

Study on Influential Factors of Adsorption and Desorption of Phenanthrene by Three Typical Soils

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Abstract

In recent years, with the development of the country's industrialization, the content of Polycyclic aromatic hydrocarbons (PAHs) in the soil has continuously increased, which has caused widespread concern in various countries around the world. PAHs are an important hydrophobic organic pollutant in the environment, and their adsorption and desorption behaviors directly affect environmental fate and ecotoxicity. In this paper, the batch equilibrium method was used to study the adsorption and desorption behaviors of PAHs and phenanthrene by coarse sand, aeolian sand and loess under different influencing factors, which are the environmental and chemical behaviors of PAHs in the soil. And migration and transformation laws provide a theoretical basis. The experimental results are as follows: ① In the studied pH range, all three soils showed that with the increase of pH, the adsorption capacity also increased. That is, when the soil is under alkaline conditions, its adsorption is more favorable. As for the desorption behavior, with the increase of pH value, the desorption effect of phenanthrene on coarse sand and loess is not obvious, and the effect on aeolian sand is greater. The optimal pH for coarse sand and aeolian sand desorption is 6.0, and the optimal pH for loess is 7.0; ② Affected by different initial concentrations, the processes of adsorption and desorption of phenanthrene by coarse sand, aeolian sand, and loess are basically the same, all of which are coarse. The desorption amount of aeolian sand and loess increased with the increase concentration.

Keywords

Phenanthrene; adsorption desorption; influencing factors; soil.

1. INTRODUCTION

PAHs are a class of persistent organic pollutants that are widely distributed in the environment. Diet and other ways into the body. PAHs in soil mainly come from dry and wet sedimentation of the atmosphere, chemical application, agricultural and industrial sewage sludge or accidental leakage. Therefore, the polycyclic aromatic hydrocarbons enriched in the soil not only damage the normal function of the soil and reduce the quality of the soil, but also can be bioaccumulated and biomagnified through biological enrichment into the food chain, endangering human health and the ecological environment. The effects of soil composition, temperature, and concentration of pollutants on the adsorption and desorption of polycyclic aromatic hydrocarbons in the soil are different. The distribution of PAHs concentration in the state was studied. The results showed that when the extraction temperature increased from 25°C to 100°C, the aqueous phase concentration of PAHs increased from 0.1 µg/L to 3.0 µg/L. At different temperature gradients (25 °C -100 °C), the increase of water-soluble PAHs

concentration conforms to the Van'tHoff equation, especially the fitting of Phe in 3-ring and F1 in 4-ring is good. The desorption enthalpy of Phe is from -32kJ/mol to -58kJ/mol, the desorption enthalpy of F1 is from -44kJ/mol to -76kJ/mol, and as the molecular weight increases, the desorption enthalpy also increases[1,2]. Studies have shown that the 16 types of PAHs that are controlled by USEPA in different particle size components are similar. The average content of PAHs decreases with decreasing particle size. Coarse flour has the strongest ability to enrich PAHs. There was a significant positive correlation between the content in different particle size components and the content of organic matter in the particle size components [3].

There are many researches on the adsorption and desorption behavior of PAHs in soil at home and abroad, mainly focusing on the source of PAHs, its distribution in the environment, the existence form, migration and hazards, etc., but the specific effects of various factors on PAHs adsorption and desorption The impact is not deep enough. Philippine is one of the 16 internationally recognized PAHs for priority control of pollutants. It has a typical PAHs structure, is a representative of PAHs tricyclics, and constitutes a variety of carcinogenic, teratogenic, and mutagenic. The basic unit of PAHs is widely used to study the role of PAHs in the environment. Therefore, this paper uses phenanthrene as a typical pollutant to conduct research, and selects coarse sand, aeolian sand, and loess to influence the adsorption and desorption of phenanthrene in soil, so as to further investigate the migration and transformation of PAHs in soil and groundwater. Theoretical basis.

2. METHODOLOGY

2.1. Test Soils

The three soil samples used in the test were coarse sand, aeolian sand, and loess. The samples were air-dried and ground. The coarse sand was sieved with 4 meshes, and the aeolian sand and loess were sieved with 70 meshes, and stored in the sample bag for later use. The physical and chemical properties of soil samples are shown in Table 1.

