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Chemical Behaviors of Benzene Series in Arid Soil and Impact Factors

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BTEX in soil can be detrimental to human health directly by ways of plant absorption and groundwater irrigation. This paper takes benzene, toluene, ethylbenzene and xylene as the study cases to determine the content of BTEX in soil by the headspace-gas chromatography-mass spectrometry (GC-MS), based on which to investigate the impacts of the soil alkaline, salinity, organic matter content and ambient temperature in arid areas on the absorption of BTEX. In this way, the law of the migration of BTEX in the solution with different concentrations of components is revealed. Studies show that the adsorption isotherm coincides with the Henry (linear) adsorption model; the content of organic matter in soil is a leading factor that affects the adsorption. Migrations of BTEX in the solutions with different concentrations generally first increase and then decrease. This study may provide a valuable reference for remedying BTEX contamination in arid areas.

1. Introduction

Currently, BTEX is more common in the petrochemical, coal chemical, paint, pharmaceutical, pesticide and other industries. Such pollutants enter soil from industrial water discharged and leaked and sewage irrigation and are degraded and volatilized by adsorption and desorption. As the industrial economy advances rapidly, it is unaware that the contamination the BTEX does in soil has increasingly exacerbated, especially in arid areas. Soil has a poor natural recovery but often suffers from further intensified contamination (Koschel, et al., 1999). Thus it is of great significance for us to drill down the destruction mechanism of BTEX on soil and control environment pollution.

In recent years, many scholars have conducted some studies on the volatility of BTEX in soil. These studies show that the volatilization rate of benzene solution is higher in about 2d on the threshold, and progressively slower thereafter (Choma et al., 2004). Migration and transformation of organic matter in soil are closely correlated to adsorption, such that this trend must be predicted with a good adsorption model (Blass 1987, Ranke 2006, Asada 1996). However, with regard to BTEX measurement and control, the quantitative analysis in air and water was often underscored in some studies (Chen et al., 2006), there are relatively few studies on the content and adsorption-desorption behaviors of BTEX in soil; additionally, some experiments are mostly static with single factor, and unable to reflect the actual environmental conditions so that the study results contribute to a limited promotional value.

In view of this, the headspace-gas chromatography-mass spectrometry (GC-MS) was adopted to demonstrate the BTEX adsorption process of solutions containing multiple components, given that the four factors of alkaline, salinity, organic matter and temperature produce different effects on this process, as well as the law of effect of multiple factors on BTEX adsorption. It is of great significance to soil remediation.

2. Experiment investigation

Adsorption kinetics: The basic parameters and relevant instruments chosen in this paper are shown in Table 1. Headspace and gas chromatography-mass spectrometry (GC-MS) is used to determine the content of BTEX. The absorption capacity is calculated with subtraction method as follows (Chen and Wu, 1999), $q_e = (C_0 - C_e)V/m$.
Where:

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q_e-The absorption capacity of BTEX when the absorption reaches equilibrium (μg/kg)
C_0- The initial mass concentration of BTEX in the original solution (μg/L)
C_e-The mass concentration of BTEX at an equilibrium (μg/L)
V-Added liquid volume (m L);
m-The mass of soil added to the vial (g).

Table 1: Test parameters

Parameters	Indicators	Remarks
Soil Sample Weight, Solution Volume	2g, 20ml	20ml Head Space Bottle; Blank Test deducts soil dissolved matters and volatilization tolerances
Shaker Temperature	15℃	
Shake Speed	180 rpm/min	
Shake Time	5min/10min/2h/3h/5h/6h/	
Instruments	Model	Manufacturers
Gas Chromatography-Mass Spectrum(GC-MS)	GS-MS7893A/5975c	USA Agilent
Headspace Autosampler	HSS86.50	Italy DANI
Electro-Thermostatic Blast Oven	DHG-9140B	An Ting Science Instruments Co., Ltd
Ultra Pure Water Machine	UPH-I-20T	Chao Chun Science Co., Ltd
Centrifuge	TDL-5A	Xing Ke Science Co., Ltd
PH Gauge	PB-21	Sartorius Instruments (Beijing) Co., Ltd
Electronic Balance	PL-203	Mettler Toledo
Digital Display Water Bath Thermostatic Shaker	SHA-CA	Rong Yi Instruments Co., Ltd

