

Adsorption Kinetics, Equilibrium and Thermodynamics of Naphthalene onto Loess Soil

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Abstract. Adsorption behavior of naphthalene onto loess soil was investigated based on adsorption kinetic and adsorption isothermal experiments. The saturated adsorption capacity of naphthalene onto soil from Lanzhou (LZ) was higher than those onto loess soil from Jiayuguan (JYG). The soil properties have an obvious influence on adsorption of naphthalene on loess soil. The naphthalene adsorption equilibrium was reached within 24h, and the adsorption kinetics was well described by the pseudo-second-order model, and also followed the intraparticle diffusion model. The adsorption processes were controlled by the external liquid film diffusion, surface adsorption, intra-particle diffusion, etc. Besides, the adsorption equilibrium data were fitted well with the Henry and Freundlich isothermal model. The saturated adsorption capacity was weakened with the decrease of temperature, suggesting a spontaneous endothermic process. The results of thermodynamic parameters analysis showed the adsorption was mainly a physical process and was enhanced by chemical adsorption.

Introduction

Petroleum substances have seriously polluted in the environment, especially soil ecosystem during their mining, refining, storage, transport and use. The petroleum pollutants percolated through the soil will damage by damaging the soil structure, and reduce soil permeability to nutrients and water. The pollutants residing in the soil will be absorbed by minerals and organic matters. The behaviors and fate of petroleum pollutants can be severely affected by minerals adsorption and the natural organic matters in the soil [1].

The Loess Plateau is the only accumulated plateau in the world and widely distributed in Northwest China. It is composed of hundred meters depth of loess, which was accumulated throughout the Quaternary, and even the Paleocene. Loess soils are featured with homogeneously fine grain size, high porosity, softness and strong permeability, but generally low content of organic matter and poor agglomeration ability [2]. Because of petroleum industrial activities in Northwest China, however, many petroleum pollutants are released into the environment, deteriorating ecosystems, especially soil ecosystem [3]. There were various organic pollutants, such as paraffins, aromatics, heterocyclic compounds and phenols in the loess soils [4]. Therefore, understanding the adsorption behavior of petroleum pollutants in loess soil is vital for us to predict their transport and fate of these pollutants in Northwest China.

The objective of this study was to investigate the adsorption behavior of naphthalene onto loess soil. The Henry, Langmuir, Freundlich and Dubinin-Radushkevich (D-R) equations were used to fit the equilibrium isotherm process. The adsorption kinetic process was determined using various kinetic models. The thermodynamics parameters were evaluated from the adsorption measurements.

Materials and Methods

Preparation of Soil Samples

The samples were collected from uncontaminated soil (0-20cm) from Lanzhou (LZ) and Jiayuguan (JYG), Gansu province. All soil samples were sieved through 100 meshes and stored for further use. The soil chemical and physical properties are showed in Tab. 1.

Table 1. Properties of the Tested Loess Soils.

Soil	pH	Soil moisture content (%)	Organic matter content (g/kg)	Clay (%)	Silt (%)	Sand (%)
JYG	8.34	1.94	9.16	4.881	46.616	48.503
LZ	8.02	1.85	10.84	4.509	54.329	41.161

Adsorption Experiments

The kinetics and thermodynamics adsorption of naphthalene by loess soil were tested using a batch equilibrium method, as described in references [5, 6]. The kinetics of the adsorption process was studied by carrying out a separate set of experiments with constant temperature ($25\pm 0.5^\circ\text{C}$), soil amount (each 0.500 g) and initial naphthalene concentrations (50 mL, $25\text{ mg}\cdot\text{L}^{-1}$). Each reactor was withdrawn at suitable time intervals (0, 0.5, 2, 6, 10, 20, 24, 48, and 72 h). Batch experiments of adsorption kinetics were conducted by 100-mL plastic screw-capped bottles separately in an incubator shaker. The adsorption isotherm experiments were conducted under constant agitation rate (200 rpm), and three temperatures (25, 35, and 45°C). The solid and liquid phases in all experiments were separated at 4000 rpm by a centrifuge after a given time period. Finally naphthalene concentration in the liquid phase was detected by a UV spectrophotometer at 275 nm. All experiments were carried out in triplicate.

Results and Discussions

Kinetics of Adsorption

The adsorption capacity of naphthalene onto loess soil versus contact time is illustrated in Fig. 1. It can be seen that the adsorbed capacity of naphthalene significantly increased with contact time up to 10 h. While the adsorption capacity of naphthalene increased slowly after 10 h, and then the adsorption process reached equilibrium within 24 h. Therefore, 24 h was selected as the optimum contact time for all further experiment.

