Study on the Influence of Solid Medium Adsorption on the Migration and Transformation of Chlorinated Hydrocarbons in the Groundwater System

Shuaiji Zhang¹², Ruibao Jia³, Shaohua Sun³, Zhenmin Ma¹²*, Shusen Liu¹²

¹School of Water Conservancy and Environment, University of Jinan, Jinan 250022, China.
²Shandong Provincial Engineering Technology Research Center for Groundwater. Numerical. Simulation. and Contamination Control, Jinan 250022, China.
³Shandong Province City Water Supply and Drainage Water Quality Monitoring Center, Jinan 250022, China.

*stu mazm@ujn.edu.cn
*Corresponding author E-mail: 398523871@qq.com (Z. Ma)

Abstract. In this paper, the pollution of chlorinated hydrocarbons in the groundwater system is taken as the main research object. According to the adsorption characteristics of chlorinated hydrocarbons in different aquifer media, carbon tetrachloride is taken as an example to carry out isothermal adsorption experiments under different solid medium conditions. The concentration data are obtained by fitting the standard curves of linear, Langmuir, Freundlich, and Temkin types to study the mechanism of chlorinated hydrocarbons in different media. The results show that the adsorption capacity of silty clay is greater than that of limestone at the same initial concentration. Therefore, before the pollutants enter the karst water, the silty clay will "intercept" the pollutants. However, once the karst water is polluted, the limestone medium has a small adsorption capacity, which will bring difficulties to pollution control and treatment.

1. Introduction

The adsorption of organic pollutants by solid-phase media is an extremely complex process, which includes a variety of action modes and mechanisms, including surface adsorption, distribution, void filling, or interaction with special adsorption sites of minerals and soil organic matter[1]. The adsorption of organic pollutants by the solid-phase medium of aquifer affects the migration and return of pollutants in the groundwater system. When the adsorption process reaches equilibrium, the unit amount of solute adsorbed by the solid medium reflects the adsorption capacity of the medium. The adsorption capacity and the kinetic mechanism of adsorption/resolution are the key factors of the adsorption effect. To study the migration and transformation of pollutants in the groundwater system, the first step is to study the adsorption process. When hydrochlorination hydrocarbons migrate in aquifers or low-permeability media, the adsorption effect affects the migration rate and diffusion of hydrochlorination hydrocarbons[2]. A great deal of research has been done on the adsorption characteristics of chlorophyll hydrocarbons in different aquifers[3-5]. The limestone aquifers in the study area are widely distributed, and the adsorption of chlorinated hydrocarbons by limestone during migration in karst water is seldom studied. In this paper, carbon tetrachloride is taken as an example to...
study the adsorption effect of silty clay and limestone on carbon tetrachloride in the main aquifer medium, to lay a theoretical foundation for further monitoring of groundwater organic pollution and exploring the control methods of groundwater organic pollutants.

2. Overview of the study area
The study area is located in the north of Taishan anticline uplift and the east wing of Jinan monocline structure. Quaternary and Yanshanian igneous rocks and Ordovician limestone are developed in the area. The quaternary system is mainly distributed in the northern plain area of the study area, and the lithology is mainly composed of silty clay and clayey sand. Igneous rocks are mainly distributed in the marginal zone of Jinan igneous rock mass in the northern part of the study area. They are mainly gabbro and diorite, which are concealed in the Quaternary system and limestone, and most of them intrude into the limestone layer in multilayer. The Ordovician is mainly composed of limestone. The Quaternary pore water-rock group and carbonate rock fracture karst water-bearing rock group are mainly distributed in the southern refinery and the exposed surface area to the south. The groundwater types are mainly Quaternary loose rock pore water and carbonate rock fracture karst water.

3. Materials and methods

3.1. Experimental preparation

3.1.1. Experimental materials and instruments
(1) Reagent: carbon tetrachloride (analytical purity, purity ≥ 99.5%), methanol (analytical purity, purity ≥ 99.5%).
(2) Instruments: TRACE 1300 gas chromatograph; JM-3 air generator; JM-3 hydrogen generator; AI 1310 automatic injector.
Analysis conditions: direct injection - split injection; Injector: 200 °C.
Carrier gas: high purity nitrogen constant pressure carrier gas, pressure: 100.0kpa.
Flow rate: 40.0ml/min; Furnace temperature: 350 °C; Running time: 20min; Shunt flow: 50.0ml/min.
Tester: FID, 150°C; Gas flow rate: air: 350 ml / min, hydrogen: 35.0 ml / min.
3.1.2. Isothermal equilibrium adsorption experiment of different media

The Quaternary pore water aquifer and karst water aquifer are distributed in the study area. The aquifer media are silty clay and limestone respectively. The south of the study area is a single karst aquifer, and the northern karst water overlies the Quaternary pore water. Therefore, isothermal adsorption equilibrium experiments were carried out for different aquifer media. Two groups of isothermal equilibrium adsorption experiments were set up, with 12 initial concentration values in each group. 2.000±0.001g silty clay and limestone were respectively added into the brown reagent bottle of 40ml headspace sample, and then carbon tetrachloride solution (0~20mg/L) with different mass concentrations was added to the bottle until there was no gas phase space in the bottle, and the silicone rubber bottle containing PVC liner was used for packing seal to reduce the loss caused by volatilization or bottle wall adsorption. The brown reagent bottle was placed in a constant temperature water bath at 25.0±0.2℃for 24h. after centrifugation, the supernatant was quickly taken out and the mass concentration of carbon tetrachloride was determined by GC.

