UDK (УДК) 554.723.212:546.76
JEL Classification: Q 24

Гумницький Ярослав Михайлович,
доктор технічних наук,
професор кафедри екології
та збалансованого природокористування
Національного університету «Львівська політехніка»
e-mail: jgumnitsky@ukr.net
ORCID ID : 0000-0003- 0464-9782

Сабадаш Віра Василівна,
кандидат технічних наук,
доцент кафедри екології та
збалансованого природокористування
Національного університету «Львівська політехніка»
e-mail: virasabadash@gmail.com
ORCID ID: 0000-0002- 6091-4053

Леськів Галина Зіновіївна,
кандидат технічних наук,
доцент кафедри менеджменту
Львівського державного університету внутрішніх справ
e-mail: galuna.leskiv2015@ukr.net
ORCID ID: 0000-0002- 4900-9466

МАТЕМАТИЧНА МОДЕЛЬ МІГРАЦІЇ ЗАБРУДНЕННЯ В ЕКОЛОГІЇ З РОЗГЛЯДОМ АДСОРБЦІЙНИХ ПРОЦЕСІВ

Анотація. Моделювання процесів міграції токсичних речовин у ґрунтах має величезне значення для забезпечення екологічної безпеки довкілля. У літературі представлено безліч моделей опису процесів міграції, але вони переважно мають теоретичний характер і не піддаються реалізації на практиці. Інший клас моделей базується на припущенні, що процес акумуляції забруднень у ґрунтах можна описати рівняннями для опису хімічних процесів першого, другого, псевдо другого та вищих порядків. У таких моделях процес взаємодії полютанта з ґрунтовим середовищем враховується з точки зору хімічної взаємодії, але зовсім не враховуються дифузійні процеси, що мають місце під час процесів міграції. У роботі проаналізовано проблеми забруднення навколишнього середовища важкими металами, мінеральними добривами як джерелами важких металів, оцінено ступінь забруднення важкими металами та антропогенне забруднення ґрунтового покриву, описані механізми накопичення рослинами важких металів, нормування токсичних речовин у ґрунті. Розроблено математичну модель для прогнозування міграції важких металів у ґрунтовому середовищі з урахуванням адсорбції. Запропонована модель дозволяє прогнозувати розподіл компоненту на межі розділу фаз тверде тіло-рідина у безрозмірній висоті шару сорбенту з урахуванням процесу адсорбції. Розроблена модель адекватна для зовнішньодифузійної області. Враховуючи, що встановлення рівноваги адсорбційної системи супроводжується процесами адсорбції та десорбції компоненту в шарі сорбента, у динамічних умовах адсорбційний процес буде ускладнюватися гідродинамікою рухомого матеріального потоку в шарі сорбента. Експериментальні дослідження процесу адсорбції катіонів важких металів у апараті колонного типу показали, що процес відбувається у зовнішньо дифузійній області. Критерій Біо в умовах експерименту становив Ві=900, коефіцієнт дифузії D=2,3·10⁻¹⁰ м²/с, коефіцієнт масовіддачі β=3·10⁻⁵ м/с. Порівняння експериментальних та теоретичних даних показало хорошу збіжність результатів та адекватність математичної моделі для її застосування для базового алгоритму у програмах для моделювання стану довкілля.

Ключові слова: важкі метали, міграція, адсорбція, грунт, математична модель.

Gumnitsky Jaroslav,

Doctor of Technical Sciences,
Professor Department of Applied Ecology
and Sustainable Environmental Management
Lviv Polytechnic National University,
e-mail: jgumnitsky@ukr.net
ORCID ID : 0000-0003- 0464-9782

Sabadash Vira,

Candidate of Technical Sciences (PhD),
Docent Department of Applied Ecology
and Sustainable Environmental Management,
Lviv State University of Internal Affairs,
e-mail: virasabadash@gmail.com
ORCID ID: 0000-0002- 6091-4053

Les'kiv Halyna,

Candidate of Technical Sciences (PhD),
Docent Department of Management,
Lviv State University of Internal Affairs,
e-mail: galuna.leskiv2015@ukr.net
ORCID ID: 0000-0002- 4900-9466

