

Article

Adsorption Characteristics and Influencing Factors of Chlorinated and Aromatic Hydrocarbons on Aquifer Medium

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Abstract: To determine the competitive adsorption characteristics and influencing factors of chlorinated and aromatic hydrocarbons on the aquifer medium, toluene, benzene, 1,2–dichloropropane, and 1,2,3–trichloropropane (TCP) were selected as typical pollutants for adsorption tests. The results showed that the adsorption process of pollutants on the aquifer medium conformed to the first–order kinetic and Henry linear model equation, and the adsorption capacity decreased in the order of toluene, benzene, 1,2–dichloropropane, and TCP. Benzene promoted the adsorption of toluene on the aquifer medium, while toluene reduced the adsorption of benzene conversely. 1,2–dichloropropane restrained the adsorption of TCP, and TCP had no significant effect on the adsorption of 1,2–dichloropropane. The adsorption capacity of TCP on the aquifer increased with the concentration of toluene. TCP acted as a stimulus for the adsorption of toluene when the initial concentration of toluene was lower than 2 mg/L. In contrast, TCP served as an inhibitor for the adsorption of toluene on the aquifer medium. Furthermore, the adsorption of all pollutants increased with decreasing medium size. The promotion rates for aromatic and chlorinated hydrocarbons were 7.2~41.1% and 2.7~27.1%, suggesting that the promotion effect on aromatic hydrocarbons was stronger than that on chlorinated hydrocarbons. Natural organic matter (NOM) inhibited the adsorption of pollutants on the aquifer medium (especially for high concentrations of chlorinated hydrocarbons), and the adsorption rate increased by more than 60% when OM decreased from 0.25% to 0.08%. Clay minerals improved the adsorption of organic pollutants in different compound pollution systems, and montmorillonite exhibited a stronger promoting effect than kaolin.

Keywords: chlorinated hydrocarbons; aromatic hydrocarbons; competitive adsorption; aquifer medium; influencing factors



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1. Introduction

With the development of productivity, the organic pollution of groundwater caused by the production and the use of organics is becoming increasingly serious in China [1–3]. An investigation and evaluation of groundwater pollution in the North China Plain indicates that the detection rate of organic pollutants in groundwater has reached 40% [4], of which chlorinated hydrocarbons and aromatic hydrocarbons account for approximately 30% and 25% [5], respectively. Moreover, the organic–contaminated groundwater in China generally contains multiple types of pollutants, exhibiting different mechanisms of adsorption, migration, and influence compared with single pollution [6,7]. Therefore, it is more difficult to define their trending and fate for further remediation work.

For multiple organic pollutants, earlier studies believed that they had no competitive adsorption behavior in soils, aquifers, and various sediments [8], while later studies

indicated that the adsorption–desorption kinetics of different organics were significantly affected by competitive adsorption. Xia et al. [9] analyzed the adsorption behavior of pyrene, phenanthrene, naphthalene, and other compounds in silty loam soil and found that the fitting parameters of the model equation under competitive adsorption were significantly different from those of a single group. David et al. [10] studied the effects of competitive adsorption on the adsorption–desorption kinetics of tetracycline, oxytetracycline, and aureomycin in acidic soil, and demonstrated the descending order of competitive adsorption strength was aureomycin, oxytetracycline, and tetracycline. Baytar et al. investigated the adsorption processes of benzene and toluene, both as sole components and in a binary mixture, and found that the adsorption behaviors of benzene and toluene against activated carbon were quite different when they were in the competition (in a binary mixture) and without competition (sole components) [11].

At present, there are few studies on the competitive adsorption of chlorinated and aromatic hydrocarbons, and most limited studies focus on single or similar components [12,13]. However, combined pollutions caused by two or more types of organic pollutants are more common in actual contaminated sites. Since 2013, our research team has been conducting continuous investigation and remediation work at a contaminated site in Jixian County, Tianjin [14]. This site presents typical compound pollution of chlorinated and aromatic hydrocarbons, including 1,2,3–trichloropropane (TCP), 1,2–dichloropropane, dichloromethane, benzene, toluene, ethylbenzene, xylene (BTEX), and naphthalene in its groundwater. TCP is an emerging organic pollutant, and its migration, transformation, and final fate in soil environments have been studied by WHO (2003) [15], but most of the studies on TCP in groundwater focus on how to reduce its concentration through remediation materials or techniques to improve the safety of drinking water [16,17], and the adsorption behavior of TCP on typical aquifer media is rarely studied. Furthermore, when TCP exists as one of the pollutants of organic composite contamination, the competitive adsorption characteristics of TCP, the influence of TCP on co-existing pollutants adsorption, and the influence of characteristic parameters of typical aquifer media are still unclear, which all need to be studied urgently. According to existing problems, benzene, toluene, 1,2–dichloropropane, and TCP representing aromatic hydrocarbons and chlorinated hydrocarbon pollutants were selected to analyze their competitive adsorption behaviors on typical aquifer media, as well as the influence of characteristic parameters of typical aquifer media, including medium particle size, natural organic matter (NOM) content, and clay mineral composition, on competitive adsorption. The order of adsorption strength of each pollutant was determined, and the rule of competitive adsorption of pollutants was revealed through the competitive adsorption experiment of combined pollutants. The study provided an important theoretical basis for exploring the migration behavior of aromatic hydrocarbons and chlorinated hydrocarbon combined pollutants in aquifer media, identifying potential risks, and conducting scientific and rational restoration.

2. Materials and Methods

2.1. Materials

Natural sand collected from 10 m underground in Zhengding County, Hebei Province was used as the aquifer medium in the experiments. The sand was sieved to obtain homogeneous particles with an average grain size of 0.075~0.1 mm, 0.1~0.25 mm, and 0.5~1 mm, and their physical and chemical properties are shown in Table 1. After cleaning with deionized water, the sand was sterilized by an autoclave at the pressure and temperature of 102.9 kPa and 121.3 °C for 25 min to remove surface impurities, aiming to exclude the effect of microorganisms. All reagents with analytical grades, including 1,2,3–trichloropropane, 1,2–dichloropropane, benzene, toluene, calcium chloride, and methanol, were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd., Tianjin, China. The deionized water was also sterilized under the same condition as natural sand.

