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Analysis of Factors for Compacted Clay Liner Performance Considering Isothermal Adsorption

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Abstract: The concentration profiles and breakthrough curves of the 2 m thick compacted clay liner (CCL) given in the specification were compared, considering three different adsorption isotherms (upper convex, linear, and lower concave). In addition, the effects of transport parameters, sorption isotherms, and source concentrations on pollutant migration were analyzed. The results showed that the dimensionless breakthrough curves of different source concentrations considering the linear adsorption isotherm coincided with each other, as the partition coefficient of the linear adsorption isotherm was constant. For the lower concave isotherm, the migration of a large source concentration was slowest, because the partition coefficient of the lower concave isotherm increased with an increase in concentration. For the upper convex isotherm, the migration of a large source concentration was fastest, because the partition coefficient decreased with an increase in concentration. The effects of the nonlinear isotherms on the shape of the outflow curve were similar to the effects of a change in the hydrodynamic dispersion (D_h): the concentration front of the upper convex isotherm was narrower, which was similar to the effect of a reduction in D_h (i.e., P_L), and the concentration front of the lower concave isotherm was wider and similar to the effect of an increase D_h (i.e., P_L). Therefore, the diffusion and adsorption parameters were fitted separately in the study, in case the nonlinear adsorption behavior was mistakenly defined as linear adsorption.

Keywords: CCL; adsorption; hydraulic conductivity; numerical modeling



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1. Introduction

Soil column tests and centrifugal model tests were both used for studying the migration of pollutants in soil. The soil column test was used to obtain migration parameters such as hydrodynamic dispersion and adsorption in the soil column state [1–4]. And the centrifuge model test was used to obtain migration parameters in the prototype stress state, and it could simulate and predict the migration behavior of pollutants in the prototype [5–7]. These studies must be simulated and analyzed via theoretical models. The fitting results of different theoretical models are different. Thus it is critical to select the appropriate advection–dispersion analytical model for the analysis of the results.

Many studies have been performed on mathematical simulations of pollutant migration [8–18]. The effect of boundary conditions on the simulation results has been discussed through theoretical analysis [8–10]. Solute transport experiments have been conducted to study suitable boundary conditions [1,4,15–18]. Zeng et al. [18] adopted soil column tests to verify that the combination of the continuous input flux boundary condition and the infinite far-zero gradient of the outflow was suitable for simulating the pore water concentration in the soil column, and the boundary combination of a continuous inlet

concentration and infinite far-zero gradient of the outflow was suitable for simulating the outflow concentration at the bottom of the soil column. All these studies are based on the linear sorption property of the pollutant on the material.

Isothermal adsorption lines can be classified into three types: the straight type, the upper convex type, and the lower concave type, according to the change in the slope of the curve closest to the origin of the isothermal adsorption line [19–21]. Many studies in the literature assumed that the adsorption behavior in the tests was linear, and therefore the test results were fitted based on a linear adsorption model [1–3,16,17,22]. However, most of the batch test results reported in the literature show that the isothermal adsorption curves of heavy-metal ions are mostly nonlinear [1,23–26]. Dou et al. [27] simulated the breakthrough curve with a retardation factor that gradually decreased over time, i.e., considering nonlinear adsorption as linear adsorption. Xie et al. [28] presented analytical solutions considering a piecewise linear adsorption. Serrano et al. [29] presented approximate analytical solutions for four nonlinear adsorptions. Mojid et al. [30] discussed the effect of the retarding factor of the nonlinear adsorption model on the migration of instantaneous injection-type pollutants. Maraqa et al. [31] used numerical methods to analyze the effect on pollutant migration of considering nonlinear adsorption as linear adsorption.

Many theoretical analyses and experiments have been conducted on the performance of the compacted clay liner (CCL) [11,13,32,33]. However, the effect of the isothermal line type on the CCL's performance has rarely been discussed. In this paper, the effects of transport parameters, isothermal line type, and source concentrations on the CCL's performance were investigated synthetically. This research could provide an insight into the migration characteristics of different isothermal line types and the regression of migration parameters.

2. Introduction of Theory

The mechanisms of pollutant migration include advection, hydrodynamic dispersion (including molecular diffusion and mechanical dispersion), and adsorption. The parameter representing advection is the pore flow velocity v_s , the parameters representing hydrodynamic dispersion are the effective molecular diffusion coefficient D_d^* (bending factor τ) and the diffusivity α , and the parameters representing the adsorption action are the retardation factor R_d and the nonlinear adsorption parameters. The flow velocity determines the appearance of the pollution front, the hydrodynamic dispersion parameter determines the width of the pollution front, and the adsorption has a retardation effect on migration, which delays the appearance of the pollution front. Figure 1 shows the breakthrough curves with a continuous source C_0 at the top of the soil column. As shown in Figure 1, when only advection exists, the pollution front is pushed vertically like a piston; this is called piston flow, and the occurrence time is $t_c = L/v_s$, where L is the length of the column and v_s is the seepage velocity. When there is both advection and hydrodynamic dispersion, the pollution front is a curve, and when there is also adsorption, the occurrence time of the pollution front is pushed backward, $t_c^* = t_c/R_d$. Whether the hysteresis phenomenon caused by adsorption with different adsorption models is the same has not been discussed.

The one-dimensional transient solute transport through homogeneous soil can be described as

$$\frac{\partial C_w(x, t)}{\partial t} = \frac{D_h}{R_d} \cdot \frac{\partial^2 C_w(x, t)}{\partial x^2} - \frac{v_s}{R_d} \frac{\partial C_w(x, t)}{\partial x} \quad (1)$$

where D_h is coefficient of hydrodynamic dispersion, $D_h = D_d^* + D_m$, $D_d^* = \tau D_d$, $D_m = \alpha v_s$, where D_d is free diffusion coefficient, D_m is mechanical dispersion. $R_d = 1$ when it is nonabsorbable, R_d is a constant greater than 1 under linear adsorption, and R_d is a function of pore water concentration under nonlinear adsorption, with its value changing with pore water concentration.

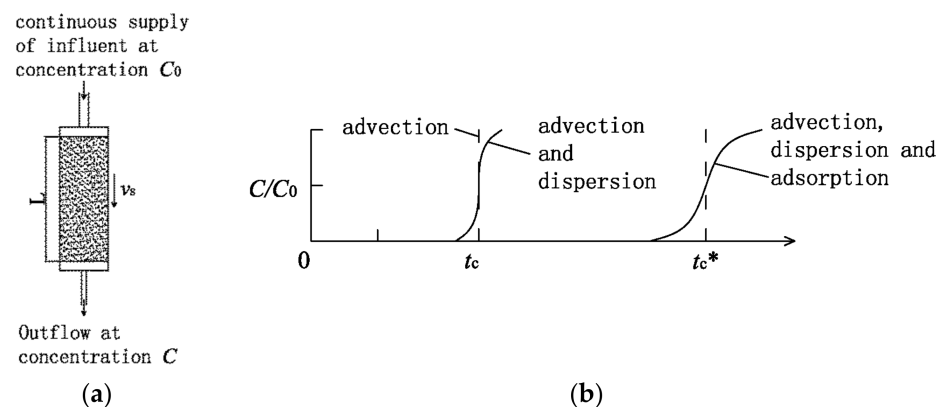


Figure 1. One-dimensional transport for continuous source: (a) column permeated continuously at concentration C_0 ; (b) breakthrough curves under advection alone, under advection and dispersion, and under advection, dispersion, and adsorption.