The curves of the concentration of four BTEXs as a function of time are shown in Fig. 1 below. It is obvious that the concentration of each BTEX decreases first and then increases with time and gradually tends to be stable. After 16 hours or so, the concentrations of BTEXs reach equilibrium. In order to verify the availability of experimental data, the adsorption equilibrium time is taken as 48 h.

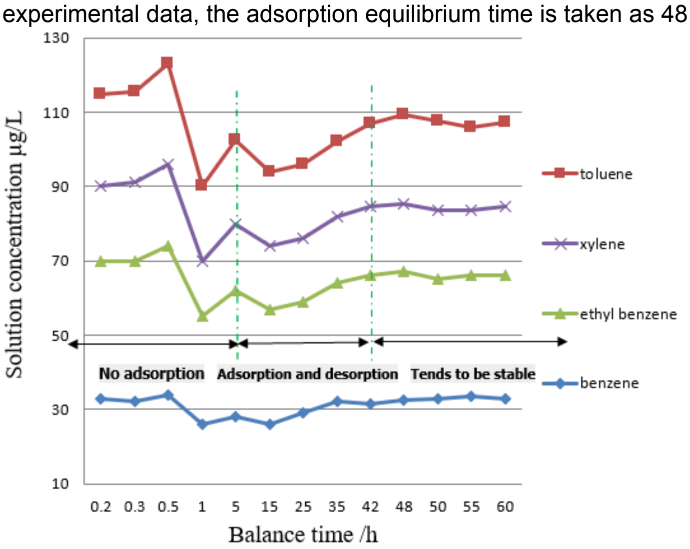

Figure 1: Adsorption kinetics of BTEX on soil

3. Determination of isothermal adsorption model

Many scholars have made a lot of theoretical studies on such adsorption with many models as proposed (Babiker 1977, Dumat 2010, Charles 2006). Studies show that the adsorption capacity is correlated to the medium concentration or temperature. At the time of constant temperature, the functional relationship between the absorption capacity and the concentrations is known as the adsorption isotherm, i.e. the isothermal adsorption model. There are three types of commonly used adsorption models: Henry, Langmuir and Freundlich, whose expressions are respectively given as follows:
Model 1: Linear adsorption isotherm Henry qe = KdCe + a

Where: q_e-The equilibrium absorption capacity (μg/kg);
K_d- The distribution coefficient, or linear adsorption coefficient (L/kg)
C_e-The concentration of balanced solution (μg/L)
Model 2: Nonlinear adsorption isotherm Langmuir $q_e=Q_m b\ C_e/\ (1+b\ C_e)$
Where:
q_e- The equilibrium absorption capacity (μg/kg);
C_e- The concentration of balanced solution (μg/L);
Q_m-The maximum adsorption capacity (μg/kg);
b-The constant.
Model 3: Nonlinear adsorption isotherm Freundlich $q_e=K_F C_e^n$
Where:
q_e-The equilibrium absorption capacity (μg/kg)
C_e- The concentration of balanced solution (μg/L)
K_F-The constant of adsorption capacity, the greater the value, the greater the adsorption capacity;
n-The parameters of adsorption strength, the greater the value, the greater the intensity.