Table 1. Chemical composition of the tested soil (average%)

| Soil | Size(mm) | SiO ₂ | CaO | MgO | P ₂ O ₅ | CO ₂ | K ₂ O+Na ₂ O ₂ |
|--------------|------------|------------------|-----|-----|-------------------------------|-----------------|---|
| Coarse sand | 1-0.2 | 93.9 | 0.4 | 0.5 | 0.05 | 0 | 0.8 |
| Aeolian sand | 0.25-0.05 | 84.3 | 3.2 | 0.6 | - | 2.5 | - |
| Loess | 0.01-0.005 | 62.2 | 7.6 | 2.0 | 0.2 | 5.3 | 5.0 |

2.2. Experimental Instruments and Reagents

The main instruments used in the experiment are shown in Table 2 below.

Table 2. Experimental instruments and models

| Number | Equipment | Model |
|--------|------------------------------------|---|
| 1 | Thermostatic water bath oscillator | SHA-B |
| 2 | Bench-top centrifuge | TGL-15B |
| 3 | UV-visible spectrophotometer | Anke |
| 4 | Magnetic stirrer | DF-101SCollecting thermostatic heating magnetic stirrer |
| 5 | Electronic balance | LE204EI02 |

The main reagents used in the experiment are shown in Table 3 below.

Table 3. Chemical reagent list

| Number | Reagent | Purity grade | Manufacturer |
|--------|-------------------|--------------|---|
| 1 | Methanol | Analytical | Guangdong Chemical Reagent Engineering Technology Research and Development Center |
| 2 | Phenanthrene | Analytical | Aladdin Industrial Corporation |
| 3 | CaCl ₂ | Analytical | Tianjin Kemiou Chemical Reagent Co., Ltd. |
| 4 | NaOH | Analytical | Shandong Haozhong Chemical Technology Co., Ltd. |
| 5 | HCl | Analytical | Hangzhou Shuanglin Chemical Reagent Factory |

2.3. Experimental Part

In this paper, the ultraviolet-visible spectrophotometer is mainly used to determine the phenanthrene content in the soil. The optimum wavelength of the phenanthrene solution is 250nm determined by scanning. Therefore, the ultraviolet spectrophotometry was used to measure the phenanthrene solution at 250nm. Determination.

Effects of different pH on adsorption and desorption: ① Weigh accurately 5g of three different types of soil, adjust pH = 3.0, and add them to 500mL conical flasks; ② Move 100mL phenanthrene containing 1.0mg/L The electrolyte and the conical flask are covered with a sealing film, and the temperature was shaken (200r/min) at 30°C in a constant temperature and protected from light. The shaking time is the adsorption equilibrium time determined by the kinetic experiment (the equilibrium time is 18h from the kinetic measurement), and the shaking ends Then take 10mL of the mixed solution from various soil samples; ③ Take the mixed solution and centrifuge at 4000r/min for 15min. After centrifugation, take the supernatant, and measure the concentration of phenanthrene in the supernatant at 250nm using a UV spectrophotometer and record the data; Change the soil pH value in order 4, 5, 6, 7, 8, 9, repeat steps ①②③, record the data. After the end of the adsorption experiment, the supernatant was decanted, and an equal weight background electrolyte was added to carry out the desorption experiment. The specific experimental steps are the same as above. The experimental steps for different concentrations, different temperatures and different dosages are the same as above.

Calculate the adsorption capacity of Philippine on different soils according to the following formula:

$$q = \frac{V(C_0 - C_e)}{M} \quad (1)$$

Where, q_e (mg/g) is the amount of phenanthrene absorbed; c_0 (mg/L) and c_e (mg/L) are the initial and equilibrium aqueous concentrations, respectively; V (mL) is the solution volume; and m (g) is the mass of soil in the centrifuge tubes.

3. RESULTS AND DISCUSSION

3.1. Effect of pH on Adsorption and Desorption

In general, the pH value of the solution will have a certain effect on the existence of organic pollutants, and then affect the adsorption of organic pollutants by the soil. Therefore, in this experiment, the adsorption and desorption processes of phenanthrene on six soil samples with pH of 4, 5, 6, 7, 8, 9, and 6 were studied and analyzed. The pH was plotted on the horizontal axis, and the adsorption amount was plotted on the vertical axis.