According to the adsorption model, a relationship between the total concentration in the soil and the pore water concentration can be established. The relationships for all three adsorption isotherms have been derived. The linear isotherm is the straight type, the Langmuir isotherm is the upper convex type, and the Freundlich isotherm (taking n_f greater than 1) represents the lower concave type.

(1) Linear isotherm (straight type).

The linear isotherm is expressed mathematically as

$$C_s = K_d C_w \quad (2)$$

where C_s is the mass of contaminants adsorbed per unit dry mass of soil, K_d is the distribution coefficient, and C_w is the pore water concentration.

The corresponding retardation factor expression is:

$$R_d = 1 + \frac{\rho_d K_d}{n} \quad (3)$$

where ρ_d is dry density, K_d is distribution coefficient, n is porosity.

According to the mass balance, the total concentration of pollutants C_{sto} can be expressed as

$$C_{sto} = \frac{n}{\rho_d} \left(S_r + \frac{\rho_d}{n} K_d \right) C_w \quad (4)$$

In saturated soil, $S_r = 1$, so

$$C_{sto} = \frac{n}{\rho_d} R_d C_w \quad (5)$$

Substituting Equation (5) into Equation (1), the governing equation for the mass concentration of pollutants in the soil can be obtained as follows:

$$R_d \frac{\partial C_{sto}}{\partial t} = D_h \left(\frac{\partial^2 C_{sto}}{\partial x^2} \right) - v_s \left(\frac{\partial C_{sto}}{\partial x} \right) \quad (6)$$

Therefore, the analytical solution of the total concentration in the soil is equal to the analytical solution of the pore water multiplied by $\frac{n}{\rho_d} R_d$. Furthermore, the analytical solution can be used to fit the total concentration profile.

(2) Langmuir sorption isotherm as upper convex type.

$$C_s = \frac{Q_0 b C_w}{1 + b C_w} C_s = \frac{Q_0 b C_w}{1 + b C_w} \quad (7)$$

$$R_d = 1 + \frac{\rho_d}{n} \cdot \frac{Q_0 b}{(1 + bC_w)^2} \quad (8)$$

$$C_{sto} = C_s + C_w V = \frac{Q_0 b C_w}{1 + bC_w} + C_w \frac{w}{\rho_w} \quad (9)$$

(3) Freundlich sorption isotherm as lower concave type.

$$C_s = K_F C_w^{n_f} \quad (10)$$

$$R_d = 1 + \frac{\rho_d}{n} K_F n_f C_w^{n_f-1} \quad (11)$$

$$C_{sto} = C_s + C_w V = K_F C_w^{n_f} + C_w \frac{w}{\rho_w} \quad (12)$$

For a nonlinear sorption isotherm, because C_{sto} and C_w are not simple linear relationships, it is impossible to obtain an analytical solution for the total concentration; however, the numerical method can be used to simulate C_{sto} .

3. Scheme for Analyses and Discussion of Results

In this paper, the transport of pollutants considering a linear isotherm was analyzed based on the analytical solution, and the transport of pollutants considering nonlinear isotherms was analyzed by the finite difference method. Firstly, the pore water concentration C_w was calculated, and then the C_{sto} profile was obtained based on the relationship between C_w and C_{sto} . For the one-dimensional transport problem, the expressions for the pore water concentration C_w and the effluent concentration C_e adopted the boundary combination recommended by Zeng et al. [18]: the boundary combination of a continuous inlet flux and an infinite far-zero gradient of the outflow was used to simulate the pore water concentration C_w profile, and the boundary combination of a continuous inlet concentration and an infinite far-zero gradient of the outflow was used to analyze the effluent concentration C_e curve.

According to the compacted clay liner parameters given in the specification [34] and the relevant parameters reported in the literature [35,36], the main basic calculation parameters are shown in Table 1. The adsorption parameters are presented in the following sections.

Table 1. Model calculation parameters.

ρ_d (g/cm ³)	1.04
n	0.62
k (m/s)	1×10^{-9}
L (m)	2
h (m)	40
C_0 (mg/L)	1000
α (m)	0.047
D_d^* (m/s ²)	3.3×10^{-10}

3.1. Analysis of Influencing Factors of Advection–Dispersion Model for Linear Isotherm

According to the expressions for the pore water concentration C_w and effluent concentration C_e recommended by Zeng et al. [18], the dimensionless expressions are shown in Equations (13) and (14).

$$\frac{C_w(x,t) - C_i}{C_0 - C_i} = \frac{1}{2} \operatorname{erfc} \left(\frac{\frac{x}{L} - \frac{T}{R_d}}{2\sqrt{T/(R_d P_L)}} \right) + \sqrt{\frac{TP_L}{\pi R_d}} \exp \left[-\frac{\left(\frac{x}{L} - \frac{T}{R_d} \right)^2}{4T/(R_d P_L)} \right] - \frac{1}{2} \left(1 + P_L \frac{x}{L} + \frac{TP_L}{R_d} \right) \exp(P_L \frac{x}{L}) \operatorname{erfc} \left(\frac{\frac{x}{L} + \frac{T}{R_d}}{2\sqrt{T/(R_d P_L)}} \right) \quad (13)$$

$$\frac{C_e(L, t)}{C_0} = \frac{1}{2} \operatorname{erfc} \left(\frac{1 - \frac{T}{R_d}}{2\sqrt{T/(R_d P_L)}} \right) + \frac{1}{2} \exp(P_L) \operatorname{erfc} \left(\frac{1 + \frac{T}{R_d}}{2\sqrt{T/(R_d P_L)}} \right) \quad (14)$$

where $T = \frac{v_s t}{L}$, $P_L = \frac{v_s L}{D_h}$, T is the number of pore volumes of the flow, and P_L is the Peclet number of soil columns representing the relative effect of advection with respect to the dispersive/diffusive transport.

The effluent concentration can be calculated according to Equation (16). In addition, the expression for the effluent concentration can be simplified when $T_R = T/R_d$ is substituted into Equations (13) and (14). It is then found that the expressions in Equations (13) and (14) for adsorbing solutes and non-adsorbing solutes are exactly the same. Dimensionless parameters were used directly in the following discussion. Dry density, porosity, and water content were taken from Table 1.

Figure 2a,b show the pore water and total concentration profiles in the clay liner corresponding to different retardation factors, respectively. Figure 2a shows that the larger the value of K_d (i.e., R_d), the shallower the contaminant front. Figure 2b shows that the larger the value of K_d (i.e., R_d), the shallower the total concentration profile curve in the soil and the bigger the peak value at the top.

