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Study of water pollution in river-groundwater systems

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Abstract: *Groundwater resources and other important resources indispensable for human production and life play a very important role. This paper takes organic pollutants in river-groundwater system as the research object, establishes the model of convection and dispersion through mass conservation and mass transfer equation, and analyzes the adsorption based on Langmuir model and Freundlich model to study the migration and transformation mechanism of organic pollutants in river-groundwater systems, and the effect of biodegradation on the transformation of organic pollutants is also analyzed by Monod model.*

Keywords: *Mass Conservation, Mass Transfer, Langmuir Model, Freundlich Model, Monod Model*

1. Introduction

Rivers have a direct impact on groundwater, and when rivers recharge groundwater, once they are polluted, groundwater and the water sources close to rivers will be polluted to different degrees, which will seriously affect the normal operation of agriculture and industry, social and economic development and drinking water safety. The most difficult and harmful groundwater pollution is organic pollution [1], so it is of great theoretical significance and practical value to study the behavior of organic pollutants in the river-groundwater system.

It has been shown that the behavioral characteristics of organic pollutants in river-groundwater systems mainly involve physical processes such as convective transport, hydrodynamic dispersion, adsorption and hindrance, chemical reaction processes and biological transformation processes [2]. In this paper, the migration and transformation laws of organic pollutants are studied and explored by using the groundwater seepage field as an isotropic homogeneous steady-state flow, analyzing and establishing the convection, dispersion and adsorption of organic pollutants in the river-groundwater system, and studying the migration and transformation mechanism of organic pollutants in the river-groundwater system and analyzing the effect of biodegradation on the transformation of organic pollutants.

2. Modeling and empirical analysis

2.1 Empirical study of organic pollutants in river-groundwater systems

Fluid refers to the process of groundwater flow that carries away the mass of organic contaminants. Convective flow is usually modeled according to Darcy's law, which mainly describes the flow of groundwater. In order to establish a mathematical model of convection, dispersion and adsorption of organic pollutants in the river-groundwater system, this paper uses the mass conservation equation and mass transfer equation, assuming that $c(x,y,z,t)$ denotes the concentration of organic pollutants, (x,y,z) denotes the spatial coordinate and t denotes time; u denotes the mean pore flow rate; v denotes the groundwater infiltration rate; k denotes the infiltration parameter; D denotes the dispersion parameter; ρ denotes the aquifer sample density; and n denotes porosity.

The mass conservation equation and mass transfer equation are used to derive mathematical models of convection, dispersion and adsorption processes of organic pollutants in river-groundwater systems.

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2.1.1 Convection modeling

FThe convective term describes the transport of organic contaminants with the motion of the fluid, which can be derived from the mass conservation equation to derive the equation for the convective term.

The conservation of mass equation is given by:

$$\frac{\partial C}{\partial t} + \nabla \bullet (uC) = S \tag{1}$$

Including, C denotes the concentration of organic pollutants, t denotes time, u denotes the fluid velocity vector, and S denotes the source term.

In the one-dimensional case, the equation can be transformed into:

$$\frac{\partial C}{\partial t} + \frac{\partial (uc)}{\partial x} = S \tag{2}$$

Including, x denotes the spatial coordinate.

Replacing u in the mass conservation equation with $u * \partial C / \partial x$, u is the average flow rate in the void, the equation for the convection term is obtained as:

$$\frac{\partial C}{\partial t} + u * \frac{\partial C}{\partial x} = S \tag{3}$$

When deriving the convective term, the mass conservation equation is applied and the transport of organic pollutants with fluid velocity changes is considered. This study is important for understanding the behavioral characteristics of organic pollutants in river-groundwater systems and has practical applications.

2.1.2 Dispersion modeling

Dispersion is the phenomenon of dispersed diffusion of solutes in groundwater due to the heterogeneity of the properties of different media and the stochastic nature of fluid movement, which can affect the transport and migration of organic contaminants in groundwater [3]. Dispersion is usually modeled using Fick's law, where the diffusion coefficient is one of the important parameters.

