Adsorption and Desorption Behavior of Chemical Residues in Soils

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Abstract. In order to prevent the influence of residual volatile organics from chemical plant on metro environment and population health, phenol was selected as a typical intermediate. And the adsorption and desorption of phenol in the surrounding soil of subway were investigated, which benefit for understanding pollutants transportation law and truncation of pollutants transportation. Adsorptive dynamics, adsorption-desorption behavior of phenol in soil, and the effect of different factors on adsorptive behavior were studied. The results showed that the linear adsorption equation can better meet the adsorption behavior of phenol in soil. When the equilibrium concentration was 85 mg L\textsuperscript{-1}, the adsorption amount of no. 1 and no. 2 soils were 15.7 mg g\textsuperscript{-1} and 17.2 mg g\textsuperscript{-1} respectively. And the adsorption of phenol in soils was dependent on pH and temperature. Desorption 4 h can basically achieve desorption balance, the desorption efficiency of no. 1 and no. 2 soils were 14 % and 10 % respectively. Because there is less humus in the deep soil, desorption of phenol in deep soils was weak, which maybe reduce the transportation speed of phenol in soils.

1. Introduction

With the acceleration of urban construction, many subways or other modes of transportation will be constructed through historically industrial land. Therefore, residual pollutants from the original enterprise (e.g., arsenic, phenolic substances, and petroleum hydrocarbons) can be transported and diffused into internal environments where they can exert detrimental effects on human health [1-5]. To prevent pollutants from entering subway environments effectively and minimize hazards to the public, it is necessary to study pollutant transportation and transformation [6-8]. Studies have shown that pollutant adsorption and desorption in soil are important factors affecting transportation and transformation [9-11]. Therefore, it is important to study the adsorption-desorption behavior of pollutants in soils to explore the transportation and transformation of pollutants in the environment.

In this study, the adsorption and desorption kinetics and transportation behavior of phenol in the surrounding soil of subway were studied by using the phenol which were important
intermediate used in chemical plant. The results of this study will provide a theoretical guide to study the transportation and transformation of phenolic compounds in the environment and truncation of phenols transportation in soil.

2. Materials and Methods

2.1 Material

The soil samples used in the tests were collected from the shallow (No. 1) and deeper (No. 2) subterranean soil in an uncontaminated area near the subway. The soil was dried and impurities were removed, and the remaining samples were stored after sifting through 20-mesh and 40-mesh sieves. Before use, the moisture content of the soil samples was measured using a freeze-drying apparatus, and the moisture content of the two soils was below 0.05%. Therefore, the impact of moisture was not considered in the experiments.

2.2 Method

2.2.1 Adsorption Kinetics

First, 8.00 g of soil sample was added to a 250 mL Erlenmeyer flask, and approximately 100 mL of phenol (50 mg/L) was measured in a measuring cylinder and added to the flask, which was sealed. At a water temperature of 25°C and oscillation frequency of 150 rmin⁻¹, phenol adsorption was quantified under different adsorption times. During the adsorption process, to eliminate the effect of dissolved matter in the soil, a blank experiment was used as a reference.

2.2.2 Adsorption Isotherms

First, 100 mL of phenol solution at various concentrations (1mg/L, 2mg/L, 4mg/L, 5mg/L, 8mg/L, 9mg/L and 10mg/L) was placed in a 250 mL Erlenmeyer flask, 8 g of soil sample was added, and the adsorption experiment was performed at a temperature of 25 °C and oscillation speed of 150 rmin⁻¹. The solutions were centrifuged immediately after the equilibrium time was reached, and the amount of phenol adsorbed was determined by measuring the amount of phenol in the supernatant. The blank experiment was used as a reference. The adsorption isotherms were fitted with linear and Freundlich isotherms.

Linear model equation:

\[ q_L = K_L C_e \]  \hspace{1cm} (1)

where \( q_L \) is the adsorption capacity, \( K_L \) is the partition coefficient, which refers to degree of pollutant adsorption onto soil, and \( C_e \) is the liquid phenol concentration at equilibrium.

The Freundlich model was expressed as:

\[ q_f = K_f C_e^{1/n} \]  \hspace{1cm} (2)

Where \( q_f \) is adsorption capacity, \( K_f \) and \( n \) are Freundlich adsorption constant.

2.2.3 Factors of Adsorption

In order to study the effects of various factors on the adsorption, the effects of different pH (2.65,3.41,7.25,10.44,12.21), different salinity (0.05 mg / L and 0.1 mg / L) and different temperature (25, 35, 55 °C) under the adsorption capacity of the experimental study. Take 100 mL of the phenol solution in a 250 mL Erlenmeyer flask and add 8 g of soil sample. The sample
was placed in a constant temperature oscillator at a constant temperature oscillation, the oscillation speed was 170 rmin\(^{-1}\), the oscillation time was 3 h, and the sampling time was 0,5,15,25,30,45,120, 180, 240 min.

2.2.4 Desorption Experiment

Desorption experiments were carried out with 100ml of deionized water to desorb the saturated soil. Desorption temperature is 25\(^{\circ}\)C, the oscillation frequency is 150rmin\(^{-1}\), and the blank experiment is used as reference to determine the desorption law.

3. Results and Discussion

3.1 Adsorption Kinetics

The adsorption rate directly affects the transport rate of chemicals in soil, and has a decisive role in the adsorption time for adsorption isotherm tests [12,13]. Therefore, we first studied the adsorption kinetics of soil samples No. 1 and No. 2 to phenol. The results of the adsorption kinetics (Fig. 1) showed that the phenol adsorption onto soil underwent two obvious stages, a rapid adsorption stage and slow adsorption stage. At the beginning of the experiment, phenol was rapidly adsorbed onto soil, which gradually slowed after 1 h. The concentration of the aqueous phase was near equilibrium within 3 h, and balance was obtained after 4 h. Therefore, the experiment duration of adsorption was set to 4 h.

