Adsorption Thermodynamics and Transport Dynamics of Nitrogen and Phosphorus in Small and Medium-Sized Rivers: An Analytical Study

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ABSTRACT

Small and medium-sized rivers, pivotal in connecting terrestrial environments with larger water bodies, play a crucial role in regional water security and biodiversity. The escalation of human activities has led to nitrogen and phosphorus pollution becoming a critical factor affecting the water quality of these rivers, thereby posing a threat to the stability of their ecosystems. This study is dedicated to examining the adsorption characteristics of river sediments for nitrogen and phosphorus and their transport behavior under varying temperature conditions, aiming to guide water quality improvement and ecological restoration. The adsorption mechanisms for monolayer and multilayer coverage, as well as the influence of adsorbent pore volume on nitrogen and phosphorus adsorption, were systematically analyzed through the construction of Langmuir, Freundlich, and D-R adsorption isotherm models. Adsorption processes were characterized using thermodynamic parameters such as enthalpy change, entropy change, free energy, and activation energy. Additionally, the impact of temperature on the transport behavior of nitrogen and phosphorus was described using a one-dimensional mathematical model. The findings indicate that the adsorption behavior of nitrogen and phosphorus in river sediments is significantly influenced by temperature, revealing a complex temperature dependency in both adsorption processes and transport patterns. These insights contribute to more accurate predictions and management of nitrogen and phosphorus pollution in small and medium-sized rivers, offering a vital reference for sustainable water environment management.

1. INTRODUCTION

With the rapid development of industrialization and urbanization, small and medium-sized rivers are increasingly burdened with severe nitrogen and phosphorus pollution [1-3]. Nitrogen and phosphorus, as primary nutrients for eutrophication in water bodies, their excessive discharge not only disrupts the ecological balance of water bodies but also triggers environmental issues such as red tides [4-6]. However, as natural purification systems, rivers regulate the concentration of nitrogen and phosphorus in the water to a certain extent through the adsorption by sediments. Hence, an in-depth understanding of the adsorption mechanisms of river sediments for nitrogen and phosphorus and their thermodynamic behavior is of significant theoretical and practical importance for the protection and restoration of water environments [7, 8].

Research on the environmental behavior of nitrogen and phosphorus is crucial for devising effective water environment management strategies [9]. Current studies mainly focus on the distribution characteristics of nitrogen and phosphorus in rivers, source analysis, and assessment of their environmental effects [10-12]. However, there is a relative paucity of research on the adsorption process of nitrogen and phosphorus in river sediments and their response mechanisms to environmental factors, particularly thermodynamic analysis and transport dynamics under varying temperature conditions [13, 14]. This

limits our comprehensive understanding of the behavior of nitrogen and phosphorus in small and medium-sized rivers and impacts our ability to predict and control water eutrophication.

Existing studies generally employ laboratory simulations or field sampling to examine the adsorption characteristics of nitrogen and phosphorus, often overlooking the thermodynamic characteristics of the adsorption process under complex natural conditions [15-18]. Additionally, current methods tend to use static or assumed homogeneous condition models to describe the transport and transformation processes of nitrogen and phosphorus, which are inadequate for accurately predicting the effects of environmental factors such as temperature fluctuations on nitrogen and phosphorus transport behavior. These limitations and deficiencies restrict the application of these models in actual river management [19-21].

Addressing these issues, this study initially constructs Langmuir, Freundlich, and D-R models to describe the adsorption process of nitrogen and phosphorus in river sediments, aiming to reveal the factors influencing monolayer and multilayer adsorption characteristics, as well as the impact of adsorbent pore volume. By analyzing thermodynamic parameters such as entropy change, enthalpy change, free energy, and activation energy of nitrogen and phosphorus adsorption, the influence of temperature on the adsorption process is deeply explored. Subsequently, a one-dimensional mathematical model for the transport of nitrogen and

phosphorus is established, systematically examining the impact of temperature fluctuations on the transport patterns of nitrogen and phosphorus in rivers. The methods and conclusions of this study provide a theoretical basis and technical support for the control and ecological restoration of nitrogen and phosphorus pollution in small and medium-sized rivers, having significant research value and application prospects.

2. NITROGEN AND PHOSPHORUS ADSORPTION ISOTHERM MODELS AND THERMODYNAMIC ANALYSIS

2.1 Analysis of monolayer adsorption process

Figure 1 presents a schematic diagram of the nitrogen and phosphorus adsorption model for small and medium-sized rivers. To gain a deeper understanding of the adsorption behavior and thermodynamic characteristics of nitrogen and phosphorus in river sediments, this paper constructs a Langmuir model to describe the monolayer adsorption process of nitrogen and phosphorus in small and medium-sized rivers. The Langmuir model assumes that all adsorption sites are uniform, with each site capable of adsorbing only one molecule, making it suitable for describing the monolayer adsorption process. This assumption aligns with the potential uniform adsorption sites on the surface of sediments in small and medium-sized rivers, especially under conditions of low concentration nitrogen and phosphorus pollutants, where adsorption is likely to occur predominantly at specific sites on the surface of sediment particles. The Langmuir model provides a clear theoretical framework to quantify adsorption capacity and strength. Thus, it enables the assessment of the maximum adsorption capacity and adsorption equilibrium constant of nitrogen and phosphorus through Langmuir model parameters, thereby enhancing the understanding of the adsorption potential of nitrogen and phosphorus in river sediments.
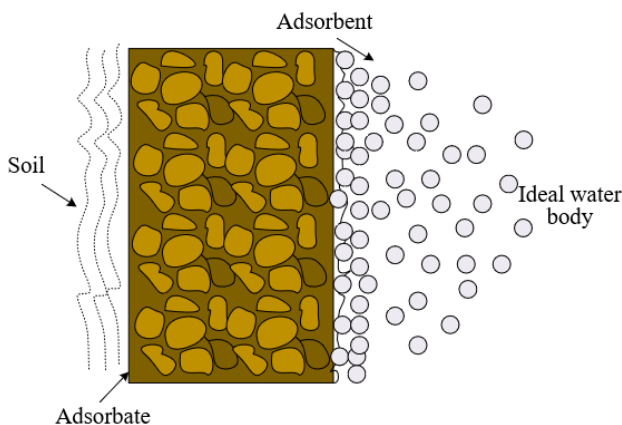

Figure 1. Schematic diagram of the nitrogen and phosphorus adsorption model in small and medium-sized rivers

The construction of the Langmuir model is based on the following three core assumptions:

(1) The surface of the adsorbent is assumed to be homogeneous, with all adsorption sites possessing the same adsorption capability, and each adsorption site exhibits consistent adsorption capacity without any energy difference between sites.

