Journal of Hazardous Materials 244–245 (2013) 77–85

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Study of dynamic sorption and desorption of polycyclic aromatic hydrocarbons in silty-clay soil

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HIGHLIGHTS

- ► The Langmuir model can describe the mechanism of isothermal sorption of fluorene.
- ► The desorption hysteresis of fluorene was evident.
- ► The hysteresis phenomenon is attributed to the sorption of PAHs onto clay mineral.

ARTICLE INFO

Article history:
Received 10 May 2012
Received in revised form
11 November 2012
Accepted 12 November 2012
Available online 21 November 2012

Keywords:
Hysteresis
Langmuir
PAHs
Soil column
Sorption and desorption

ABSTRACT

This study reported a well controlled laboratory experiment of high concentration PAHs solute, containing fluorene, phenanthrene, fluoranthene and pyrene, through a nearly homogeneous soil column to reveal sorption and desorption behavior of these four PAHs in soil. The duration of the experiment was 64 days and the flow rate through the soil column was a constant which equals to 2000 mL d^{-1}. The result showed that the mechanism of isothermal sorption and desorption of fluorene can be perfectly described by the Langmuir model, and the correlation coefficients were greater than 0.997. The first-order Lagergren and the Bangham equation can precisely describe the rate of sorption of PAHs, while the rate of desorption can be represented by the second-order kinetics model. The results of the desorption experiment indicated that the desorption hysteresis of fluorene was evident. Few phenanthrene, fluoranthene and pyrene were desorpted to the aqueous phase for the chemical bond with the clay minerals. The most important process determining the behavior of PAHs in soils and their availability to further transformations was the sorption to soil solids with further sequestration and desorption to the aqueous phase.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of hydrophobic organic contaminants (HOC), which mainly contains two or more fused aromatic rings of carbon and hydrogen atoms [1]. PAHs are of environmental concern due to their toxic and carcinogenic effects in many animals including human beings, act as anti-estrogens in mammals, and induce reproductive toxicity in women.

PAHs have been described as ubiquitous contaminants, and they can be introduced into the environment by various processes. The primary sources of PAHs are incomplete combustion of fossil fuels or biomass. One way for PAHs entering soil is through atmospheric deposition, and the other way is via landfill leachate which contains much of PAHs [2].

The most important processes determining the behavior of PAHs in soils and their availability to further transformations are sorption to soil and desorption to the aqueous phase [3]. Due to low solubility and high octanol–water partition coefficients (K_{ow}), PAHs in aqueous environment can be strongly absorbed by soil. Desorption of PAHs from soil to the aqueous phase tends to show hysteresis phenomenon [4]. To the best knowledge of us, the existing studies have not been able to unequivocally ascertain the specific mechanisms of hysteresis for a given situation up to now.

Dynamic sorption is different from static sorption by the way of contact and separation between the sorbent and the absorbate [5]. Static sorption in which the sorbent and absorbate are agitated for mixing without steady flow of absorbent in the sorbent, is carried out by the means of batch technique. Dynamic sorption with steady flow of absorbent in the sorbent is studied by the column method.

The batch technique and the column method have been commonly used to study the sorption and desorption of PAHs. For instance, Hwang et al. [4] studied the role of soil properties in

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http://dx.doi.org/10.1016/j.jhazmat.2012.11.029

pyrene sorption and desorption through batch arrays, and found that soil type would greatly affect the sorption-desorption of HOCs. In investigation of naphthalene sorption in soils and soil fractions using batch and column assays, Bayard et al. [6] found that these two methods provided extremely consistent evaluation of naphthalene sorption on soil under the condition of fully saturated media and short contact time (24 h), with the internal diameter and the height of the soil column of 2.5 cm and 7 cm (corresponding to 50 g of soil), respectively. In addition, apparent equilibrium was reached in batch experiments within 10–15 h and could be represented by linear isotherms, where adsorption of naphthalene mainly took place on the organic matter of the soils. However, the dynamic sorption was with short contact time (24 h) and limited flow rate. Mon et al. [7] found that the sorption isotherm of triarylmethane obtained from the column method did agree fairly well with the batch isotherms, except at small dye concentrations with the internal diameter and the height of the column of 1.5 cm and 12.2 cm, respectively. In that study, column experiments were conducted to study the vertical transport of selected PAHs in different particle-size fraction of sandy soils, the inner diameter and the length of the column were 5 cm and 30 cm, respectively. The elution was mixture of 12 PAHs at a total concentration of 14.4 g kg^{-1} [8]. Bueno et al. [9] conducted a column experiment with 5 cm inner diameter and 20 cm length, and obtained good correlation coefficients when the experimental sorption data were fit with Langmuir model. The dynamic sorption experiments were performed using column reactors filled with quartz sand and equilibrium times were short.