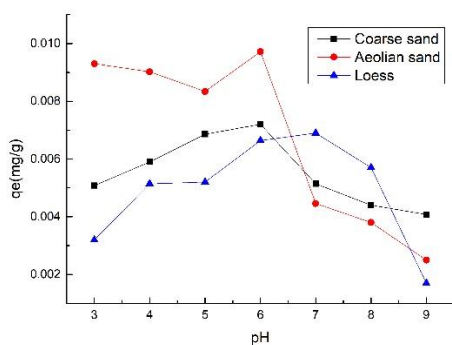


Figure 1. Effect of pH on soil adsorption of phenanthrene

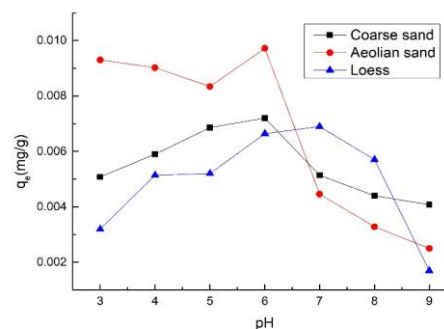


Figure 2. Effect of pH on soil desorption of phenanthrene

It can be seen from Figure 1 that in the pH range, the equilibrium adsorption capacity of the three soils to phenanthrene increased with increasing pH. For coarse sand, when the pH value is increased from 4 to 9, the equilibrium adsorption capacity is increased from 0.00154mg/g to 0.00756mg/g, and it is obtained that when pH = 9, the coarse sand is more favorable for phenanthrene adsorption; For aeolian sand, when the pH value is increased from 4 to 9, the equilibrium adsorption capacity is increased from 0.00606mg/g to 0.01052mg/g. From this, when pH = 9, the adsorption of phenanthrene on phenanthrene is relatively beneficial; For the loess, when the pH value increases from 4 to 7, the equilibrium adsorption capacity increases from 0.00116 mg/g to 0.00938 mg/g, and when the pH value increases from 7 to 9, the equilibrium adsorption capacity increases from 0.00938 mg/g decreased to 0.01052 mg/g, which shows that when pH = 7, the adsorption of phenanthrene by loess is more favorable.

Guo Hongdong [4] studied the effect of sediments on the adsorption of organic pollutants in the Lanzhou section of the Yellow River by setting three different pHs of 4.8, 7.0, and 10.0. There is an upward trend. The results of this experimental study are consistent with those of Guo Hongdong. In addition, some literatures have suggested that soil adsorption of phenanthrene will decrease with increasing pH. Wang Xiaolong[5] found that the PAH content and distribution in urban forestry soils in Nanjing showed that the increase of pH value would reduce the soil's ability to adsorb phenanthrene. In addition, many experimental results show that an increase in pH will also release organic matter in the soil into the water, leading to a decrease in its adsorption capacity [6,7].

It can be seen from Figure 2. that when pH = 6.0, the desorption amount of phenanthrene on coarse sand and aeolian sand reaches the maximum value, while the desorption amount of loess reaches the maximum when pH = 7.0. The change of pH has less effect on coarse sand and loess. At pH value of 3.0~6.0, coarse sand increases as the pH is worth increasing, and when pH value is 6.0~ 9.0, it decreases as pH is worth increasing. Compared with coarse sand, the desorption

amount of loess began to decrease at pH = 7.0; the overall trend of aeolian sand changed greatly, and the equilibrium desorption amount decreased with the increase of pH, then increased and then decreased. The reason why the desorption amount changes with the pH value may be that when the pH is less than 7, the increase of hydrogen ions in the natural soil sample destroys the water and action of the aqueous ions, the surface water film of the soil is damaged, and the desorption sites in the reaction are exposed. The desorption of organic matter by soil is strengthened; when the pH is greater than 7, the reaction is in an alkaline environment. A part of Ca^{2+} in the original solution can combine with OH^- , but its solubility is far less than CaCl_2 . Therefore, the concentration of calcium ions in the water decreases, which makes the solution Of organic matter changed from flocculated to adsorbed aggregates, reducing the desorption effect of the soil.

