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THEORETICAL MODEL OF COMPOUNDS RELEASE FROM CAPSULATED PARTICLES AND ITS EXPERIMENTAL CHECK

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Abstract. Mathematical model of solid phase diffusive release during dissolving of capsulated spherical particle has been developed. The adequacy of the model to experimental data obtained for different compounds has been checked.

Keywords: mathematical model, capsulated particle, release kinetics.

1. Introduction

Development of compounds with controlled or prolonged solubility is one of the ways of dispersed materials capsulation [1-3]. Capsulated granulated mineral fertilizers and chemical pharmaceutical preparations are among them. The membrane over the capsulated particles surface produces additional resistance to mass transfer, changing the intensity of compounds solubility and movement in a solvent medium during its diffusion release. Various scientific papers are devoted to the problem of compounds diffusion through polymer capsules during solid phase dissolving [4-6]. However, theoretical developments have limited application because of the introduced simplifications and assumptions, especially while compounds modification by new film-forming compositions. The theoretical investigations of diffusive release of solid phase from capsulated particles are of considerable practical interest as they allow to develop analytical dependencies which would give the possibility to predict kinetics within a wide range of investigated objects properties. The polymeric capsule is a membrane, diffusion flux through which is determined by concentration difference, which is the motive force of this mass transfer.

2. Results and Discussion

Commonly the capsulated materials have rounded form, close to spherical one. While developing the theoretical model we consider a single spherical particle (Fig. 1) in the solvent medium.

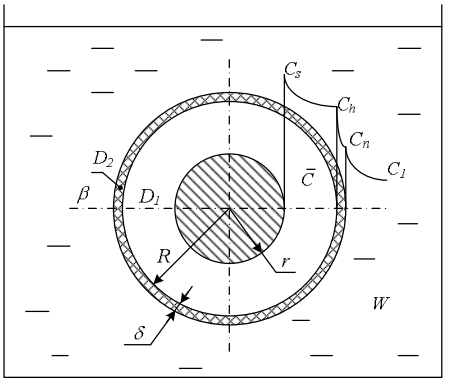


Fig. 1. Scheme of the components concentration distribution during their release from capsulated spherical particle through polymeric capsule with *d* thickness at time *t*

The material balance of components release from capsulated particles for any time t is described by the Eq. (1) [7, 8]:

$$WC_1 + \frac{4}{3}\pi(R^3 - r^3)\bar{C} = \frac{4}{3}\rho_s\pi(R^3 - r^3) \qquad (1)$$

where $\bar{C}$ – compound average concentration in the middle of the capsule, kg/m^3; C_1 – compound concentration in the solvent medium, kg/m^3; r_s – solid phase density, kg/m^3; W – solvent volume, m^3; R – radius of solid phase at the process beginning, m; r – running radius of solid phase for release time t, m.

Let us designate the ratio between linear sizes of the solid phase in the middle of the capsule and obtain dimensionless simplex j:

$$\frac{r}{R} = \varphi \quad (0 \le \varphi \le 1) \qquad (2)$$

Taking into account simplex j (2) the Eq. (1) takes the form of:

$$\frac{3WC_1}{4\pi R^3} + (1 - \varphi^3)\bar{C} = \rho_s(1 - \varphi^3) \qquad (3)$$

Kinetics of the release process is described by the equations of compound diffusion from the dissolving surface to the internal boundary of the capsule, diffusion through the capsule and mass transfer to the solvent medium [7, 8]:

$$-\frac{dM}{Fd\tau} = D_1\frac{C_s - C_h}{R-r} = D_2\frac{C_h - C_n}{\delta} = \beta(C_n - C_1) \quad (4)$$

where M – mass of soluble solid phase, kg; F – area of soluble solid phase, m^2; C_s – saturation concentration on the dissolving boundary, kg/m^3; C_h – concentration of the compound in the solution at internal boundary of membrane, kg/m^3; C_n – concentration at the external boundary of membrane, kg/m^3; d – capsule thickness, m; D_1 – diffusion coefficient in the middle of the particle, m^2/s; D_2 – coefficient of mass conductivity through membrane, m^2/s; b – mass transfer from external surface to the solvent medium, m/s; r_s – solid phase density, kg/m^3; t – process time, s.