MATHEMATICAL MODEL OF MIGRATION OF POLLUTION IN THE ENVIRONMENT WITH CONSIDERATION OF ADSORPTION PROCESSES

Abstract. Simulation of the processes of migration of toxic substances in soils is of great importance for the environmental safety of the environment. The literature presents many models of description of migration processes, but they are predominantly theoretical and can not be implemented in practice. Another class of models is based on the assumption that the process of accumulation of soil contamination can be described by equations for the description of chemical processes of the first, second, pseudo second and higher orders. In such models, the process of interaction of the pollutant with the soil environment is taken into account from the point of view of chemical interaction, but does not take into account the diffusion processes taking place during the migration processes at all. The problem of environmental pollution with heavy metals, mineral fertilizers as sources of heavy metals, the degree of contamination by heavy metals and anthropogenic contamination of soil cover, the mechanisms of accumulation of heavy metals by plants, and the valuation of toxic substances in the soil are described. A mathematical model was developed for predicting the migration of heavy metals in the soil environment, taking into account adsorption. The proposed model allows to predict the distribution of the component at the interface between the solids and the liquid in the dimensionless height of the sorbent layer, taking into account the adsorption process. The developed model is adequate for the external diffusion region. Taking into account that the establishment of the equilibrium of the adsorption system is accompanied by adsorption and desorption processes of the component in the sorbent layer, under dynamic conditions the adsorption process will be complicated by the hydrodynamics of the moving material flow in the sorbent layer. Experimental studies of the process of adsorption of heavy metal cations in a column type device showed that the process takes place in the exterior diffusion region. Bio criterion in the experimental conditions was Bi = 900, diffusion coefficient $D = 2,3 \cdot 10^{-10}$ m²/s, coefficient of mass tansfer $\beta = 3 \cdot 10^{-5}$ m/s. The comparison of experimental and theoretical data showed good convergence of results and the adequacy of the mathematical model for its application for the basic algorithm in environmental modeling programs.

Key words: heavy metals, migration, adsorption, soil, mathematical model

Introduction

One of the key points of modern environmental regulation is the idea of the soil as a depositing and buffer environment on the path of man-made streams of harmful substances, in particular of heavy metals (Ltifi et al., 2017). This protective biosphere function of the soil has a barrier character in general, because at a distance of several centimeters of soil profile, acid and oxidation-reducing conditions, carbonate content can change significantly. The adsorption properties of the soil are equally important, as a result of which the largest amount of metal cations is concentrated in the upper layers of the

soil. Typically, soils with high adsorption capacity due to the content of organic matter and clay minerals are highly buffered in terms of translocation and water migration of such dangerous elements as Pb, Cd, Cu, Zn, Ni, Co, and others. Despite the reversal nature of ion-exchange processes, the desorption of soils absorbed by heavy metals in the natural environment is very weak and is determined primarily by the acidity of precipitation and soil solution. The main mechanisms of soil functioning as an adsorption barrier can be considered as ion exchange (with alkaline earth, alkaline and hydrogen leaching) and specifically sorption (with leaching of H +) (Burghardt & Schneider, 2018). Reactions of ion exchange of heavy metals and H + in soils are reversible. The absorption of heavy metal cations is accompanied by the removal of hydrogen cation from the so-called The soil picking complex, which is represented by aluminosilicates, humic and fulvic acids, leads to a decrease in the pH of the soil solution (Hunt et al., 1984). This, in particular, reduces the ionization of the groups -COO- and the negative charge of the colloids, the strength of the cations to the soil and influences the absorption of soil nutrients (Osmani & Bani, 2018). When the soluble metal salts (chlorides, nitrates, sulfates) enter the soil, the changes in the hydrolytic acidity of the solution are imposed on the process of diffusion (migration) (Volesky, & Holan, 1995).

The purpose of the study is to develop an adequate mathematical model for studying the processes of migration of toxic emissions in the soil environment, taking into account adsorption and experimental study of the migration of heavy metals by soil profile.

Methodology and equipment for conducting experimental research
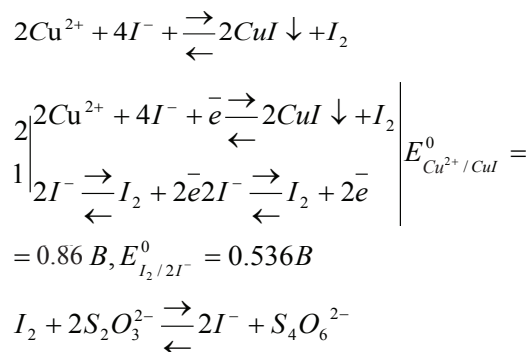
To investigate the mechanism of migration of heavy metals in the soil environment, we consider the zone with the concentration C^1 = const on the surface of the soil. The distribution of matter takes place in a stationary layer of soil with a porosity $\varepsilon = 0{,}4$. Medium pores are filled with water. To study migration of heavy metals in the soil environment, kumpanum sulfate was used. To ensure a constant concentration of Cu^{2+} on the surface of the soil, 50 g of salt was added to the measuring cells.

