

## USE OF MODIFIED ADSORBENTS TO REMOVE PESTICIDES FROM WASTEWATER

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**Abstract.** The migration of highly concentrated pesticide solutions in the soil has been experimentally studied. A mathematical model of the diffusion process in the soil environment has been developed. Based on the mathematical model, a system of equations for calculating the duration and intensity of the process depending on environmental parameters was obtained. The dependence of the process velocity on the direction of the diffusion front is determined, and the diffusion coefficients, kinetic coefficients of the diffusion process and the diffusion front velocity were calculated. Environmental aspects of pesticide migration were analysed. The diffusion coefficient of glyphosate in the model soil environment is established. Under the experimental conditions, the diffusion coefficient value was  $D = 1.755 \cdot 10^{-12} \text{ m}^2/\text{s}$ . The study results of the process of migration of the component up the soil profile indicate the mechanism of molecular diffusion of glyphosate in the soil environment. The results of experimental research and the solution of the mathematical model were used to model the migration process in the Comsol Multiphysics environment. Analysis of theoretical and experimental results showed that the developed model could be used to calculate the dynamics of the spread of the pesticide front in the soil with sufficient accuracy.

**Keywords:** diffusion, pesticides, soil, groundwaters, environmental protection.

## 1. Introduction

The discovery of pesticides - chemicals used to protect plants and animals from various pests and diseases - is one of the most significant achievements of modern science. Today in the world on 1 hectare. 300 kg of

chemicals are used. However, long-term use of pesticides in agriculture (pest control) is almost universally less effective, as resistant pests develop and “new” problems spread, whose natural enemies and competitors have been destroyed by pesticides. At the same time, the effects of pesticides have begun to manifest themselves on a global scale (Rajmohan et al., 2021; Jiang et al., 2022). Of the considerable number of insects, only 0.3 % or 5.000 species are harmful. Resistance to pesticides was found in 1.250 species. There is also a phenomenon of cross-resistance, i.e. increasing resistance to one active ingredient is accompanied by resistance to active ingredients of other classes. From a general biological point of view, resistance can be considered a change in populations resulting from the transition from a susceptible strain to a resistant strain of the same species due to selection caused by pesticides. This phenomenon is associated with organisms' genetic, physiological and biochemical changes (Lopes-Ferreira et al., 2022; Kang et al., 2017).

Excessive use of pesticides (herbicides, insecticides, defoliants) affects soil quality. In this context, the fate of pesticides in soils and the possibility of their destruction by chemical and biological means is being intensively studied. Producing and using only active ingredients with a short shelf life is essential, measured in weeks or

months. In this case, some progress has already been made, and agents with a high rate of destruction are being introduced, but the problem has not yet been resolved (Borgohain et al., 2020; Wongmaneepratip et al., 2022).

Ways of glyphosate degradation (Roundup) in the environment and plants include photochemical and chemical decomposition and destruction by microorganisms. When using preparations based on glyphosate, there is no air pollution due to evaporation of the active substance from the surface of soil, plants or water due to the low volatility of the chemical substance (vapour pressure  $1.31 \cdot 10^{-2}$  MPa at 25 °C) (Arias-Estévez et al., 2008; Jiang et al., 2022). The low value of the Henry glyphosate constant ( $E = 2.1 \cdot 10^{-7}$  Pa·m<sup>3</sup>/mol) indicates the possibility of glyphosate migration from air to water and rapid adsorption of glyphosate on soil particles. Glyphosate has a high solubility in water (12 g/l at 25 °C) and a very low partition coefficient in the n-octanol-water system ( $\log P < -3.2$  at pH 2-5; 20 °C). The solubility of glyphosate in water is 105 g/l at pH 19; 20 °C; ammonium salt -  $(144 \pm 19)$  g/l at pH 32; (Lopes-Ferreira et al., 2022) isopropylamine salt – 1050 g/l at pH 4.3; 25 °C. Glyphosate is chemically stable in water and causes contamination of groundwater with this herbicide. The bulk quantity of glyphosate found in surface water sources results from leaching from the surface of treated plants, wear during agricultural or forestry herbicide application and intentional or unintentional direct treatment of water sources to kill aquatic weeds. Glyphosate can be transported several kilometres downstream by water flow from the treatment site in the form of suspended solid particles when applied directly to water sources (Hyvlud et al., 2019; Borgohain, et al., 2020).