The dispersion term describes the mixing process of organic contaminants in fluids due to molecular diffusion, and the expression of the dispersion term can be derived from the mass transfer equation and dispersion theory.

The mass transfer equation is given by:

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{4}$$

Including, C denotes the concentration of organic pollutants, t denotes time, D denotes the dispersion coefficient, and ∇^2 denotes the Laplace operator.

In the one-dimensional case, the equation can be transformed into:

$$\frac{\partial C}{\partial t} = D\partial^2 C / \partial x^2 \tag{5}$$

Treating the dispersion coefficient D as a constant, the equation for the dispersion term is obtained as:

$$\frac{\partial C}{\partial t} = D\partial^2 C / \partial x^2 \tag{6}$$

The derivation of dispersion terms is based on mass transfer equations and dispersion theory to describe the mixing processes of organic pollutants in fluids due to molecular diffusion, and these studies have both theoretical and practical value.

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2.1.3 Adsorption modeling

Adsorption is usually the process by which organic contaminant molecules are adsorbed by pore spaces and chemical functional groups on the surface of soil or rock particles. This process slows the transport and diffusion of organic contaminants in groundwater. Sorption is usually represented using isothermal sorption models (e.g. Langmuir or Freundlich models), where the sorption isotherm parameters can be fitted to experimental data [4].

Adsorption is a process in groundwater contamination that describes the interaction of organic contaminants with the surface of aquifer particles. If organic contaminants are adsorbed in the aquifer, the equations for the adsorption term can be derived using adsorption isotherms and subsurface diffusion theory.

For the k -movement in the vertical direction of the river groundwater system, it can be divided into several discrete nodes or levels with the positive z -axis direction. At each discrete node, the interaction of organic pollutants between liquid and solid phases needs to be considered.

According to the adsorption isotherm theory, the following equation can be used to describe the adsorption process of organic pollutants:

$$q = k * C(1-\theta) \tag{7}$$

Including, q is the adsorption mass per unit mass of the solid phase, K is the adsorption isotherm constant, C is the concentration of organic pollutants in the liquid phase, and θ is the porosity (indicating the proportion of the solid phase to the total volume).

According to the diffusion theory of subsurfaces, the diffusion process of adsorbed substances in the void can be described as:

$$\partial q/\partial t = Ds * \partial^2 q/\partial z^2 \tag{8}$$

Including, Ds is the subsurface diffusion coefficient.

To combine these equations with the mass transfer equation, the solid phase adsorption mass per unit mass q, is divided by the porosity θ, to obtain the solid phase adsorption mass fraction per unit volume ρs:

$$\rho s = (q/\theta) \tag{9}$$

Then, using mass conservation for ρs and considering flow and diffusion in the vertical direction, the equation for the adsorption term can be obtained as:

$$\partial(\rho s\theta)/\partial t = -\rho nku\partial^2(\rho s\theta)/\partial z^2 + Ds\theta\partial^2(\rho s\theta)/\partial z^2 \tag{10}$$

The above equations are processed and organized to obtain the final adsorption term equation:

$$\partial C/\partial t = \rho nku\partial^2 C/\partial z^2 \tag{11}$$

The adsorption term explains the adsorption and desorption behavior of organic pollutants on the surface of soil particles, which is modeled and calculated over adsorption isotherms and subsurface diffusion theory.

2.1.4 Establishment of the final theoretical model

The convection, dispersion and adsorption terms were combined to construct an integrated mathematical model to describe the convection, dispersion and adsorption of organic pollutants in the river-groundwater system. The final model equations are as follows:

Convecting:

$$\partial C/\partial t + u * \partial C/\partial x + v * \partial C/\partial y = -w * \partial C/\partial z \tag{12}$$

Dispersing:

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$$\partial C/\partial t = D*(\partial^2 C/\partial x^2 + \partial^2 C/\partial y^2 + \partial^2 C/\partial z^2) \tag{13}$$

Adsorpting:

$$\partial C/\partial t = \rho nku\,\partial^2 C/\partial z^2 \tag{14}$$

These methods use partial differential equations to describe the movement and transformation processes of organic contaminants in riverine groundwater systems, considering the main physical and chemical processes such as convection, diffusion and adsorption.