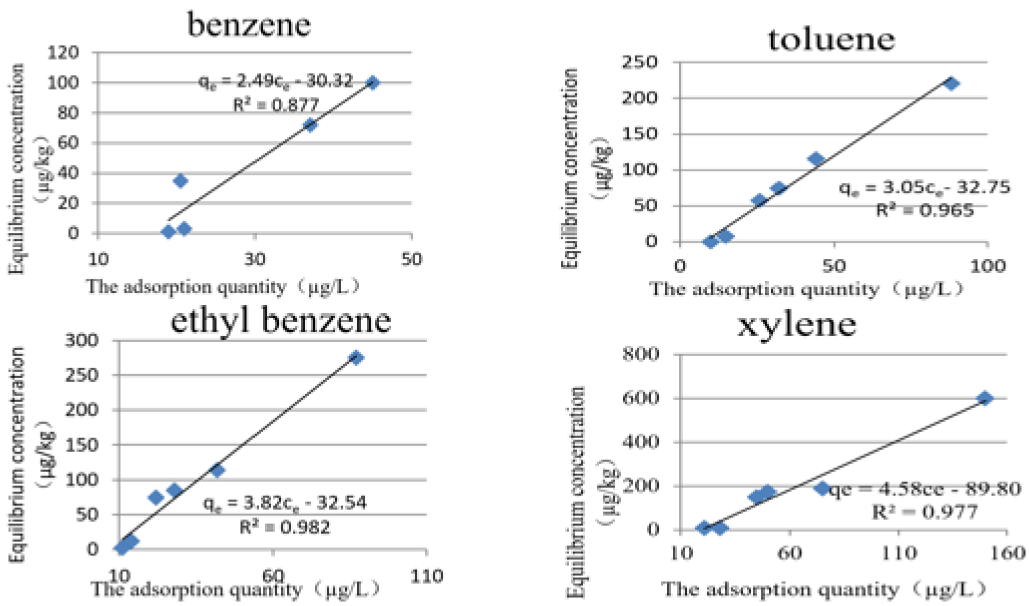

Figure 2: Henry isotherm adsorption of BTEX on soil

To a certain extent, the veracity of experimental data depends on the choice of models (Gonzalez 1996, Ren 2011). In order to avoid this effect, three models are used to obtain the isotherms respectively from which the optimal adsorption model is chosen. In the paper, BTEX mixed solution with different concentrations are prepared. After the adsorption equilibrium (48 h), the concentration of BTEX component is determined by the GC-MS instrument so that the equilibrium equations (see Table 2) and the isotherms (See Fig. 2 and 3) for individual models are available. It is proved that Henry linear equation achieves a better effect of fitting to the adsorption process than the other two models, as shown in Fig. 2 and 3.

Table 2: Parameters of isothermal adsorption equations of BTEX on soil

Material	Henry equations $[q_e=K_dC_e+a]$			Langmuir equations $[q_e=Q_m b\ C_e/\ (1+b\ C_e)]$			Freundlich equations $[q_e=K_FC_e^n]$		
	K_d	a	R^2	Q_m	b	R^2	K_F	n	R^2
benzene	0.62	-7.58	0.877	1.76×10^5	2.66×10^{-6}	0.783	0.15	1.29	0.833
toluene	0.76	-8.19	0.965	2.32×10^5	2.63×10^{-6}	0.894	0.21	1.25	0.935
Ethyl benzene	0.95	-8.14	0.982	2.67×10^5	2.98×10^{-6}	0.929	0.28	1.25	0.968
xylene	1.14	-22.45	0.977	9.5×10^5	9.46×10^{-7}	0.893	0.13	1.41	0.975

