Biosystems Engineering (2004) **88** (3), 395–400
doi:10.1016/j.biosystemseng.2004.03.004
SW—Soil and Water

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Mathematical Model for Potassium Release from Polymer-coated Fertiliser

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(Received 24 June 2003; received in revised form 2 March 2004; published online 11 June 2004)

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:

$$\frac{M_t}{M_0} = 4\left(\frac{Dt}{\pi l^2}\right)^{0\cdot 5} \quad \text{for } 0 \leqslant \frac{M_t}{M_0} \leqslant 0\cdot 4 \tag{1}$$

$$\frac{M_t}{M_0} = 1 - \left(\frac{8}{\pi^2}\right)\exp\left(-\frac{\pi^2 Dt}{l^2}\right) \quad \text{for } 0\cdot 4 \leqslant \frac{M_t}{M_0} \leqslant 1\cdot 0 \tag{2}$$

where: D is the diffusion coefficient for the polymer in $mm^2\,d^{-1}$; l is the thickness of the polymer membrane in 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:

$$\frac{M_t}{M_0} = 6(1+\alpha)\,\frac{tD^{0\cdot 5}}{(\pi b)^{0\cdot 5}} \tag{3}$$

where: D is the diffusion coefficient for the polymer in $mm^2\,d^{-1}$; b is radius of the fertiliser granule in mm; and α is a constant. This model is simple, but the parameter α 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.

Notation

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

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.

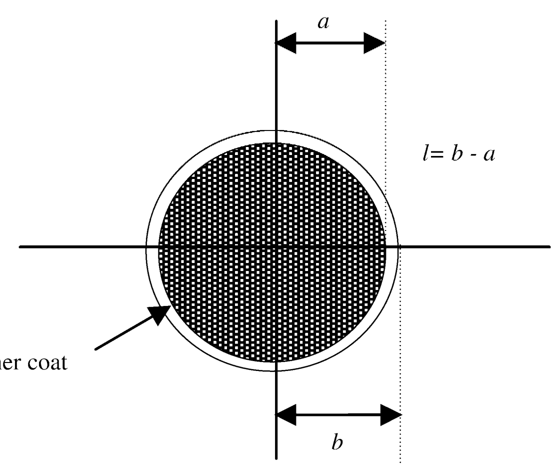

Fig. 1. Schematic diagram of a cross-section view of a fertiliser granule: a, radius of granule; b, radius of coated granule; l, thickness of membrane

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:

$$t' = \frac{\gamma r l}{3 p_h \Delta P} \tag{4}$$

where: γ 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 $mm^2\,Pa^{-1}\,d^{-1}$, ΔP 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

$$g_t = \frac{Q_t}{M_0} = 0 \quad \text{for } t \leqslant t' \tag{5}$$

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

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 Fick's second law

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \tag{6}$$

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

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial r^2} \tag{7}$$

Eqn (7) defines linear flow in one dimension.

The diffusion distance x in mm in the membrane is defined as

$$x = r - a \tag{8}$$

In the region $0 < x < l$, the boundary conditions are

$$u(0, t) = c_1 a \quad t > 0 \tag{9}$$

$$u(l, t) = c_2 b \quad t > 0 \tag{10}$$

and the initial condition is

$$u(x, 0) = 0 \tag{11}$$

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

$$u(x, t) = X(x)T(t) \tag{12}$$

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

$$\frac{1}{DT}\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{1}{X}\frac{\mathrm{d}^2 X}{\mathrm{d}x^2} = -\lambda^2 \tag{13}$$

where λ is a constant.

From Eqn (12)

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\lambda^2 DT \tag{14}$$

$$\frac{\mathrm{d}^2 X}{x^2} = -\lambda^2 X \tag{15}$$

Solving Eqns (14) and (15) gives

$$X = \begin{cases} A_1 x + A_2 & \text{for } \lambda = 0 \\ B_1 \sin \lambda x + B_2 \cos \lambda x & \text{for } \lambda \neq 0 \end{cases} \tag{16}$$

where A_1, A_2, B_1, B_2 are constants, and

$$T = \begin{cases} \text{const} & \text{for } \lambda = 0 \\ B_3 \exp(-\lambda^2 Dt) & \text{for } \lambda \neq 0 \end{cases} \tag{17}$$

where B_3 is a constant.