(2) Monolayer adsorption: Each site on the adsorbent can adsorb only one adsorbate molecule, forming a monolayer, and multilayer adsorption does not occur.

(3) No interaction during adsorption: In the adsorption process, there are no interactions between adsorbed molecules, meaning that the repulsion or attraction forces between adsorbates are ignored.

The Langmuir model posits that the surface of the adsorbent has a finite and uniform number of adsorption sites, with each site capable of adsorbing only one molecule. The model describes the relationship between the adsorption amount and the concentration of nitrogen and phosphorus in the solution through an adsorption isotherm equation. This relationship indicates that the adsorption amount increases with concentration but does not exceed a maximum value. Assuming the adsorption amount of the adsorbent at equilibrium is represented by w_r, the remaining concentration of the adsorbate in the solution at equilibrium is denoted by V_r, the maximum adsorption capacity that the adsorbent can achieve is represented by W_r, and the Langmuir adsorption equilibrium constant is denoted by J_M. The following equation presents the Langmuir adsorption isotherm expression:

$$w_r = \frac{J_M W_l V_r}{1 + J_M V_r} \tag{1}$$

The linear form of the above equation is given as:

$$\frac{V_r}{w_r} = \frac{1}{W_l} V_r + \frac{1}{W_l J_M} \tag{2}$$

By determining the adsorption amount at equilibrium for different concentrations and using these data to plot a fitting line, W_l and J_M can be calculated from the slope and intercept of this curve, provided the adsorption process conforms to the model. Observing the shape of the adsorption isotherm line can determine the type of the model. If the curve shows an initial rise followed by a plateau, it indicates that after a certain point, all adsorption sites on the surface of the adsorbent are occupied, suggesting a monolayer adsorption. The Langmuir model defines a separation factor, which aids in understanding the feasibility of the adsorption process. This dimensionless value depends on the initial nitrogen and phosphorus concentration and the adsorption strength constant. Based on the value of this separation factor, the adsorption process can be assessed as favorable or unfavorable, reversible or irreversible. Assuming the separation factor is represented by E_M and the initial concentration of the adsorbate is denoted by V_0, the calculation formula for E_M is as follows:

$$E_M = \frac{1}{1 + J_M V_0} \tag{3}$$

2.2 Analysis of multilayer adsorption process

Sediments in small and medium-sized rivers often have a complex and diverse composition, including organic matter, clay minerals, and oxides, which provide heterogeneous adsorption sites. Additionally, multilayer adsorption may occur when the concentration of nitrogen and phosphorus in the river is high, or when the adsorption sites on the surface of the sediment are partially saturated. In this paper, a Freundlich model is constructed to describe the multilayer adsorption

process of nitrogen and phosphorus in small and medium-sized rivers. The Freundlich model assumes that the adsorption surface is heterogeneous, suitable for describing the adsorption characteristics of such complex surfaces. It allows for different adsorption capacities at different adsorption sites, thereby better reflecting the non-uniform distribution of energy at the adsorption sites on the surface of the adsorbent.

When applied to describe the adsorption process of nitrogen and phosphorus in small and medium-sized rivers, the assumptions of the Freundlich model might include:

(1) The adsorbent surface is capable of multilayer adsorption, meaning that under certain conditions, adsorbate molecules can form multiple layers by continuing to adsorb on top of already adsorbed molecules, not just a single layer.

(2) The adsorption capacity of the adsorbent decreases as the concentration of adsorbate on the adsorbent surface increases, reflected in the model by an adsorption constant exponent less than 1.

(3) The model describes adsorption behavior at low and medium concentrations, not at very high concentrations. This aligns with the typical scenario in small and medium-sized rivers where nitrogen and phosphorus concentrations are usually not very high.

The core of the Freundlich model is a mathematical expression that describes the relationship between the amount of adsorption and the concentration of the adsorbate. Assuming the adsorption amount of the adsorbent at equilibrium is represented by w_r, the Freundlich adsorption equilibrium constant is denoted by J_D, the adsorption equilibrium constant related to adsorption strength is represented by b, and the remaining concentration of the adsorbate at equilibrium is denoted by V_r. Its expression is as follows:

$$w_r = J_D V_r^{\frac{1}{b}} \tag{4}$$

The linear form of the above equation is given as:

$$\ln w_r = \ln J_D + \frac{1}{b} \ln J_r \tag{5}$$

To extract the parameters of the Freundlich model from experimental data, similar to the Langmuir model, the adsorption isotherm is linearized by plotting $ln(w_r)$ against $ln(V_r)$ to calculate the slope and intercept. The slope of the curve represents the exponent of the Freundlich adsorption isotherm, related to the heterogeneity of adsorption capacity. The intercept, on the other hand, is related to the adsorption capacity and can be used to calculate the adsorption equilibrium constant. The equilibrium constant J_D can be used to assess the adsorption capacity of the adsorbent for nitrogen and phosphorus at a certain concentration.

2.3 Determination of adsorbent pore volume

To understand how nitrogen and phosphorus are adsorbed by bed sediments or other adsorbents in small and medium-sized rivers, it is essential to determine the pore volume, which aids in understanding the transport and fate of nitrogen and phosphorus in the sediments. This paper constructs a Dubinin-Radushkevich (D-R) model to determine the adsorbent pore volume through adsorption isotherms. The D-R model does not rely on a specific adsorption mechanism, making it

adaptable for handling non-ideal adsorption situations. Additionally, this model can be used to calculate the mean free energy of adsorption, thereby providing information about the adsorption mechanism. Lower adsorption energy suggests that the adsorption process is likely governed by physical forces; higher adsorption energy may involve the formation of chemical bonds.

When applying this model to measure nitrogen and phosphorus adsorption and the adsorbent pore volume in the sediments of small and medium-sized rivers, it is based on the following assumptions:

(1) The adsorbent is assumed to have a porous structure, with these pores being crucial for the adsorption process. They provide adsorption sites, enabling the adsorption of pollutants like nitrogen and phosphorus.

(2) The pore structure is assumed to be uniform, meaning the pores of the adsorbent have consistent size and shape. Also, the energy of adsorption sites is uniformly distributed without concentrations of high-energy or low-energy sites.

(3) The adsorption process is presumed to be physical rather than chemical, implying that the adsorption involves intermolecular forces rather than the formation of chemical bonds.