From the container, with the pipette, remove excess liquid (saturated solution) and filter. Select 5 ml., filtrate and analyze it (Ure, 1990).

Samples of soil are taken at a depth of 1, 5, 10, 15, 20 and 25 cm from the surface.

Weigh is weighed, placed in a 250 ml flask. and 100 mL of distilled water was added.

Method of determination of Cu^{2+} in solution. The following reactions are the bases of the determination

$$2Cu^{2+} + 4I^- + \underset{\longleftarrow}{\longrightarrow} 2CuI \downarrow + I_2$$

$$2\begin{vmatrix} 2Cu^{2+} + 4I^- + \overline{e} \underset{\longleftarrow}{\longrightarrow} 2CuI \downarrow + I_2 \\ 1 \begin{vmatrix} 2I^- \underset{\longleftarrow}{\longrightarrow} I_2 + 2\overline{e} 2I^- \underset{\longleftarrow}{\longrightarrow} I_2 + 2\overline{e} \end{vmatrix} \end{vmatrix} E^0_{Cu^{2+}/CuI} =$$

$$= 0.86\, B, E^0_{I_2/2I^-} = 0.536 B$$

$$I_2 + 2S_2O_3^{2-} \underset{\longleftarrow}{\longrightarrow} 2I^- + S_4O_6^{2-}$$

To reduce the flow of KI to the copper (II) solution add a mixture of KI + KCSN. At the same time, the following reaction proceeds

$$2Cu^{2+} + 2I^- + 2CSN^- \underset{\longleftarrow}{\longrightarrow} 2CuSCN \downarrow + I_2$$

Starch solution is the indicator.

Progress of analysis. In a flask with the analyzed solution Cu^{2+} add 10 ml of IM solution of H_2SO_4, 10 ml of K1 + KSSN mixture and immediately titrate with sodium thiosulfate solution until the transition of the yellow-brown coloration to light yellow. Then add 5 ml of starch solution and continue to titrate until the transition of the blue color to the lilac (pinkish-white color of the *CuCSN* precipitate). Record the volume of thiosulfate sodium spent on titration, and calculate the amount of copper (II) in solution.

1. Physical model of the process of migration of heavy metals in soils

The process of migration of heavy metals in the soil is divided into several stages:

– diffusion of solvent molecules to a source of pollution;

– solvation of heavy metal ions;

– dissociation of the compound from the area of C = Cs to C = C1, with 0 <C1 <Cs.

When dissolving the compound in the system there are mutually opposite flows – the flow of of the dissolved substance and the flow of solvent. When crossing these two streams, a diffusion resistance is created, which slows down the process of mass transfer of the component in the volume of the soil environment.

When dissolving compounds of heavy metals, depending on the product of their solubility, to a greater or lesser extent, there is a change in the density of the liquid. The gravity, surface tension and intermolecular interaction of water molecules and solvated heavy metal ions with the pore surface, i.e., adsorption, and

friction forces, are applied to the liquid. Since the diameter of the pores is quite significant – $d_e = 2 \cdot 10^{-3}$ m, then the forces of surface tension can be neglected. In the conditions of the task set for the study of migration of heavy metal components in the soil environment, the concentration of $CuSO_4$ is 3450 kg / m³, and the difference in the densities of the saturated solution and pure substance $\rho_s - \rho_B = 110$ kg/m³, which means that the flow will have a significant effect of the acceleration of the earth's gravity. Consequently, the hypothetical migration of a component in a soil environment in the negative direction of the Z axis will pass through the mechanism of turbulent diffusion. In the case of diffusion in a horizontal direction along the x and y axes, the gravitational contribution will be somewhat reduced, and if we consider a section of infinitesimal height with respect to the Z axis, then the effect of gravity forces will be leveled. Thus, one can expect the process to pass through the mechanism of molecular diffusion. When diffusion of a component from a thicker soil to its surface on the solution will be significantly affected by gravity, and at $C \approx C_s$, that is, at the upper boundary of the layer of salt will create significant resistance in the diffusion of the component, which reduces the motive force of the process.