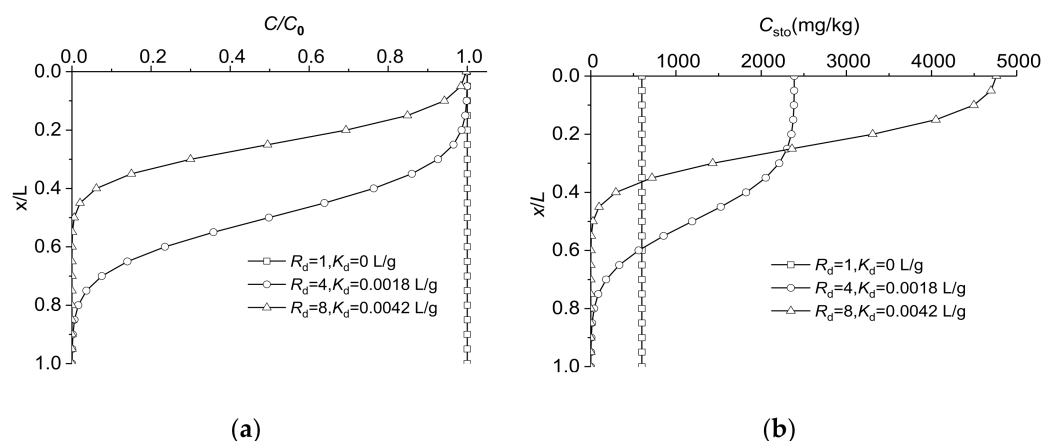


Figure 2. Concentration profiles in soil with different R_d values ($P_L = 50$, $T = 2$): (a) pore water concentration; (b) total concentration.

Figure 3 shows the breakthrough curves in terms of dimensionless parameters. As shown in Figure 3a, when T is taken as the abscissa, the greater the value of K_d , the later the effluent front appears and the wider the contaminant front in shape. When P_L is the same, the concentration values corresponding to $T = R_d$ on the breakthrough curves for different K_d values are equal: the greater the $P_L = v_s L/D_h$ corresponding to the same K_d , the narrower the contaminant front. This is because a greater P_L leads to a stronger advection effect; thus, its front is narrower. As shown in Figure 3b, when the abscissa is $T_R = v_s t/(LR_d)$, the outflow concentration curves for different R_d values coincide, indicating that the effect of R_d on advection and dispersion is as shown in the control equation, that is, both v_s and D_h are $1/R_d$ of the past, so that the effect of R_d on advection and dispersion migration is a linear superposition.

Figure 4 shows the relative outflow concentration values for different values of P_L at $T = R_d$. When $T = R_d$, C_e/C_0 is closer to 0.5. This is because the greater the P_L , the greater the relative importance of advection and dispersion, and the sharper the concentration interface as a piston.

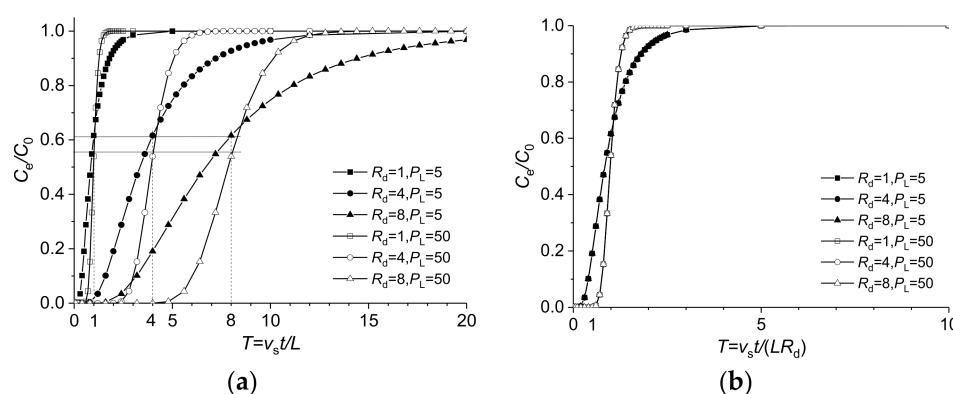


Figure 3. Concentration profiles in soil with different values of R_d ($P_L = 50$, $T = 2$): (a) pore water concentration; (b) total concentration.

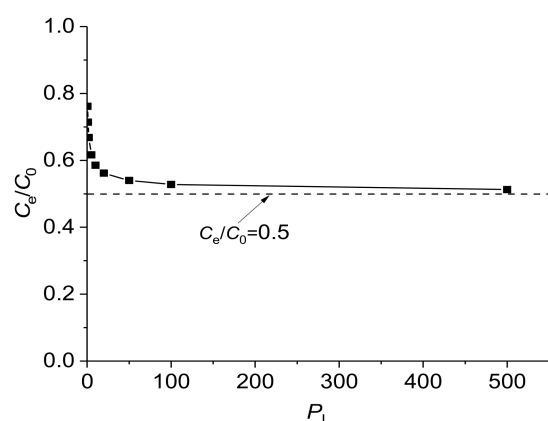


Figure 4. Relative outflow concentration values for different values of P_L at $T = R_d$.

The effects of the two diffusion parameters $D_d^*(\tau)$ and α are compared separately below. Figure 5a–c show the corresponding outflow curves with a 4-fold change of D_d^* and α with three values of v_s ($v_s = 1 \times 10^{-9}$ m/s, 1×10^{-7} m/s, and 1×10^{-8} m/s), respectively, with a barrier thickness of 2 m. The values of D_d^* and α are shown in the legends. As shown in Figure 5, when $v_s = 1 \times 10^{-9}$ m/s, the effect of a 4-fold change in D_d^* on the outflow curve was significantly greater than that of a 4-fold change in α . When $v_s = 1 \times 10^{-7}$ m/s, the effect of a 4-fold change in α on the outflow curve was significantly greater than that of a 4-fold change in D_d^* . When $v_s = 1 \times 10^{-8}$ m/s, the outflow curves corresponding to 4-fold changes in D_d^* and α coincided, that is, the effect was the same. According to the dimensionless parameters $P_L = \frac{v_s L}{D_h} = \frac{L}{\frac{D_d^*}{v_s} + \alpha}$, the effects of D_d^* and α are manifested in the change of P_L , so that outflow curves with the same P_L coincide. The smaller the flow rate, the greater the effect of D_d^* , and conversely for the effect of α .

3.2. Analysis of Influencing Factors of Advection–Dispersion Model for Lower Concave Type

The Freundlich model has two parameters: K_F and n_f . The effects of the two parameters were compared separately, and in this section, C_0 is assumed to be 1000 mg/L. The values of K_F and n_f used in the analysis are given in Table 2. All values of n_f were greater than 1, so the isotherm is a lower concave curve. The corresponding adsorption isotherms are shown in Figure 6. When the effects of different source concentrations were compared, three source concentrations (1000 mg/L, 100 mg/L, and 10 mg/L) were considered, with K_F and n_f adsorption parameters taken from F1 in Table 2.

