

Jarosław BOBEK*¹, Andrzej POLAŃSKI¹

Chapter 1. NUMERICAL MODELING OF THE LIESEGANG PRECIPITATION PATTERNS WITH LINEAR AND RADIAL GEOMETRIES

1.1. Introduction

Liesegang patterns are stripes, bands or rings [1] formed by moving fronts of chemical reactions. Processes involved in formation of Liesegang patterns are diffusion, reaction and precipitation. Liesegang patterns occur in many reactions/processes and can be seen in all types of media, hard substances, gels, liquids or gases. Due to variety of possible media and processes/scenarios Liesegang patterns are reported and researched in many systems in chemistry, geology, biology [2]. Occurrence of the Liesegang phenomenon requires at least two chemical reactants, called inner and outer electrolytes. Outer electrolyte, of higher concentration diffuses into the medium and reaction with inner electrolyte takes place. Under certain conditions precipitation of the reaction product then occurs leading to formation of layers of separate precipitates.

Formation of precipitation patterns [1, 3] in reaction – diffusion systems have always gained a lot of interest of researches, motivated both by challenges of experimental and modeling problems and wide range of potential applications. A very interesting and motivating recent application of precipitation phenomena is designing reaction – diffusion – precipitation processes for oscillatory drug release systems [4]. It can involve different chemical reagents and different geometries. Developing such systems poses several challenges. The first challenge is developing reliable mathematical/computational models of reaction – diffusion – precipitation reactions. The second one is using the developed model as a control system that allows obtaining desired

* Corresponding author: jaroslaw.bobek@polsl.pl, Akademicka 16, 44-100 Gliwice, PL.

¹ Department of Computer Graphics, Vision and Digital Systems, Silesian University of Technology.

parameters of time and space distributions of concentrations. Finally, the third one is experimental validation.

In this paper we present a mathematical and computational model of reaction – diffusion – precipitation systems with linear and radial geometries. Our mathematical and computational system allows validations of reaction – diffusion – precipitation reactions modeling assumptions and fitting model parameters to data. In order to verify our modeling environment we use experimental data on formation of Liesegang patterns [5], [6-8]. We solve partial differential equations of reaction-difusion-precipitation processes by using discretization based on suitable 1D or 2D meshes. We confront computational predictions of percipitation patterns with experimental measurements by evaluating Matalon-Packter laws, i.e., laws concerning precipitation bands spacing, their time occurence and their widths.

In contrast to the literature, where only 1D Liesegang patterns are studied numerically, our research has led to creating a stable computational environment allowing predicting outcomes of both 1D and 2D diffusion – precipitation chemical reactions.

Chemical and mathematical model

Liesegang patterns are based on reaction process of two diffusing substances. The effect of reaction is stationary product which precipitate periodically in time. Basic reaction could be represented as



where:

A, B – inner/outer electrolyte

P – reaction product.

The inner electrolyte can be understood as substance equally distributed in the whole reaction system and the outer electrolyte as substance delivered from outside of reaction system.

So, the whole chemical process can be divided in three mainly operations [9]:

1. Diffusion of outer electrolyte into and inner electrolyte inside reaction system [10].
2. Precipitation of reaction product.
3. Agglomeration of diffusing substances on precipitated product.

The first one point is substance diffusion. In accordance to second Fick's law the diffusion equation for chemical system can be described as

$$\frac{\partial c}{\partial t} = D * \nabla^2 c$$

Simultaneously when substances concentration ratio exceeds critical value the precipitation process occurs. Important information is that whole product doesn't appear in same time. That process is stationary and can be described as

$$\frac{\partial c}{\partial t} = k_p * ([A] * [B] - K_{SO}) * \theta([A] * [B] - K_{SO})$$

where:

[A], [B] – concentration of substrates

k_p – reaction rate constant

K_{SO} – product solubility constant

$\theta(x)$ – Heaviside step function

The second point references to supersaturation theory [11] which is simplest method to describe precipitation of Liesegang rings. When substrates concentration ratio exceeds critical value the precipitation process occurs. That is one-way reaction – product doesn't dissolve into substrates.