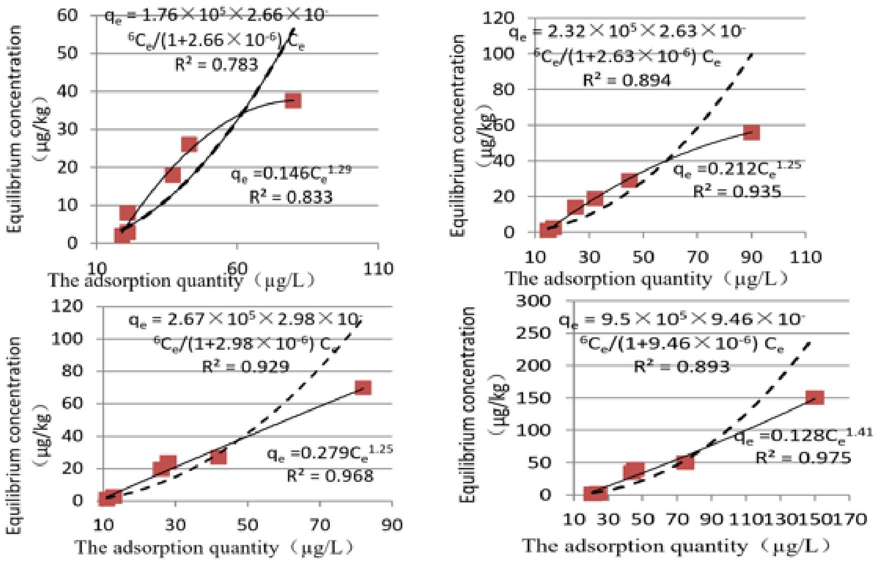

Figure 3: Langmuir and Freundlich isotherm adsorption of BTEX on soil

4. Factors affecting the adsorption behaviors of BTEX in soil

The adsorption of BTEXs in soil has concern with many factors. Studies (Charles et al., 2008) show that organic matter, adjusted solution pH, salinity and temperature in soil have a significant impact on its adsorption. To investigate the comprehensive effect of these factors, a four-factor orthogonal experiment is designed in this paper to get the adsorption capacities of BTEXs under different conditions respectively. The adsorption isotherms of BTEXs in the four groups of experiments are measured, as shown in Fig. 4, 5, 6 and 7, respectively. Experiment design is shown in Table 3, and individual indicators for the original soil are shown in Table 4.

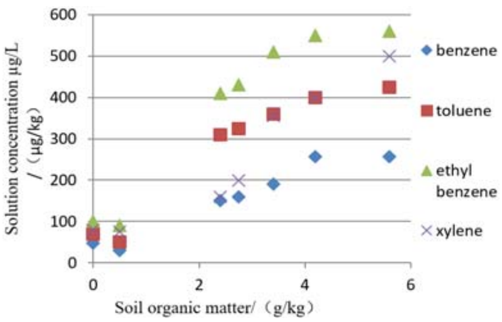

Figure 4: Relationship between adsorption capacity of BTEX and soil organic matter Content

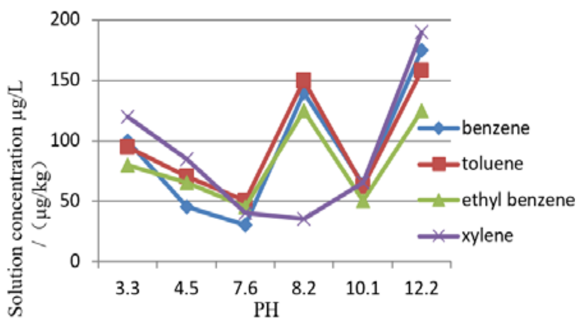

Figure 5: Relationship between adsorption capacity of BTEX and salt content of Solutions

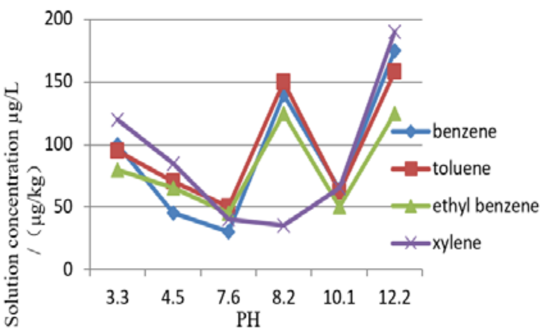

Figure 6: Relationship between adsorption capacity of BTEX and pH values of Solutions