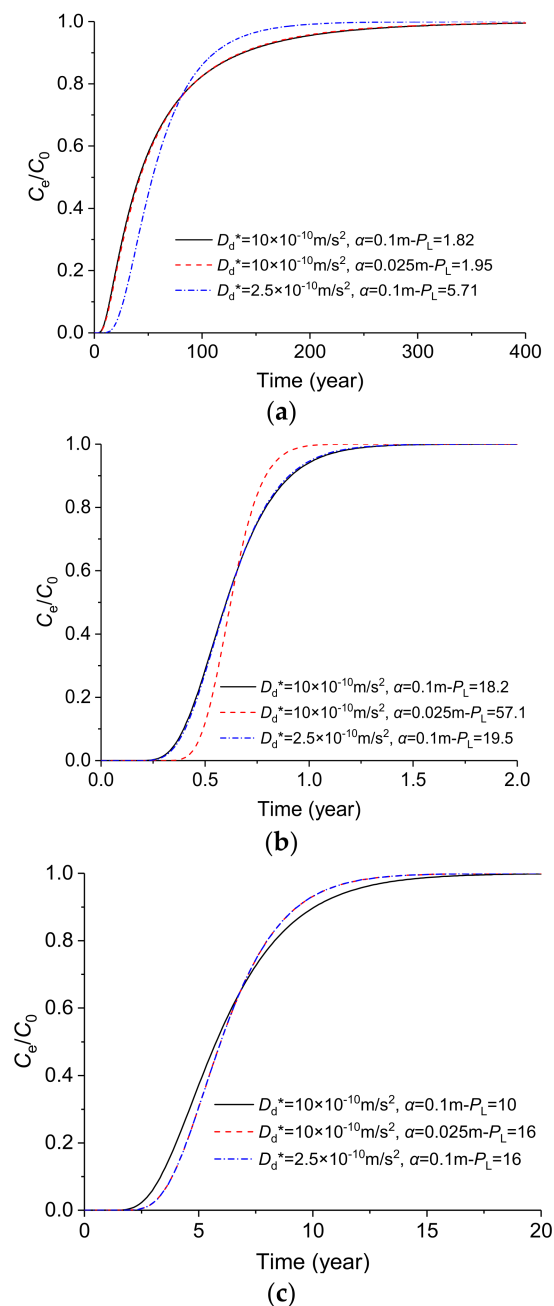


Figure 5. Comparison of outflow curves for different values of $D_d^*(\tau)$ and α : (a) $v_s = 1 \times 10^{-9}$ m/s; (b) $v_s = 1 \times 10^{-7}$ m/s; (c) $v_s = 1 \times 10^{-8}$ m/s.

Table 2. Freundlich adsorption model parameters.

Model Number	F1	F2
K_F (L/g)	0.00025	0.0004
n_f	1.39	1.39

3.2.1. Effect of K_F and n_f

Figure 7a,b show the pore water concentration profiles and the total concentration profiles in soil with different values of K_F at $t = 24$ h. As shown in Figure 7a, the larger the value K_F (i.e., the higher the isotherm), the greater the adsorption and the shallower the pore water concentration front. As shown in Figure 7b, the larger the value of K_F , the

shallower the total concentration profile curve in the soil and the greater the maximum value at the top.

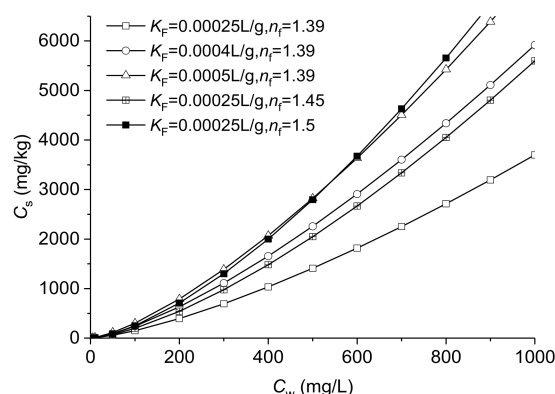


Figure 6. Adsorption isotherms.

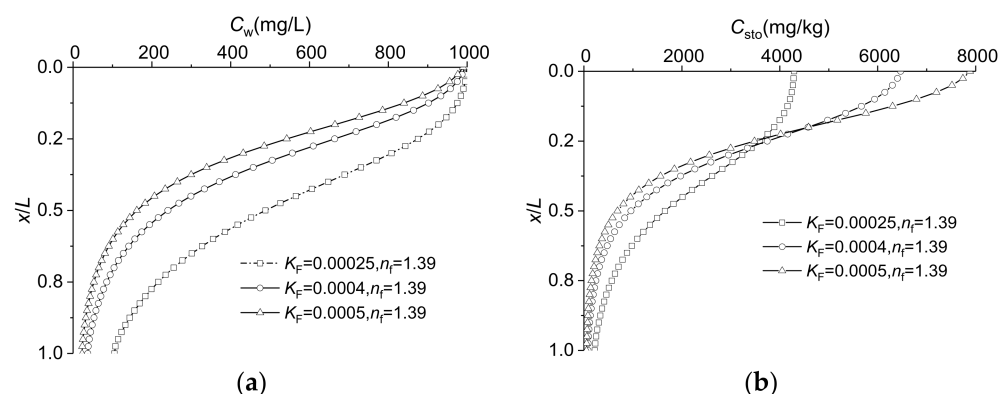


Figure 7. Concentration profiles in soil at $t = 24$ h with different values of n_f : (a) pore water concentration; (b) total concentration.

Figure 8a,b show the outflow concentration curves with $T = v_s t / L$ as the abscissa and the outflow curves with $T_R = v_s t / (LR_d)$ as the x -axis, respectively. The outflow curves with T_R as the abscissa were obtained by substituting the R_d value calculated from Equation (13) into the outflow curve with T as the abscissa. As shown in Figure 8a, the larger the value of K_F , the later the outflow curve appears. As shown in Figure 8b, when T_R is taken as the abscissa, all the outflow curves basically coincide.

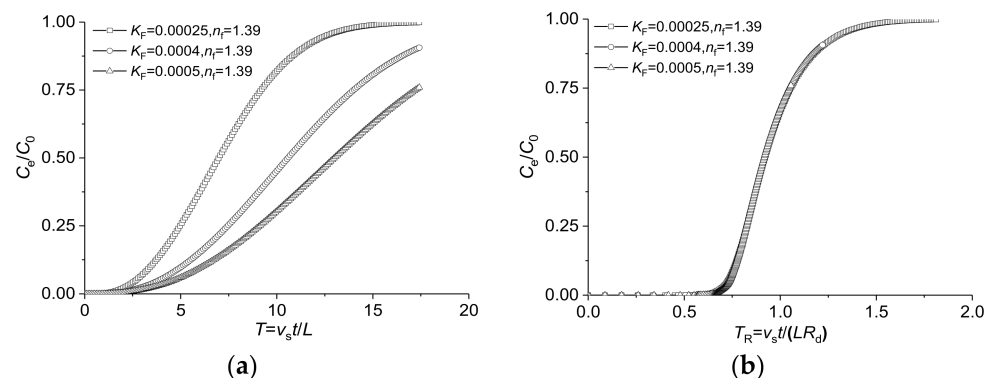


Figure 8. Dimensionless outflow curves for the Freundlich model with different values of K_F : (a) T as abscissa; (b) T_R as abscissa.

Figure 9a,b show the pore water profiles and the total concentration profiles in soil with different values of n_f at $t = 24$ h. As shown in Figure 9a, the larger the value of n_f ,

(i.e., the higher the isotherm), the greater the adsorption and the shallower the pore water concentration front. As shown in Figure 9b, the larger the value of n_f , the shallower the total concentration profile curve in the soil and the greater the maximum value at the top.