To complete mathematical description of diffusion-precipitation-agglomeration system we need to provide agglomeration equation. First of all, the crystal product is needed because surrounding ions agglomerate on precipitated crystals. When substrates accumulate on crystal surfaces precipitation process still occurs so agglomeration process can be described as

$$\frac{\partial c}{\partial t} = \lambda * [A] * [B] * [P]$$

where:

[A], [B], [P] – concentration of substrates and product

λ – aggregation rate

Summarizing all of equations (2), (3) and (4) whole model can be described as

$$\frac{\partial a}{\partial t} = D_a \nabla^2 a - k_p * (a * b - K_{SO}) * \theta(a * b - K_{SO}) - \lambda * a * b$$

$$\frac{\partial b}{\partial t} = D_a \nabla^2 b - k_p * (a * b - K_{SO}) * \theta(a * b - K_{SO}) - \lambda * a * b$$

$$\frac{\partial p}{\partial t} = k_p * (a * b - K_{SO}) * \theta(a * b - K_{SO}) + \lambda * a * b * p$$

which includes diffusion of inner and outer electrolyte, product precipitation and agglomeration (reducing concentration of substrates and increasing concentration of product) and product stationarity [12, 13].

Initial condition of substances concentration in system should be assumed as

$$\begin{aligned} a(x, 0) &= a_0 * \theta(x > 0 \& x < L) \quad \text{or} \quad a(x, 0) = a_0 * \theta(x < R) \\ b(x, 0) &= b_0 * \theta(x \leq 0 | x \geq L) \quad \text{or} \quad b(x, 0) = b_0 * \theta(x \geq R) \\ p(x, 0) &= 0 \end{aligned}$$

At the beginning there's no product, the inner electrolyte (a) is equally distributed in whole system and the outer electrolyte (b) is only outside of system.

Next point is to define boundary conditions. The outer electrolyte has to be continuously delivered into system. The product should never exit whole reaction environment such as inner electrolyte, but boundary condition for inner electrolyte is little more difficult. When product appears, it's behavior should be as boundary for inner electrolyte. It can be defined as high agglomeration rate but also high reaction rate constant [12, 14]. The general boundaries can be defined as

$$\begin{aligned} a(x == 0 | x == L, t) &= a_0 \\ \frac{\partial b(x == 0 | x == L)}{\partial x} &= 0 \\ \frac{\partial p(x == 0 | x == L)}{\partial x} &= 0 \end{aligned}$$

but also, important boundary named "moving boundary condition" [9, 12] which represents precipitating product at position x_n and at time t_n behaving as limit of system

$$b(x == x_n, t > t_n) = 0$$

where:

x_n – appearing band position

t_n – appearing band time

Geometry

In experiments we tested one- (1D) and two-dimensional (2D) geometry [15]. In 1D system the assumption that length is much greater than width is needed. Hence, we can interpret the diffusion process as depending only on one coordinate. The concentration of inner electrolyte was equally distributed along reaction environment and outer electrolyte was delivered at both ends. For 2D geometry to minimize dependencies the circle geometry with same assumption of electrolytes distribution was prepared. 1D geometry was prepared with length parameter of the reaction area equal to 200 mm and 2D geometry was prepared with radius equal to 10 mm.

Mesh generation

For generating 2D mesh was used Matlab implementation of the Delaunay triangulation algorithm with maximal edge length set to 0.25. Algorithm is based on linear geometric order. For 1D geometry reaction area length was divided into 0.1 mm fragments [15].

Computational method

Calculations were made using Matlab R2020b software and more specifically using Partial Differential Equation (PDE) toolbox. The first step was to implement equations (5). PDE toolbox interpret equation as

$$m \frac{\partial^2 u}{\partial t^2} + d \frac{\partial u}{\partial t} - \nabla * (c \nabla u) + au = f$$

so, we can write (5) system as

$$\begin{aligned} 0 \frac{\partial^2 a}{\partial t^2} + 1 \frac{\partial a}{\partial t} - \nabla * (D_a \nabla u) + 0 * a \\ &= -k_p * (a * b - K_{SO}) * \theta(a * b - K_{SO}) - \lambda * a * b * p \\ 0 \frac{\partial^2 b}{\partial t^2} + 1 \frac{\partial b}{\partial t} - \nabla * (D_b \nabla u) + 0 * b \\ &= -k_p * (a * b - K_{SO}) * \theta(a * b - K_{SO}) - \lambda * a * b * p \\ 0 \frac{\partial^2 b}{\partial t^2} + 1 \frac{\partial b}{\partial t} - \nabla * (0 * \nabla u) + 0 * p \\ &= k_p * (a * b - K_{SO}) * \theta(a * b - K_{SO}) + \lambda * a * b * p \end{aligned}$$

In both geometries system of equation coefficients m, d, c, a and f are matrixes. For our setup the m parameter is equal 0, d is identity matrix, c is diagonal matrix of diffusion coefficients, a is equal 0 and f is no derivate dependent part.