2.2 Migration and transformation mechanism of river-groundwater system

2.2.1 Test parameters and test results

(1) Convection and dispersion test parameters

The parameters related to the convection and dispersion of an organic pollutant in the river-groundwater system measured by the test are shown in Table 1.

Table 1: Convection and dispersion test parameters

Average pore flow rate u	Groundwater seepage flow rate v	Permeability coefficient k	Dispersion coefficient D	Dry density of aquifer samples ρ	Porosity n
38.67cm/d	5.01cm/d	6.32m/d	0.38cm^2/min	1.67(g/cm^3)	37.5%

(2) Adsorption kinetic test results

The adsorption kinetics of four different river sediments on an organic pollutant adsorption system with an initial concentration of about 0.5 mg/L and the concentrations of an organic substance in the solid and liquid phases measured at different adsorption times are listed in Table 2.

Table 2: Liquid and solid phase concentrations (liquid ml/L, solid mg/kg) of an organic material in the adsorption system of river X section at different times

Sample Number & Concentration / Time	S1		S2		S3		S4	
	liquid phase	solid phase	liquid phase	solid phase	liquid phase	solid phase	liquid phase	solid phase
0	0.495		0.495		0.495		0.495	
0.5	0.355	2.30	0.401	1.84	0.225	3.60	0.367	2.18
1.0	0.312	2.73	0.327	2.58	0.086	5.09	0.284	3.01
1.5	0.305	2.80	0.280	3.05	0.080	5.05	0.224	3.61

(3) Isothermal equilibrium adsorption test results

The sorption behavior of organic pollutants in groundwater was described by a mathematical model of isothermal equilibrium sorption, and the results of isothermal equilibrium sorption tests of four different sediments on 10 different initial concentrations of an organic pollutant for 24 h are listed in Table 3.

Table 1 shows the migration and transformation mechanism of organic pollutants in the river-groundwater system, simulating the parameter conditions of migration and transformation. According to the experimental parameters in Table 1, the values of convective velocity u, permeability coefficient k and dispersion coefficient D are obtained; Table 2 is the adsorption kinetic model established in a river-groundwater system for an organic substance, and the empirical adsorption model, such as linear adsorption model or Langmuir adsorption model, can be selected and the parameters such as adsorption rate constant and equilibrium adsorption concentration are obtained by parameter fitting using the experimental data and further applied in the mathematical model; Table 3 shows the results of isothermal equilibrium sorption tests to establish an isothermal equilibrium sorption model for an organic substance in a river-groundwater system. The Langmuir isothermal adsorption model or Freundlich isothermal adsorption model can be chosen and parameters such as adsorption isotherm constant and maximum adsorption amount can be obtained by parameter fitting using the experimental data, which can be used in the model to describe the adsorption.

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Table 3: Concentration of an organic substance in liquid and solid phases after 24h isothermal equilibrium adsorption in river section X (liquid ml/L, solid mg/kg)

Sample Number & Concentration / Initial concentration	S1		S2		S3		S4	
	liquid phase	solid phase	liquid phase	solid phase	liquid phase	solid phase	liquid phase	solid phase
0.0681	0.0461	0.1702	0.0246	0.1852	0.0424	0.2071	0.0354	0.2772
0.1372	0.0722	0.6005	0.0492	0.8301	0.0654	0.6683	0.0613	0.7101
0.2177	0.1235	0.8921	0.0903	1.224	0.1091	1.036	0.0993	1.134

2.2.2 Adsorption modeling

One of the commonly used models of adsorption kinetic theory is the Langmuir model, which assumes that there is only one adsorption site on the adsorbent surface and that the adsorption between the adsorbent and the organic material is a single molecular layer adsorption.