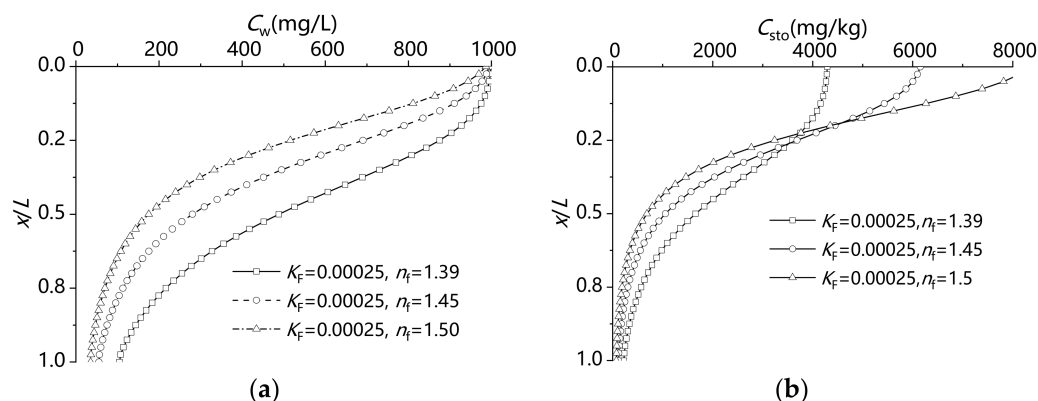


Figure 9. Concentration profiles in soil at $t = 24$ h with different values of n_f : (a) pore water concentration; (b) total concentration.

Figure 10a,b show the outflow concentration curves with $T = v_s t / L$ as the abscissa and the outflow curves with $T_R = v_s t / (LR_d)$ as the x -axis, respectively. As shown in Figure 10a, the larger the value of n_f , the later the outflow curve appears. As shown in Figure 10b, when T_R is taken as the abscissa, all the outflow curves basically coincide.

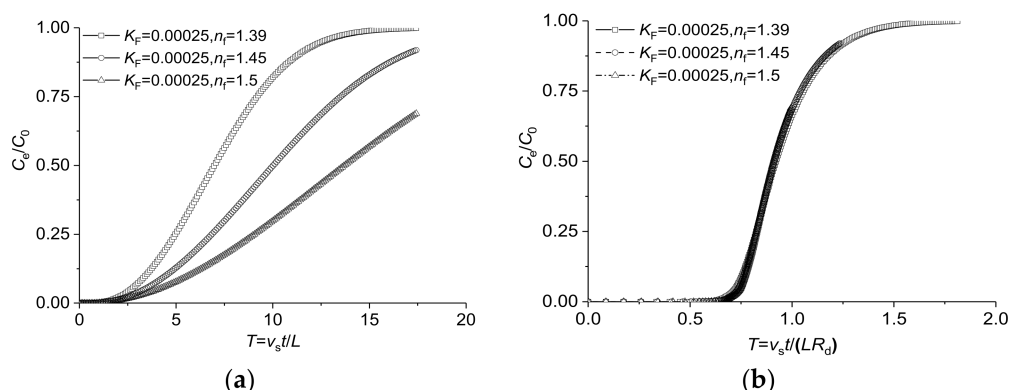


Figure 10. Dimensionless outflow curves for the Freundlich model with different values of n_f : (a) T as abscissa; (b) T_R as abscissa.

3.2.2. Effect of Source Concentration

Figure 11a,b show the outflow concentration curves with $T = v_s t / L$ as the abscissa and the outflow curves with $T_R = v_s t / (LR_d)$ as the x -axis, respectively. As shown in Figure 11a, when T is taken as the abscissa, the smaller the source concentration, the earlier the outflow curve appears. As shown in Figure 11b, when T_R is taken as the abscissa, the outflow curves corresponding to different source concentrations are relatively close, but do not coincide, which indicates that the effect of C_0 on advection and dispersion migration in the nonlinear adsorption model is nonlinear.

3.3. Analysis of Influencing Factors of Advection–Dispersion Model for Upper Convex Type

The Langmuir model has two parameters: Q_0 and b . The effects of these two adsorption parameters were compared separately in the analysis, and in this section, C_0 is assumed to be 1000 mg/L. The values of Q_0 and b used in the analysis are given in Table 3, and the corresponding adsorption isotherms are shown in Figure 12. The effects of different source concentrations for the same adsorption parameter were compared. Three source

concentrations (1000 mg/L, 100 mg/L, and 10 mg/L) were considered, with the adsorption parameters Q_0 and b taken from L1 in Table 3.

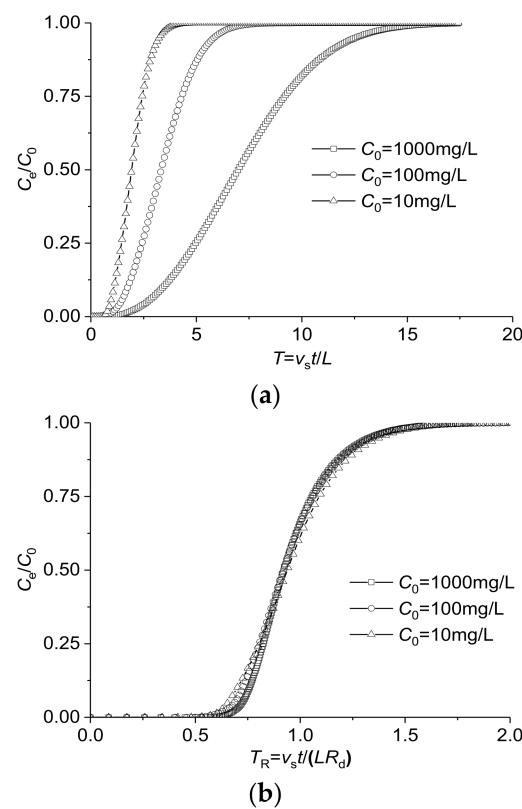


Figure 11. Dimensionless outflow curves for the Freundlich model with different source concentrations: (a) T as abscissa; (b) T_R as abscissa.

Table 3. Langmuir adsorption model parameters.

Model Number	L1	L2	L3	L4	L5
Q_0 (mg/g)	5.19	5.19	5.19	3	7
b (L/mg)	0.0015	0.003	0.006	0.0015	0.0015

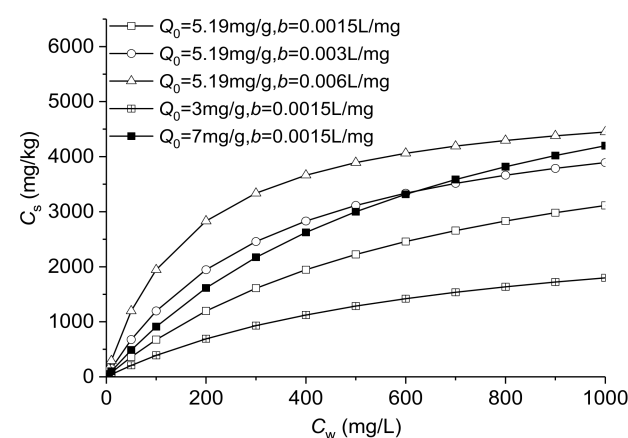


Figure 12. Isothermal adsorption curves.

3.3.1. Effect of Q_0 and b

Figure 13a,b show the pore water concentration profiles and the total concentration profiles in soil with different values of Q_0 at $t = 24$ h. As shown in Figure 13a, the larger the

value of Q_0 (i.e., the higher the isotherm), the higher the isothermal adsorption curve, the greater the adsorption, and the shallower the pore water concentration front. As shown in Figure 13b, the larger the value of Q_0 , the shallower the total concentration profile curve in the soil and the greater the maximum value at the top.