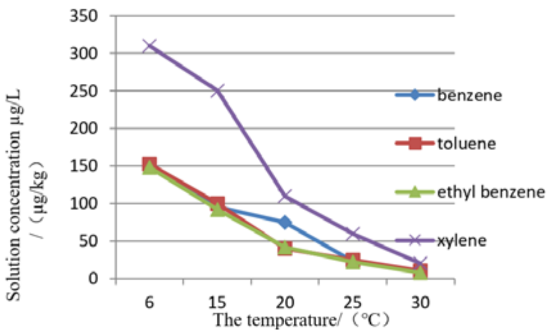

Figure 7: Relationship between adsorption capacity of BTEX and temperature

Table 3: Experimental design of impact factors of adsorption of BTEX

Organic Matters Content Experiment		pH Influence Experiment		Salinity Influence Experiment		Temperature Influence Experiment	
SL.	Organic / (g/kg)	SL.	Solution pH	SL.	Salinity/ (g/L)	SL.	Temperature/ (℃)
O1	0.017	P1	3.3	S1	0.5	W1	6
O2	0.5	P 2	4.5	S2	1	W 2	15
O3	2.4	P 3	7.6	S3	3	W 3	20
O4	2.7	P 4	8.2	S4	6	W 4	25
O5	3.4	P 5	10.1	S5	10	W 5	30
O6	4.1	P 6	12.2	S6	12.6	W 6	
O7	5.7	P 7					

Table 4: Soil indicators

Parameter	Value	Measure
Organic in Soil	5.7 g/kg	$K_2Cr_2O_7$ Method
Salinity	35.5 g/kg	Weight
Benzeni series Mixture PH	7.02	pH Gauge

The relationship between the content of organic matter and the BTEX adsorption capacity in soil is shown in Fig. 4. It is obvious that the content of organic matter and the adsorption capacity is positively correlated, that is, when the content of organic matter increases, the BTEX adsorption in soil also climbs up, which coincides with studies of domestic and foreign scholars Outcomes (Chen et. Al, 2003), Chiou CT et al. (Karickhoff 1979; Chiou et al 1983). As can be seen clearly from Fig. 5, as the salinity in the solution increases, the amount of BTEX adsorbed by soil first decreases and then tends to stabilize. The relationship between PH value and the absorption capacity is shown in Fig. 6. Obviously, when the solution is acidic, PH increases while the adsorption capacity decreases; when the PH value exceeds 7, there is no clear law about relationship between BTEX adsorption capacity and PH value, which is basically consistent with the studies of Maria Tung Ling (Tong et al, 2007) and others. Set five temperature gradients, a curve of the relationship between temperature and BTEX adsorption capacity is plotted, as shown in Fig. 7. The results show that when the temperature increases, the BTEX adsorption capacity decreases. The reason for this phenomenon is that the high temperature inhibits the adsorption from physical behavior to chemical behavior, but with reduced adsorption capacity.

5. Conclusions

(1) Determinate the adsorption equilibrium time: the concentrations of benzene, toluene, ethylbenzene, xylene benzene all decrease and then increase over time, and tend to be stable, reaching equilibrium after 16 hours or so.
(2) Determine the optimal adsorption model: Henry linear equation has a better fitting effect to the absorption process than Langmuir29 and Freundlich, that is, as the concentration increases, the BTEX adsorption capacity in soil increases with the increase of the content of organic matter in soil.
(3) Get the law of effect of soil on the BTEX adsorption capacity: the organic matter in soil is the leading factor affecting the adsorption capacity, and its content is significantly and positively correlated with the adsorption capacity. The pH value of the solution has no obvious law of effect on the adsorption process; when the salinity in soil increases, the solution absorption capacity shows the first decrease and then tends to be stable; adsorption process is exothermic, the higher the temperature, the lower the BETX adsorption capacity.

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