The D-R model distinguishes the type of adsorption by calculating the mean free energy during adsorption. If this value falls between 8-16 kJ/mol, the adsorption process is likely chemical, as this energy range involves the formation of chemical bonds. If the value is less than 8 kJ/mol, the adsorption process primarily involves physical forces. The D-R model, based on the characteristic of micropore adsorption being a volume-filling process, is a model that can determine the adsorbent pore volume through adsorption isotherms. Assuming the constant related to adsorption energy is represented by J_F, and Polanyi potential energy is denoted by γ, where $\gamma = EYLN(1+(1/V_r))$, its expression is:

$$\ln w_r = \ln w_l - J_F \gamma^2 \tag{6}$$

The D-R model involves expressing the relationship between adsorption quantity and adsorption potential. By fitting experimental data to derive model parameters, these parameters can help researchers estimate the average energy change per molecule during the adsorption process. Assuming the mean adsorption energy is represented by R, its calculation formula is:

$$R = (2J_F)^{-\frac{1}{2}} \tag{7}$$

Through these steps, the D-R model not only helps researchers determine the adsorption mechanism of nitrogen and phosphorus in small and medium-sized rivers (physical or chemical) but also provides necessary parameters for quantifying the pore volume of the adsorbent. Understanding these aspects is crucial for designing effective water treatment strategies and predicting the behavior of pollutants in riverine environments.

2.4 Thermodynamic parameter analysis

Figure 2 illustrates the technical route adopted in this study. Studying the adsorption and transport of nitrogen and phosphorus in small and medium-sized rivers, thermodynamic equations and parameter analyses are crucial tools. By

calculating and analyzing thermodynamic parameters, a comprehensive understanding of the nature of interactions between nitrogen, phosphorus, and the adsorbent during the adsorption process can be obtained, including the driving forces and spontaneity of the process.
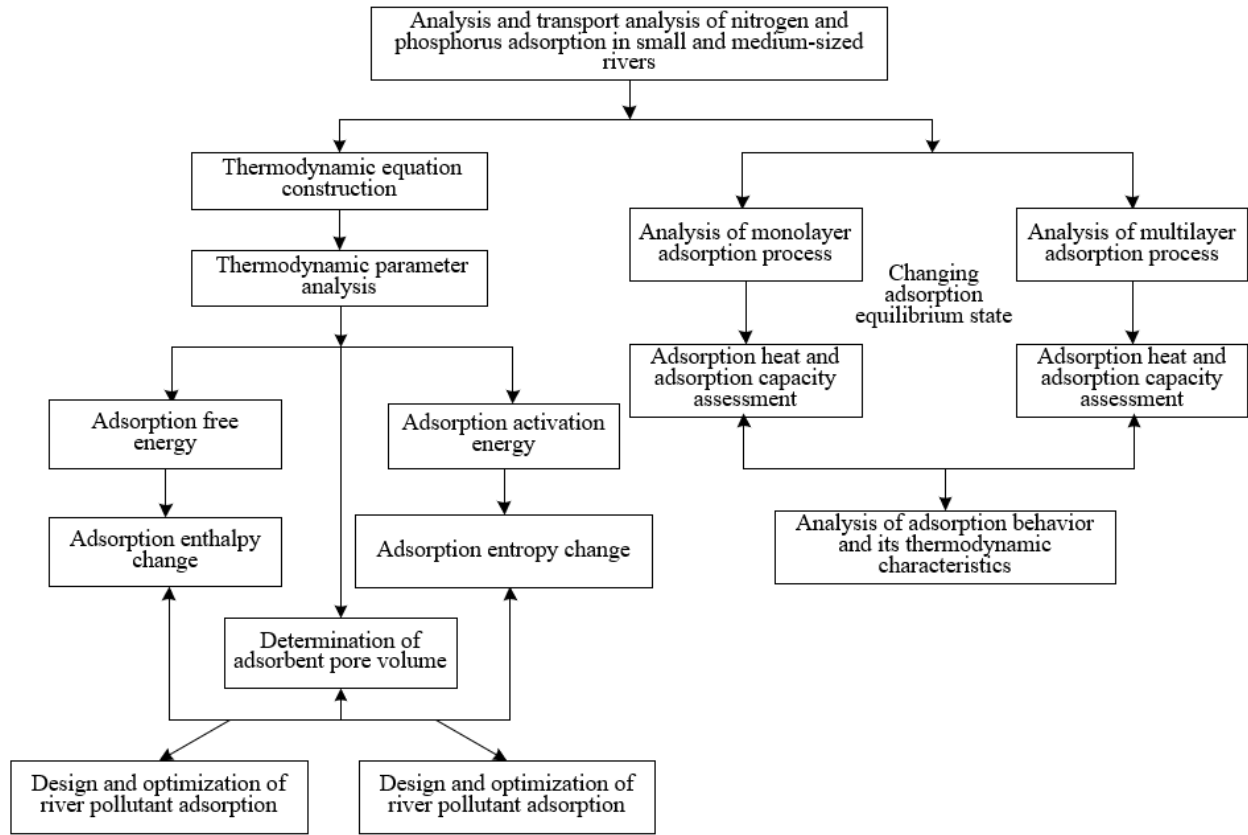

Figure 2. Technical route of this study

The change in adsorption free energy is a key parameter to determine whether the adsorption process is spontaneous. If the adsorption free energy is negative, it indicates that nitrogen and phosphorus molecules will be spontaneously captured by the adsorbent medium without the need for external energy input. The calculation of free energy change is usually based on adsorption isotherms, which can be obtained from experimental data. Assuming Gibbs free energy is represented by ΔH, the ideal gas constant by E, the absolute temperature by Y, and the distribution coefficient by Jr (where $J_r = V_S/V_A$), with V_S and V_A representing the concentration of the adsorbate adsorbed by the adsorbent and the remaining concentration of the adsorbate in the solution at equilibrium, respectively, the calculation formula is:

$$\Delta H = -EY \ln J_r \qquad (8)$$

Adsorption enthalpy change refers to the change in system energy during the adsorption process. If the adsorption process releases energy, it is exothermic, typically associated with chemical adsorption; if it requires energy absorption, the process is endothermic, common in physical adsorption. Analyzing the adsorption enthalpy change enables researchers to determine the nature of the adsorption process and the interaction strength between nitrogen, phosphorus pollutants, and the adsorbent medium. Adsorption entropy change describes the change in system disorder during the adsorption process. Typically, if the adsorption process leads to a decrease in system disorder, the entropy change is negative. The sign and magnitude of the entropy change can help understand the changes in molecular structure and motion during the adsorption process. Assuming adsorption enthalpy change is represented by ΔG and adsorption entropy change by ΔA, this paper calculates these based on the Van't Hoff equation, as follows:

$$\ln J_r = -\frac{\Delta G}{EY} + \frac{\Delta A}{E} \qquad (9)$$

Adsorption activation energy refers to the energy required to initiate the adsorption process. Lower adsorption activation energy means that nitrogen and phosphorus molecules are more readily captured by the adsorbent medium. The magnitude of adsorption activation energy can reflect the rate and potential mechanism of the adsorption process, being an important parameter in understanding adsorption kinetics. Assuming the reaction rate constant for the u-level reaction is represented by k_i, the pre-exponential factor by j_0, and the adsorption activation energy by R_s, this paper calculates the adsorption activation energy based on the Arrhenius equation, with the calculation formula as:

$$j_u = j_0 \exp\left(-\frac{R_s}{EY}\right) \qquad (10)$$

The linear form of the above equation is:

$$\ln(J_u) = \ln(j_0) - \frac{R_s}{EY} \qquad (11)$$

Through in-depth analysis of these thermodynamic parameters, better design and optimization of methods for adsorption and removal of pollutants in rivers can be achieved, and predictions can be made about the behavior of pollutants under different conditions, providing important information for the protection and restoration of river ecosystems.

3. ONE-DIMENSIONAL TRANSPORT ANALYSIS OF NITROGEN AND PHOSPHORUS UNDER TEMPERATURE EFFECTS

Figure 3 presents the schematic diagram of the nitrogen and phosphorus transport model in small and medium-sized rivers under temperature effects. The following assumptions are made while constructing the one-dimensional transport analysis model for nitrogen and phosphorus in small and medium-sized rivers:

(1) It is assumed that the transport of nitrogen and phosphorus occurs only in the main flow direction of the river. This means the model neglects lateral and vertical variations in the river, simplifying it to a one-dimensional problem.

(2) The flow velocity of the river is assumed to be constant and unchanging. This implies that within the entire analysis range of the model, the velocity of the water flow is consistent, unaffected by seasonal changes, rainfall events, or changes in the riverbed's topography.

(3) It is assumed that the molecular diffusion of nitrogen and phosphorus in the water body is uniform. Diffusion causes nitrogen and phosphorus to move from areas of high concentration to areas of lower concentration, in order to achieve concentration equilibrium.
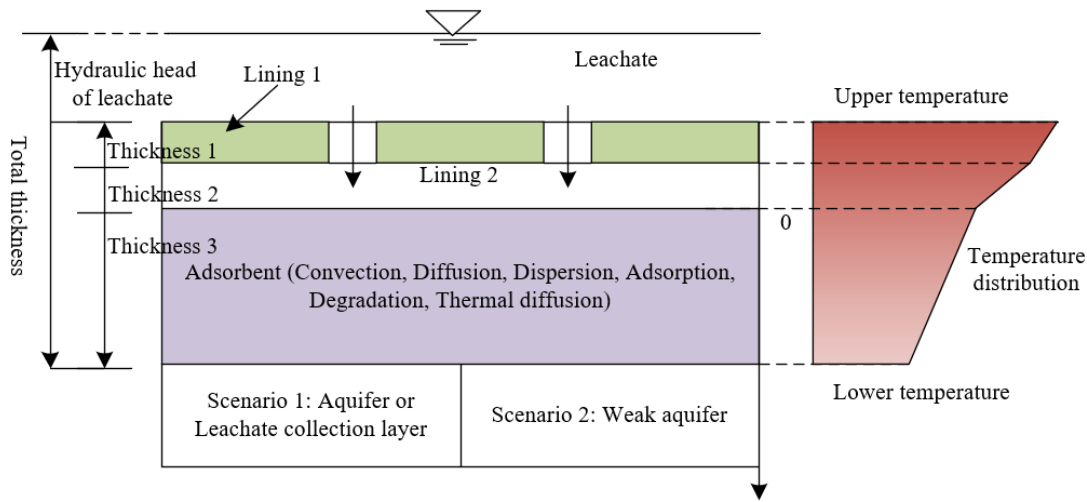

Figure 3. Schematic diagram of the nitrogen and phosphorus transport model in small and medium-sized rivers under temperature effects

Assuming the concentration of nitrogen and phosphorus leachate is represented by V_0, the temperatures at the upper and lower surfaces of the adsorbent are denoted by Y_1 and Y_2, the hydraulic head of the leachate is represented by g_q, the thickness of the adsorbent is denoted by M, the porosity of the adsorbent is represented by b, the seepage velocity of water through the adsorbent is denoted by c_a, the effective diffusion coefficient of the adsorbent is represented by F^*, the Soret coefficient is denoted by A_Y, and the obstruction factor is represented by E_f.

The law of mass conservation is the foundation of constructing any pollutant transport model. The law of mass conservation states that in the absence of sources or sinks, the change in the mass of a pollutant within a control volume over time is equal to its net inflow minus its net outflow. This means that the change in the amount of nitrogen and phosphorus is equal to their inflow minus their outflow. The convection-diffusion equation describes the transport of a substance in a fluid due to flow and concentration gradients. For nitrogen and phosphorus in rivers, convection describes their movement with the water flow, while diffusion describes their movement from areas of higher concentration to lower concentration due to concentration gradients. Assuming the concentration of nitrogen and phosphorus is represented by V, time by y, the vertical distance between the pollutant and the adsorbent surface by x, the diffusion coefficient of the medium by F_Y, and the temperature of the adsorbent by Y. Based on the law of mass conservation and the convection-diffusion equation, this paper simplifies the one-dimensional transport equation of nitrogen and phosphorus under temperature effects as follows:

$$\frac{\partial V}{\partial y} = \frac{F^*}{E_f}\frac{\partial^2 V}{\partial x^2} + \frac{1}{E_f}\frac{\partial}{\partial x}\left(F_Y\frac{\partial Y}{\partial x}\right) - \frac{c_a}{E_f}\frac{\partial V}{\partial x} \qquad (12)$$

In the one-dimensional transport analysis model of nitrogen and phosphorus in small and medium-sized rivers, the seepage velocity of the water flow is an important parameter affecting the transport and transformation of nitrogen and phosphorus. Seepage velocity refers to the rate at which water passes through the riverbed matrix. It involves the exchange process between river water and the riverbed, having a direct impact on the adsorption, desorption, and biochemical reactions of pollutants. Assuming the porosity of the riverbed soil is represented by b, and the permeability coefficient of the adsorbent lining layer is denoted by j, the calculation formula is:

$$c_a = \frac{j(M + g_q)}{bM} \qquad (13)$$

Temperature significantly affects the biochemical reaction rates of nitrogen and phosphorus, including nitrification, denitrification, phosphorus release, and fixation. These

processes usually follow the Arrhenius Law, i.e., the reaction rate increases with an increase in temperature. The solubility of nitrogen and phosphorus in water is also influenced by temperature. With rising temperatures, the solubility of certain forms of nitrogen and phosphorus may decrease, potentially leading to a transfer from the aqueous to the gaseous phase. The thermal diffusion coefficient usually describes the ability of heat to propagate in a medium, rather than the propagation of mass. However, the concept of the thermal diffusion coefficient can be indirectly associated with some processes affecting the transport of nitrogen and phosphorus. The following formula provides the calculation for the medium's thermal diffusion coefficient represented by F_Y:

$$F_Y = VA_Y F^*$$ (14)