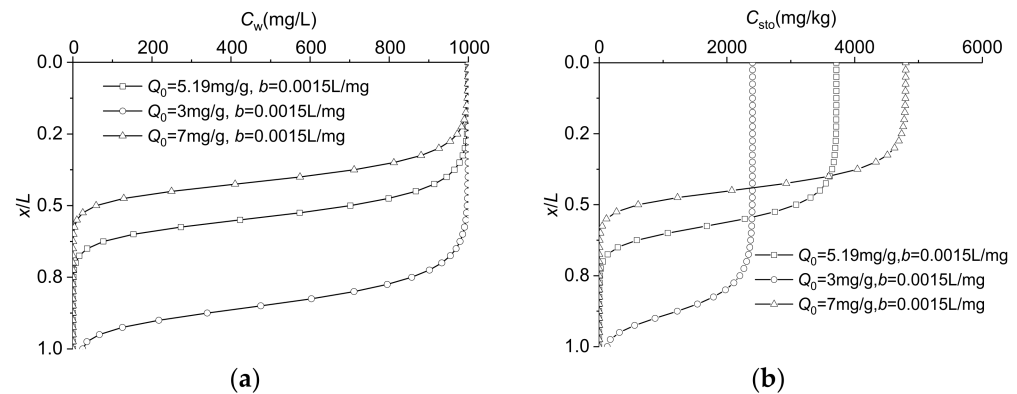


Figure 13. Concentration profiles in soil at $t = 24$ h with different values of Q_0 : (a) pore water concentration; (b) total concentration.

Figure 14a,b show the outflow concentration curves with T as the abscissa and the outflow curves with T_R as the x -axis, respectively. As shown in Figure 14a, the larger the value of Q_0 , the higher the isothermal adsorption curve, the later the outflow curve appears, and the flatter the concentration front. As shown in Figure 14b, when T_R is taken as the abscissa, all the corresponding flow curves are very close.

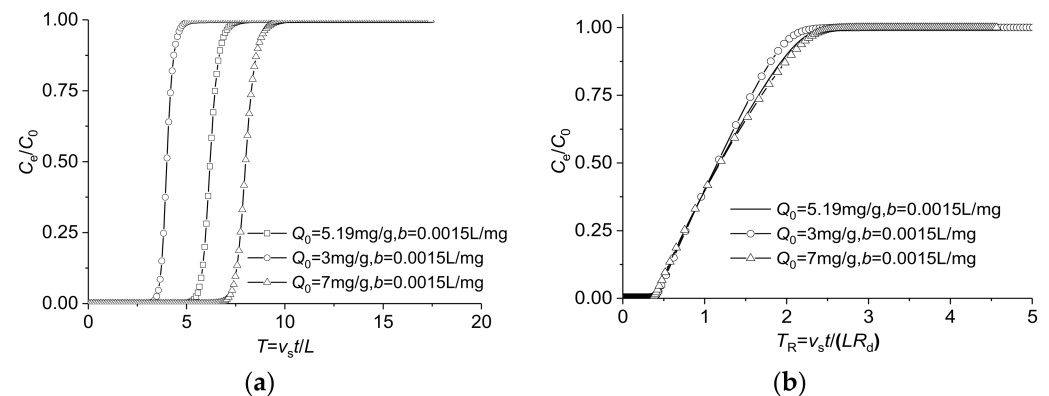


Figure 14. Dimensionless outflow curves for the Langmuir model with different values of Q_0 : (a) T as abscissa; (b) T_R as abscissa.

Figure 15a,b show the pore water profiles and the total concentration profiles in soil with different values of b at $t = 24$ h. As shown in Figure 15a, the larger the value of b , (i.e., the higher the isotherm), the greater the adsorption and the shallower the pore water concentration front. As shown in Figure 15b, the larger the value of b , the shallower the total concentration profile curve in the soil and the greater the maximum value at the top.

Figure 16a,b show the outflow concentration curves with T as the abscissa and the outflow curves with T_R as the x -axis, respectively. As shown in Figure 16a, the larger the value of b , the later the outflow curve appears. As shown in Figure 16b, when T_R is taken as the abscissa, all the outflow curves of the Langmuir model are quite different, and there is an intersection point.

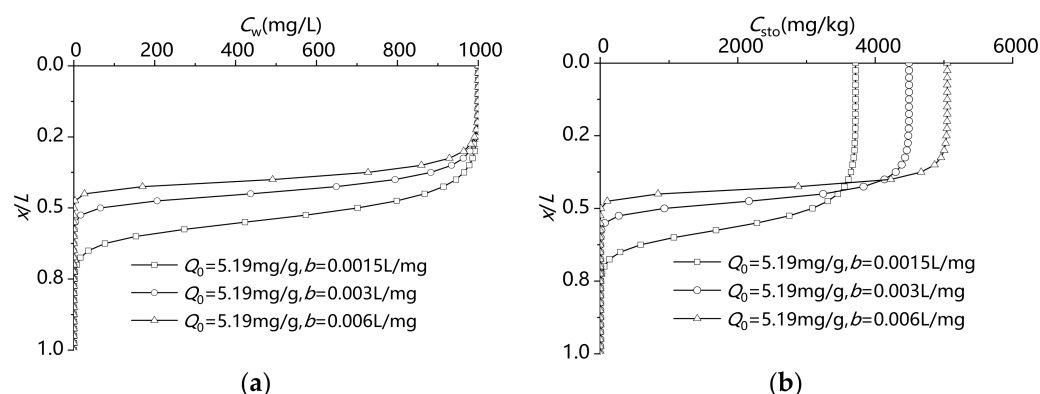


Figure 15. Dimensionless outflow curves for the Langmuir model with different values of Q_0 : (a) T as abscissa; (b) T_R as abscissa.

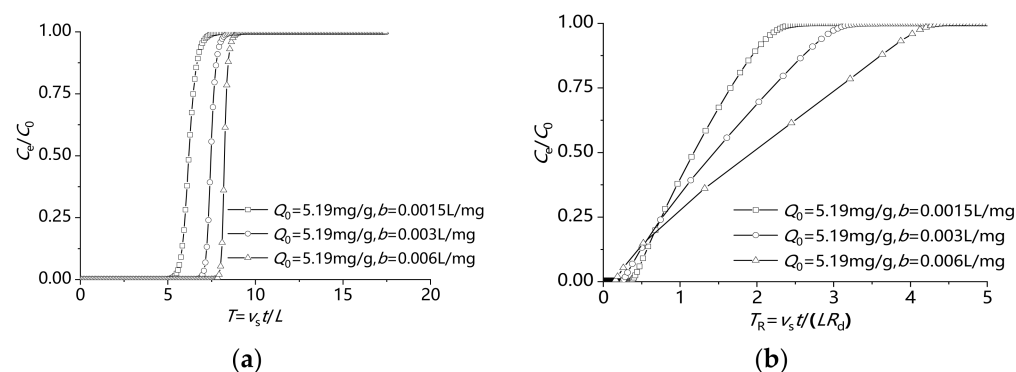


Figure 16. Dimensionless outflow curves of the Langmuir model with different values of Q_0 : (a) T as abscissa; (b) T_R as abscissa.

3.3.2. Effect of Source Concentration

Figure 17a,b show the outflow concentration curves with T as the abscissa and the outflow curves with T_R as the x -axis, respectively. As shown in Figure 17a, when T is taken as the abscissa, the smaller the source concentration, the later the outflow curve appears. As shown in Figure 17b, when T_R is taken as the abscissa, the outflow curves corresponding to the different source concentrations do not coincide and are quite different.