Recently, much attention is devoted to the development of effective numerical schemes for constructing approximate solutions of problems of migration of impurities with dominant convection. In this case, solutions of tasks can have internal and boundary layers - very narrow areas, where the solutions themselves and their gradients change sharply. As a result, numerical solutions based on the Galerkin scheme, where the sampling parameter is too large to take into account all these layers, can strongly oscillate throughout the definition area. In order to achieve a satisfactory approximation, you must use the values of the sampling parameter to be proportional to the ratio between diffusion and convection. In many cases, such an approach leads to an enormous amount of degrees of freedom, and thus to the impossibility of effectively finding a numerical solution. Therefore, many authors proposed different counter-flow schemes of the finite element method (FEM), which are based on the addition of a certain amount of artificial diffusion in the direction of flow to the original numerical circuit. The most widely used anti-flow scheme of the Petrova-Galerkina method and approach based on the concept of functions-bubbles. Recent studies [20] suggest that these approaches are equivalent.

An important point in assessing the migration of heavy metals is the mathematical interpretation of the process, which allows really calculating the rate of penetration of heavy metals into the environment.
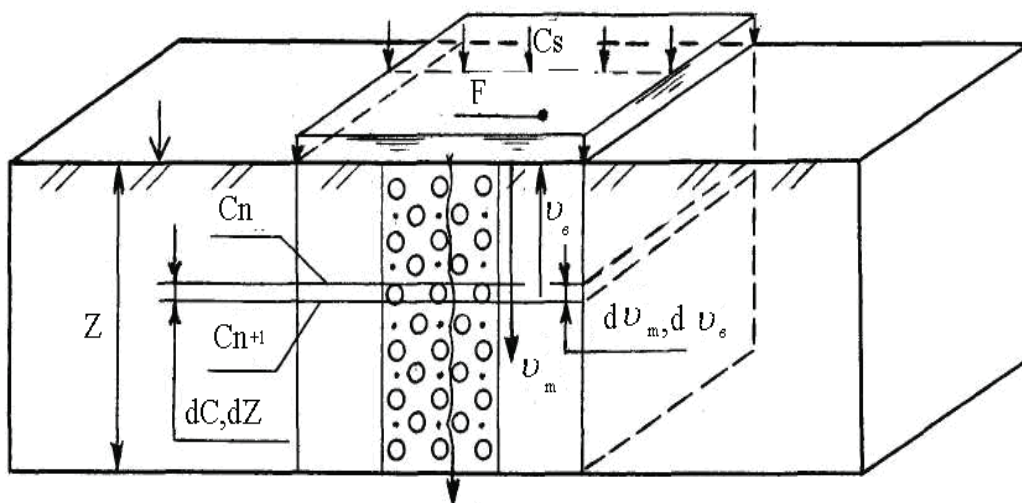

Fig. 1. Схема міграції водного розчину важких металів у ґрунті

Z – the calculated layer of soil; F –area unit, m²; υ_m – velocity of the VM solution m / s;

q_m – specific costs of a solution of VM with a concentration of C.

The process of diffusion of heavy metals by a system of equations to be described:

$$\begin{cases} \dfrac{\partial C}{\partial \tau} = D \cdot \dfrac{\partial^2 C}{\partial z^2} \\ C(0,0) = C_{n0} \\ C(\infty, \tau) = 0 \\ \left(\dfrac{\partial C}{\partial z} \right)_{z=\infty} = 0 \end{cases} \qquad (1)$$

Having applied the method of separating the variables for the solution of this system, taking $a^2 = D$, we obtain the value of concentration at the time τ at a distance Z from the surface of the soil (Gumnitsky at al., 2009).

$$C(Z, \tau) = \int_0^\infty e^{-a^2 \lambda^2 \tau} [C_1 \cos \lambda Z + C_2 \sin \lambda Z] d\lambda \quad (2)$$

where λ – constant ones that need to be found for a given differential equation.