Experimental model

Experimental parameters were idealized to point precipitation of product in result of reaction-diffusion process. Initial value of substrates concentration was: 0.5 mol/dm³ for outer electrolyte and 0.05 (0.1) mol/dm³ for inner electrolyte in 1D system (2D) [15]. Boundary conditions were implemented as equations (7) and (8). 1D and 2D parameters are presented in Table 1.1. [5-8].

Table 1.1

Experimental models' parameters

	1D model	2D model
Inner electrolyte diffusion coefficient	$1 * 10^{-3} [mm^2 * s^{-1}]$	$0.8 * 10^{-3} [mm^2 * s^{-1}]$
Outer electrolyte diffusion coefficient	$1 * 10^{-3} [mm^2 * s^{-1}]$	$1.2 * 10^{-3} [mm^2 * s^{-1}]$
Solubility constant	$3.5 * 10^{-5} [mol^2 * dm^{-6}]$	$3.5 * 10^{-3} [mol^2 * dm^{-6}]$
Reaction rate constant	$1 * 10^1 [dm^3 * mol^{-1} * s^{-1}]$	$1 * 10^1 [dm^3 * mol^{-1} * s^{-1}]$
Aggregation rate constant	$1 * 10^1 [dm^6 * mol^{-2} * s^{-1}]$	$1 * 10^1 [dm^6 * mol^{-2} * s^{-1}]$
Experiment time	$2 * 10^6 [s]$	86400 [s] (24 h)

Results and discussion

Using parameters described in Table 1.1., two models (1D and 2D) was tested and verified against Matalon-Packter law (spacing law), width law and time law. Both models are suitable to be good description of diffusion-precipitation-agglomeration system.

1D model

One dimensional model was predicated using described geometry and parameters to predict creation of rings. However, problem is only described on one coordinate, rings aren't noticeable – only where product precipitate.

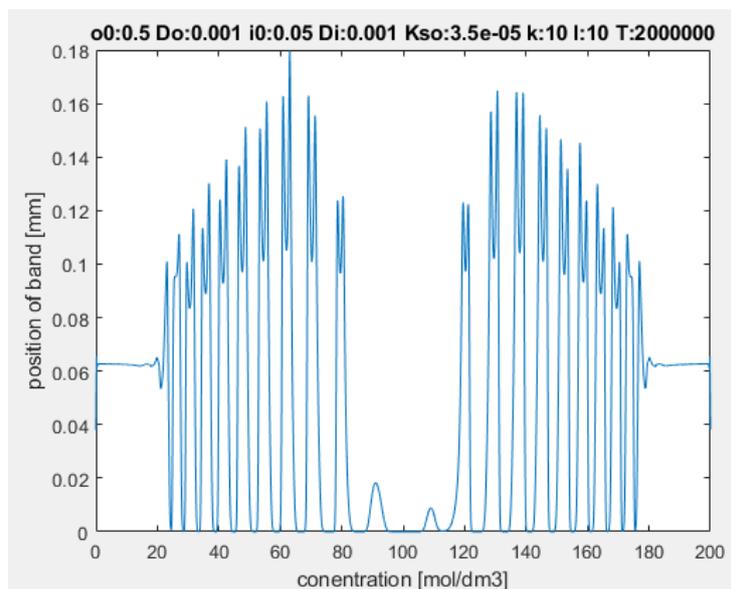


Fig. 1.1. Predicated bands with 1D model

Rys. 1.1. Wzorce przewidziane modelem 1D

Table 1.2

Predicted bands in 1D model

band no.	position X_n [mm]	width [mm]	time T_n [s]
1	26.5	4.1	150000
2	30.8	4.8	200000
3	36.1	4.9	280000
4	41.8	4.9	360000
5	48.2	5.5	470000
6	55.1	5.7	610000
7	62.7	5.8	800000
8	71.1	6.1	1000000
9	80.7	6.3	1260000

Table 1.2 contains bands description seen on Fig. 1.1. That data was used to prove that model explain Liesegang rings, precipitating bands should fulfill spacing, time and width law (Matalon-Packter law). The time law is presented in Fig. 1.2 as linear dependency position of precipitating band against root precipitation time. The width law is presented in Fig. 1.3 as linear dependency position of precipitating band against width of this band. The spacing law can be simplest presented as linear dependency of band position difference against band position what is shown in Fig. 1.4.