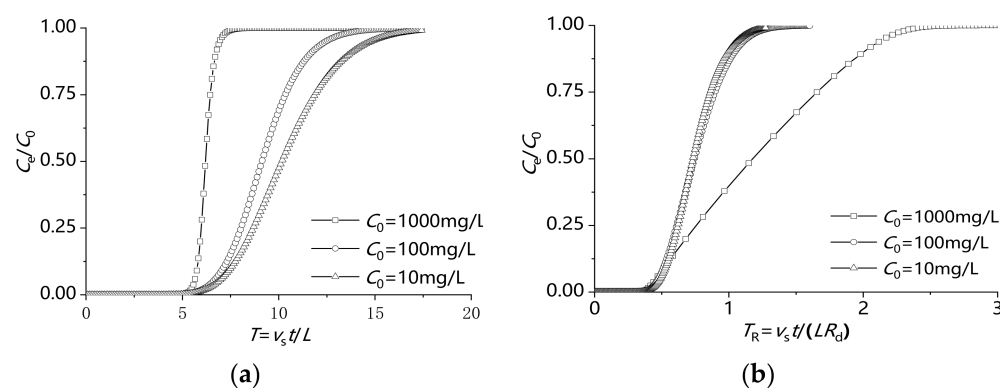


Figure 17. Dimensionless outflow curves for Langmuir models with different C_0 : (a) T as abscissa; (b) T_R as abscissa.

3.4. Effect of Different Types of Sorption Isotherms with the Same Maximum Adsorption Capacity

Three types of isotherms: upper convex, linear, and lower concave, with the same maximum adsorption capacity, are compared below, represented by the Langmuir model,

the linear model, and the Freundlich model, respectively. The specific adsorption parameters are shown in Figure 18. The other parameters used in the calculation are given in Table 1.

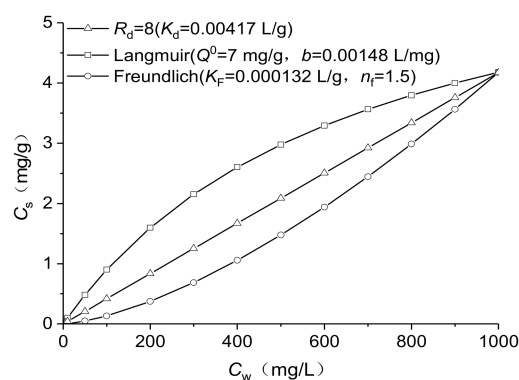


Figure 18. Three types of sorption isotherms.

Figure 19 shows the pore water concentration profiles. As shown in Figure 19, there is a common intersection point in the three concentration profiles: above the intersection point, the concentration front of the upper convex (Langmuir model) is the deepest, and the concentration front of the lower concave (Freundlich model) is the shallowest; below the intersection point, the concentration front of the upper convex (Langmuir model) is the shallowest, and the concentration front of the lower concave (Freundlich model) is the deepest. With increasing time, the intersection-point position on the profile gradually moves downward. As a whole, the concentration front of the upper convex (Langmuir model) is the narrowest, followed by the linear model, and the lower concave (Freundlich model) is the widest.

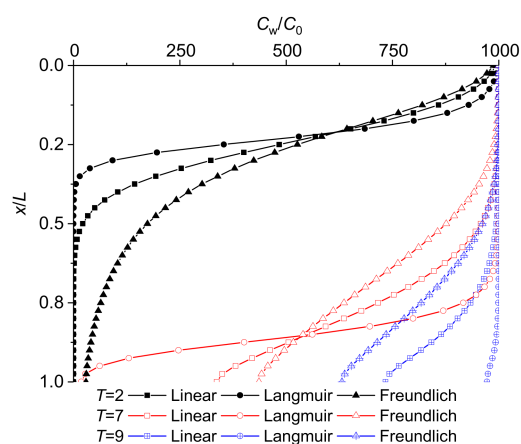


Figure 19. Pore water profiles in soil for the three isotherms.

The slopes (partition coefficients) for each isotherm are as follows: in the low pore water concentration segment, the upper convex type (Langmuir model) > linear model > lower concave type (Freundlich model), that is, the upper convex adsorption rate is largest and the lower concave adsorption rate is smallest; in the high pore water concentration segment, the upper convex type (Langmuir model) < linear model < lower concave type (Freundlich model), that is, the upper convex adsorption rate is smallest and the lower concave adsorption rate is largest. Therefore, there is an intersection point in the pore water concentration front of different models.

Figure 20a,b show the outflow concentration curves with T as the abscissa and the outflow curves with T_R as the x -axis, respectively. As shown in Figure 20a, when T is taken as the abscissa, there is a common intersection point in the three curves, and

before the intersection point, the order of the outflow concentration is lower concave (Freundlich model) > linear > upper convex (Langmuir model), with the opposite after the intersection point. The lower concave (Freundlich model) outflow concentration appeared first, followed by the linear model, with the upper convex (Langmuir model) appearing latest. The upper convex (Langmuir model) reached equilibrium first, the linear model in the middle, and the lower concave (Freundlich model) latest. This is consistent with the distribution of pore water concentrations shown in Figure 19. As shown in Figure 20b, when T_R is taken as the abscissa, the outflow curves of different isotherms do not coincide and there are intersections.

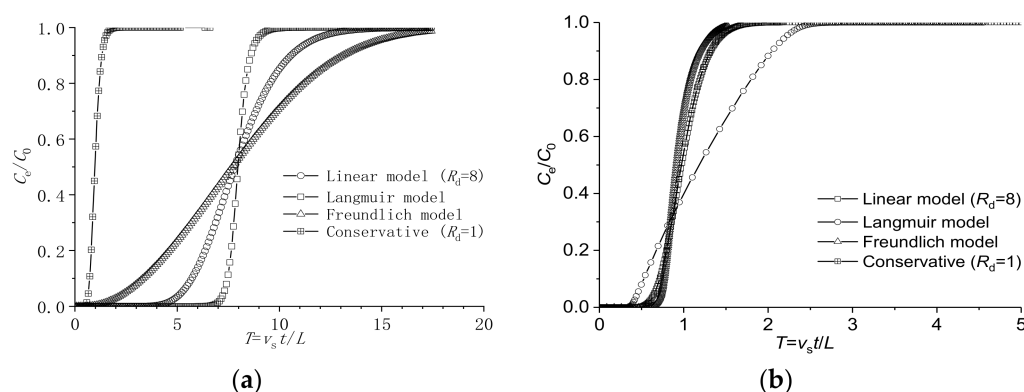


Figure 20. Dimensionless outflow curves for for the three isotherms ($C_0 = 1000$ mg/L): (a) T as abscissa; (b) T_R as abscissa.

Comparing Figure 20a with Figure 3a, it can be seen that compared with the linear model, the Langmuir model corresponds to a narrower concentration front, which is similar to the effect of a smaller D_h (i.e., P_L), and the Freundlich model corresponds to a wider concentration front, which is similar to the effect of a larger D_h (i.e., P_L), that is, the nonlinear adsorption model has a similar effect on the shape of the outflow curve as changing D_h . Therefore, the nonlinear adsorption behavior may be mistakenly defined as linear adsorption by fitting the diffusion parameters and adsorption parameters at the same time. For this reason, univariate analysis is recommended in the analysis of the test results. That is, migration parameters should be fitted one by one in the study.