By combining the above formulas, there is:

$$\frac{\partial V}{\partial y} = \frac{F^*}{E_f}\frac{\partial^2 V}{\partial x^2} + \frac{A_Y F^*}{E_f}\frac{\partial}{\partial x}\left(V\frac{\partial Y}{\partial x}\right) - \frac{c_a}{E_f}\frac{\partial V}{\partial x}$$ (15)

In the one-dimensional transport analysis model of nitrogen and phosphorus in small and medium-sized rivers, the construction of a thermal diffusion control equation is indirectly related to the environmental factors of substance transport in water. The thermal diffusion control equation is typically used to describe and predict the distribution of temperature in a medium over time and space. This paper constructs the thermal diffusion equation based on Fourier's Law, characterizing the rate at which heat passes through a region as being directly proportional to the temperature gradient of that region. This means that heat always flows from higher to lower temperature areas, and this flow rate is related to the thermal conductivity of the medium and the magnitude of the temperature gradient. This paper simplifies thermal diffusion as a one-dimensional variation process, with the specific equation expression as follows:

$$Y = S_u x + N_u$$ (16)

To solve the thermal diffusion equation, boundary conditions and initial conditions must be set. Boundary conditions describe the temperature or heat flow characteristics at the system's edges, while the initial conditions define the temperature distribution at the start of the system.

4. EXPERIMENTAL RESULTS AND ANALYSIS

Figure 4 displays the nitrogen and phosphorus adsorption isotherms for different adsorbents at three different temperatures (25°C, 35°C, and 45°C). Scenario 1 involves natural sediments, Scenario 2 involves artificially added zeolite, and Scenario 3 involves artificially added activated carbon. The data points in the figure represent experimental observations, while the two curves represent the fitting results of the Langmuir and Freundlich models, respectively. It is evident from the graph that at all temperatures, as the initial concentration increases, the adsorption capacity also correspondingly increases, indicating that the adsorption capacity of the sediments enhances with the increase in pollutant concentration.
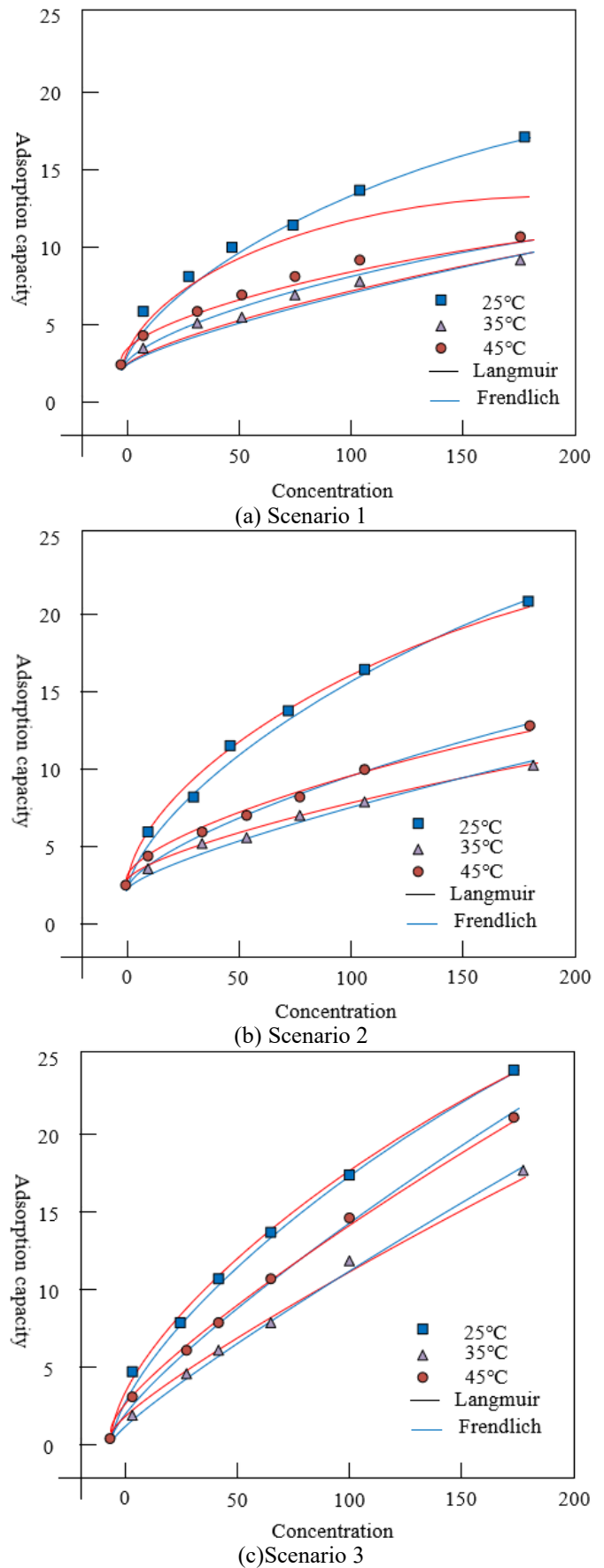

(a) Scenario 1

(b) Scenario 2

(c) Scenario 3

Figure 4. Isotherms of nitrogen and phosphorus adsorption in rivers

At the same concentration, as the temperature rises, the adsorption capacity also increases, suggesting that the adsorption process of nitrogen and phosphorus on river

sediments is endothermic. In other words, higher temperatures promote the adsorption process. This preliminary inference suggests that the adsorption capacity of river sediments for nitrogen and phosphorus is positively correlated with temperature, and both models are suitable for describing this adsorption process, although further data analysis is required to confirm which model is more appropriate. Comparing the three graphs, it is apparent that the isotherm of activated carbon shows the highest adsorption capacity at all concentrations. The isotherm of natural sediments is the lowest, as its adsorption capacity is the weakest among the three materials. The isotherm of zeolite lies between activated carbon and natural sediments.