Table 1. Physical and chemical properties of the experimental soils.

Soil Type	Medium Size (mm)	TOC (%)	pH	Cation Exchange Capacity (CEC, mol/kg)
Un-sieved sand	-	0.22	7.15	9.82
Silty sand	0.075~0.1	0.27	7.10	10.21
Fine sand	0.1~0.25	0.25	7.20	10.10
Coarse sand	0.5~1	0.19	7.18	9.24

2.2. Adsorption Kinetics of Pollutants on Aquifer Medium

To ensure the accurate and stable concentration of organic pollutants, 100 mg/L stock solutions of benzene, toluene, TCP, and 1,2-dichloropropane were prepared by methanol and then diluted with 0.005 mol/L CaCl_2 solution to a certain concentration for adsorption experiments. The concentration of methanol in diluted solutions was less than 0.1% to avoid its influence on the adsorption process of organic pollutants [18].

In the kinetic adsorption tests, benzene, toluene, TCP, and 1,2-dichloropropane solutions of 5.30, 5.45, 6.93, and 6.32 mg/L were prepared by diluting the corresponding stock solution with CaCl_2 solution. A total of 5 g of sand was accurately weighed and placed in a series of 40 mL brown headspace bottles, and then 25 mL of pollutant solution was added. The headspace bottles were sealed and placed in a shaker at a constant speed and temperature of 150 rpm and 25 °C. The control and duplicate tests were performed under the same conditions. Sampling was carried out at a specific time to determine the concentration of pollutants in the solution.

2.3. Competitive Isothermal Adsorption of Pollutants on Aquifer Medium

Each pollutant solution of 1, 2, 4, 6, 8, and 10 mg/L measurements were prepared for the isothermal adsorption tests. The control and duplicate tests were performed under the same conditions. Sampling was carried out at 24 h to determine the concentration of each pollutant.

The isothermal competitive adsorption experiments were conducted according to the above steps and the following special sets: ① Each pollutant solution of 2, 4, 8, 12, 16, and 20 mg/L measurements were prepared for the same type of pollutant tests (benzene and toluene, TCP and 1,2-dichloropropane). A specific concentration (4 mg/L) of one pollutant and a series of concentrations (2–20 mg/L) of another pollutant were mixed for competitive adsorption isotherm tests (e.g., a benzene solution of 4 mg/L was mixed with a series of concentrations of toluene solution to analyze the competitive adsorption effect of benzene on toluene). The effect of toluene on benzene and the competitive adsorption characteristics between TCP and 1,2-dichloropropane were obtained in the same way. ② The 2, 4, 10, 20, and 40 mg/L toluene and TCP solutions were prepared for testing different types of pollutants (toluene and TCP). Two pollutant solutions with different concentrations were mixed in pairs, and orthogonal isothermal adsorption experiments were carried out to investigate the competitive adsorption of toluene and TCP on the aquifer medium. Synchronized single-component tests and duplicate tests were conducted for control and verification.

2.4. Influencing Factors of Competitive Adsorption

The various 1, 2, 5, 10, and 20 mg/L pollutant solutions were prepared to determine the influence of medium particle size, NOM, and clay minerals on the competitive adsorption of benzene and toluene, 1,2-dichloropropane and TCP, and toluene and TCP. According to the main methods and steps in Section 2.3, two kinds of pollutant solutions with same concentration were mixed to carry out the following three groups of isothermal adsorption experiments, namely, (1) coarse sand and silty sand; (2) fine sand with NOM removed; and (3) fine sand with 10% kaolinite or montmorillonite.

2.5. Analysis Methods

The concentrations of the samples were measured by a gas chromatograph (Shimadzu GC2010 Plus, Kyoto, Japan) equipped with a DB–624 capture column (30 m × 0.32 mm × 0.5 mm), a flame ionization detector (FID), and a DK–3001 automatic headspace injector. The chromatography conditions were set as a column temperature of 250 °C, detector temperature of 260 °C, injector temperature of 200 °C, carrier gas of nitrogen with a flow rate of 23 mL/min, transmission line temperature of 90 °C, sample loop temperature of 85 °C, and balance chamber temperature of 70 °C.

A pseudo first–order kinetics model was used to fit the kinetic curves of organic pollutants on the aquifer medium, which was expressed as Equation (1) [19]:

$$\frac{Q_t}{Q_e} = 1 - e^{-kt} \quad (1)$$

where Q_t is the adsorption amount at time t (mg/kg), Q_e is the equilibrium adsorption amount (mg/kg), and k is the adsorption rate constant (h^{-1}).

The Henry, Temkin, Freundlich, and Langmuir models were employed to describe the competitive adsorption properties of organic pollutants. The mechanism of them was ① Henry: low coverage adsorption and regardless of the interaction between adsorbent molecules; ② Temkin: surface heterogeneity adsorption, and the adsorption heat decreases linearly with the adsorption amount; ③ Freundlich: surface heterogeneity adsorption, and the adsorption heat decreases logarithmically with the adsorption amount; ④ Langmuir: surface homogeneity adsorption; their expressions are in Equations (2)–(5) [20]:

$$Q_e = K_d C_e \quad (2)$$

$$Q_e = K_1 \ln C_e + K_2 \quad (3)$$

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max}} C_e + \frac{1}{K_L Q_{\max}} \quad (5)$$

where C_e represents the equilibrium concentration of pollutant (mg/L) in solution, and K_d denotes the partition coefficient of pollutant on the medium, which shows better adsorption for larger values in the Henry model. K_1 and K_2 are Temkin isotherm adsorption constants, which are related to the adsorption heat and illustrate the interactions between the pollutant and medium. K_f and n indicate the constants of the Freundlich model, which are related to the capacity and strength of adsorption. K_L refers to the constant of the Langmuir model. $Q_{\max}$ is the maximum adsorption capacity of the medium.