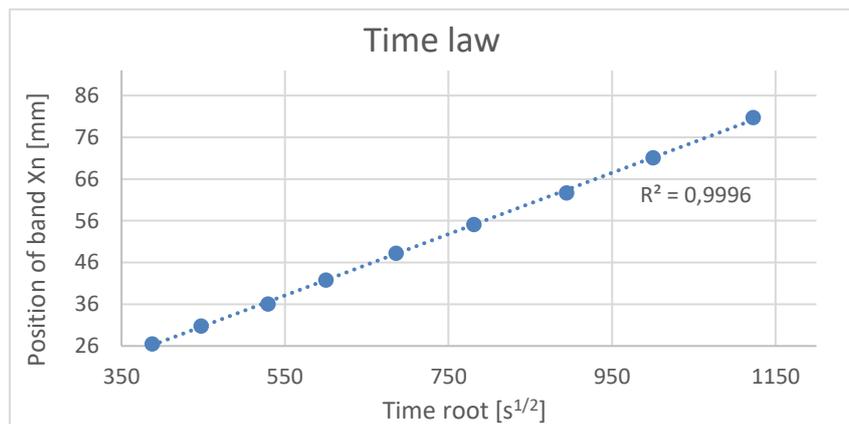


Fig. 1.2. Time law verification for 1D model

Rys. 1.2. Weryfikacja zależności odstępów czasowych dla modelu 1D

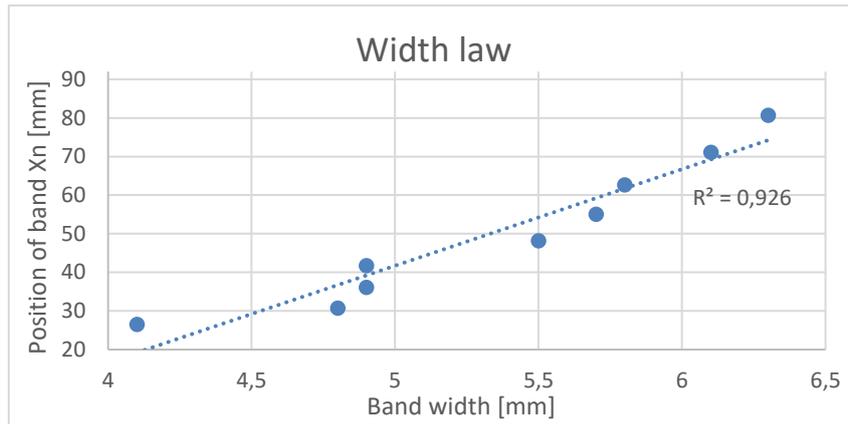


Fig. 1.3. Width law verification for 1D model

Rys. 1.3. Weryfikacja zależności grubości wzorców dla modelu 1D

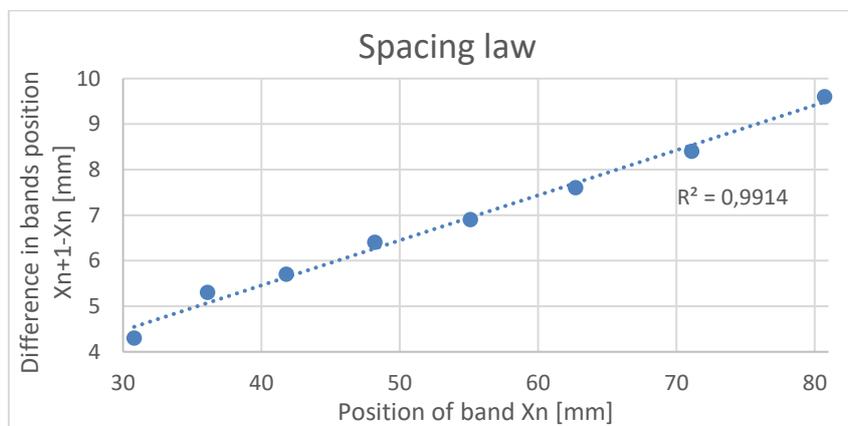


Fig. 1.4. Spacing law verification for 1D model

Rys. 1.4. Weryfikacja zależności odstępów między wzorcami dla modelu 1D

All three figures contains linear dependency. The R-square parameter informs about good data fir to linear function. Model can be interpreted as good description of precipitation Liesegang rings in one dimension.