Table 1. Parameters of ammonia nitrogen adsorption isotherm fitting equations for different adsorbents

Adsorbent Usage Scenario	Temperature	*Langmuir* Equation			*Freundlich* Equation		
		Maximum Adsorption Capacity	Adsorption Equilibrium Constant	R^2	Heterogeneity Factor	Empirical Coefficient	R^2
Scenario 1	25°C	11.23	0.006	0.9568	0.62	0.22	0.9451
	35°C	11.35	0.011	0.9632	0.55	0.37	0.9325
	45°C	21.44	0.009	0.9784	0.57	0.66	0.9587
Scenario 2	25°C	11.36	0.012	0.9856	0.56	0.45	0.9521
	35°C	13.25	0.012	0.9852	0.47	0.66	0.9562
	45°C	23.68	0.013	0.9826	0.47	1.23	0.9487
Scenario 3	25°C	27.85	0.011	0.9741	0.53	1.14	0.9362
	35°C	31.24	0.012	0.9763	0.51	1.23	0.9452
	45°C	32.58	0.012	0.9859	0.52	1.51	0.9563

Table 2. Adsorption thermodynamic parameters of ammonia nitrogen for different adsorbents

Adsorbent Usage Scenario	Temperature	Adsorption Free Energy	Adsorption Enthalpy Change	Adsorption Entropy Change
Scenario 1	25°C	-4.69		
	35°C	-5.85	0.0389	6.78
	45°C	-5.79		
Scenario 2	25°C	-5.88		
	35°C	-6.53	0.0334	3.45
	45°C	-6.78		
Scenario 3	25°C	-5.81		
	35°C	-6.32	0.0215	0.89
	45°C	-6.38		

Based on the data from Table 1, the parameters of two fitted isotherm equations for ammonia nitrogen adsorption—Langmuir and Freundlich equations—can be observed for three different adsorbent usage scenarios at various temperatures. Analysis of the Langmuir equation indicates that for all three scenarios, the maximum adsorption capacity increases with rising temperature, suggesting that higher temperatures enhance the monolayer adsorption of ammonia nitrogen on the adsorbent surface. For scenarios 1 and 3, the adsorption equilibrium constant is the highest at 35°C, whereas for scenario 2, it slightly increases with rising temperature. An increase in the adsorption equilibrium constant implies that at higher temperatures, the affinity of the adsorbent for ammonia nitrogen is enhanced. In all three scenarios, the R^2 values for the Langmuir equation are generally high, especially at 45°C, indicating that the Langmuir model accurately describes the adsorption process at these temperatures.

In the analysis of the Freundlich equation, there is no clear trend in the heterogeneity factor with rising temperature for all three scenarios, but it is generally lower at medium temperatures, indicating a complex impact of temperature on the non-uniformity of the adsorbent surface. The empirical coefficient increases with temperature in all scenarios, suggesting that the multilayer adsorption capacity of ammonia nitrogen on the adsorbent surface is enhanced at higher temperatures. The R^2 values for the Freundlich equation also indicate a good fit, although they are generally slightly lower than those of the Langmuir model.

Based on the data from Table 2, it can be concluded that the values of adsorption free energy are negative in all scenarios, indicating that the adsorption process is spontaneous. As the temperature increases, the absolute value of adsorption free energy also increases (with a slight decrease before increasing in Scenario 1), suggesting that higher temperatures are favorable for adsorption. This is due to the higher energy of active sites on the adsorbent at high temperatures, or the increased activity of ammonia nitrogen molecules, making them more easily adsorbed. The values of adsorption enthalpy change are positive in all scenarios, indicating that the adsorption process is endothermic. A positive value of enthalpy change typically implies a physical adsorption process, as chemical adsorption usually accompanies a larger exothermic effect. Relatively low positive values of enthalpy change indicate that the adsorption process is predominantly driven by physical forces. Scenario 1 has the highest entropy change, suggesting the greatest increase in system disorder during the adsorption process, likely due to the adsorbed molecules having more degrees of freedom on the solid phase surface or more water molecules being released during adsorption. Scenarios 2 and 3 have smaller entropy changes, indicating a less significant increase in system disorder

compared to Scenario 1.

In conclusion, the adsorption process in all scenarios is spontaneous, and the adsorption capacity generally improves with increasing temperature. The process is endothermic, primarily driven by physical adsorption. The adsorption process leads to an increase in system disorder, with the most significant increase in Scenario 1. When selecting adsorbents in practical applications, factors such as cost, regeneration capability, and the actual operating temperature conditions should also be considered. Typically, adsorbents with more negative adsorption free energy, moderate adsorption enthalpy change, and greater adsorption entropy change are more favorable, as this implies good spontaneity of the adsorption process, strong adsorption capacity, and beneficial increase in system disorder for the adsorption process. According to these criteria, Scenario 1 performs best at 25°C, but it's necessary to weigh its performance at other temperatures and real-world operating conditions.
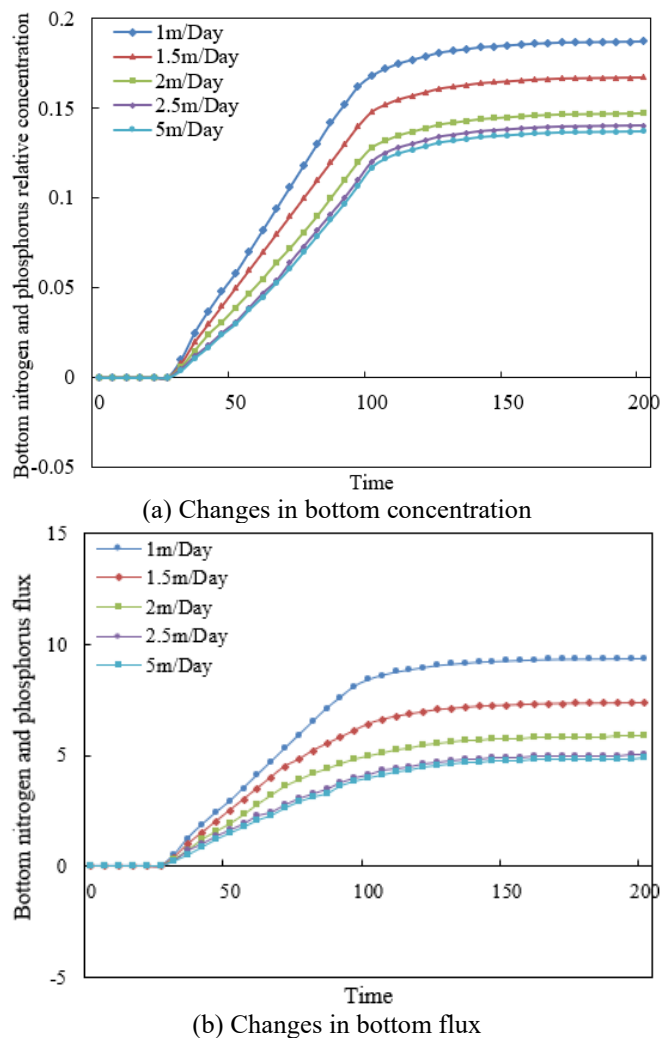