Numerous results show that the pH of phenanthrene adsorption process is different in different soils. Therefore, it is inferred that the change law of phreatic sand, aeolian sand and loess pH on adsorption and desorption of phenanthrene is mainly related to the physical and chemical properties of the soil.

3.2. Effect of Initial Concentration on Adsorption and Desorption

In this experiment, the effect of 5 initial concentrations on the adsorption and desorption of phenanthrene in soil was studied. The initial concentration of phenanthrene-containing electrolyte was 0.5, 1, 1.5, 2, 2.5, and 3 mg/L. The initial concentration was used as the horizontal axis, and the adsorption amount was taken as the vertical value. The coordinates are plotted in Figure 3.

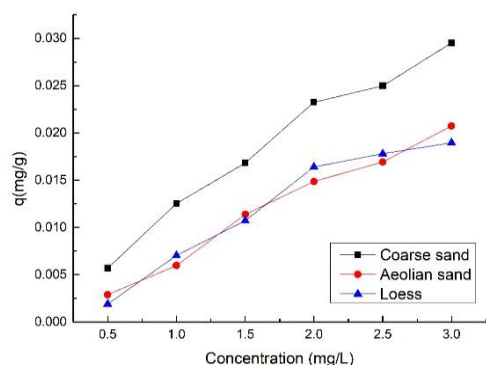


Figure 3. Effect of initial concentration on phenanthrene adsorption in soil

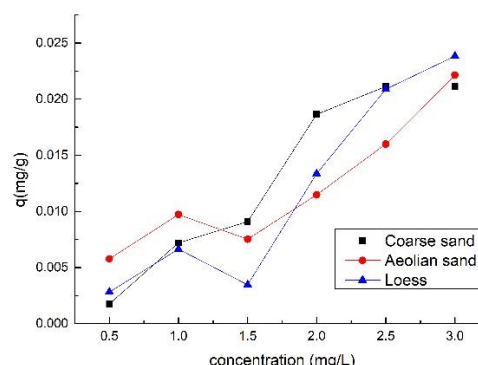


Figure 4. Effect of initial concentration on phenanthrene desorption in soil

It can be seen from Figure 3 that as the initial concentration increases, the adsorption amount of phenanthrene by coarse sand, aeolian sand, and loess gradually increases, and the adsorption law is basically the same. Among them, for coarse sand and aeolian sand, the adsorption amount is increasing with the increase of the initial concentration, while the adsorption rate of the loess gradually slows down from 2mg/L to 3mg/L; With the increase of initial concentration, the adsorption amount of coarse sand is the largest, and the adsorption amount of aeolian sand and loess is smaller. When the initial concentration of phenanthrene is in a certain range, the equilibrium adsorption amount gradually increases with the increase of the initial concentration. On the one hand, it may be because as the initial concentration of phenanthrene increases, the more phenanthrene provided to the soil is adsorbed, Therefore, the greater the difference between the concentration of the phenanthrene solution and the liquid film on the outer surface of the soil, the greater the kinetics of phenanthrene's migration to the soil surface. On the other hand, it may be because as the concentration of the phenanthrene solution increases, The possibility of collisions between sorbents increases. Under the influence of these

two factors, the adsorption of phenanthrene on soil increased. That is, the increase of the initial concentration of phenanthrene significantly promoted the adsorption process; but when the initial concentration of phenanthrene was from 2 mg/L to 3 mg/L, the increase in the amount of loess adsorption gradually decreased. This result may be due to the adsorption. When the initial concentration rises to a certain value, the available adsorption sites on the adsorbent will soon reach the limit. When the adsorbent reaches its own saturated adsorption amount, the adsorption amount will not increase with the initial concentration. High while continuing to increase [8].

It can be seen from Figure 4 that the equilibrium desorption amount of phenanthrene on coarse sand increases with the increase of the initial concentration. When the initial concentration of phenanthrene is in the range of 0.5 to 2.0 mg/L, the equilibrium desorption amount increases more obviously. At 2.0 to 3.0 mg/L, the increasing trend of the equilibrium desorption amount decreases and remains basically unchanged. The desorption rules of aeolian sand and loess are the same. As the initial concentration of phenanthrene increases, the equilibrium desorption amount decreases at the initial concentration of 1.5 mg/L, and increases at other concentrations without reaching the saturated desorption amount.