2D model

Two dimensional model was analyzed by using described geometry and parameters to predict creation of rings. Diffusion process occurs in both x and y coordinates which makes whole prediction faster. It was needed to shorten experiment time. The used solubility rate constant is greater than in 1D model cause of higher initial concentration of substrates and to avoid local supersaturation. The diffusion coefficients have to differ from each other to avoid continously precipitation of product caused by process happening in both dimensions.

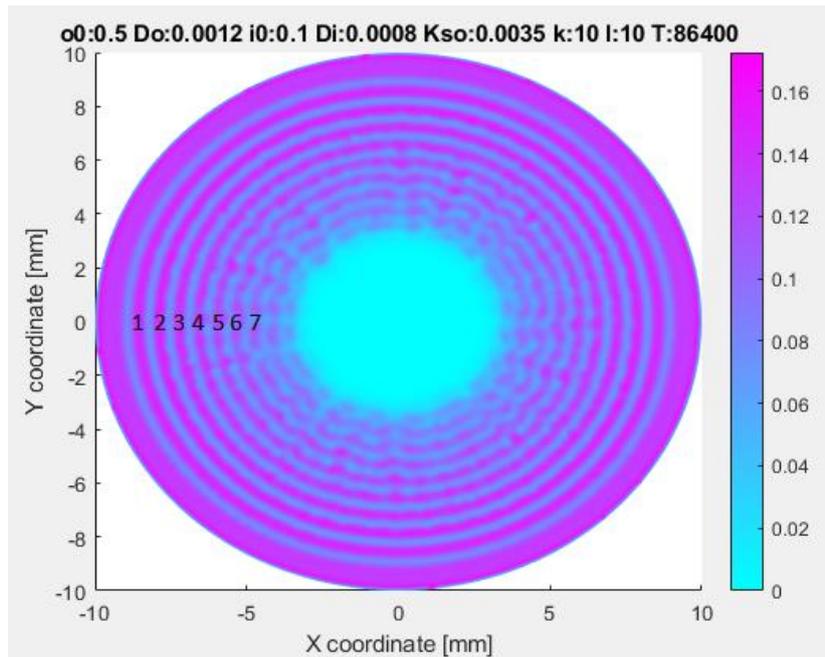


Fig. 1.5. Predicted bands in 2D model

Rys. 1.5. Wzorce przewidziane modelem 2D

Fig. 1.5 contains predicted rings in two dimensional circular geometry. The bands which can be interpreted as good precipitated product were marked. Outside precipitated product cannot be interpreted as ring because of high initial concentration of electrolytes. The seventh ring is not completely continuous but still can be interpreted as a ring since it is well visible. The inner bands cannot be interpreted as Liesegang ring because the concentration of product is low (may be not noticeable). In Table 1.3 parameters of precipitated bands with precipitation time are presented.

Table 1.3

Predicted bands in 2D model

band no.	position R [mm]	width [mm]	time [s]
1	8.54	0.4	840
2	7.87	0.4	1380
3	7.2	0.38	1980
4	6.58	0.35	2700
5	5.99	0.32	3540
6	5.43	0.31	4440
7	4.84	0.31	5520

Model was verified against time law (Fig. 1.6), width law (Fig. 1.7) and spacing law (Fig. 1.8). The model well describes the two-dimensional diffusion process – all laws verifications fits to linear dependency. Analogously to 1D model, values of R-square parameter were shown on figures.