Therefore

$$u(x, t) = \begin{cases} a_1 x + a_2 & \text{for } \lambda = 0 \\ (A_3 \sin \lambda x + B_4 \cos \lambda x)\exp(-\lambda^2 Dt) & \text{for } \lambda \neq 0 \end{cases} \tag{18}$$

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:

$$u(x, t) = c_1 a + \frac{(c_2 b - c_1 a)}{l}x + (A_3 \sin \lambda x + B_4 \cos \lambda x)\exp(-\lambda^2 Dt) \tag{19}$$

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

$$\lambda = \lambda_n = \frac{n\pi}{l} \quad n = 1, 2, 3 \ldots \tag{20}$$

Therefore

$$u(x, t) = c_1 a + \frac{(c_2 b - c_1 a)}{l}x + \sum_{n=1}^{\infty} A_n \sin \lambda_n x \exp(-\lambda^2 Dt) \tag{21}$$

The initial condition, Eqn (11), requires that

$$-c_1 a - \frac{(c_2 b - c_1 a)}{l}x = \sum_{n=1}^{\infty} A_n \sin \lambda_n x \tag{22}$$

Using the Fourier series expansion yields

$$\begin{aligned} A_n &= \frac{2}{l}\int_0^l \left[-c_1 a - \frac{(c_2 b - c_1 a)}{l}x\right] \sin \frac{n\pi x}{l}\,\mathrm{d}x \\ &= \frac{2}{n\pi}[(-1)^n c_2 b - c_1 a], \quad n = 1, 2, 3... \end{aligned} \tag{23}$$

Thus the final solution is

$$\begin{aligned} u(x, t) = c_1 a &+ \frac{(c_2 b - c_1 a)}{l}x \\ &+ \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}((-1)^n c_2 b - c_1 a) \sin \frac{n\pi x}{l} \\ &\times \exp[-n^2 \pi D t / l^2] \end{aligned} \tag{24}$$

From Eqns (8) and (24)

$$\begin{aligned} c(r, t) = \frac{a c_1}{r} &+ \frac{(c_2 b - c_1 a)}{rl}(r - a) \\ &+ \frac{2}{\pi r}\sum_{n=1}^{\infty}\frac{1}{n}((-1)^n c_2 b - c_1 a) \sin \frac{n\pi(r - a)}{l} \\ &\times \exp(-n^2 \pi D t / l^2) \end{aligned} \tag{25}$$

From this expression, $D(\partial c/\partial r)|_{r=a}$ 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

$$J_0 = \frac{D}{lr}(c_2 b - c_1 a) + \frac{2D}{\pi r}\sum_{n=1}^{\infty}\frac{1}{n}((-1)^n c_2 b - c_1 a) \times \exp\,(-n^2\pi Dt/l^2) \quad (26)$$

and

$$Q_t = J_0 4\pi abt \quad (27)$$

From Eqns (26) and (27)

$$Q_t = 4\pi ab\left[\frac{Dt}{lr}(c_2 b - c_1 a) + \frac{2Dt}{\pi r}\sum_{n=1}^{\infty}\frac{1}{n}((-1)^n c_2 b - c_1 a)\exp\,(-n^2\pi Dt/l^2)\right] \quad (28)$$

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 Dt/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 $c_1 \cong 0$.

As $t \to \infty$, approaches the line:

$$Q_t = 4\pi ab\left[\frac{Dt}{lr}(c_2 b - c_1 a) - \frac{l}{6}\right] = \frac{4\pi Dab^2 c_2}{lr}\left(t - \frac{l^2}{6D}\right) \quad (29)$$

This has an intercept on the t axis given by

$$t_1 = \frac{l^2}{6D} \quad (30)$$

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 $Dt_1/l_2 \cong 0{\cdot}45$ 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, $a \cong b \cong r$, therefore

$$Q_t = 4\pi r^2\left[\frac{Dt}{l}(c_2 - c_1) - \frac{l}{6}\right] \quad (31)$$

and

$$g_t = \frac{Q_t}{M_0} \quad (32)$$

where M_0 is the total mass of nutrient density ρ_s in kg m^{-3}

$$M_0 = \frac{4}{3}\pi r^3 \rho_s \quad (33)$$

From Eqns (32) and (33)

$$g_t = \frac{3}{\rho_s r}\left[\frac{D(t-t')}{l}(c_2 - c_1) - \frac{l}{6}\right] \quad (34)$$