3.5. Column Test with Pb^{2+}

In order to illustrate the different types of isotherms, a breakthrough column test with a source solution of $Pb(II)$ was carried out. Kaolin clay slurry was consolidated for preparing the clay liner model in a model cylinder. The physical parameters of kaolin are given in Table 4.

Table 4. Physical parameters of Jiangsu kaolin.

Property	Value
Specific gravity, G_s	2.61
Mean particle size, d (mm)	0.003
Clay fraction, CF (%)	67.8
Liquid limit, w_L (%)	67.1
Plastic limit, w_p (%)	34.6
Specific surface area (m^2/g)	2.1
pH	4.4

As shown in Figure 21, after completion of the consolidation, the model cylinder was connected to a modified Mariotte bottle which was used to contain the designed hydraulic head. The source concentration C_0 of Pb(II) was kept constant at 892.3 mg/L. The test was started by turning on the two control valves for inflow and outflow. The effluent from the bottom of the model cylinder was collected at a series of different times. The effluent concentration was measured using an atomic absorption spectrophotometer (TAS-990).

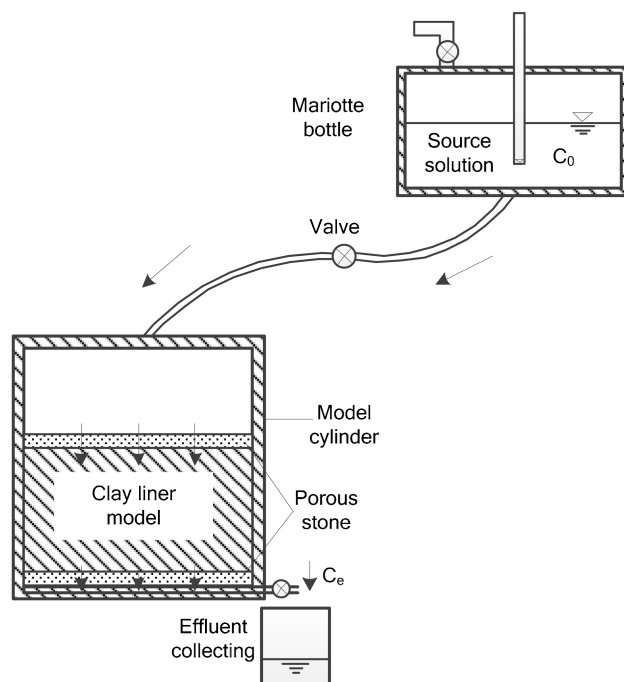


Figure 21. Schematic diagram of soil column test.

Table 5 shows the parameters of the column test. The height of the column was 21.9 mm, and the hydraulic head difference was 16m, corresponding to an advection velocity of 9.01×10^{-7} m/s. Figure 22 shows a comparison of the measured breakthrough curve and the fitting breakthrough curves. The best-fit value of R_d was 7.5 as shown in Figure 22. Meanwhile, the Langmuir isotherm and the Freundlich isotherm with the same maximum adsorption capacity were compared, as shown in Figure 23. As shown in Figure 22, the Langmuir isotherm was able to fit the measured curve very well (determination coefficient $R^2 = 0.992$). However, the best-fit value of D_h was 5.45×10^{-9} m²/s, which was much larger than a reasonable value. The Freundlich isotherm fit the measured curve somewhat less well ($R^2 = 0.984$) than the other two isotherms, and the fitted value of D_h was 2.8546×10^{-10} m²/s, which was much smaller than a reasonable value. Hence, it was verified that the nonlinear adsorption model had a similar effect on the shape of the outflow curve as changing the value of D_h .

Table 5. Parameters of the column test.

h_c (mm)	Δh_w (m)	n	ρ_d	v_s ($\times 10^{-7}$ m/s)	D_d^* ($\times 10^{-10}$ m ² /s)	α (m)	Test Duration (h)
21.9	16	0.55	1.17	9.01	2.8546	0.00128	222.25

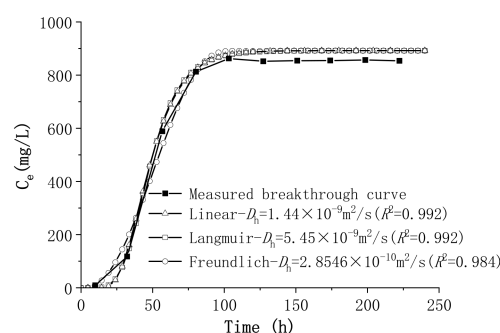


Figure 22. Comparison of the measured breakthrough curve and the fitting breakthrough curves.

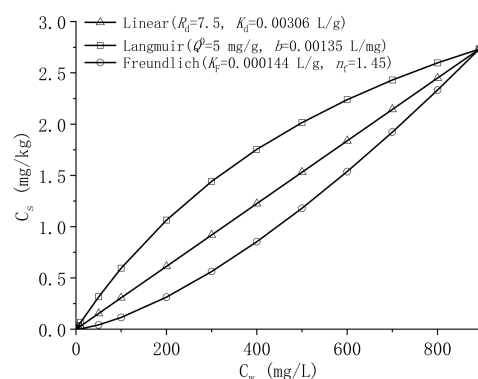


Figure 23. Three types of sorption isotherms used in fitting.

4. Conclusions

The concentration profiles and outflow curves of the 2 m thick compacted clay liner (CCL) given in the specification were calculated, considering three different sorption isotherms (upper convex, linear, and lower concave). The effects of transport parameters, sorption isotherms, and source concentrations on pollutant migration were analyzed. The results showed that the effect of source concentrations on pollutant migration was different for different adsorption models. Source concentration values had no effect on the migration of the linear adsorption model, but for the Langmuir model, migration was slow for small source concentrations, and for the Freundlich model, migration was slow for large source concentrations. Because the partition coefficient of the linear isothermal adsorption curve was constant and did not change with concentration, the upper convex (Langmuir model) isothermal adsorption curve had a larger partition coefficient at smaller concentrations, and the lower concave (Freundlich model) isothermal adsorption curve had a smaller partition coefficient at smaller concentrations. With a small partition coefficient, the adsorption was low and the concentration front was deep; conversely, the concentration front was shallow with a larger partition coefficient.

When the adsorption capacity corresponding to the source concentration was the same as in the linear model, the effect of the nonlinear adsorption model on the shape of the outflow curve was similar to the effect of a change in diffusion (D_h): the concentration front corresponding to the upper convex model was narrower, which was similar to the effect of D_h (i.e., P_L) reduction, and the concentration front corresponding to the lower concave model was wider, which was similar to the effect of an increased D_h (i.e., P_L). These results were verified using a column test. Therefore, the nonlinear adsorption behavior may be mistakenly defined as linear adsorption by fitting the diffusion parameters and adsorption parameters at the same time. For this reason, univariate analysis was recommended for analysis of the results. In other words, the diffusion and adsorption parameters should be fitted separately in the study.

When the flow rate was small, the effect of D_d^* on the curve was large, and the effect of α was small, while there were opposite effects when the flow rate was large. The adsorption

had a significant effect on the outflow curve, so it is very important to obtain the correct adsorption parameters for the prediction of the CCL's performance.

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