In the adsorption process, organic pollutants are removed from the aqueous phase by adsorption with the solid surface. The adsorption rate constant describes the rate at which adsorption of organic molecules occurs with the solid surface per unit time, and according to the mass balance principle and isotherm equation, it is assumed that after the organic substances reach equilibrium in the liquid and solid phases, their concentrations are C_l and C_s, respectively. The Freundlich model is the adsorption isotherm. One of the empirical models used to describe the non-uniform adsorption behavior of solutions on adsorbents, the following adsorption isotherm equations can be obtained:

$$q = K \bullet C\hat{}b \tag{15}$$

Including, q denotes the amount of organic matter adsorbed per unit mass of solid, K denotes the adsorption coefficient, b denotes the adsorption index, and C denotes the equilibrium concentration of organic pollutants in solution.

Considering the four different sediments, the Langmuir model can be fitted using the equations of the Langmuir model as shown below:

$$q = \frac{q_{\max} \cdot K_{ads} \cdot CC_l}{1 + K_{ads} \cdot C_l} \tag{16}$$

In the formula, $q_{\max}$ is the adsorption amount of organic pollutants.

Simplifying the above equation yields that:

$$\frac{q}{C_l} = \frac{q_{\max} \cdot K_{ads}}{1 + K_{ads} \cdot C_l} \tag{17}$$

Let $y = \frac{q}{C_l}$ and $x = C_l$. Then the above equation can be written in the form:

$$y = \frac{q_{\max} \cdot K_{ads}}{1 + K_{ads} \cdot x} \tag{18}$$

This is a classical Langmuir isotherm equation whose parameters $q_{\max}$ and K_{ads} can be determined by fitting experimental data.

2.2.3 Weighted flow rate modeling

Establishing weighted flow rate v:

$$v_w = n \cdot v_{mac} + (1-n) \cdot v_{mic} \tag{19}$$

Including, v_{mac} is the average flow rate of macropores = groundwater seepage flow rate = 5.01 cm/d, v_{mic} is the average flow rate of micropores = average pore flow rate = 38.67 cm/d, and n is the porosity

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so that the effect of macroscopic pores and microscopic pores in aquifer samples can be reflected more accurately.

2.2.4 Study results

Combining the data in Table 3, the data were plotted in two dimensions using Matlab to derive the results of the Duncan equilibrium tests for S1-S4.