The decrease in the amount of glyphosate and primary metabolite is mainly due to the adsorption of the substance by precipitation and decomposition by microorganisms. The decomposition rate of glyphosate in water is usually less than in soil. There are far fewer microorganisms in water than in most soil types. Although glyphosate is quite soluble in water, it, unlike most water-soluble herbicides, has an extremely high ability to bind soil particles. This ability increases with increasing clay soil content, and soil cation exchange capacity decreases pH and phosphate (Srivastav et al., 2013; Jiang et al., 2022). The main factor determining the amount of glyphosate isolated by soil particles is the level of ophosphate in the soil, which leads to the binding of herbicide molecules. Glyphosate competes with inorganic phosphate for soil binding centres; the

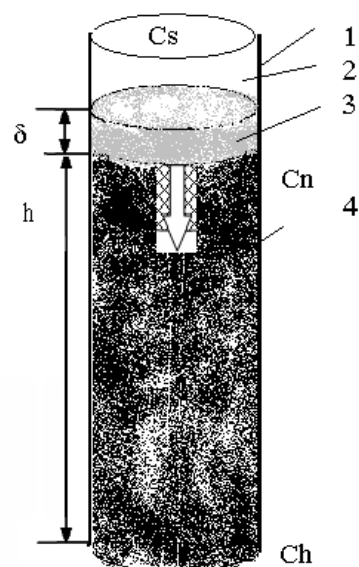
degree of its binding depends on the availability of unoccupied acute centres. In the adsorbed state, glyphosate shows no herbicidal activity (Ajiboye et al., 2022; Yorlano et al., 2022; Sabadash et al., 2017). Depending on the type of soil, the half-life of glyphosate in the ground, as determined by US EPA, is 3 to 130 days, which poses a threat to the environment.

The work aims to study the mechanism of diffusion of pesticides and their metabolites in the soil environment and determine the diffusion coefficient of the component in the dispersed solid-liquid system in the steady-state.

## 2. Experimental part

### 2.1. Methods for studying the migration of pesticides in the soil environment

To study the migration of pesticides in the environment, we research the example of glyphosate. The research installation we arranged as the measuring cell with an area of  $F = 0.023$  m<sup>2</sup> was filled with sand (porosity 0.4). The height of the layer of granular material was  $h = 0.2$  m. Glyphosate was sprayed on the surface of the model soil for  $3.45 \cdot 10^{-6}$  l. This concentration of glyphosate corresponds to the application rate of 1.5 l/ha.



**Fig. 1.** Experimental installation for the study of fertiliser migration,

where 1 – cell housing; 2 – saturated solution; 3 – the source of pollution; 4 – soil;  $C_s$  – saturation concentration;  $C_n$  – concentration on the surface of contact with the head of contamination;  $C_h$  – concentration at a distance  $h$  from the source of pollution

The concentration of glyphosate and its metabolites in the soil was determined by liquid chromatography.

## 2.2. Mathematical model of pesticide distribution in soil

The main task was to develop a mathematical model of pesticides on the ground.

When compiling a mathematical model, a particle of spherical shape is considered.

The mathematical model of glyphosate migration in soil solution includes the material balance equation and a system of kinetic equations describing mass flows in the middle of the capsule, through the polymer shell and in an inert moist environment.

Equation of material balance at any time  $\tau$  :

$$\begin{aligned} \frac{4}{3}\pi R^3 \rho_T &= \frac{4}{3}\pi r^3 \rho_T + \\ &+ \frac{4}{3}\pi(R^3 - r^3) \frac{(C_s + C_h)}{2} + W\varepsilon \bar{C}_1. \end{aligned} \quad (1)$$

Write the expression for mass flows in the soil:

$$-\frac{dM}{d\tau} \frac{1}{F} \frac{R-r}{D_3} = C_s - C_h, \quad (2)$$

In the soil solution:

$$-\frac{dM}{d\tau} \frac{1}{F} \frac{\delta}{D_2} = C_h - C_n, \quad (3)$$

and in the environment:

$$-\frac{dM}{d\tau} \frac{1}{F} \frac{l}{D_1} = C_n - C_1. \quad (4)$$

The solution of this system will be the equation:

$$\frac{dM}{d\tau} = \frac{1}{\frac{R-r}{D_3} + \frac{\delta}{D_2} + \frac{l}{D_1}} F(C_s - C_1). \quad (5)$$