![Figure 1. Adsorption kinetics of phenol in soil.](image)

3.2 Adsorption Isotherms

Adsorption isotherms reflect the soil adsorption capacity of pollutants, from which transport law of pollutants in soil can be understood [14]. From the fitting results, phenol adsorption by the two types of soil around the subway coincided with both adsorption isotherm models, but the linear model has a higher correlation coefficient, and all correlation coefficients were...
greater than 0.98. The adsorption capacity of samples No. 1 and No. 2 were similar under low phenol concentrations, but the adsorption capacity of No. 2 soil increased more than that of No. 1 as the concentration increased. This indicated that the affinity of No. 2 soil to phenol was greater than that of No. 1. It was further speculated that the transport of phenol in No. 2 soil would be slower than that in No. 1.

3.3 Factors of Adsorption

Fig. 2(a) shows the effect of pH on soil adsorption of phenol. The amount of phenol adsorbed onto both soil samples decreased with increasing solution pH. The effect of pH on phenol adsorption can be explained by the soil structure and composition. Soil material mainly includes minerals and organic matter, where humic substances are the main component of organic matter, which have a greater impact on the adsorption of organic matter. Humus contains numerous benzene rings, but also contains carboxyl, alcohol, and phenolic hydroxyl groups, which can become dissociated in water. Moreover, the morphological configuration of humus is related to the dissociation degree of the functional groups [15]. In alkaline solutions, a large proportion of hydroxyl and carboxyl groups are dissociated in the solution, the structure is stretched, and hydrophilicity is strong; therefore, humus tends to dissolve, reducing the adsorption capacity for pollutants. In acidic solutions, the functional groups do not dissociate as readily, reducing their charge. As a result, the macromolecules condense into groups, and their hydrophilicity is weakened, enabling precipitation and agglomeration, which enhances the adsorption capacity for pollutants.

Fig. 2(b) shows the effect of salinity on phenol adsorption in both soils. With increasing salinity, the solubility of organic matter in the water phase decreased, showing a "salting out" effect. The amount of phenol adsorbed onto the two soils increased with increasing salt content, indicating that phenol was affected by the salting out effect. Although salinity does not alter the physicochemical properties of the adsorbate, it can change its solubility in solution. When NaCl is added to aqueous solutions, the solubility of phenol in water is reduced, and its adsorption onto soil increases [16]. After adding salt, the adsorption capacity of phenol on No. 2 soil was higher than that of No. 1 soil but the difference between adsorption onto the two soils did not change with salinity, indicating that the addition of salt did not change the adsorption capacity of phenol to soil.

Fig. 2(c) shows the effect of temperature on the adsorption of phenol onto both soils. With increasing solution temperature, the adsorption capacity of phenol in samples No. 1 and No. 2 both showed marked decreasing tendencies, especially at higher temperatures. This may be due to the increased solubility of phenol with increasing temperature, resulting in a decrease in the adsorption capacity of the soil. In addition, adsorption is generally an exothermic process, and an increase in temperature may have inhibited the adsorption of phenol onto soil.
Figure 2. Effects of (a) pH, (b) salinity, and (c) temperature on phenol adsorption onto soil.

3.4 Experiment Analysis

Phenol adsorption onto soil occurs via two types of adsorption processes, physical adsorption processes and chemical adsorption processes. Under certain conditions, phenol adsorption can be desorbed, resulting in transport via rainwater leaching. Figure 3 shows the desorption kinetics curves of phenol in soil samples No. 1 and No. 2. The rate of desorption was faster, and the concentration in the water phase was near equilibrium within 3 h, and desorption equilibrium was reached after 4 h. In the process of desorption, phenol is desorbed from soil under the action of diffusion forces, where it re-enters the aqueous phase. At first, the desorption rate was fast due to the large concentration gradient between soil and water, and desorption process gradually became balanced as the concentration gradient decreased. The desorption rate of sample No. 2 was faster than that of No. 1 at first, but it ultimately became much slower than that of No. 1. This may have been due to the larger amount of phenol adsorbed onto the soil in sample No. 2 than that of No. 1, resulting in a greater initial driving force of desorption. However, once the phenol in the soil reached a certain concentration, the desorption
rate was lower than that of No. 1 soil, because the affinity of the soil in sample No. 2 for phenol was stronger than that of No. 1.

![Graph](image_url)

**Figure 3. Desorption kinetics of phenol in soil.**

4. Conclusion

The following conclusions can be drawn on the adsorption / desorption of phenol in different soils:

1. The soil adsorption rate of phenol, desorption rate are fast. In the soil adsorption test of phenol, the systems nearly reached dynamic equilibrium after about 3 h, and the desorption test generally reached a balance around 4 h. Moreover, soil sample No. 1 had a smaller adsorption capacity than No. 2.

2. Temperature and pH had strong influences on phenol adsorption onto soil, while salinity had little effect on the phenol adsorption rate. As pH increased, the adsorption capacity of phenol decreased, indicating that acidic soil is more conducive to phenol adsorption, while alkaline soil is not conducive to phenol adsorption. An increase in temperature is not conducive to phenol adsorption onto soil, suggesting that the migration of phenol may be faster in summer.

3. Deep soil (No. 2) had a stronger affinity for phenol and a slightly less desorption capacity, probably due to the less humus contained in the deep soil.

References