Kinetic modeling of the experimental data helps finding out the potential rate-controlling steps involved in the sorption process. There are several kinetic models about adsorption of organic pollutants onto loess soil. The adsorption kinetics of naphthalene on loess soil was fitted using three common kinetic models, named the pseudo-first order models, pseudo-second order model, and intraparticle model. The kinetic parameters for the adsorption of naphthalene onto loess soil are given in Tab. 2. The correlation coefficients for the pseudo-first order models and intraparticle model are lower than pseudo-second order model; therefore, this implies that the adsorption of naphthalene onto loess soil does not follow the pseudo-first order models and intraparticle model. The adsorption system studied follows to the pseudo-second order model at all time intervals, which means that the adsorption process were controlled by the external liquid film diffusion, surface adsorption, intraparticle diffusion and so on.

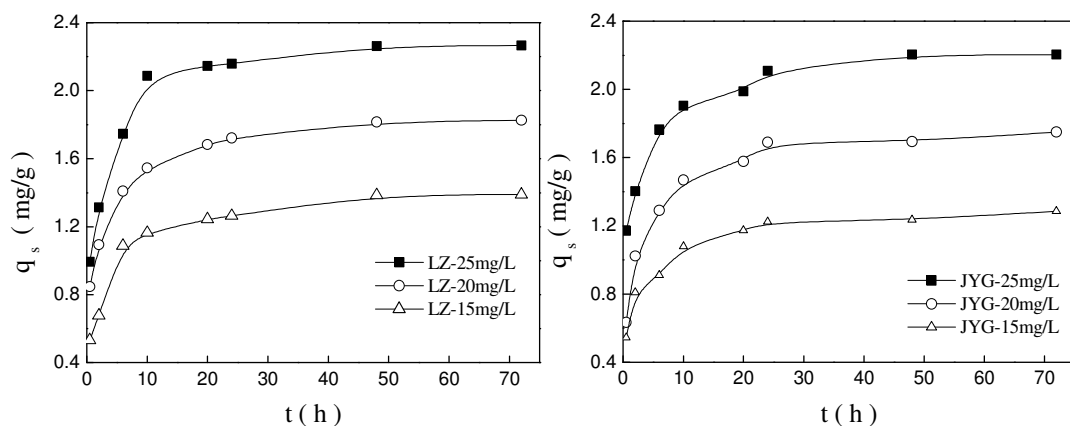


Figure 1. Kinetics Curves for the Adsorption of Naphthalene onto Loess Soil at Different Concentrations.

Adsorption Isotherms

The adsorption capacity of naphthalene onto loess soil versus contact time is illustrated in Fig. 2. The equilibrium adsorption capacity of naphthalene onto loess soil was favored at higher temperatures. An increase of the temperature from 25 to 45°C leads to an increase in the adsorption capacity of loess soil (LZ) from 2.58 to 2.79 mg g⁻¹ at an equilibrium time of 24 h, besides the loess soil from JYG has similar variation trend. Below equilibrium time, an increase in the temperature leads to an increase in the naphthalene adsorption, which indicates kinetically controlling process. After the equilibrium attained, the uptake increases with increasing temperature, this effect may be explained by availability of more active sites of adsorbent at higher temperatures.

The equilibrium adsorption is one of the most important data to understand the mechanism of the adsorption. Several isotherm equations are available and four important isotherms are chosen in this study, which are namely the Henry, Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms. All of the isotherm model parameters for the adsorption of naphthalene onto loess soil at the temperatures of 25-45°C are tabulated in Tab. 3. The maximum adsorption capacity (Q_m) of adsorbent calculated from Langmuir isotherm equation defines the total capacity of the adsorption of loess soil for naphthalene, but Q_m is negative. It indicating that Langmuir isotherm is not applicable to naphthalene adsorption on loess soil. So the absorption of naphthalene onto loess soil is not a monolayer adsorption reaction.

All of the other isotherm models fit very well when the r^2 values are compared in Tab. 3. It concluded that the adsorption of naphthalene onto loess soil is thus complex, involving more than one mechanism. In other words, the surface of loess soil is made up of homogeneous and heterogeneous adsorption patches. The values of k_D , k_F , n and $Q_{m(D-R)}$ are increased with the increase in the temperature, revealing that the sorption capacity of naphthalene onto loess soil increased with the increase in the temperature. The nonlinearity coefficient n values are nearly 1, indicating that the sorption isotherms of naphthalene to loess soil are linear in the experiments condition, and distribution plays a leading role.