By integrating the equation over λ in the range from 0 to ∞ and substituting the constant integer values C_1 and C_2 into the equation, we obtain:

$$C(Z, \tau) = \frac{1}{\pi} \int_0^\infty e^{-a^2 \lambda^2 \tau} \int_{-\infty}^\infty [\phi(\alpha) \cos \lambda (\alpha - Z) d\alpha] d\lambda \quad (3)$$

Having made a substitution $a\lambda\sqrt{\tau} = x$ $\dfrac{a - Z}{\alpha\sqrt{\tau}} = \beta$ we calculate the following

$$K(\beta) = \int_0^\infty e^{-a^2 \lambda^2 \tau} \cos \lambda (\alpha - Z) d\lambda$$

$$K(\beta) = \frac{\sqrt{\pi}}{2} e^{-\frac{\beta^2}{4}} \qquad (4)$$

If substitute (4.4) to (4.3) we will obtain the following:

$$\int_0^\infty e^{-a^2 \lambda^2 \tau} \cos \lambda (\alpha - Z) d\lambda = \frac{1}{2a} \sqrt{\frac{\pi}{\tau}} e^{-\frac{(\alpha - Z)^2}{4a^2 \tau}} \qquad (5)$$

If substitute (4.5) to (4.2) we will obtain the following:

$$C(Z, \tau) = \frac{1}{2a\sqrt{\pi\tau}} \int_0^\infty f(\phi) e^{\frac{(Z - \varphi)^2}{4a^2 \tau}} - e^{\frac{(Z - \varphi)^2}{4a^2 \tau}} d\varphi \quad (6)$$

where φ, α – constant ones that need to be found for a given differential equation.

After integrating equation (6), by substituting the initial conditions, we obtain an expression for determining the concentration of the released component at a distance Z from the surface of the soil at the time τ:

$$\frac{C_n - C}{C_n} = erf \left(\frac{Z}{2a\sqrt{\tau}} \right) \text{ by substituting to } a^2 = D$$

we will obtain:

$$\frac{C_n - C_0}{C_n} = erf \left(\frac{Z}{2\sqrt{D\tau}} \right)$$

whereof $\qquad C = C_\Pi \left(1 - erf \left(\frac{Z}{2\sqrt{D\tau}} \right) \right) \qquad (7)$

At the initial time τ_0 the mass of the dissolved heavy metal salt $\qquad M_0 = F dZ \cdot C_{\Pi 0}$, where F – is the surface area of the particle of the heavy metal salt.

At the time τ $\quad M = F dZ \cdot C_\Pi$

$M = jF \tau$

$M_0 - M = M_0 - jF \tau$

Given that the density of the mass flow is:

$$J_F = -D \cdot \left(\frac{\partial C}{\partial z} \right)_{z=0} \cdot \varepsilon \cdot F \qquad (8)$$

where ε – porosity of the soil.

$$M_0 - M = \int_0^\tau -D \cdot \left(\frac{\partial C}{\partial z} \right)_{z=0} \cdot d\phi$$

$$1 - \frac{M}{M_0} = \frac{1}{M_0} \int_0^\tau -D \cdot \left(\frac{\partial C}{\partial z} \right)_{z=0} \cdot d\phi$$

$$\frac{C_\Pi}{C_{\Pi 0}} = 1 - \frac{1}{M_0} \int_0^\tau -D \cdot \left(\frac{\partial C}{\partial z} \right)_{z=0} \cdot d\phi$$

The solution will look the following:

$$C_\Pi = C_{\Pi 0} - \frac{2 \cdot \varepsilon}{M_0} \cdot \sqrt{\frac{D}{\pi}} \cdot \sqrt{\tau} \qquad (9)$$

Average concentration of metal ion in the soil solution $C^* = \dfrac{M_0}{\varepsilon}$

$$C_\Pi = C_{\Pi 0} - \frac{2}{C^*} \cdot \sqrt{\frac{D}{\pi} \cdot \sqrt{\tau}} \qquad (10)$$

By substituting expression (10) to (7) we obtain an equation for calculating the concentration of heavy metals at a depth Z from the surface of the soil

$$C = \left(C_{\Pi 0} - \frac{2}{C^*} \cdot \sqrt{\frac{D}{\pi}} \cdot \sqrt{\tau} \right) \cdot \left(1 - erf \cdot \frac{z}{2 \cdot \sqrt{D \cdot \tau}} \right) (11)$$

The mass transfer process of the released component runs smoothly, in the form of the so-called diffusion front, in a zone of length l=Z, which, in the experiment, is limit`ed to the overall dimensions of the measuring cell. At the initial time in all areas of the measuring cell, the concentration of the target component will be zero.

The change of the diffusion front in time is the curves for the distribution of the concentration of the released component in a solution placed in the pores of an inert medium along the length l of immovable layer of wet granular material, with $\tau_1 < \tau_2 < \tau_3$ …where $<\tau_i$ is the time. Taking into account that the establishment of system equilibrium is accompanied by processes of adsorption and desorption of a component in a sorbent layer, under dynamic conditions the adsorption process will be complicated by the hydrodynamics of the moving material flow in the sorbent layer (Harmsen, 2017).