3. Results and Discussion

3.1. Adsorption Kinetic Characteristics

There were different degrees of volatilization in the sampling and testing process of volatile organic compound (VOC). The multiple groups of parallel samples were performed to reduce errors. The adsorption kinetic curves of benzene, toluene, 1,2–dichloropropane, and TCP on natural sand are shown in Figure 1. The adsorption equilibrium time of benzene and toluene was 4–6 h, and 1,2–dichloropropane and TCP reached the adsorption equilibrium slowly, which was 8–12 h, indicating that aromatic hydrocarbons were more easily adsorbed on the aquifer medium. Ma Yuejiao et al. [21] demonstrated that the adsorption equilibrium time of BTEX in soil was 24–48 h. Wang Wei [20] investigated the adsorption characteristics of chlorohydrocarbon on soil with an adsorption equilibrium time of 16 h. Compared with the surface soil, the gravel medium of a typical aquifer possesses a low content of organic carbon and clay minerals, which led to a weak adsorption capacity

of pollutants and accelerated the adsorption equilibrium [22]. The calculated results of fitting parameters of the adsorption kinetics showed that the maximum adsorption capacity of benzene, toluene, 1,2-dichloropropane and TCP were 5.40, 6.58, 2.87, and 1.10 mg/kg, and the adsorption rate constants (k) of them were 0.86, 0.90, 0.82, and 0.74 h^{-1} , respectively. Therefore, aromatic hydrocarbons were easier to be adsorbed on aquifer media than chlorinated hydrocarbons.

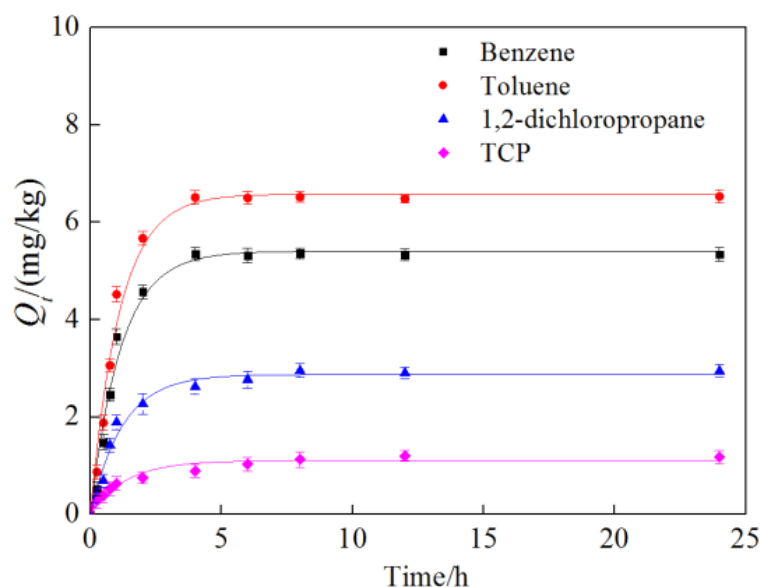


Figure 1. Adsorption kinetic curves of benzene, toluene, 1,2-dichloropropane, and TCP on natural sand. (The initial concentration of them was 5.30, 5.45, 6.93, and 6.32 mg/L, respectively. A total of 5 g of sand was added to 25 mL of pollutant solution).

3.2. Isothermal Adsorption Characteristics

The fitting results of different models for the isothermal adsorption of pollutants are shown in Figure 2 and Table 2. Within the preset concentration range in the tests, the Henry and Freundlich models had a higher degree of fitting than the Freundlich and Langmuir models. The Henry model fitted best for all correlation coefficients above 0.98, indicating a linear adsorption relation between the aquifer medium and pollutants. The adsorption process could be better described by the linear model and Freundlich model, which was consistent with some previous studies on the adsorption behavior of aromatic and chlorinated hydrocarbons on different soil media [23–26].

The isotherm adsorption of organic pollutants included nonlinear surface adsorption at low concentrations and linear distribution adsorption at high concentrations [27]. The adsorption process could be analyzed using the Henry linear model when the pollutant concentration was relatively high or the required simulation accuracy for low concentration was relatively low. Aquifers exhibited a limited adsorption capacity for relatively low-concentration organic pollutants, which might be removed by natural attenuation of microorganism degradation. Therefore, the adsorption behaviors of organic pollutants with relative high concentration in aquifer were explored by the Henry model, which is more meaningful for actual aquifers contaminated by organic pollutants. As listed in Table 2, the K_d values of toluene, benzene, 1,2-dichloropropane, and TCP were 1.89, 2.07, 0.93, and 1.84 L/kg, and their adsorption strength on the aquifer media decreased in the order of toluene, benzene, 1,2-difluoropropane, and TCP, which was consistent with the results of the kinetic study.