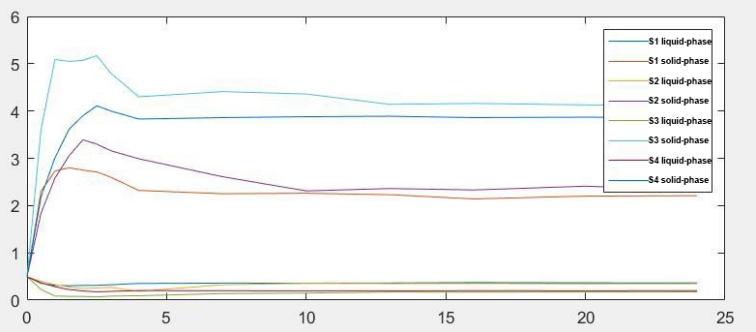

Figure 1: Plotting the results of S1-S4 adsorption kinetics test

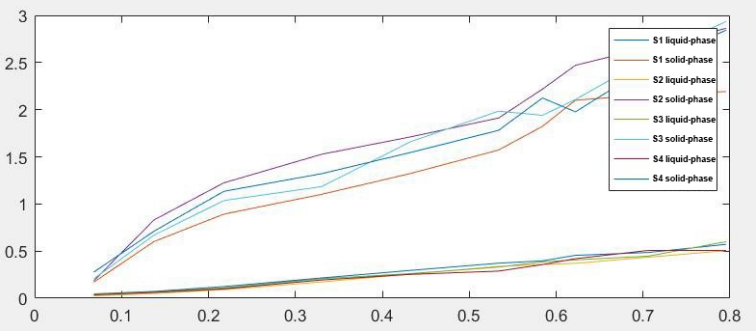

Figure 2: Plotting the results of S1-S4 isothermal equilibrium adsorption test

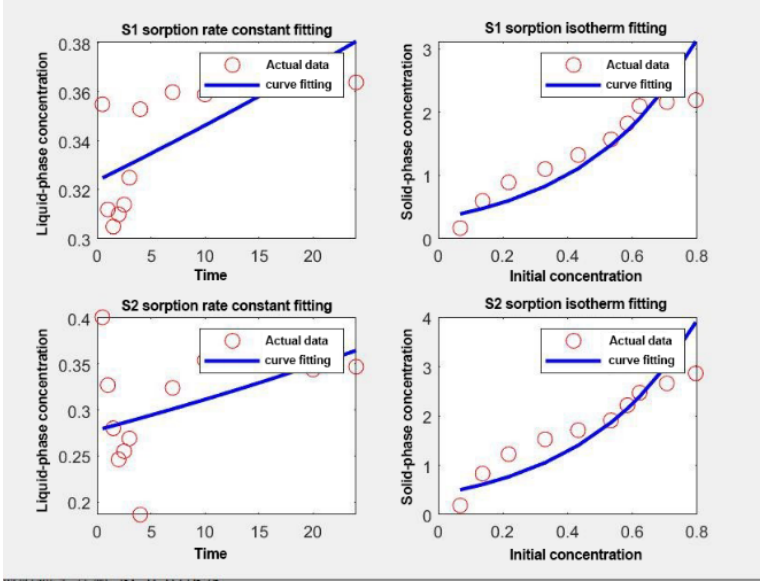

Figure 3: S1-S2 adsorption rate constants and isotherm fit

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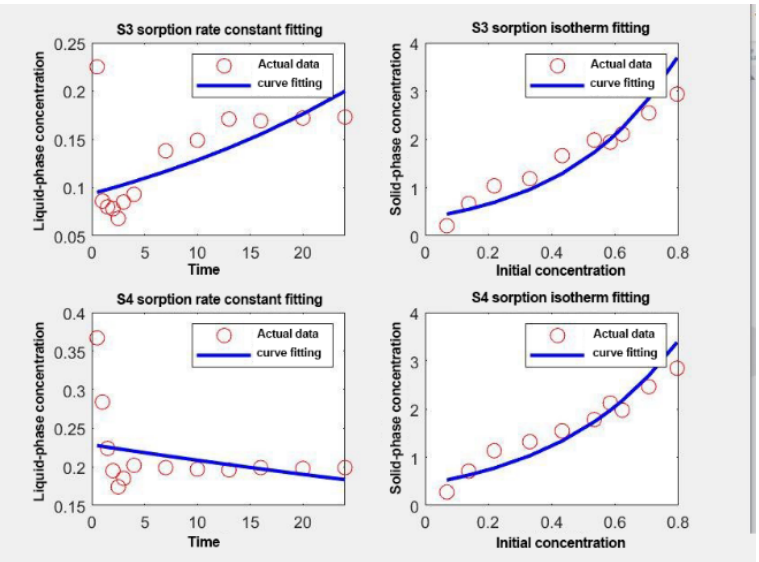