The distribution of adsorbate in the sorbent layer was calculated by the following equation:

$$1 - \frac{C}{C_0} = \frac{1}{2} \left[1 + erf \frac{Fo - \omega}{\sqrt{\frac{4}{3} \omega \left(\frac{1}{Bi} + \frac{1}{5} \right)}} \right] \qquad (12)$$

where C_0 and C – the initial and running concentration of adsorbate in solution; μ_n – the roots of the characteristic equation; Fo – Fourier criterion; $Fo = \frac{D_{e\phi} \cdot t}{R^2}$; D – diffusion coefficient, m²/s;

$$\omega = (1 + A) \frac{\sigma D x}{\upsilon R^2} \qquad (13)$$

A – parameter that considers the phenomenon of adsorption. For processes that are not accompanied by adsorption A=0; x – height of the layer, m; R – particle radius, m; υ – flow rate in the layer; σ – porosity of sorbent, m³/m³.

2. Experimental studies of heavy metal migration

Investigation of the mechanism of migration of heavy metals in a soil environment with a concentration of C_1 = const on the soil surface was conducted according to the procedure described in section 2. The distribution of matter occurs in a fixed layer of soil with porosity ε = 0,4:

– from the surface of the measuring cell to the volume of the medium in the negative direction of the Z axis;

– along the horizontal plane of the cell, that is, in the direction of the X axis;

– from the bottom of the cell to the surface, that is, in the positive direction of the Z axis.

Medium pores are filled with water. To study the migration of heavy metals migration in the soil environment, kurpum sulfate was used. To ensure a constant concentration of Cu^{2+} on the surface of the soil, 50 g of salt was added to the measuring cells. Experimental studies of the adsorption process of heavy metal cations in the experimental conditions have shown that the process takes place in the exterior diffusion region. The Bio criterion in the experimental conditions was Bi = 900, the diffusion coefficient D=1·10⁻¹⁰m²/s, the coefficient of mass return β=3·10⁻⁵m/s [2]. Comparison of the calculated data and experimental results on an example of adsorption of Cu (II) ions is shown in Fig. 2, 3, 4.

Analyzing the data of experimental research with the help of the solution of the mathematical model, the value of the diffusion coefficient Cu^{2+} in the soil environment on the vertical profile was obtained in the negative direction of the coordinate axis Z – D=2·10⁻⁶ Fig. 2. This indicates the migration of the component in the soil environment by the mechanism of turbulent mass transfer.

Distribution of Cu^{2+} concentration on the profile of the soil along the horizontal plane of the cell in the direction of the X axis at t = const, fig.3. It also passes through the mechanism of turbulent diffusion, which indicates the value of the diffusion coefficient – D=1·10⁻⁷. This is explained by the fact that the solution, which diffuses in the pores of the soil environment, is significantly heavier than water, and the gravitational force will have an effect on the velocity of the diffusion front.

The results of the study of the migration process of the component up along the soil profile indicate that there is a molecular diffusion of the dissolved component in the soil environment, although the process will be slowed down by the force of gravity and hydrostatic pressure of the liquid in the pores of the soil environment. Coefficient of diffusion of Cu^{2+} in the soil environment on the vertical profile in the positive direction of the coordinate axis D=2,27·10⁻¹¹ (Sabadash at al., 2017).