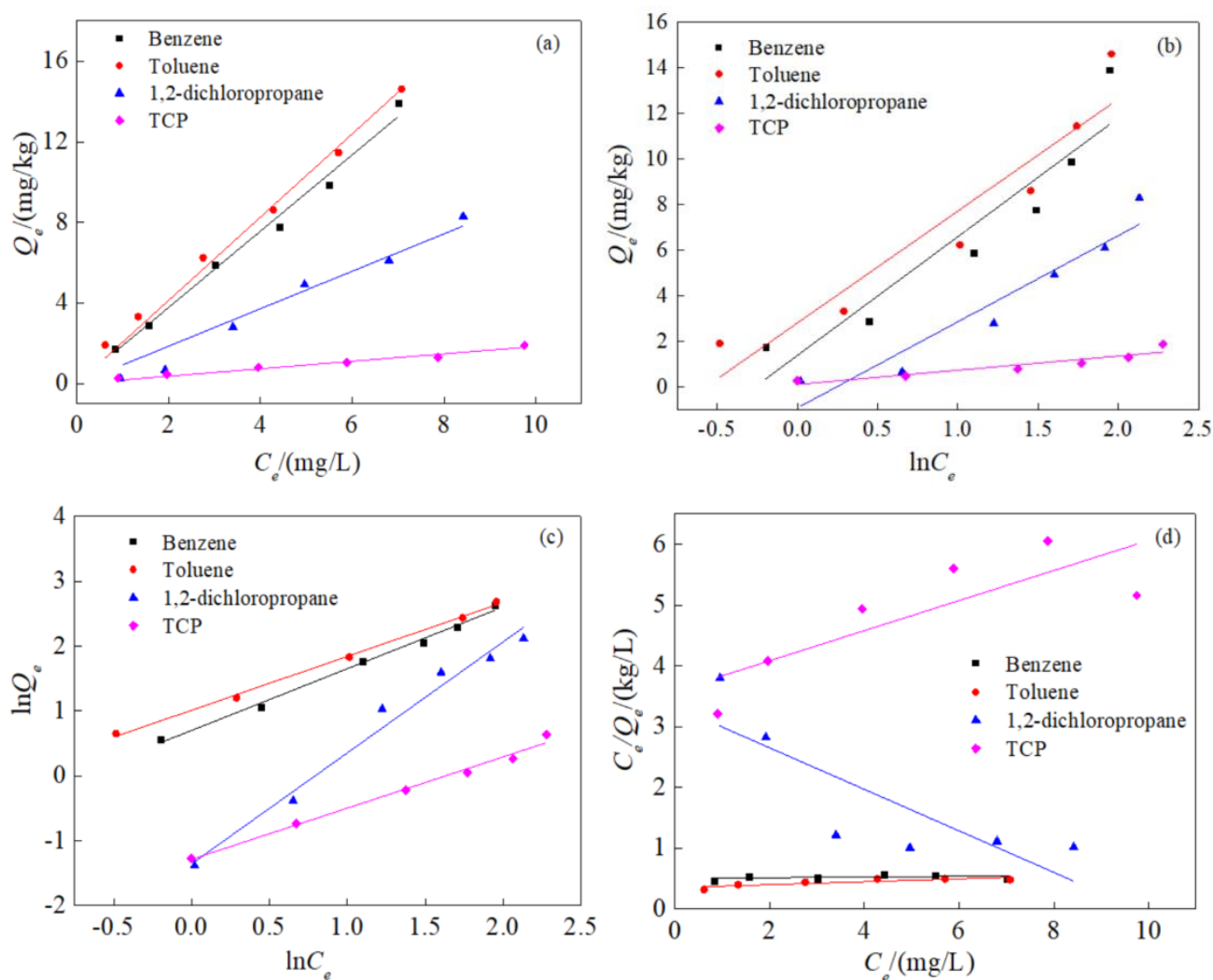


Figure 2. Isotherm fitting curves for each pollutant (The initial concentration of individual benzene, toluene, 1,2–dichloropropane and TCP was 1, 2, 4, 6, 8, and 10 mg/L, respectively. A total of 5 g of sand was added to 25 mL of pollutant solution). (a) Henry model; (b) Temkin model; (c) Freundlich model; (d) Langmuir model.

Table 2. Fitting parameters of isothermal adsorption models.

Pollutants	Henry		K_1	Temkin		K_f	Freundlich		Langmuir	
	K_d (L/kg)	R^2		K_2	R^2		n	R^2	K_L	R^2
Benzene	1.8920	0.9965	5.2066	1.3958	0.9531	5.0130	1.0502	0.9923	0.0113	−0.0905
Toluene	2.0658	0.9969	4.9083	2.8177	0.9182	10.2754	1.2039	0.9967	0.0673	0.6824
1,2–dichloropropane	0.9292	0.9809	3.7784	−0.9096	0.9526	0.0440	0.5842	0.9743	−0.1024	0.5979
TCP	0.1849	0.9900	0.6223	0.1205	0.9594	0.0516	1.2668	0.9859	0.0673	0.5858

3.3. Competitive Adsorption Characteristics

In the environmental system containing one or more adsorbents, the target compound is considered to be the main solute, and the other components that compete with them for adsorption sites are called coexisting solutes. The competitive adsorption experiments of binary components were carried out to investigate the competitive adsorption characteristics of aromatic hydrocarbons and chlorinated hydrocarbons on the aquifer medium, as shown in Figure 3.

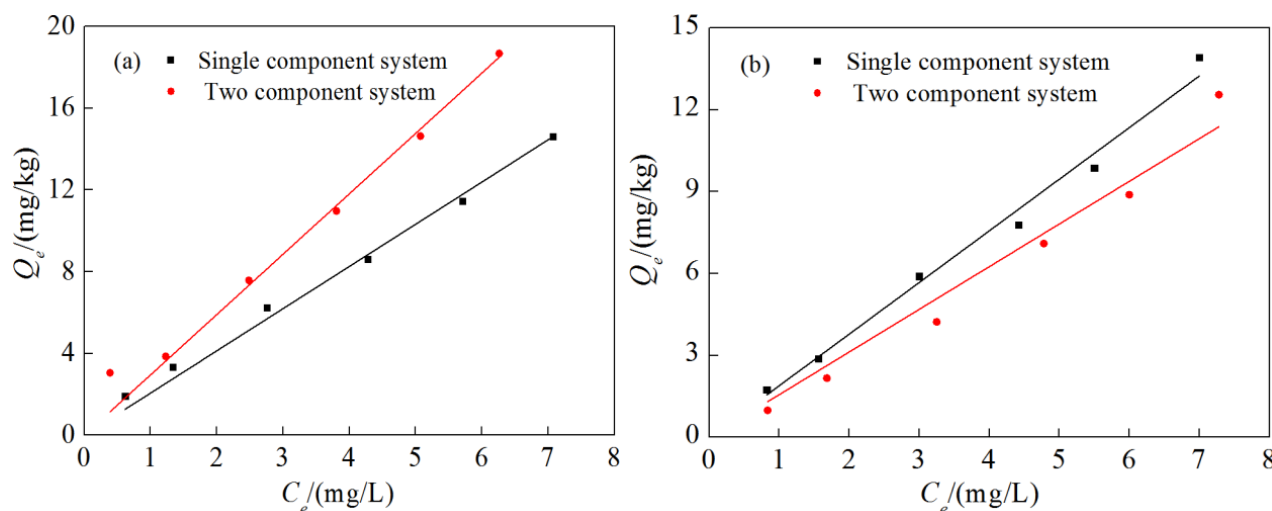


Figure 3. Competitive adsorption of benzene and toluene on the aquifer medium. (The initial concentration of the target compound was 1, 2, 4, 6, 8, and 10 mg/L, and the concentration of the coexisting solute was 2 mg/L). (a) Effect of benzene on the adsorption of toluene on the aquifer medium; (b) Effect of toluene on the adsorption of benzene on the aquifer medium.

