 6}\right] = \frac{4\pi D a b^2 c_2}{lr} \left(t - \frac{l^2}{6D}\right)
\]

(29)

This has an intercept on the \( t \) axis given by

\[
t_1 = \frac{l^2}{6D}
\]

(30)

where \( t_1 \) in \( d \) was defined as the lag period after diffusion of nutrient starts.

From an observation of the intercept, \( D \) is deduced. When \( D t_1 / l_2 \approx 0.45 \) approximately the steady state is achieved (Crank, 1967). However, in some cases \( l \) is very small, so \( t_1 \) is also small, and the total lag period is still decided by \( t' \).

When \( l \) is very small, \( a \approx b \approx r \), therefore

\[
Q_t = 4\pi a^2 \left[\frac{D}{l} (c_2 - c_1) - \frac{l}{6}\right]
\]

(31)

and

\[
g_t = \frac{Q_t}{M_0}
\]

(32)

where \( M_0 \) is the total mass of nutrient density \( \rho_s \) in kg m\(^{-3}\)

\[
M_0 = \frac{4}{3} \pi r^3 \rho_s
\]

(33)

From Eqns (32) and (33)

\[
g_t = \frac{3}{\rho_s r} \left[\frac{D(t - t')}{l} (c_2 - c_1) - \frac{l}{6}\right]
\]

(34)

In case of polymer-coated fertiliser, assuming that: \( c_1 \to 0 \), and \( c_2 \to c_s \) (Saturated concentration), then

\[
g_t = \frac{3}{\rho_s r} \left[\frac{D(t - t')}{l} c_s - \frac{l}{6}\right]
\]

(35)

From Eqn (35)

\[
\frac{d g_t}{dt} = \frac{3D c_s}{\rho_s r l} (1 - g_t)
\]

(36)

where \( c_s \) is the saturated concentration of nutrients in kg m\(^{-3}\).

When there is no solid fertiliser in the granule \( (t \geq Y) \), the concentration in the granule is no longer saturated:

\[
c_s = \frac{(1 - g_t) M_0}{V} = \rho_s (1 - g_t)
\]

(37)

where: \( c_s \) is the nutrient concentration in the granule in kg m\(^{-3}\); \( Y \) is the time when all the solid nutrients dissolved in \( d \); and \( V \) is the granule volume in m\(^3\):

\[
\frac{d g_t}{dt} = \frac{3D c_s}{\rho_s r l} (1 - g_t) = \frac{3D}{r l} (1 - g_t)
\]

(38)

When \( t = Y \), the boundary value for the cumulative percentage of nutrient release \( g_Y \) is

\[
g_Y = \frac{M_0 - c_s V}{M_0} = 1 - \frac{c_s}{\rho_s}
\]

(39)

From Eqns (38) and (39)

\[
g_t = 1 - \frac{c_s}{\rho_s} \exp \left(-\frac{3D}{r l} (t - Y)\right)
\]

(40)

Therefore, the nutrient release from polymer-coated granule is as follows:

\[
g_t = \begin{cases} 
0 & t \leq t' \\
\frac{3}{\rho_s r} \left[\frac{D(t - t')}{l} c_s - \frac{l}{6}\right] & t' < t \leq Y \\
1 - \frac{c_s}{\rho_s} \exp \left(-\frac{3D}{r l} (t - Y)\right) & t > Y
\end{cases}
\]

(41)

3. Model verification

A polymer-coated fertiliser was provided by Haifa Chemical Ltd, Israel. The release of potassium in distilled water was determined with flame photometer. The K content was 10.79%, and the thickness was
Four uniform fertiliser granules were chosen, immersed in 10 ml distilled water for release at 30°C. When sampling all the solution was obtained, and another 10 ml of distilled water added, then kept releasing at 30°C. Different radii of fertiliser granules were carefully chosen to verify the influence of radius on release. The diffusion coefficients were determined according to Zhang et al. (1994).

Figure 2 shows that the experimental results are close to the mathematical prediction to a satisfactory extent. The slope of release curve in Fig. 2(a) is sharper than that in Fig. 2(b), which means that the nutrient release rate increases when the granule radius decreases. However, there still are some differences between modelling and the experimental results due to two factors: one is granularity shape which is not exactly spherical. Since the surface area of spherical granule is the smallest under a certain mass, so the surface area (diffusion area) of granule used in the experiment will be larger than that for modelling and, therefore, the modelling cumulative percentage of nutrient release is lower than experimental one. The other factor is the granule thickness which is not completely uniform, and nutrient will easily release from thinner part of the membrane, which also leads to faster nutrient release than predicted.

In addition, this model also can evaluate lag period through the intercept of the release equation in the linear stage, this evaluation method is much easier than the theoretical calculation, although there remains some error which is of acceptable magnitude. Further sensitivity analysis should be done to check the model.

4. Conclusions

A mathematical model was established to predict the nutrient release from polymer-coated fertiliser. The modelling result agreed with the experimental release on the whole. There still existed a few differences, because some granule conditions do not completely agree with the model assumptions. Further sensitivity analysis should also be done to check or improve the model. However, as a theoretical model, it was satisfactory to assist in improving the production of polymer-coated fertiliser.

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