The calculation of the value of the mean-square deviation showed that this value varies within 5–7%.
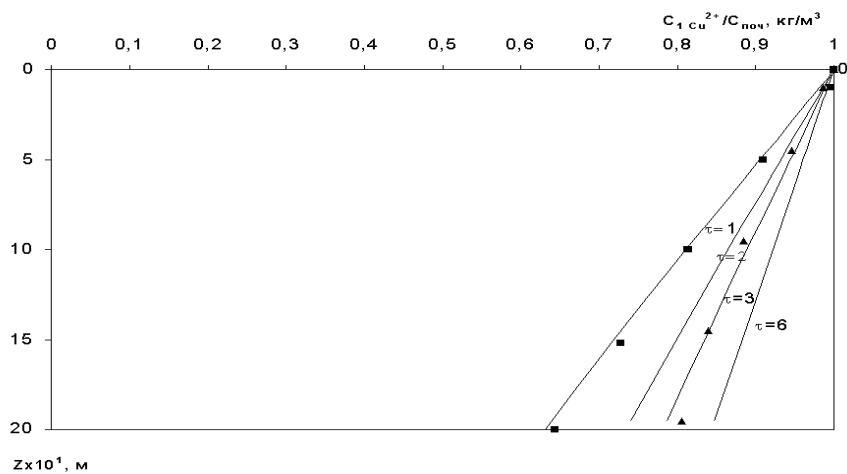
Fig. 2. Distribution of the concentration of Cu^{2+} by the profile of the soil from the surface
of the measuring cell in the volume of the medium in the negative direction of the Z axis at t=const,
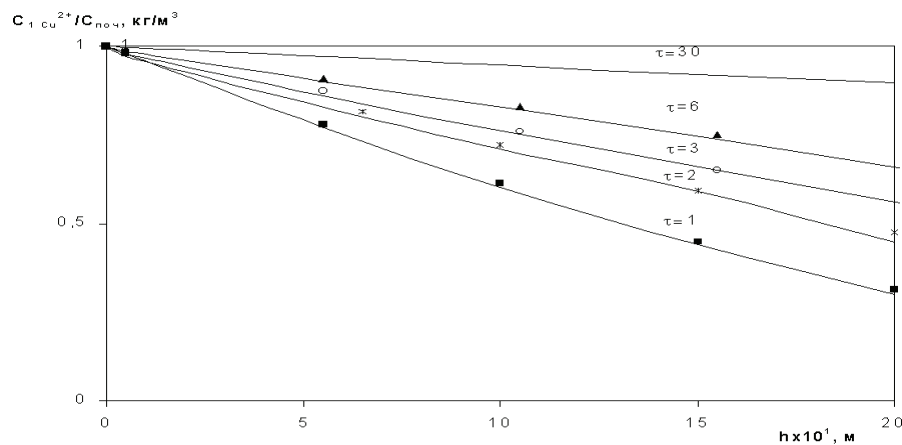bottom, where ■– τ=3, ▲ - τ=6, D=2·10^{-6}.

Fig. 3. Distribution of the concentration of Cu^{2+} by the profile of the soil along the horizontal plane
of the cell in the direction of the X axis at t=const, bottom,
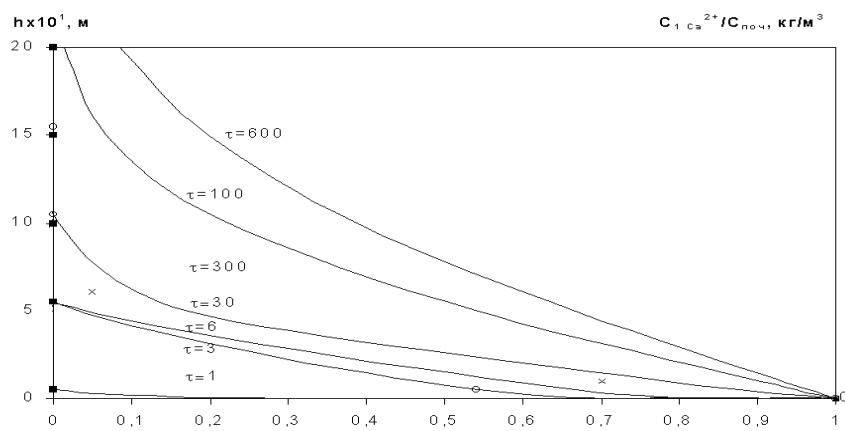where ■– τ=1, *- τ=2, ○- τ=3, ▲ - τ=6, D=1·10^{-7}.

Fig. 4. Distribution of the concentration of Cu^{2+} by the profile of the soil from the bottom
of the cell to the surface in the positive direction of the Z axis at t=const, bottom,
where ■– τ=1, ○- τ=3, x- τ=30, D=2,27·10^{-11}.

Conclusion

Comparison of theoretical and experimental data indicates a satisfactory convergence of results. The correspondence of the developed mathematical model with experimental data points to the validity of the simplifications introduced and allows prediction of the time and speed of migration of soil contamination with sufficient accuracy for practical purposes.