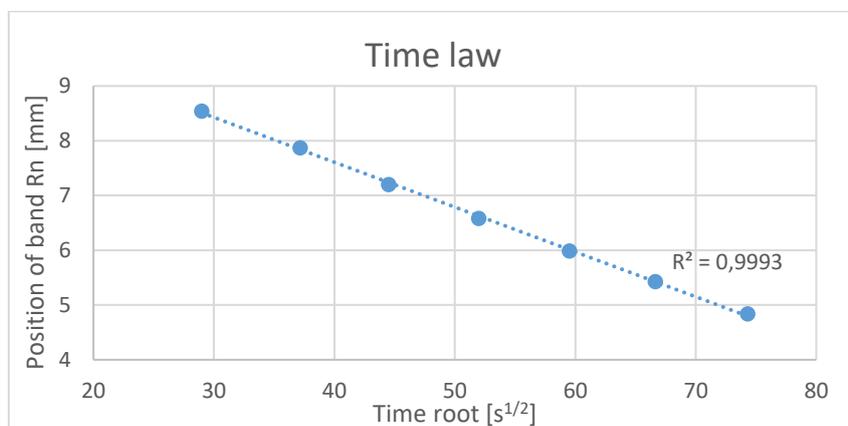


Fig. 1.6. Time law verification for 2D model

Rys. 1.6. Weryfikacja zależności odstępów czasowych dla modelu 2D

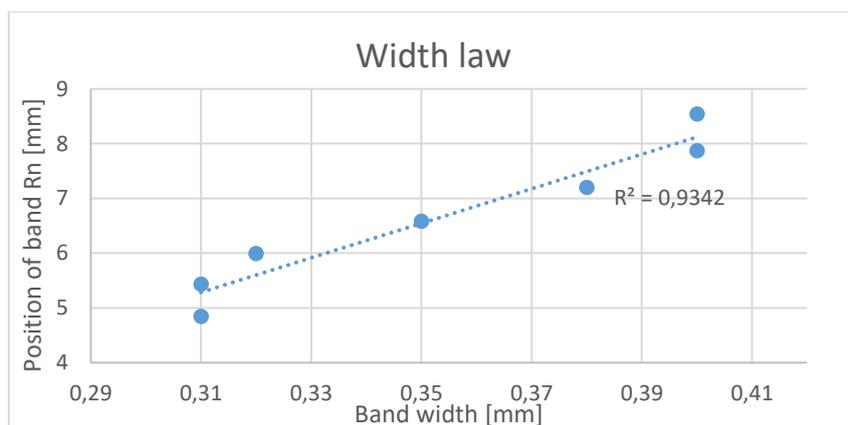


Fig. 1.7. Width law verification for 2D model

Rys. 1.7. Weryfikacja zależności grubości wzorców dla modelu 2D

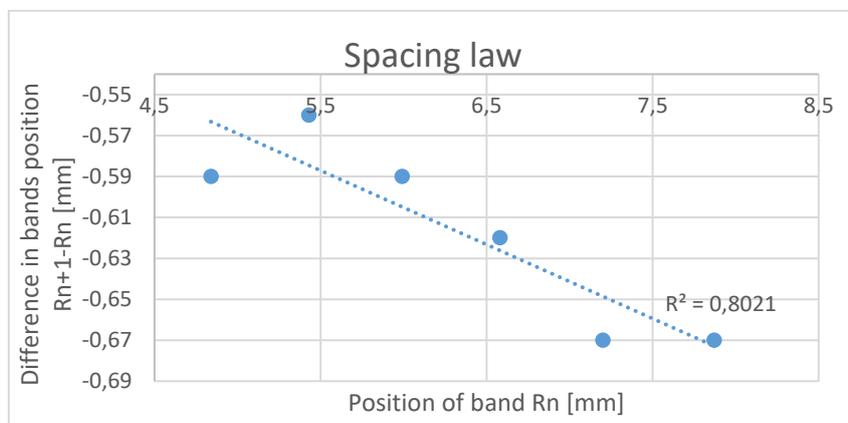


Fig. 1.8. Spacing law verification for 2D model

Rys. 1.8. Weryfikacja zależności odstępów między wzorcami dla modelu 2D

1.2. Conclusion

We have validated our diffusion – precipitation modeling procedures by predicting values of parameters of precipitation patterns, bands spacing, time occurrence of precipitation strips or rings and sizes of their widths. Parameters of the reactions obtained from the literature [5-8] were listed in Table 1.1 Predicted values versus experimental measurements are shown in Figures 1.2, 1.3, and 1.4 for 1D geometry and in Figures 1.6, 1.7 and 1.8 for 2D geometry of the reaction. One can see good correlation between predicted and measured values.