(a) Changes in bottom concentration

(b) Changes in bottom flux

Figure 5. The impact of water flow seepage velocity on nitrogen and phosphorus transport patterns in small and medium-sized rivers

Based on the analysis of Figure 5, we can understand the impact of different water flow seepage velocities on the transport patterns of nitrogen and phosphorus in small and medium-sized rivers. From the trends in the data of Figure 5(a), under different seepage velocities, the concentration of nitrogen and phosphorus shows an increasing trend over time but with a gradually slowing growth rate, until it approaches a

stable value. This indicates the existence of a balance state of nitrogen and phosphorus release into the river, where, over time, the release rate of nitrogen and phosphorus gradually balances with other removal processes. Comparing the final stable values of nitrogen and phosphorus concentrations at different seepage velocities, it's found that the faster the seepage velocity, the lower the stable concentration of nitrogen and phosphorus. This is because a faster water flow increases the diffusion capacity and dilution effect of the water body, thus reducing the bottom concentration of nitrogen and phosphorus. Moreover, according to the initial growth rate of the data, a slower seepage velocity results in a more significant increase in nitrogen and phosphorus concentration, due to reduced dilution and diffusion, leading to more accumulation of nitrogen and phosphorus at the river bottom.

Figure 5(b) shows that, after the start of data recording (around 50 time units), the flux of nitrogen and phosphorus under each seepage velocity increases over time, indicating that the flux of nitrogen and phosphorus gradually increases with time. As seepage velocity increases, the time required to reach the same nitrogen and phosphorus flux decreases, meaning that higher seepage velocities accelerate the transfer of nitrogen and phosphorus. Although the flux of nitrogen and phosphorus increases over time, in all scenarios, the growth rate seems to slow down over time, suggesting that a steady state is being approached, i.e., a balance between the input and output of nitrogen and phosphorus. After 200 time units, the flux of nitrogen and phosphorus under different seepage velocities tends to stabilize, and the faster the seepage velocity, the lower the steady-state flux of nitrogen and phosphorus. For instance, the nitrogen and phosphorus flux at 1m/Day stabilizes around 9.36, while at 5m/Day, it stabilizes around 4.86.

In summary, the following conclusions can be drawn: Over time, the concentration of nitrogen and phosphorus at the bottom of the river gradually increases until it reaches a relatively stable level. The faster the seepage velocity, the lower the stable concentration of nitrogen and phosphorus, indicating that faster water flow helps dilute and disperse nitrogen and phosphorus, thereby reducing their concentration. Higher water flow seepage velocities lead to faster increases in nitrogen and phosphorus flux in the short term but more effectively dilute or remove nitrogen and phosphorus in the long term, resulting in lower steady-state fluxes. All seepage velocities tend towards a steady-state flux after a certain time, meaning that the input and removal of nitrogen and phosphorus are balanced.

From Figure 6(a), it can be seen that during the initial 50 time units, the nitrogen and phosphorus concentrations are zero under all conditions, suggesting that there was no thermal diffusion, or the concentration changes were below the detection limit during this period. As time progresses, the nitrogen and phosphorus concentrations start to increase under all conditions, indicating that thermal diffusion begins to take effect, and nitrogen and phosphorus start to diffuse from the bottom into the river. A higher thermal diffusion coefficient results in a slower rate of increase in nitrogen and phosphorus concentration. Initially, the concentration of nitrogen and phosphorus grows more rapidly, but later the growth rate begins to slow down, indicating a trend towards equilibrium. Eventually, these concentrations tend towards a steady state value, dependent on the supply of nitrogen and phosphorus from the bottom, river flow characteristics, and the efficiency of thermal diffusion. In the process of reaching a steady state,

a higher thermal diffusion coefficient seems to lead to a lower steady-state concentration, due to the higher coefficient promoting rapid dispersion of nitrogen and phosphorus, thereby reducing local concentration at the river bottom.
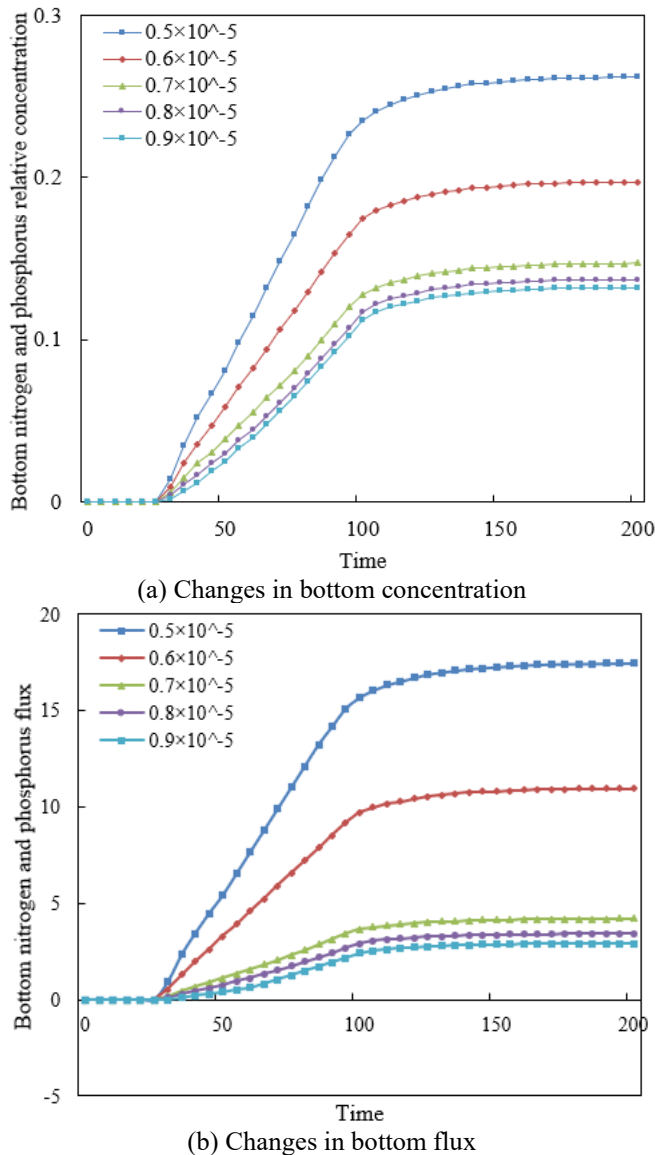