As shown in Figure 3a, the adsorption of toluene on the aquifer medium was promoted by benzene. When the initial concentration of toluene was 1, 2, 4, 6, 8, and 10 mg/L, the adsorption capacity of toluene increased by 59.2%, 15.9%, 21.4%, 27.3%, 27.7%, and 27.8%, compared to that of a single component. Benzene had a stronger promoting effect on the adsorption of relative lower concentrations (<2 mg/L) of toluene, and the promoting effect increased with increasing toluene concentration, accompanied by a gradual weakening and stable increment. Correspondingly, toluene inhibited the adsorption of benzene on the aquifer medium, as shown in Figure 3b. The adsorption of benzene at different concentrations was 28.7%, 21.2%, 19.2%, 7.7%, 4.3%, and 6.2% lower than that of the single component, respectively. Generally, the inhibition effect decreased with increasing concentrations of benzene. The molecular weight and molecular diameter of toluene were higher than those of benzene (as the same type of aromatic hydrocarbon pollutant), which caused toluene to be more easily adsorbed on the surface of the medium [28]. Furthermore, the adsorption capacity of organic pollutants was related to its solubility in water. The solubility of benzene was about three times than that of toluene, thus toluene had a stronger adsorption affinity in soil than benzene [21]. Therefore, toluene preferentially occupied the adsorption sites on the surface of the medium, further inhibiting the adsorption of benzene. Organic matter was supplied to the medium by the adsorption of benzene, which promoted the partition of toluene in the organic phase of the medium, thus enhancing the adsorption of toluene [29]. However, the adsorption sites continued to decrease as the concentration of toluene increased, thus the effect of benzene decreased and the growth of toluene adsorption gradually slowed and stabilized.

Similarly, 1,2-dichloropropane was adsorbed more easily than TCP, as shown in Figure 4. The adsorption process was significantly inhibited, and the adsorbing capacity decreased by 26.3%, 48.6%, 48.8%, 53.4%, 56.0%, and 61.9% for different initial concentrations. Moreover, the adsorption of 1,2-dichloropropane was not enhanced by adding TCP to the medium, indicating that the competitive adsorption between chlorinated hydrocarbons mainly occurred on the surface sites, while the effect of partition was relatively small.

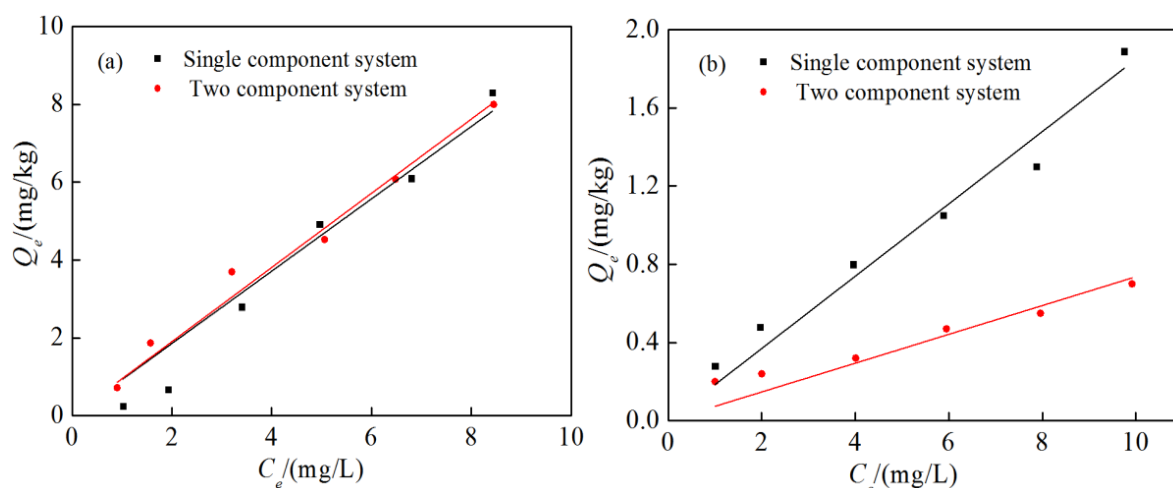


Figure 4. Competitive adsorption of 1,2-dichloropropane and TCP on aquifer medium. (The initial concentration of the target compound was 1, 2, 4, 6, 8, and 10 mg/L, and the concentration of the coexisting solute was 2 mg/L). (a) Effect of TCP on the adsorption of 1,2-dichloropropane on the aquifer medium; (b) Effect of 1,2-dichloropropane on the adsorption of TCP on the aquifer medium.

The competitive adsorption effect of toluene on TCP is shown in Figure 5a. The adsorption of TCP increased with increasing toluene concentration, indicating that toluene promoted the adsorption of TCP on the aquifer medium. Compared with the single component, the adsorption of 10 mg/L TCP increased by 10.3%, 35.1%, 72.7%, 79.0%, and 83.0% when toluene was added. Analogously, a study on the competitive adsorption of benzene, trichloromethane, and dichloromethane demonstrated that the adsorption of chlorinated hydrocarbons on the aquifer medium was promoted by the increasing concentration of benzene [20]. The increase in organic matter content in the medium resulted from aromatic hydrocarbon adsorption, and the partition of organic pollutants in the medium increased, thereby promoting the adsorption of chlorinated hydrocarbons. Aromatic hydrocarbons mainly affected the partition process of chlorinated hydrocarbon adsorption on aquifer media, while the competition of adsorption sites on the surface was relatively weak.