Our system is ready for further development concerning controlling times and shapes of precipitation patterns by boundary conditions.

Bibliography

1. M.I.I.L. Hideki Nabika, „Pattern Formation in Precipitation Reactions: The”, Langmuir, tom 36, pp. 481-497, 2020.
2. E. Ramírez-Álvarez, F. Montoya, T. Buhse, W. Rios-Herrera, J. Torres-Guzmán, M. Rivera, G. Martínez-Mekler, M.F. Müller, „On the dynamics of Liesegang-type pattern formation in a gaseous system”, Scientific Reports, tom 6, nr 23402, 2016.
3. K.S. Jinxing Jiang, „Formation of Ultrathin Liesegang Patterns”, Langmuir, tom 32, pp. 9126-9134, 2016.
4. H. Ni, M. Pan, K. Shi, „Preparation of isometric Liesegang patterns and application in multi-pulsed drug release system”, J Sol-Gel Sci Technol, nr 91, pp. 216-224, 2019.
5. D. Granjon, O. Bonny, A. Edwards, „Coupling between phosphate and calcium homeostasis: a mathematical model”, Renal Physiology, nr 313, pp. F1181-F1199, 2017.
6. S.C.A. Das, „Tracer diffusion studies in the system phosphoric acid-disodium hydrogen phosphate-water by a radioactive method”, Radiation Physics and Chemistry, nr 45, pp. 773-778, 1995.
7. H.S. Harne, H.W. Parker, „The Diffusion Coefficient of Calcium Chloride in Dilute and Moderately Dilute Solutions at 25°”, Journal of the American Chemical Society, nr 77, pp. 265-266, 1955.

8. S. Recillas, V.R. Lugo, M.L. Montero, S. Viquez, „Studies on the precipitation behavior of calcium phosphate solutions”, *Journal of Ceramic Processing Research*, nr 13, pp. 5-10, 2012.
9. J. George, I. Paul, P.A. Varughese, G. Varghese, „Rhythmic pattern formations in gels and Matalon–Packter law: A fresh perspective”, *Pramana*, nr 60, p. 1259-1271, 2003.
10. J. Crank, *The Mathematics of diffusion*, Oxford: Oxford university press, 1975.
11. H.W. Morse, G.W. Pierce, „Diffusion and Supersaturation in Gelatine”, *Physical Review (Series I)*, nr 17, p. 129, 1903.
12. T. Antal, M. Drozd, J. Magnin, Z. Rácz, M. Zrinyi, „Derivation of the Matalon–Packter law for Liesegang patterns”, *The Journal of Chemical Physics*, nr 109, p. 9479, 1998.
13. A. Büki, É. Kárpáti-Smidróczki, K. Meiszel, M. Zrínyi, „Experimental and theoretical investigation of static and dynamic chemical pattern formations in gels”, *Gels. Progress in Colloid & Polymer Science*, nr 102, pp. 110-117, 1996.
14. M. Al-Ghoul, R. Sultan, „Front Propagation in Patterned Precipitation. 1. Simulation of a Migrating $\text{Co}(\text{OH})_2$ Liesegang Pattern”, *The Journal of Chemical Physics*, nr 105, pp. 8053-8058, 2001.
15. H. Zhang, K. Zhan, Y. Chen, G. Chen, X. Zhou, J. Liu, M. Wu, H. Ni, „Three dimension Liesegang rings of calcium hydrophosphate in gelatin”, *Journal of Sol-Gel Science and Technology*, nr 71, pp. 597-605, 2014.

NUMERICAL MODELING OF THE LIESEGANG PRECIPITATION PATTERNS WITH LINEAR AND RADIAL GEOMETRIES

Abstract

We present a computational study of reaction – diffusion – precipitation systems for two types of geometries, linear and radial. The elaborated numerical procedures allow validations of reaction – diffusion – precipitation reactions modeling assumptions and fitting model parameters to data. We used results of our study for comparing computational predictions of the obtained precipitation patterns with experimental measurements. The main contribution of our research is creating a stable computational environment allowing predicting outcomes of both 1D and 2D diffusion – precipitation chemical reactions. One area of application of the elaborated computational

environment designing personalized, controlled drug release systems, where predicting/controlling shapes and positions of reaction fronts is of high importance.

Keywords: Reaction – diffusion systems, precipitation, Liesegang patterns, Drug release, Numerical modeling.