(a) Changes in bottom concentration

(b) Changes in bottom flux

Figure 6. Impact of the thermal diffusion coefficient on the transport patterns of nitrogen and phosphorus in small and medium-sized rivers

From Figure 6(b), it is evident that the greater the thermal diffusion coefficient, the slower the rate of increase in nitrogen and phosphorus flux. In the early stages, the increase in nitrogen and phosphorus flux is very slow. This is because it takes some time for the nitrogen and phosphorus to begin migrating from the bottom through thermal diffusion. After a certain point in time, the growth of nitrogen and phosphorus flux starts to accelerate, as the migration of nitrogen and phosphorus caused by thermal diffusion begins to accumulate to a measurable level. For each thermal diffusion coefficient, the nitrogen and phosphorus flux eventually appears to reach a stable growth rate, indicating the establishment of a dynamic equilibrium where the release of nitrogen and phosphorus from the bottom balances with other factors.

In summary, the following conclusions can be drawn. The thermal diffusion coefficient has a significant impact on the increase of bottom nitrogen and phosphorus concentrations in

small and medium-sized rivers. A lower thermal diffusion coefficient leads to a rapid increase in nitrogen and phosphorus concentration, while a higher coefficient results in a slower increase rate and eventually a lower steady-state concentration. Over time, nitrogen and phosphorus concentrations tend towards a steady state under all conditions. The thermal diffusion coefficient significantly influences the flux of nitrogen and phosphorus at the bottom of small and medium-sized rivers. A higher thermal diffusion coefficient leads to a slower growth rate of nitrogen and phosphorus flux, while a lower coefficient causes rapid increases. Under all coefficient conditions, the nitrogen and phosphorus flux increases over time, indicating that thermal diffusion is a driving force in the migration of nitrogen and phosphorus.
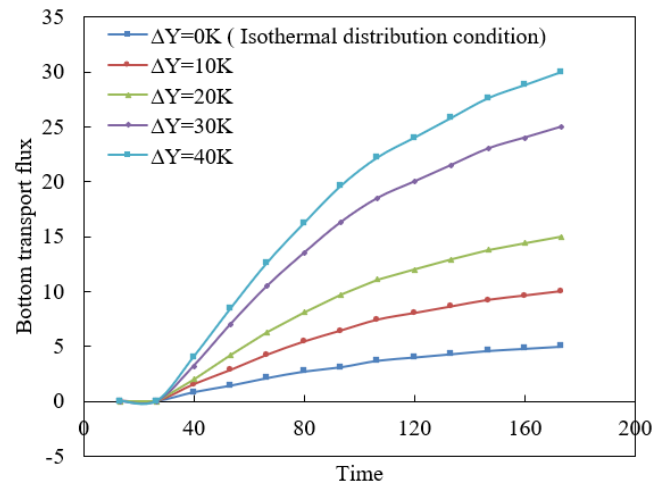

Figure 7. The influence of temperature difference between the upper and lower parts of the transport model on the migration process

Figure 7 shows the changes in nitrogen and phosphorus transport amounts in small and medium-sized rivers under different temperature differences (ΔY) over time, with temperature difference measured in Kelvin (K). The impact of temperature difference on the migration process of nitrogen and phosphorus can be analyzed by comparing the flux of nitrogen and phosphorus under different temperature differences. The graph indicates that as the temperature difference increases, so does the transport amount of nitrogen and phosphorus at the same time point. Regardless of the temperature difference, the transport amount of nitrogen and phosphorus gradually increases over time, signifying that as the system transitions to equilibrium, nitrogen and phosphorus continuously migrate from the riverbed sediments into the water body. A larger temperature gradient appears to accelerate the transport rate of nitrogen and phosphorus, likely because a larger temperature difference enhances water body convection, thereby promoting the vertical mixing and migration of nitrogen and phosphorus. Under all temperature difference conditions, the migration amount of nitrogen and phosphorus remains zero for the initial 40 time units, indicating that a certain startup time is needed for the release and migration of nitrogen and phosphorus. Once the process begins, a noticeable increase in nitrogen and phosphorus is observed. In summary, the temperature difference has a significant impact on the migration of nitrogen and phosphorus in small and medium-sized rivers. A larger temperature difference seems to promote the migration of nitrogen and phosphorus, which is related to the increase in

convective movements of the water body caused by the temperature difference, enhancing the vertical mixing of the water. This finding is crucial for water quality management and pollution control. By regulating the temperature distribution in rivers, the distribution of nutrients, including nitrogen and phosphorus, can be affected, thereby influencing the health and functionality of river ecosystems.

5. CONCLUSIONS

This study, by constructing Langmuir, Freundlich, and D-R models to describe the adsorption process of nitrogen and phosphorus in river sediments, reveals the characteristics of monolayer and multilayer adsorption and the influence of adsorbent pore volume on adsorption behavior. Through thermodynamic parameter analysis, the study examined the impact of temperature on the adsorption process of nitrogen and phosphorus and explored the effect of temperature fluctuations on their transport patterns in rivers through a one-dimensional transport mathematical model.

The experimental results attained in this study show that with increasing temperature, the adsorption capacity of nitrogen and phosphorus in river sediments is enhanced. This phenomenon is reflected in both Langmuir and Freundlich models, suggesting that higher temperatures increase the number or activity of adsorbent surface active sites. Temperature significantly influences the adsorption and migration of nitrogen and phosphorus. Thermodynamic parameters indicate that the adsorption process becomes more spontaneous with increasing temperature, while its endothermic nature suggests the presence of physical adsorption forces. Temperature fluctuations facilitate the migration of nitrogen and phosphorus in rivers. When there is a large temperature difference, the migration speed of nitrogen and phosphorus is accelerated, which is crucial for the control and management of nitrogen and phosphorus pollution in rivers. The results of this study are practically significant for understanding and predicting the behavior of nitrogen and phosphorus in river ecosystems. Grasping this information is essential for developing effective environmental policies and governance strategies, especially considering the significant impact of temperature fluctuations on the nitrogen and phosphorus cycle in the context of global climate change.

This research provides a theoretical foundation for understanding and predicting the behavior of nitrogen and phosphorus in river ecosystems and offers references for future environmental management and pollution control. Through in-depth analysis of adsorption characteristics and migration patterns, the paper emphasizes the crucial role of temperature in regulating the dynamics of nitrogen and phosphorus in rivers.

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