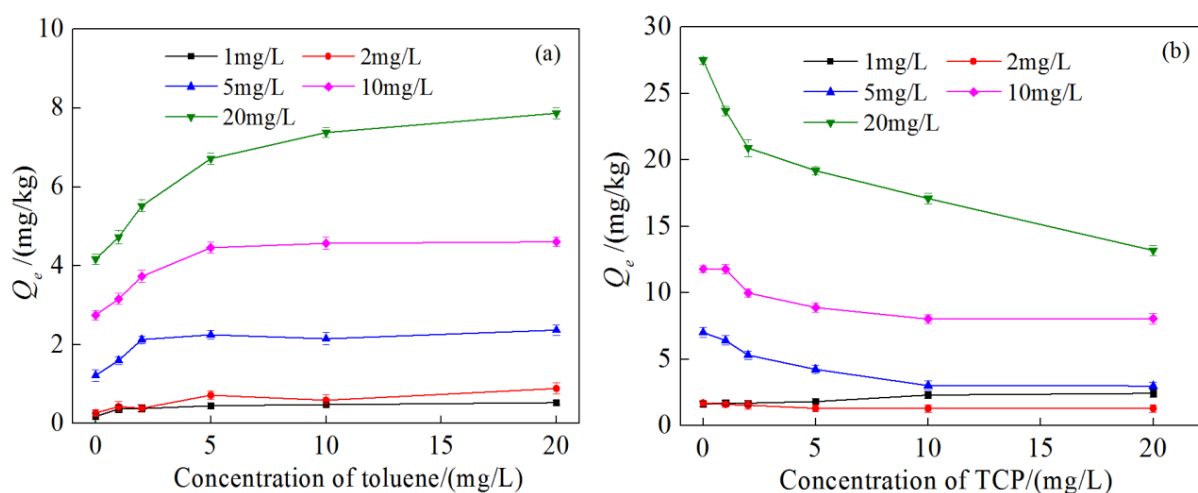


Figure 5. Competitive adsorption of TCP and toluene on the aquifer medium. (The initial concentration of the target compound and coexisting solute was 1, 2, 5, 10, and 20 mg/L, respectively. A total of 5 g of sand was added to 25 mL of pollutant solution). (a) Effect of toluene on the adsorption of TCP with different concentrations; (b) Effect of TCP on the adsorption of toluene with different concentrations.

The influence of TCP on toluene adsorption is shown in Figure 5b. TCP improved the adsorption of toluene at a lower concentration (<2 mg/L), but it was the opposite at a higher concentration. The adsorption sites at the pores on the surface of the medium were still sufficient when the concentration of toluene in water was relatively low; therefore, the adsorption of toluene on the medium was enhanced by promoting partition. However, when the concentration of toluene was higher, the adsorption sites gradually became saturated with increasing concentration of chlorinated hydrocarbons, which enhanced the surface competitive adsorption and resulted in a gradual decrease in the adsorption of toluene.

3.4. Effect of Medium Particle Size on Competitive Adsorption

To clarify the influence of medium particle size on the competitive adsorption of aromatic hydrocarbon and chlorinated hydrocarbon pollutants on aquifer medium, coarse and silty sand were used as the aquifer medium to carry out competitive adsorption tests, as shown in Figure 6. The adsorption capacity of all pollutants on silty sand was significantly improved compared with that on coarse sand. Specifically, in the benzene and toluene solution system, the adsorption capacities of the benzene and toluene increased by 10.2%, 23.6%, 33.9%, 41.1%, and 41.2%, as well as 7.2%, 10.1%, 21.9%, 32.2%, and 30.3% for different concentrations, respectively. In a TCP and 1, 2–dichloropropane solution system, the adsorption capacities of TCP and 1, 2–dichloropropane increased by 2.7%, 5.2%, 15.6%, 20.9%, and 27.1%, as well as 3.6%, 9.3%, 19.5%, 28.6%, and 26.7%, respectively. In the toluene and TCP solution system, the adsorption capacities of the toluene and the TCP increased by 1.4%, 7.3%, 17.9%, 25.5%, and 26.8%, as well as 0.6%, 4.5%, 18.4%, 18.3%, and 24.5%, respectively. Therefore, the smaller the particle size of the medium was the more conducive it was to the adsorption of organic pollutants, which was due to a larger specific surface area and more adsorption sites provided by a smaller medium particle size [30,31]. Furthermore, the effect of a smaller size on the adsorption of pollutants was related to the competitive adsorbability of pollutants. The promotion effect for the pollutants decreased, in turn, from toluene, benzene, 1,2–dichloropropane, and TCP, meaning that the adsorption of aromatic hydrocarbons and chlorinated hydrocarbons was mainly affected by medium size through the surface adsorption sites rather than the partition effect.

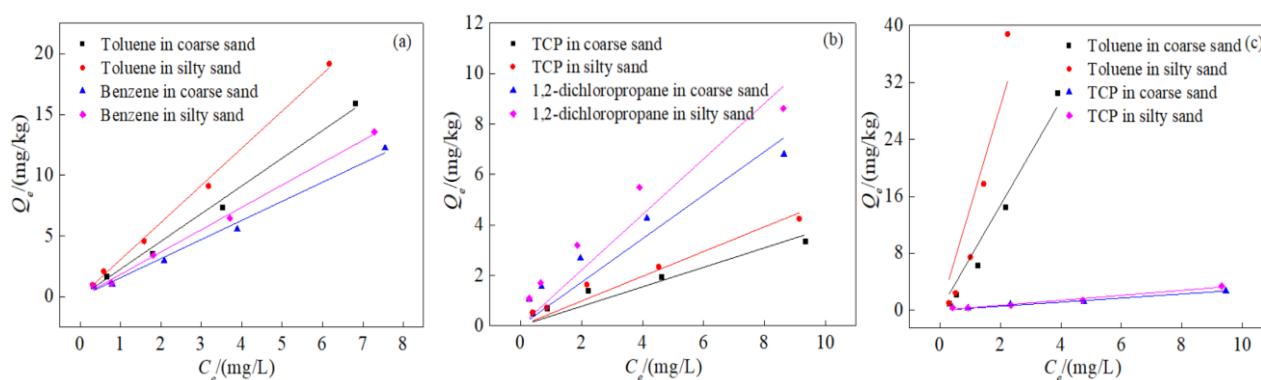


Figure 6. The effect of medium particle size on the competitive adsorption of (a) benzene and toluene, (b) TCP and 1,2–dichloropropane, and (c) toluene and TCP in different two–component systems. (The particle size of medium was 0.5~1 mm and 0.075~0.1 mm).