Wang and Liu [10] pointed out that the sorption and migration of contaminants in soil was important to evaluate their distribution in the environment. The soil used in the column experiments was calcareous soil. Although the batch method is used very often because of its simplicity, the parameters obtained from the column method had great utility [11] and can be directly applied to solute transport. There are evidences that the parameter obtained from the batch method may not be representative of the realistic transport process which is dynamic in nature [12].

Researches on sorption characteristics of PAHs have caught increasing attention among investigators from various disciplines recently [13,14]. However, most of those studies chose the batch method. Some studies included the column method as a supplementary means for verification of the batch results. Besides, the internal diameter of the columns in previous sorption studies was generally very small (usually less than 5 cm) [6,15], and far different from the actual conditions in the field. In the previous study, usually with short contact time and few researches used silty-clay soil in the column method.

The purpose of this study is trying to reveal the behavior and characteristics of dynamic sorption and desorption of four PAHs (fluorene, phenanthrene, fluoranthene and pyrene) in soil through a nearly homogeneous soil column with a larger size in internal diameter and height than the previous ones. Langmuir sorption isotherm model is applied to fit the mechanism of isothermal sorption, and the first-order Lagergren equation, the second-order kinetics model and the Bangham equation are applied to express the processes of dynamic sorption and desorption.

2. Materials and methods

2.1. Soil source

Soil samples were obtained near the landfill at north suburbs of Zhoukou, Henan province, P.R. China. After being transported to the laboratory in China University of Geosciences at Wuhan in sealed containers, the soil samples were air dried at room temperature and stored in a dark, dry place in order to prevent any photo-oxidation reactions. The soil sample is classified as silty-clay, as the particle size distribution ranging from 75 to 250 μm, 50 to 75 μm, 10 to 50 μm, 5 to 10 μm and below 5 μm accounted for 1.4%, 7.6%, 61.9%, 12.7%, and 16.4%, respectively. Its organic matter (SOM) was 0.378% and pH was 7.62, which was measured in a 1:2.5 soil/0.01 M $CaCl_2$ suspension. The data of particle size distribution and SOM of our soil sample were obtained from densimeter method of granulometric analysis and the method for determination of soil organic matter based on the China National Standard GB 9834-88 (method for determination of soil organic matter). The soil porosity and saturated hydraulic conductivity were 0.421 and $1.04 \times 10^{-}$ cm s^{-1} respectively. The column was filled with soil layer by layer to insure each layer with the same mass, and the specific weight was 1.41 g cm^{-3}, which was close to the specific weight of its undisturbed soil 1.48 g cm^{-3}. The key parameters influencing PAHs sorption and desorption are SOM content and soil classification or particle size distribution.

2.2. Chemical source

Fluorene, phenanthrene, fluoranthene and pyrene stock solutions, each with the concentration of 10 mg L^{-1}, were prepared in distilled water, mixed with a small amount of HPLC-grade methanol to increase their solubility. Table 1 shows some general properties of these four PAHs [16]. The background solution consisted of 5 mmol L^{-1} of $CaCl_2$, 100 mg L^{-1} of NaN_3 and 5 mg L^{-1} $NaHCO_3$ in distilled water, which were used to poise ionic strength, to prohibit the microbial activity and to hold pH steady, respectively [4].

2.3. Sorption and desorption experiments

Column experiments were carried out on a Plexiglas column with an internal diameter of 14 cm and height of 30 cm in which the soil has been placed and packed. The size of the soil column is quite larger than that of previous ones so that the experiment condition may be somewhat closer to the actual condition in the field. However, considering PAHs might be easily lost due to sorption by soil in the column, too large column resulted in more loss of PAHs and needed too long time to finish the experiment [17]. Fig. 1 is the schematic diagram of the experimental setup. The column was filled with 6500 g of soil. The washing solution was fed at the top of the column and the flow rate of 2000 mL d^{-1} was adjusted using the Mariotte bottle. More than 1000 mL water would be consumed when detected the contents of PAHs and the detection of pH and electric conductivity would consume some water, so we set flow rate at 2000 mL d^{-1}.

Table 1
Some general properties of PAHs.

PAHs	Chemical formula	Molecular weight	Aqueous solubility (mg L^{-1})	log K_{ow}
Fluorene	$C_{13}H_{10}$	166.2	1.68–1.98	4.18
Phenanthrene	$C_{14}H_{10}$	178.2	1.2	4.45
Fluoranthene	$C_{16}H_{10}$	202.26	0.20–0.26	4.9
Pyrene	$C_{16}H_{10}$	202.3	0.077	4.88