3.2. Batch equilibrium adsorption experiment

The adsorption types of pollutants on solid media can be determined by the determination of adsorption equilibrium concentration and mass balance[6]. When the adsorption equilibrium is reached, the relationship between the adsorption amount of pollutants on the solid medium and its liquid concentration conforms to a certain law, which can be quantified by adsorption isotherm. Adsorption isotherm represents the adsorption equilibrium state of a substance on a certain surface (usually referred to as the interface) at a certain room temperature. It is a curve characterizing the relationship between the liquid concentration and the solid concentration when the adsorption reaches equilibrium[7]. The adsorption capacity (Qc) can be determined by the law of conservation of mass of the adsorbed material, the formula is as follows:

\[ C_e = C_0 - \frac{q M}{V} \]

Among them: \( C_e \) - residual concentration in solution or concentration in solution at equilibrium (mg / L), the same below; \( C_0 \) - initial concentration of solution (mg / L); \( m \) - mass of adsorbed material (g); \( V \) - volume of solution (ml).

(1) Linear equilibrium adsorption

\[ Q_e = K_d * C_e \]

Where: \( Q_e \) - the mass of an adsorbed substance per unit mass of solid medium at adsorption equilibrium (mg / g), the same below; \( K_d \) - the distribution coefficient (L / g), which can be determined by plotting \( Q_e \sim C_e \) series data obtained from experiments.

(2) Freundlich equilibrium adsorption

\[ Q_e = K_f * C_e^{1/n} \]

Where: \( K_f \) - adsorption isothermal constant (mg / g); \( N \) - adsorption strength, dimensionless.

(3) Langmuir equilibrium adsorption

\[ \frac{C_e}{Q_e} = \frac{1}{b k} + \frac{C_e}{b} \]

Where: \( b \), \( k \) - L type adsorption characteristic constants; \( b \) represents the maximum saturated adsorption capacity (mg / g), \( k \) is the L-type constant (L / g) related to the binding site affinity and adsorption energy; drawing \( C_e/Q_e \sim C_e \) line diagram, then \( b \) and \( k \) can be obtained by the slope and intercept of the straight line.

(4) Temkin equilibrium adsorption

\[ Q_e = B \ln A + B \ln C_e, \ B = \frac{R T}{b_T} \]

Where: \( B \) - constant related to adsorption heat; \( R \) - gas constant, 8.314J/mol/K; \( T \) - temperature, 298K; \( b_T \) - TK type adsorption constant

4. Results and discussion

At 25°C, the concentration of carbon tetrachloride solution in different supernatant was analyzed and tested after 24 h isothermal equilibrium adsorption. According to the relationship between the adsorption capacity and equilibrium concentration of carbon tetrachloride in a solid medium, the concentration data obtained by linear, Langmuir, Freundlich, and Temkin type standard curves can be
fitted. The adsorption characteristic parameters and adsorption isotherms of different isothermal adsorption types can be obtained. The correlation coefficient and fitting degree are compared to determine the best adsorption isotherm.

Silty clay and limestone were selected for batch equilibrium adsorption test, according to the experimental data, the adsorption capacity $Q_e$ of carbon tetrachloride in different solid media was calculated, and the adsorption isotherm at 25°C was obtained by taking $Q_e$ as abscissa and $C_e$ as ordinate.

![Figure 2. Adsorption isotherm of silty clay and carbon tetrachloride solution](image)

It can be seen from figure 4.1 that when the adsorption of carbon tetrachloride on silty clay reaches equilibrium at 25°C, with the increase of liquid phase concentration, the solid concentration gradually increases and then tends to be flat. The fitting results of adsorption isotherm show that the Langmuir adsorption isotherm has the best fitting effect, and the determination coefficient $R^2$ is 0.982, as shown in table 4.1. According to the Langmuir adsorption characteristics, the saturated adsorption capacity of carbon tetrachloride on silty clay is 3.466mg/g.