3.5. Effect of NOM on Competitive Adsorption

To investigate the effect of NOM on the competitive adsorption of organic pollutants, adsorption tests were carried out using treated sand, in which NOM was removed by H_2O_2 , and the content of NOM before and after treatment was 0.25% and 0.08% (Table 1), respectively. Figure 7 shows the relative effect of NOM on competitive adsorption.

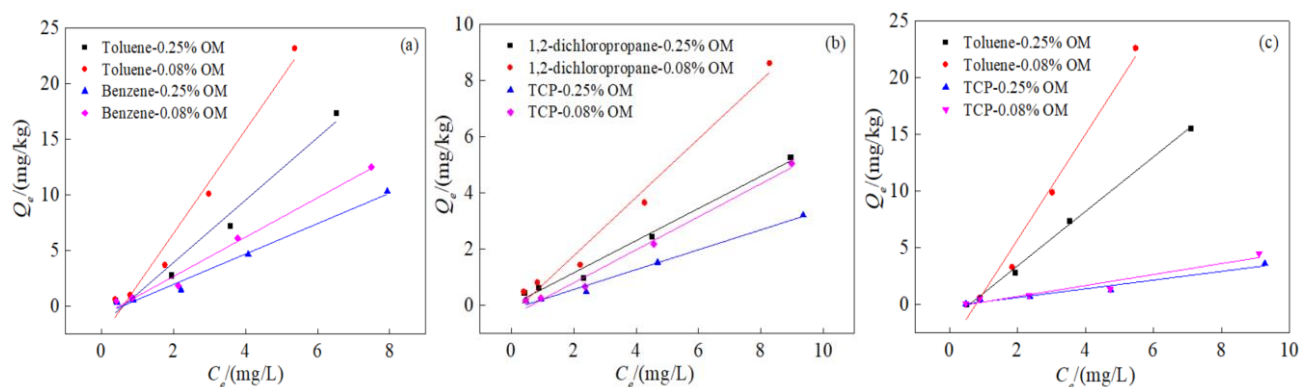


Figure 7. The effect of NOM on the competitive adsorption of (a) benzene and toluene, (b) TCP and 1,2–dichloropropane, and (c) toluene and TCP in different two–component systems. (The content of soil organic matter before and after treatment was 0.25% and 0.08%, respectively).

The adsorption capacity of all pollutants increased with the decrease in the NOM content of natural sand. The adsorption capacity of benzene and toluene increased by 15.3%, 27.1%, 32.4%, 40.2%, and 33.2%, as well as 9.1%, 25.1%, 26.2%, 31.0%, and 21.2%. The TCP and 1,2–dichloropropane increased by 5.2%, 16.2%, 37.7%, 60.2%, and 64.2%, as well as 6.6%, 27.3%, 46.9%, 67.6%, and 70.9%. The toluene and TCP increased by 3.6%, 3.0%, 16.7%, 33.9%, and 45.2%, as well as 3%, 6.6%, 15.5%, 8.2%, and 23.9%. NOM competed with organic pollutants by either site competition or pore/interstice blockage, leading to a decrease in the adsorption capacity of all pollutants [32,33]. Some studies indicated that residual natural NOM was not simply attached to the surface of sand after washing but fixed as coordination compounds. The coordination compounds were formed by the complexation of acidic functional groups (such as the carboxyl, alcohol–based, phenolic groups of NOM, and the hydroxyl groups of minerals) [34]. After oxidation by H_2O_2 , a large number of adsorption sites of sand that were previously occupied by coordination structures was employed to absorb organic pollutants. Murphy et al. [35] studied the adsorption behavior of hydrophobic organic compounds on humic minerals complexes and speculated that the complexes occupied special adsorption sites through complexation. Several studies have investigated the effect of natural NOM on the adsorption of different organic pollutants by graphene nanosheets, carbon nanotubes, and/or GACs [33,36,37], and these results showed that the presence of natural NOM in the background reduced the absorption of all adsorbents to organic pollutants.

3.6. Effect of Clay Minerals on Competitive Adsorption

As an important component of soil and aquifer media, clay minerals exhibit good adsorption performance for organic pollutants and play an important role in regulating the migration, transformation, and destination of organic pollutants in the environment. In this study, kaolin and montmorillonite were selected as the typifiers to investigate their effect on the competitive adsorption of aromatic and chlorinated hydrocarbons on the aquifer medium, as shown in Figure 8. The addition of kaolinite and montmorillonite significantly improved the adsorption capacity of benzene, toluene, TCP, and 1,2–dichloropropane in different adsorption systems. The hydrophobicity of clay minerals resulted from the microscopic structures on the surface of silica tetrahedrons; therefore, compared with the native mineral composition of natural aquifer medium, clay minerals demonstrated stronger adsorption capacity for low polarity or nonpolar organic pollutants (such as polycyclic aromatic hydrocarbons) [38]. The adsorption of organic pollutants by montmorillonite was stronger than that by kaolin, indicating organic pollutants were better adsorbed by swelling clays (such as montmorillonite and bentonite) than nonswelling clays (such as kaolinite and illite), which was due to more adsorption sites supplied by swelling clays [39]. In addition, the promoting effects of clay minerals on the adsorption of benzene and TCP

were better than those of toluene and 1,2-dichloropropane. Taking the montmorillonite test results as an example, the adsorption capacities of pollutants in benzene and toluene solutions increased by 9.8%, 25.3%, 38.9%, 40.2%, and 48.4%, as well as 10.3%, 20.4%, 35.7%, 32.2%, and 38.3%. The adsorption capacities of pollutants in 1,2-dichloropropane and TCP solutions increased by 18.3%, 28.6%, 35.2%, 32.5%, and 38.1%, as well as 15.7%, 28.4%, 42.1%, 41.9%, and 42.6%. The adsorption capacities of pollutants in toluene and the TCP solutions increased by 10.2%, 18.4%, 22.7%, 35.5%, and 30.5%, as well as 15.8%, 30.4%, 40.6%, 45.2%, and 42.7%. These results were caused by the different polarities of the pollutants, in which the competitive adsorption capacities of low-polarity toluene and 1,2-dichloropropane on clay minerals were weaker than those of nonpolar benzene and TCP. However, the adsorption capacity of toluene on the aquifer medium was much greater than that of TCP; therefore, the clay minerals showed little influence.