Figure 4: S3-S4 adsorption rate constants and isotherm fit

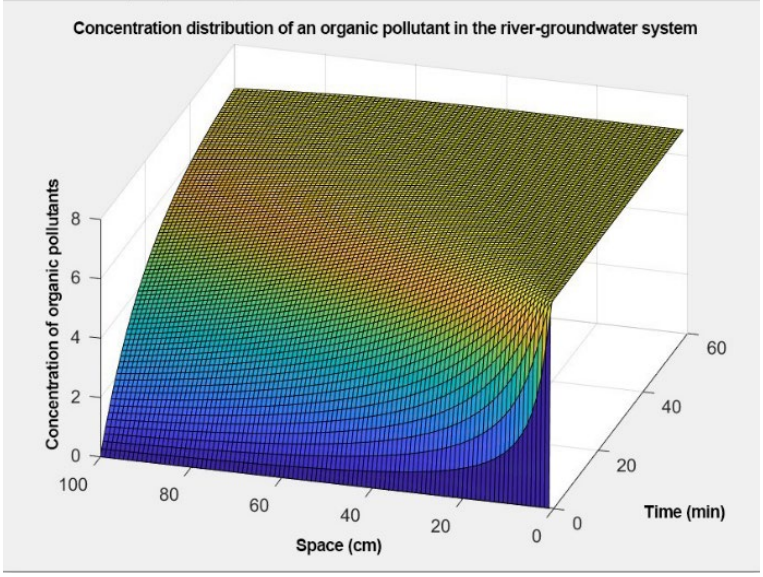

Figure 5: Three-dimensional distribution of organic pollutant concentration

From the three-dimensional diagram can be intuitively seen, the concentration of organic pollutants with the space and time change relationship, through the concentration changes in different times and different spatial changes in the concentration of fast and slow change, in the convection and dispersion changes when the concentration of organic pollutants is larger, this is a high concentration area, may be a high pollution area or may be the source of organic pollutants, and organic pollutant concentration is lower when the concentration decays faster part, may be farther away from the source of pollution or longer dispersion time.

2.3 Analysis of the degradation of organic pollutants by microorganisms

2.3.1 Establishment of the Monod model

A Monod model can be established to analyze the degradation characteristics of the organic pollutant by microorganisms using experimental data.

The mathematical equation of the Monod model is that:

$$\frac{dC}{dt} = \frac{kCM}{M + C} \tag{20}$$

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Including, C is the organic matter concentration, K is the microbial degradation rate constant, and M is the Monod constant, which indicates the affinity of microorganisms for organic matter, using experimental data to fit the parameters k and M of the Monod model.

2.3.2 Study results

The results of solving the model were determined as R^2 coefficient of 0.961648, parameter k = 3.347748; parameter M = 0.853073; parameter a = 0.067048.

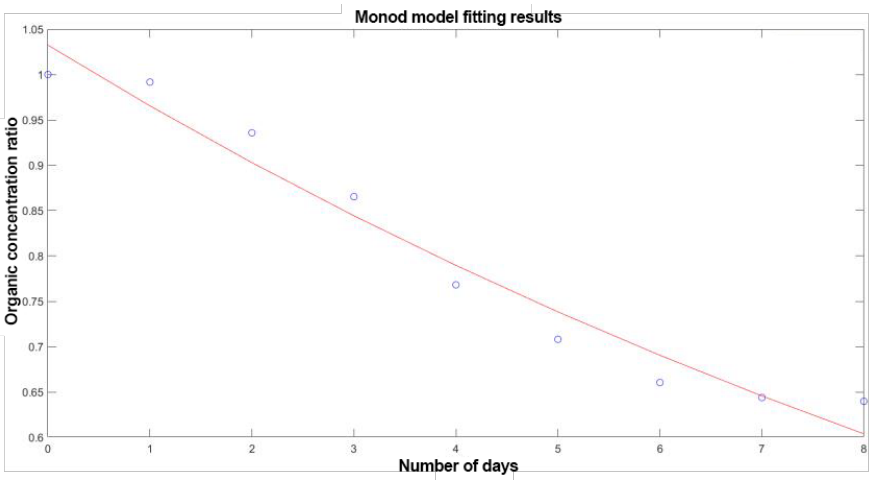

Figure 6: Monod Model

3. Conclusions

In this paper, multiple mass transfer mechanisms such as convective transport, hydrodynamic dispersion, physical adsorption and chemisorption were considered, including several theoretical models including Langmuir adsorption model and Freundlich isothermal adsorption model. In the process of data fitting using Matlab, the confidence interval was above 95% and the fitting effect was good, and three-dimensional experimental plots were established to make the results are shown more intuitively. At the same time, the results are solved by least squares fitting, and the model results are compared with the experimental data for verification to assess the accuracy and reliability of the model.

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