In addition, the change of the initial concentration has little effect on the desorption rate of aeolian sand, showing a curve that fluctuates up and down, and the maximum value of the desorption rate occurs at a concentration of 3.0 mg/L. The desorption rate curve of coarse sand and loess fluctuates very much. Large, the desorption rate of coarse sand is the lowest when the initial concentration is 0.5mg/L, and the maximum desorption rate is when the initial concentration is 2.0mg/L; the maximum desorption rate of phenanthrene in the loess is 3.0mg/L, and the value is 69.59%, the lowest desorption rate It was 20.87% at an initial concentration of 1.5mg/L. The common law of desorption of three soil samples: the increase in desorption amount from low concentration to high concentration gradually slows down. It is speculated that phenanthrene may be adsorbed at high energy points and adsorbed at high energy points by soil at low concentrations. The ratio of low-energy points decreases, and the proportion that is easier to desorb from the soil increases. When the initial concentration of phenanthrene reaches a certain height, its concentration gradient force can allow the phenanthrene molecules to enter the micropores of the soil particles, and the phenanthrene molecules enter into the micropore and adsorbed on the high-energy point inside the micropore. Or the micropore structure is deformed and the phenanthrene molecules are adsorbed in the pores and cannot be desorbed. Therefore, when the initial concentration of phenanthrene reaches a certain height, the increase of the desorption amount will decrease.

4. CONCLUSION

In this experiment, Phenanthrene was used as the research object to study the adsorption and desorption characteristics of phenanthrene from three different types of soil, coarse sand, aeolian sand and loess. The main conclusions are as follows:

① In the studied pH range, the three types of soils show that as the pH increases, the amount of adsorption also continues to increase. That is, when the soil is under alkaline conditions, its adsorption is more favorable; during the desorption process, the other operating conditions are kept unchanged and the pH value is set to 3-9. The results show that as the pH value increases, the coarse sand and the loess have an effect on the phenanthrene. The desorption amount increased first and then decreased, and the overall equilibrium desorption amount did not change significantly with the increase of pH value. The overall desorption amount of aeolian sand is very significant. In order to decrease, then increase and then decrease, the change law may be related to the physical and chemical properties of the soil.

② Affected by different initial concentrations, the processes of adsorption and desorption of phenanthrene by coarse sand, aeolian sand and loess are basically the same. All showed that the equilibrium adsorption capacity increased with the increase of the initial concentration, but when the concentration increased to a certain value, the increase of the equilibrium adsorption capacity would be relatively gentle.

REFERENCES

- [1] Rainer H, Iris M, Peter G. Proceedings of the 2nd International Workshop on Groundwater Risk Assessment at Contaminated Sites (GRACOS) and Integrated Soil and Water Protection SOWA [D]. 2002, 193-198.
- [2] Wang Xin. Enrichment Characteristics and Desorption Thermodynamics of Polycyclic Aromatic Hydrocarbons in Soil in Typical Areas of Shanghai [D]. East China Normal University, 2015. (In Chinese)
- [3] Zhou Xuhui. Effects of Different Organic Matter Components in Soil on Environmental Behavior of Polycyclic Aromatic Hydrocarbons [D]. Fujian Normal University, 2013. (In Chinese)
- [4] GUO Hongdong, YANG Yiqing, ZHOU Min, et al. Study on DAP adsorption characteristics of sediments in the Lanzhou section of the Yellow River [J]. Journal of Anhui Agricultural Sciences, 2007, 35 (31): 9993-9995. (In Chinese)
- [5] Wang Xiaolong. Study on the content and distribution of polycyclic aromatic hydrocarbons in Nanjing forestry soil [D]. Nanjing: Nanjing Forestry University, 2015: 1-56. (In Chinese)
- [6] Yun-H S. Sorption of natural dissolved organic matter on soil. Chemosphere, 1999, Vol. 38(7): 1505-1515.
- [7] Behrends T, Herrmann R. Partitioning studies of anthracene on silica in the presence of a Cationic surfactant: dependency on pH and ionic strength. Physikalische Chemie Erde, 1998, Vol. 23(2): 229-235.
- [8] Wen Zhidan. Removal and mechanism of phthalate esters from artificial wetland matrix vermiculite and its biofilm [D]. Harbin Institute of Technology, 2014. (In Chinese)