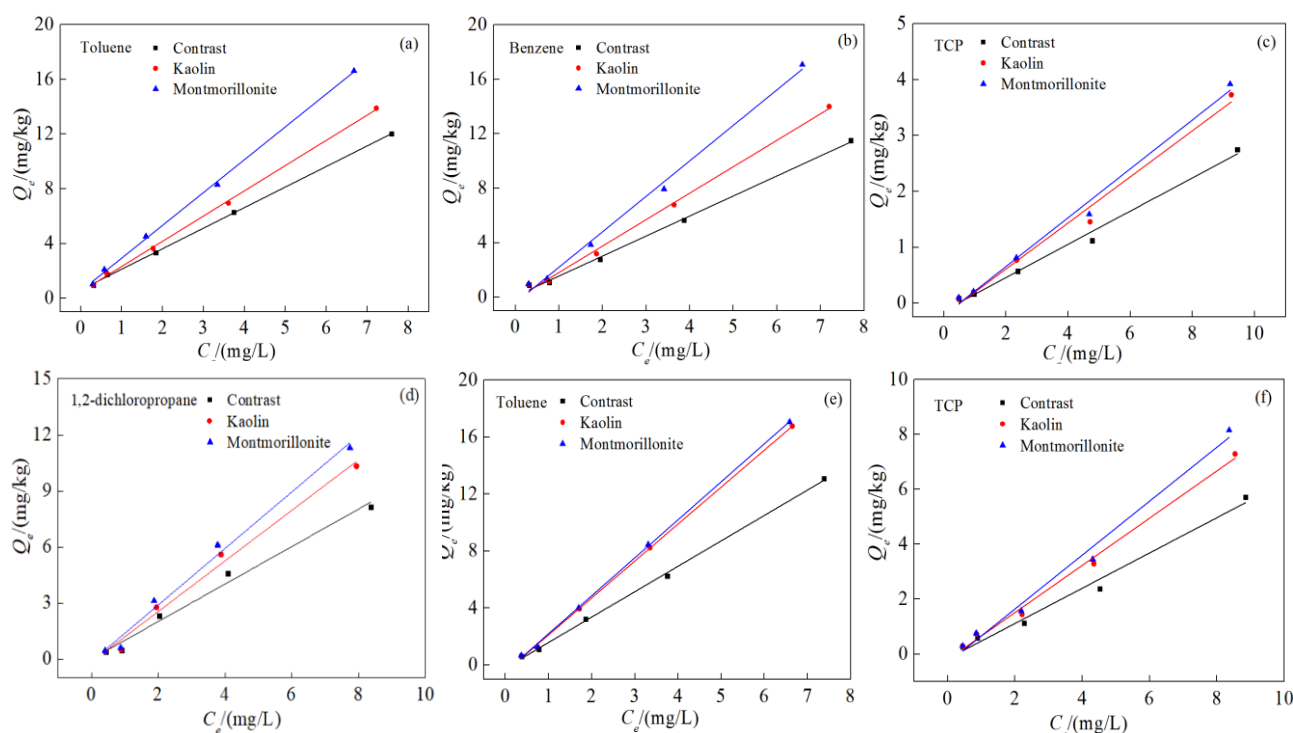


Figure 8. The effect of clay minerals on the competitive adsorption of (a,b) toluene and benzene, (c,d) TCP and 1,2-dichloropropane, and (e,f) toluene and TCP in different two-component systems. (The amount of clay minerals added was 10%).

4. Conclusions

In this study, the competitive adsorption characteristics and influencing factors of chlorinated and aromatic hydrocarbons on the aquifer medium with toluene, benzene, 1,2-dichloropropane, and TCP as typical pollutants were investigated. The conclusions were as follows.

(1) The adsorption equilibrium time of aromatic hydrocarbons was 4–6 h, and that of chlorinated hydrocarbons was 8–12 h, which indicated that aromatic hydrocarbons were more easily adsorbed on the aquifer medium than chlorinated hydrocarbons. The adsorption process of all pollutants on the aquifer medium conformed to the first-order kinetic equation with adsorption rate constants of 0.86, 0.90, 0.82, and 0.74 h^{−1}. The isothermal adsorption characteristic could be described by the Henry model, which was linear adsorption with partition coefficients of 1.89, 2.07, 0.93, and 1.84 L/kg, respectively. The adsorption strength on the aquifer medium decreased in turn as toluene, benzene, 1,2-dichloropropane, and TCP.

(2) The competitive adsorption of aromatic hydrocarbons on the aquifer medium was influenced by two mechanisms of surface site competition and distribution. Benzene promoted the adsorption of toluene on the medium, while toluene inhibited the adsorption of benzene. The competitive adsorption of 1,2-dichloropropane and TCP on the fine sand medium was mainly due to competition on the surface sites of the medium rather than the distribution. 1,2-dichloropropane obviously inhibited the adsorption of TCP, but the adsorption impact of TCP on 1,2-dichloropropane was not obvious. The adsorption capacity of TCP on the medium increased with the concentration of toluene. TCP acted as a stimulus for the adsorption of toluene when the initial concentration of toluene was lower than 2 mg/L, and it was the opposite when the initial concentration of toluene was higher than 2 mg/L.

(3) The adsorption of all pollutants increased with decreasing medium size. The promotion rates for aromatic and chlorinated hydrocarbons were 7.2–41.1% and 2.7–27.1%, respectively, and the promotion effect on aromatic hydrocarbons was stronger than that on chlorinated hydrocarbons. NOM inhibited the adsorption of pollutants on the aquifer medium, which was due to its site competition with pollutants and pore/interstice blockage of the medium. Especially for high concentrations of chlorinated hydrocarbons, an increasing rate was more than 60% when NOM decreased from 0.25% to 0.08%. Clay minerals improved the adsorption process in different compound pollution systems, and the facilitation by montmorillonite was stronger than that by kaolin.

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