List of references

1. Ltifi A., Saidi N., Rabhi M. and other. Paper Industry Effluent Short and Long Effect on Soil Heavy Metals Accumulation and Phytoremediation. In *Euro-Mediterranean Conference for Environmental Integration*. 2017. November. P. 583–584). Springer, Cham.
2. Burghardt W., Schneider, T. Bulk density and content, density and stock of carbon, nitrogen and heavy metals in vegetable patches and lawns of allotments gardens in the northwestern Ruhr area, Germany. *Journal of Soils and Sediments*. 2018. № 18 (2). P. 407–417.
3. Osmani M., Bani, A. Heavy metals concentration of dumping site soils and their accumulation in Alyssum Murale growing in selected dumping sites in Albania. *Thalassia Salentina*,. 2018. № 39. P. 83–98.
4. Volesky B., Holan, Z. R. Biosorption of heavy metals. *Biotechnology progress*. 1995. № 11 (3). P. 235–250.
5. Hunt A., Jones J., Oldfield F. Magnetic measurements and heavy metals in atmospheric particulates of anthropogenic origin. *Science of the Total Environment*. 1984. № 33 (1–4). P. 129–139.
6. Ure A. M. Methods of analysis of heavy metals in soils. *Heavy metals in soils*. 1990. № 14. P. 40–80.
7. Gumnitsky J. M., Sabadash V. V., Venher L. O. Doslidzhennya mihratsiyi mineralnykh rechovyn u gruntovomu seredovyshchi za postiynoyi kontsentratsiyi. *Scientific Bulletin of NULP*. 2009. № 644. P. 192–194.
8. Harmsen K. Long-term behavior of heavy metals in agricultural soils: a simple analytical model. *Biogeochemistry of trace metals*. 2017. P. 229–260. CRC Press.
9. Sabadash V., Mylanyk O., Matsuska O., Gumnitsky J. Kinetic regularities of copper ions adsorption by natural zeolite. *Chemistry & Chemical Technology*. 2017. № 11 (4). P. 459–462.
10. Paper Industry Effluent Short and Long Effect on Soil Heavy Metals Accumulation and Phytoremediation / A. Ltifi, N. Saidi, M. Rabhi and other. *Proceeding of Euro-Mediterranean Conference for Environmental Integration* (Sousse, Tunisia, 10–25 November 2017). 2017. P. 583–584.
11. Burghardt W. Bulk density and content, density and stock of carbon, nitrogen and heavy metals in vegetable patches and lawns of allotments gardens in the northwestern Ruhr area, Germany / W. Burghardt, T. Schneider. *Journal of Soils and Sediments*. 2018. №18. P. 407–417.
12. Osmani M. Heavy metals concentration of dumping site soils and their accumulation in Alyssum Murale growing in selected dumping sites in Albania. / M. Osmani, A. Bani. *Thalassia Salentina*. 2018. № 39. P. 83–98.
13. Volesky B., Holan Z. Biosorption of heavy metals. *Biotechnology progress*. 1995. № 11. P. 235–250.
14. Hunt A., Jones J., Oldfield F. Magnetic measurements and heavy metals in atmospheric particulates of anthropogenic origin. *Science of the Total Environment*. 1984. № 33. P. 129–139.
15. Ure A. M. Methods of analysis of heavy metals in soils. *Heavy metals in soils*. Glasgow: Blackie & Son Ltd., 1990. P. 40–80.
16. Гумницький Я. М., Сабадаш В. В., Венгер Л. О. Дослідження міграції мінеральних речовин у ґрунтовому середовищі за постійної концентрації. *Вісник Національного університету «Львівська політехніка». Хімія, технологія речовин та їх застосування*. 2009. № 644. С. 192–194. [Humnytskyi Ya. M., Sabadash V. V., Venher L. O. Doslidzhennia mihratsii mineralnykh rechovyn u gruntovomu seredovyshchi za postiinoi kontsentratsii *(Gumnitsky J. M. Investigation of migration of mineral substances in the soil environment at constant concentration)*. *Visnyk Natsionalnoho universytetu «Lvivska politekhnika». Khimiia, tekhnolohiia rechovyn ta yikh zastosuvannia (Bulletin of the National University «Lviv Polytechnic». Chemistry, technology of substances and their application)*. 2009. № 644. P. 192–194.] [in Ukr.]
17. Harmsen K. Long-term behavior of heavy metals in agricultural soils: a simple analytical model. *Biogeochemistry of trace metals*. 2017. London: CRC Press., 1990. P. 229–260.
18. Sabadash V., Mylanyk O., Matsuska O., Gumnitsky J. Kinetic appropriateness of copper ions adsorption on natural zeolite. *Chemistry & Chemical Technology*. 2017. Vol. 11, Number 4. P. 459–462.