Moreover  $C_1 = \bar{C}_1$ , where  $\bar{C}_1$  the average concentration of the released component in the inert medium will be equal:

$$\begin{aligned} \bar{C}_1 &= \frac{\int_0^l C_1 dl}{l-R}, \\ \frac{dM}{d\tau} \frac{1}{F} \left( \frac{R-r}{D_3} + \frac{\delta}{D_2} + \frac{l}{D_1} \right) &= C_s - \bar{C}_1. \end{aligned} \quad (6)$$

To describe the migration process, we equate the equations of mass flows (2) and (3)

Summarising the system of equations, we obtain:

$$\frac{dM}{d\tau} = \frac{1}{\frac{R-r}{D_3} + \frac{\delta}{D_2}} F(C_s - C_n). \quad (7)$$

Mass flow of the released component in the environment:

$$\frac{dM}{d\tau} = -D_1 \varepsilon F \frac{dC_1}{dl}, \quad (8)$$

where F is the area through which the element diffuses in the granular medium.

Therefore, equation (6) will take the form:

$$\frac{dM}{d\tau} = -D_1 \varepsilon 4\pi l^2 \frac{dC_1}{dl}. \quad (9)$$

To find the concentration of the released component in an inert medium, equate equation (9) to the sum of mass (7), we obtain:

$$-D_1 \varepsilon 4\pi l^2 \frac{dC_1}{dl} = k_1 F(C_s - C_n), \quad (10)$$

where

$$k_1 = \frac{1}{\frac{R-r}{D_3} + \frac{\delta}{D_2}}. \quad (11)$$

Assuming that  $C_n = \text{const}$ , which corresponds to the stationary conditions of the process, equation (9) can be integrated within  $l = R$ ,  $C_1 = C_n$  at  $l = R$ ,  $C_1 = C_1$

$$\int_{C_n}^{C_1} dC_1 = \frac{k_1 F(C_s - C_n)}{4\varepsilon\pi D_1} \int_{l=R}^l \frac{dl}{l^2}, \quad (12)$$

$$C_1 = C_n - \frac{k_1 F(C_s - C_n)}{4\varepsilon\pi D_1} (l - R). \quad (13)$$

Equation (13) includes the saturation concentration of  $C_n$ , which can be determined by equating the mass flows (2) and (3):

$$\frac{D_3}{R-r}(C_s - C_h) = \frac{D_2}{\delta}(C_h - C_n), \quad (14)$$

from which we find  $C_n$ :

$$C_n = C_h - \frac{D_3}{D_2} \frac{\delta}{R-r} (C_s - C_h). \quad (15)$$

The following equation describes the decomposition reaction of glyphosate:

$$\frac{dC_{\text{glyphosate}}}{d\tau} = -k_1 C_{\text{glyphosate}}. \quad (16)$$

The reaction of formation of glyphosate metabolites is described as follows:

$$\frac{dC_{\text{AMPA}}}{d\tau} = k_2 C_{\text{glyphosate}}, \quad (17)$$

$$\frac{dC_{N\text{-methyl-AMPA}}}{d\tau} = k_3 C_{AMPA}, \quad (18)$$

$$\frac{dC_{\text{methyl glyphosate}}}{d\tau} = k_4 C_{AMPA}, \quad (19)$$

$$\begin{aligned} \text{Sum of most toxic species} = \\ = \frac{dC_{AMPA}}{d\tau} + \frac{dC_{N\text{-methyl-AMPA}}}{d\tau} + \frac{dC_{\text{glyphosate}}}{d\tau}. \end{aligned} \quad (20)$$

The reaction rate constants were as follows:

$$k_1 = 5,5 \cdot 10^{-3} \text{ s}^{-1}; \quad k_2 = 5,1 \cdot 10^{-3} \text{ s}^{-1};$$

$$k_3 = 1,1 \cdot 10^{-3} \text{ s}^{-1}; \quad k_4 = 3,8 \cdot 10^{-3} \text{ s}^{-1}.$$

### 3. Results and Discussion

To study the migration process of pesticides, we used the installation (Fig.1) in which a constant concentration of glyphosate on the soil surface was provided. The change in the diffusion front in time is the curve of the distribution of the concentration of the released component in the solution placed in the pores of the inert medium along the length  $l$  of the stationary layer of wet granular material, and  $\tau_1 < \tau_2 < \tau_3 \dots < \tau_i$ . Thus, the diffusion front of the component moves over time throughout the layer of inert medium. The concentration of the released component gradually decreases with distance from

the particle. The results of experimental research and theoretical calculations were presented in graphical dependence.