![Figure 3. Adsorption isotherm of limestone and carbon tetrachloride solution](image)

| Isotherm type | Isothermal adsorption equation | Coefficient of determination $R^2$ |
|--------------|--------------------------------|-----------------------------------|
| Liner        | $Q_e = 0.154 \times C_e + 0.861$ | 0.688                             |
| Langmuir     | $Q_e = 3.466 \times 0.346 \times C_e / (1 + 0.346 \times C_e)$ | 0.982                             |
| Freundlich   | $Q_e = 1.01 \times C_e^{0.413}$ | 0.897                             |
| Temkin       | $Q_e = 0.686 \times \ln(4.62 \times C_e)$ | 0.962                             |
It can be seen from Figure 4.2 that when the adsorption process of carbon tetrachloride on limestone reaches equilibrium at 25°C, the solid concentration gradually tends to saturation with the increase of liquid phase concentration, which conforms to Langmuir type adsorption characteristics. The fitting results of different isotherms also showed that the Langmuir adsorption isotherm had the best fitting effect, and the determination coefficient R² was 0.886, as shown in Table 4.2. According to the Langmuir type adsorption characteristics, the saturated adsorption capacity of carbon tetrachloride by limestone is 2.0mg/g.

| Isotherm type | Isothermal adsorption equation | Coefficient of determination R² |
|--------------|-------------------------------|---------------------------------|
| Liner        | $Q_e = 0.061 \cdot C_e + 0.750$ | 0.569                           |
| Langmuir     | $Q_e = 2.0 \cdot 0.295 \cdot C_e/(1 + 0.295 \cdot C_e)$ | 0.886                           |
| Freundlich   | $Q_e = 1.01 \cdot C_e^{0.364}$ | 0.762                           |
| Temkin       | $Q_e = 0.479 \cdot \ln(0.191 \cdot C_e)$ | 0.872                           |

Figure 4. Comparison of adsorption isotherms between different media and carbon tetrachloride solution adsorption system

It can be seen from tables 4.1, 4.2 and figure 4.3 that under the same initial concentration, the saturated adsorption capacity of silty clay is 3.466mg/g, while that of limestone is 2.0mg/g, so the adsorption capacity of silty clay is greater than that of limestone. Therefore, before the pollutants enter the karst water, the silty clay will "intercept" the pollutants, but once the karst water is polluted, the limestone medium has less adsorption capacity, which will bring difficulties to the pollution control and treatment.

5. Conclusions
Silty clay and limestone as the main aquifer media in the study area were selected for isothermal adsorption experiment. The experimental results show that the adsorption of carbon tetrachloride in the two solid media conforms to the Langmuir isotherm adsorption equation. The saturated adsorption capacity of silty clay is 3.466mg/g, and that of limestone is 2.0mg/g.
The adsorption capacity of silty clay is greater than that of limestone. In the process of downward leakage of a chlorinated hydrocarbon containing wastewater, the upper silty clay will play a certain "blocking effect" on pollutants. This shows that in the exposed limestone area in the south of the study area, pollutants directly infiltrate into the karst fissure water system. Due to the weak adsorption capacity of limestone and the development of limestone fractures in the study area, the migration and diffusion of pollutants in karst fissure water are facilitated, resulting in a faster pollution rate and larger pollution range. In the Quaternary covered area of northern China, the infiltration of pollutants will be blocked by the strong adsorption of the silty clay layer. Once the pollutants pass through the silty clay layer and enter the karst fissure water, the migration and diffusion rate of pollutants will also be accelerated.

Acknowledgments
The authors firstly would like to express their appreciation to the anonymous reviewers. This research was financially supported by Migration and transformation model of groundwater chlorinated hydrocarbons in the eastern urban area of the sponge city water system in Jinan city research project (2016JSFW02Z0307).

Reference
[1] Simunek J, Sejna M, Van Genuchten M T, et al. HYDRUS-1D[M]. Simulating the one-dimensional moment of water, heat, and multiple solutes in variably-saturated media, version, 1998, 2.
[2] Jacques D, Genuchten M T, Mallants D. Multicomponent Geochemical Transport Modeling Using HYDRUS-1D and HP11[J]. Journal of the American Water Resources Association, 2006, 42: 1537-1547.
[3] Wanner P, Parker B L, Chapman S W, et al. Does sorption influence isotope ratios of chlorinated hydrocarbons under field conditions[J]. Applied geochemistry, 2017, 84: 348-359
[4] Foo K Y, Hameed B H. Insights into the modeling of adsorption isotherm systems[J]. Chemical engineering journal, 2010, 156(1): 2-10.
[5] Susarla S, Masunaga S, Yonezawa Y. Reductive dechlorination pathways of chloro organics under anaerobic conditions[J]. Water Science and Technology, 1996, 34(5): 489-494.
[6] Schmidt K R, Gaza S, Voropaev A, et al. Aerobic biodegradation of trichloroethene without auxiliary substrates[J]. Water Research, 2014, 59: 112-118.
[7] Cappelletti M, Frascari D, Zannoni D, et al. Microbial degradation of chloroform.[J]. Applied Microbiology & Biotechnology, 2012, 96(6): 1395-1409.