Let us express the mass of soluble solid phase (the right side of the Eq. (1)) by its volume and record it in a differential form:

$$dM = \frac{4}{3}\rho_s\pi R^3(-\varphi^3)d\varphi \ . \quad (5)$$

Dividing left and right sides of the Eq. (5) by Fdt parameter, we obtain:

$$-\frac{dM}{Fd\tau} = \frac{4\rho_s\pi R^3\varphi^2 d\varphi}{3Fd\tau} \quad (6)$$

The area of soluble solid phase is expressed by its geometrical sizes. Taking into account the Eq. (2) the following equations is obtained:

$$F = 4\pi R^2\varphi^2 \quad (7)$$

Substitution of the Eq. (7) for the right part of the Eq. (6) gives us:

$$-\frac{dM}{Fd\tau} = \rho_s\frac{R}{3}\frac{d\varphi}{d\tau} \quad (8)$$

The sum of kinetic equations (4), as well as Eqs. (2) and (8) gives us:

$$\frac{d\varphi}{d\tau}\rho_s\frac{R}{3}\left[\frac{R}{D_1}(1-\varphi) + \frac{\delta}{D_2} + \frac{1}{\beta}\right] = C_s - C_1 \quad (9)$$

The Eq. (9) contains three variable values: j, t and C_1. From the Eq. (3) we express the concentration value in the solvent medium C_1 by means of simplex j.

$$C_1 = \frac{\rho_s}{m}(1-\alpha)(1-\varphi^3) \quad (10)$$

where

$$m = \frac{3W}{4\pi R^3}; \quad \alpha = \frac{C_s}{\rho_s} \quad (11)$$

After substitution of the Eq. (10) for (9) as well as mathematical replacements and reductions the following differential equation is obtained:

$$\frac{d\varphi}{d\tau}\frac{R}{3}\left[\frac{R}{D_1}(1-\varphi) + \frac{\delta}{D_2} + \frac{1}{\beta}\right] =$$

$$= \left[\alpha - \frac{1}{m}(1-\alpha)\right] + \left[\frac{1}{m}(1-\alpha)\varphi^3\right] \quad (12)$$

Let us divide the variables and express the Eq. (12) in an integral form:

$$\int_1^{\varphi}\left[\left(\frac{R}{D_1} + r_1\right)\frac{1}{a+b\varphi^3} - \frac{R}{D_1}\frac{r_1}{a+b\varphi^3}\right]d\varphi = \frac{3}{R}\int_0^{\tau} d\tau \quad (13)$$

where

$$r_1 = \frac{\delta}{D_2} + \frac{1}{\beta}; \quad a = \alpha - \frac{1}{m}(1-\alpha); \quad b = \frac{1}{m}(1-\alpha)$$

Integration of the Eq. (13) gives the following result [9]:

$$\left\{\frac{k}{3a}\left[\frac{1}{2}ln\frac{(k+\varphi)^2}{k^2-k\varphi+\varphi^2} + \sqrt{3}arctg\frac{\varphi\sqrt{3}}{2k-\varphi}\right]\right\}\Bigg|_1^{\varphi}\left(\frac{R}{D_1} + r_1\right)$$

$$-\frac{R}{D_1}\left\{\frac{1}{3bk}\left[\frac{1}{2}ln\frac{k^2-k\varphi+\varphi^2}{(k+\varphi)^2} + \sqrt{3}arctg\frac{2\varphi-k}{k\sqrt{3}}\right]\right\}\Bigg|_1^{\varphi} = \frac{3}{R}\tau \quad (14)$$

where

$$k = \sqrt[3]{\frac{a}{b}}$$

Let us substitute the integration limits and introduce dimensionless complexes $Fo = \frac{\tau D_1}{R^2}$, $Sh = \frac{\beta R}{D_1}$, $Bi = \frac{\beta\delta}{D_2}$.