The solution of the system of differential equations can describe the migration of the component in the soil with the boundary conditions presented in (15)–(19).

To visualise the model in Comsol multiphysics, assume that glyphosate moves from the soil surface. In the ground, glyphosate decomposes according to the mechanism shown in Fig. 3. In addition, the pesticide and its decomposition products are transported by convection, dispersion, sorption and evaporation.

Fig. 4 shows the concentration profiles of glyphosate and all its decomposition products over 100 days and the sum of the three most toxic species - N-methyl-AMPK, methyl phosphonic acid, and N-methyl glyphosate. After ten days, only a small amount of glyphosate remains. Given the total contributions, pollution remains high even after a few months. The following results are based on space and time-dependent model settings.

To combine boundary conditions and sources with the formulation of Darcy's law, COMSOL Multiphysics converts the Richards equation into a SI unit and solves the pressure (SI unit: Pa). According to Fig. 4, the hydraulic head,  $H$ , head,  $H_p$  and height  $D$  are related to pressure  $p$ .

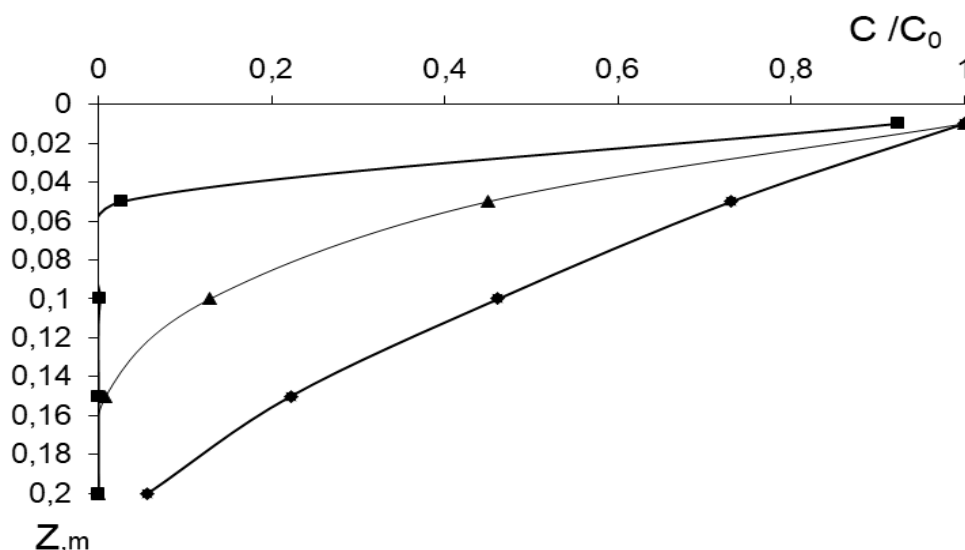
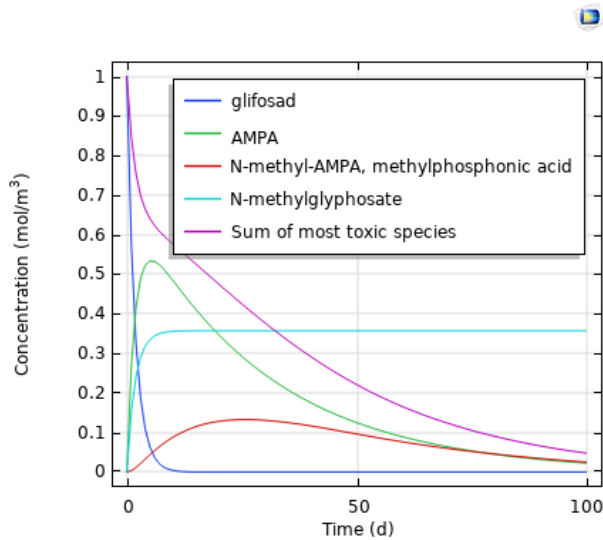