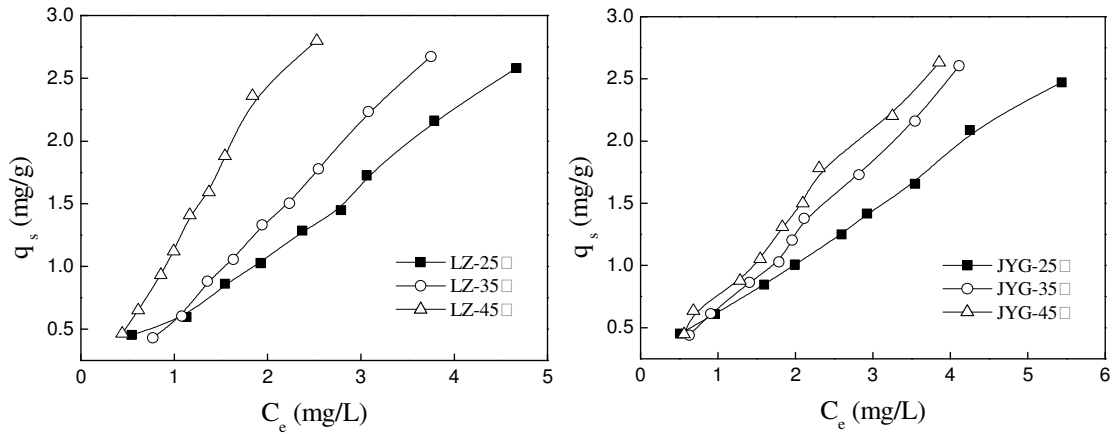


Figure 2. Effect of Temperature for the Adsorption of Naphthalene onto Loess Soil.

Table 2. Eigenvalue for the Kinetic Sorption Equation of Naphthalene Onto Loess Soil.

Adsorbent	Concentration (mg/L)	Pseudo-first-order			Pseudo-second-order			Intraparticle		
		k_1	q_e	r_1^2	k_2	q_e	r_2^2	k_p	C	r_p^2
LZ	25	0.002	1.1	0.96	0.005	2.3	1.00	0.019	1.2	0.80
		0	2	9	1	1	0	7	5	8
	20	0.001	0.8	0.95	0.005	1.8	1.00	0.015	1.0	0.79
		8	7	5	6	6	0	3	1	8
	15	0.001	0.8	0.99	0.005	1.4	0.99	0.013	0.6	0.78
		5	5	2	7	3	9	5	6	8
JYG	25	0.001	0.8	0.88	0.005	2.2	0.99	0.016	1.3	0.72
		3	7	2	1	5	9	4	2	3
	20	0.001	0.6	0.81	0.005	1.7	0.99	0.016	0.8	0.75
		1	8	4	2	8	9	4	7	8
	15	0.000	0.4	0.82	0.007	1.3	0.99	0.011	0.6	0.77
		9	7	3	3	0	9	0	8	3

Table 3. Eigenvalue of Isothermal Adsorption Equation of Naphthalene onto Loess Soil.

Adsorbent	Temperature	Henry model		Langmuir model			Freundlich model			D-R model		
		k_D	r_L^2	Q_m	k_L	r_L^2	n	k_F	r_F^2	Q_m	β	r_{D-R}^2
LZ	25°C	0.54	0.991	-5.10	0.0	0.99	1.0	0.5	0.99	2.3	0.6×10^{-6}	0.90
JYG					1	7	3	3	6	5	6	3
LZ	35°C	0.76	0.998	-7.96	0.1	0.99	1.0	0.5	0.99	2.3	0.4×10^{-6}	0.91
JYG					0	4	8	9	7	8	6	4
LZ	45°C	0.99	0.982	-10.49	0.1	0.99	1.1	1.1	0.99	2.5	0.2×10^{-6}	0.92
JYG					0	8	8	3	3	9	6	4
LZ	45°C	0.63	0.960	5.40	0.1	0.95	0.9	0.7	0.99	2.0	0.2×10^{-6}	0.81
JYG					7	0	6	5	4	9	6	5

Analysis of Thermodynamic Parameters

The calculated changes in Enthalpy (ΔH^θ), Entropy (ΔS^θ) and Gibbs free energy (ΔG^θ) in the sorption of naphthalene on loess soil are shown in Tab. 4. ΔG^θ was negative at all temperatures, confirming that the sorption of naphthalene onto losses soils was spontaneous and thermodynamically favorable. In this study, ΔG^θ ranged from -1.01 to -5.76 kJ mol⁻¹, which indicated mainly physical

adsorption[7]. The positive value of ΔH^0 suggests the endothermic nature of adsorption. The positive value of ΔS^0 suggests increased randomness at the solid/solution interface during the adsorption of naphthalene onto loess soil.