After reductions and permutations we obtain the final equation connecting solid particle dimensions and time:

$$\left(1 + 2\frac{Bi+1}{Sh}\right)\left\{\frac{k}{3a}\left[\frac{1}{2}ln\frac{(k+\varphi)^2(k^2-k+1)}{(k^2-k\varphi+\varphi^2)(k+1)^2} + \right.\right.$$

$$\left.\left. + \sqrt{3}arctg\frac{\sqrt{3}k(\varphi-1)}{2(k^2+\varphi)-k(\varphi+1)}\right]\right\}$$

$$-\frac{1}{3bk}\left[\frac{1}{2}ln\frac{(k^2-k\varphi+\varphi^2)(k+1)^2}{(k+\varphi)^2(k^2-k+1)} + \right.$$

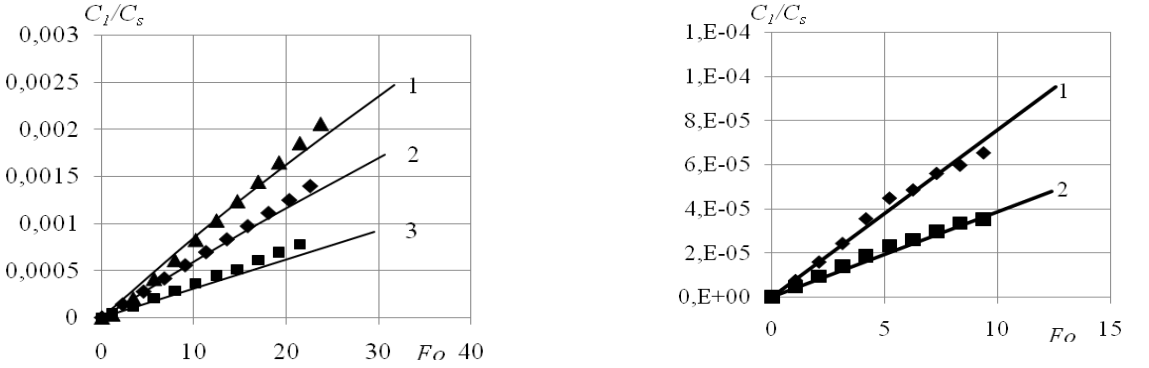
$$\left. + \sqrt{3}arctg\frac{2k\sqrt{3}(\varphi-1)}{(k\sqrt{3})^2 + (2\varphi-k)(2-k)}\right] = 3Fo \ . \quad (15)$$

The obtained equation is a theoretical model of components release from a single spherical capsulated

particle. It allows to calculate the kinetics of components release from the capsule during dissolving.

To check the adequacy of the obtained theoretical dependence (15) we compared the calculated and the experimental data on the kinetics of KNO_3 release from the particle capsulated with acetylphtalylcellulose film and $MgSO_4$ filmed with nitrocellulose of various thicknesses. The calculations were carried out taking into account the conditions of the previous experiments. The essence of those experiments is the determination of concentration C_1 for the component released from a single spherical particle [6, 10] using conductometric analysis. The results are represented in Fig. 2.

The relative error of experimental and theoretical values is within the range of 2.6–9.4 %.



a) b)

Fig. 2. Comparison of theoretical (lines) and experimental (dots) data of the component release from the capsulated spherical particles covered with insoluble capsule of various thicknesses *d*, mcm: 10 (1), 20 (2) and 30 (3) for KNO_3 (a); 10 (1) and 20 (2) for $MgSO_4$ (b)

3. Conclusions

The developed theoretical model offers a good description of the process of diffusion release of capsulated compounds through insoluble capsule. It may be used for prediction calculations with assigned rate of compounds piling up in the medium and for determination of the parameters capable of providing the necessary properties to the materials.

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ТЕОРЕТИЧНА МОДЕЛЬ ВИВІЛЬНЕННЯ РЕЧОВИН ІЗ КАПСУЛЬОВАНИХ ЧАСТИНОК ТА ЇЇ ЕКСПЕРИМЕНТАЛЬНА ПЕРЕВІРКА

Анотація. *Наведена теоретична розробка математичної моделі дифузійного вивільнення твердої фази в процесі розчинення капсульованої частинки кулястої форми. Проведена перевірка адекватності моделі експериментальним даним, отриманих для різних речовин.*

Ключові слова: *математична модель, капсульована частинка, кінетика вивільнення.*