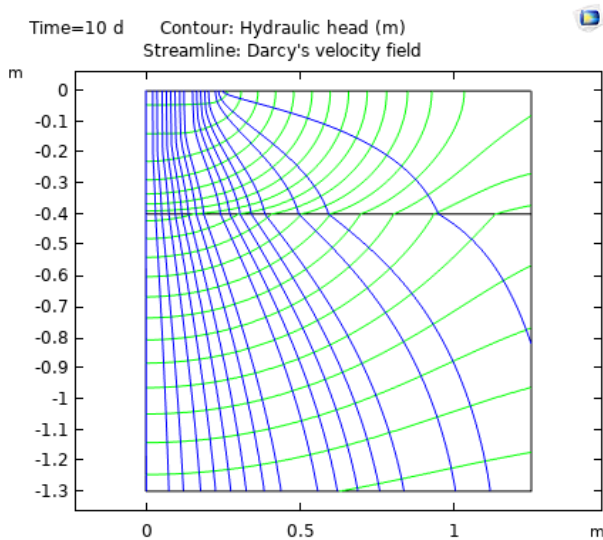
Fig. 2. Distribution of glyphosate concentration in soil at time intervals  $\tau$

where  $\blacktriangle$  – 1 day;  $\blacksquare$  – 3 days;  $\bullet$  – 8 days

The average value of the diffusion coefficient, which was calculated to visualise the model, was  $1.755 \cdot 10^{-12} \text{ m}^2/\text{s}$ .



**Fig. 3.** Dynamics of changes in the concentration of pesticide glyphosate and its decomposition products

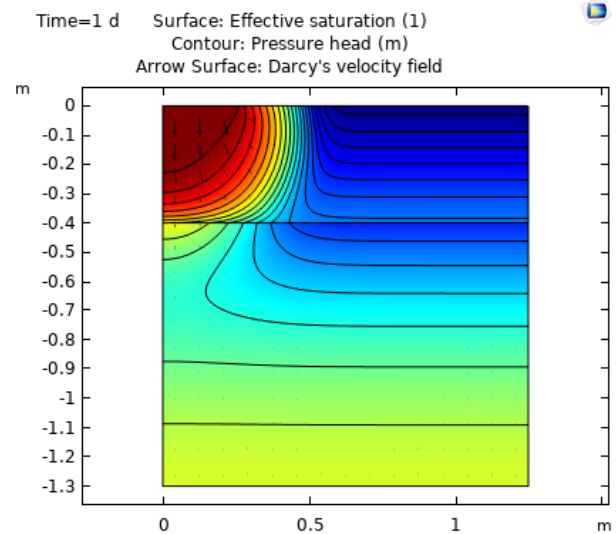


**Fig. 4.** Hydrodynamic characteristics of the environment of pesticide distribution

Fig. 5 shows the following scheme of distribution of pesticides.

Figure 5 shows the adequate saturation (surface diagram), pressure (contours) and flow rate (arrows) in variably saturated soil after one day.

Aqueous solutions of the pesticide were shown in the form of rings, and the colour corresponds to the concentration of the pesticide. The soil is layered, and the upper layer is slightly less permeable than the lower. Water moves through the bottom of the ring into the ground. The water level in the ring is known as the initial distribution of concentrations in the soil. There is no flow through the vertical walls or surface outside the ring.



**Fig.5.** Concentration profiles of pesticides in soil

The distribution of the glyphosate reached a stable state after ten days, a time frame that was also provided by the mathematical model (3). The results also show that soil contamination is relatively local to the glyphosate source. On the other hand, N-methyl glyphosate can affect a much larger soil volume for a much longer time.

Glyphosate moves with water from the reservoir into the soil at a constant concentration. In the ground, chemicals react, and are adsorbed on soil particles. Glyphosate and N-methyl glyphosate evaporate into the atmosphere. Sorption, biodegradation, and evaporation occur linearly to the water concentration. The soil is initially clean with zero concentration of chemicals involved. On the earth's surface outside the ring, evaporation into the atmosphere occurs. With the help of 2D axial symmetry, the transport of solute for one day was modelled.

The results also show that soil contamination is relatively local to the glyphosate source. On the other hand, pesticide dilution products can affect a much larger volume of soil over a much longer time.

#### 4. Conclusions

An essential step in this process is that when the diffusion front passes at a critical distance from the particle that characterises the area of distribution of the root system of plants, there is a so-called "leakage" of pesticides, which will be washed into underground aquifers. Even though according to experimental data, pesticides penetrate rather slowly into underground soil layers in actual conditions, in addition to molecular diffusion, there is convective mass transfer

of pollutants and the process of filtering groundwater through mineral rocks to underground aquifers.

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