Table 4. Thermodynamic Parameters for Naphthalene Adsorption on Different Loess Soils.

	Temperature	$\Delta G^0(\text{kJ mol}^{-1})$	$\Delta H^0(\text{kJ mol}^{-1})$	$\Delta S^0(\text{Kj}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$
LZ	25°C	-15.59	23.71	0.13
	35°C	-16.99		
	45°C	-18.23		
JYG	25°C	-14.98	15.64	0.10
	35°C	-16.01		
	45°C	-17.03		

Effect of soil Property on Adsorption of Naphthalene on Loess Soil

Zhou et al. found that the soil particle size have a significant effect on the adsorption quantity of PAHs in soils [8]. Wilche also found that the soil texture have an effect on adsorption of organic pollutants on soil, especially the soil particle size distribution [9]. The previous studies also showed that the adsorption of organic pollutants in soil are obvious influenced by soil organic matter and soil minerals [10,11,12].

Fig. 3 and 4 showed the thermodynamics and dynamic adsorption process of naphthalene onto two kinds of loess soils under the condition of 25 °C. It was indicated that the adsorption process of two kinds of loess soils have differences. At the starting point of adsorption, adsorption capacity of JYG soil samples was obviously higher than that of LZ soil samples. With the increase of concentration, the adsorption quantity of LZ soil sample was obviously higher than that of JYG soil samples. The reasons for this phenomenon can be interpreted that at low concentration stage, due to the high clay content JYG soil samples, the adsorption is given priority to with linear distribution, the naphthalene in JYG soil can quick absorption from solution. While with the increase of naphthalene concentration in solution, the function of linear distribution was abate, meanwhile, the high organic matter content in LZ soil can lead to a more naphthalene adsorption, which induced a higher adsorption of naphthalene at high concentration stage. At the same time, the differences between the silt content of two loess soils also may be lead to the adsorption difference. LZ soil samples containing high silt, resulting in significantly better than the adsorption quantity of JYG soil samples.

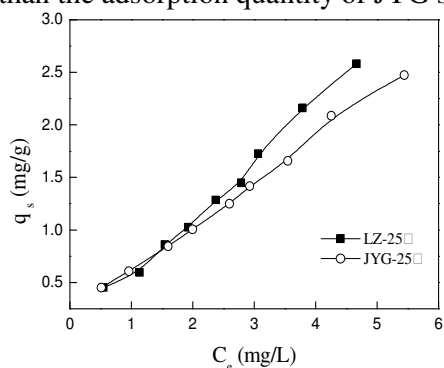


Figure 3. Effect of the Loess Properties on the Thermodynamics Adsorption Process.

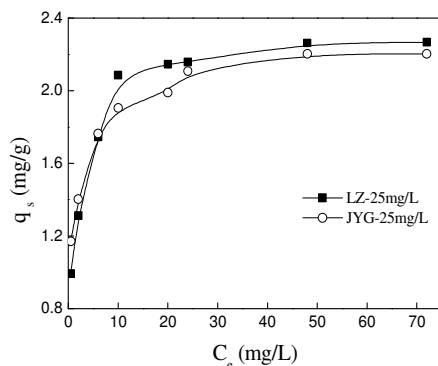


Figure 4. Effect of the Loess Properties on the Kinetic Adsorption Process.

Summary

This study has revealed the adsorption behavior of naphthalene onto loess soil. Most of the adsorption of naphthalene on loess soil occurred within 10 h and the adsorption capacity of naphthalene increased slowly after 10 h, and then the adsorption process reached equilibrium after 24 h. The adsorption of naphthalene onto loess soil fitted well with the pseudo-second-order kinetic model, the adsorption process was controlled by the external liquid film diffusion, surface adsorption, intra-particle diffusion, etc. The adsorption isotherms of naphthalene onto loess soil were linear in the experiments condition, and distribution plays a key role. The adsorption behavior is described better by Henry and Freundlich isotherm model. The adsorption of naphthalene onto loess soil is a spontaneous endothermic process. The adsorption capacity of naphthalene on loess soil increased, besides, the entropy increasing was the main driving force. It was obvious that the naphthalene was able to be adsorbed effectively by loess soil. But there was little difference for the sorption capacity of naphthalene between the two loess soils. The saturated capacity of adsorption onto soil from LZ was higher than those from JYG.

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