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

$$g_t = \frac{3}{\rho_s r}\left(\frac{D(t-t')}{l}c_s - \frac{l}{6}\right) \quad (35)$$

From Eqn (35)

$$\frac{dg_t}{dt} = \frac{3Dc_s}{\rho_s rl} \quad (36)$$

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

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

$$c_t = \frac{(1-g_t)M_0}{V} = \rho_s(1-g_t) \quad (37)$$

where: c_t 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:

$$\frac{dg_t}{dt} = \frac{3D}{\rho_s rl}\rho_s(1-g_t) = \frac{3D}{rl}(1-g_t) \quad (38)$$

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

$$g_Y = \frac{M_0 - c_s V}{M_0} = 1 - \frac{c_s}{\rho_s} \quad (39)$$

From Eqns (38) and (39)

$$g_t = 1 - \frac{c_s}{\rho_s}\exp\left(-\frac{3D}{rl}(t-Y)\right) \quad (40)$$

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

$$g_t = \begin{cases} 0 & t \leqslant t' \\ \dfrac{3}{\rho_s r}\left(\dfrac{D(t-t')}{l}c_s - \dfrac{l}{6}\right) & t' < t \leqslant Y \\ 1 - \dfrac{C_s}{\rho_s}\exp\left(-\dfrac{3D}{rl}(t-Y)\right) & t > Y \end{cases} \quad (41)$$

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

0·065 mm. 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 granule 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.

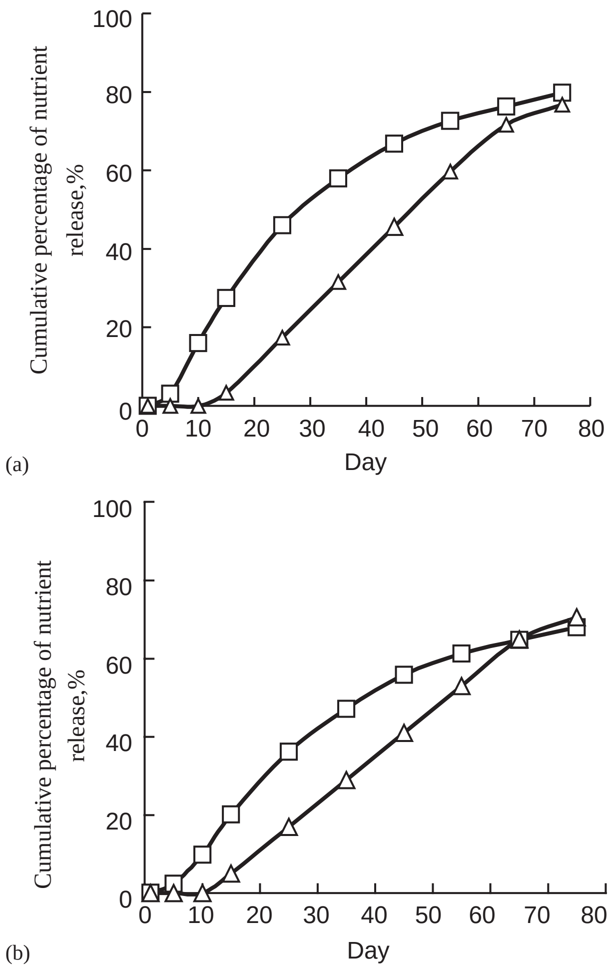

Fig. 2. Comparison of experimentally measured (—□—) and modelling (—△—) release from polymer-coated fertiliser (with membrane thickness l of 0·065 mm, nutrient density ρ_s, of 309 kg m^{-3}, diffusion coefficient D of 12·6 mm^2 d^{-1}, saturated concentration c_s of 80·4 kg m^{-3}, lag period t' of 2 d, and boundary cumulative percentage of nutrient release value g_Y of 73%) for two values of granule radius a: (a) a = 1·1 mm; (b) a = 1·4 mm

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.

Acknowledgements

We give thanks for the financial support given by Innovational Project in Environment and Resources Fields from Chinese Academy of Sciences (No. KZCX2-402) and National Natural Science Foundation (No. 39870431), and National Developing Project for High and New Technology (No. 2001AA246021); we are also very grateful to Prof. Brian Witney for his critical and kind correction.

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