SORPTION-DESORPTION BEHAVIOUR OF HYDROPHOBIC ORGANIC COMPOUNDS ON DANUBE SEDIMENT

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Abstract

The sorption-desorption hysteresis of naphthalene and phenanthrene onto Danube sediment was investigated. Hysteresis indices (*HI*) are calculated for three equilibrium concentration (C_e=1%, 5% i 50% of the solubility in water). The results of sorption-desorption hysteresis indicated that it exists for both investigated sorbates on the Danube sediment. For more hydrophobic compound, phenanthrene ($\log K_{OW}$< 4.55) hysteresis is less pronounced in comparison with naphthalene ($\log K_{OW}$< 3.36). In the case of naphthalene, the existence of hysteresis may be due to irreversible pore deformation of the sorbent which causes the formation of meta-stable states in the sorbate mesopores.

Introduction

Sorption is one of the major processes influencing the fate of hydrophobic organic compounds (HOCs) in soils and sediments. It has been shown that sorption of HOCs is directly related to soil/sediment organic matter (SOM), and SOM comprises of two important heterogeneous sorption domains: a "rubbery", soft, or amorphous and a "glass", hard, or condensed domain [1]. In addition, investigating sorption reversibility can provide additional information on sorption and desorption mechanisms. Understanding the mechanism of desorption is an essential step towards assess the risk of releasing of pollutants from sediment which is important in assessing the risk of the release of pollutants into the aquatic environment [2].

The aim of this study was to determine sorption-desorption characteristics of the Danube for two selected polycyclic aromatic hydrocarbons (PAHs). Adsorption-desorption hysteresis, the mismatch between the sorption and desorption isotherms, was investigated for naphthalene and phenanthrene on the Danube sediment.

Experimental

Characterization of sediment

The organic carbon (OC) content was determined by TOC analyzer (LiquiTOCII, Elementar, Germany) after acid pre-treatment of the sediment to remove inorganic carbon. The multi-point BET (Brunauer–Emmett–Teller) specific surface area (SSA) of Danube sediment was determined by nitrogen adsorption at 77 K by Autosorb iQ Surface Area Analyzer (Quantachrome Instruments, USA). Samples were outgassed at 200 ºC for 2 h before running the isotherms. Mesopore volumes (V_{mes}) were derived from desorption isotherms using the BJH (Barrett–Joyner–Halenda) model. Micropore volumes of both sorbents were calculated by t-test method.

Physicochemical properties of PAHs

Two PAHs (naphthalene and phenanthrene) were used as sorbates. Both PAHs(purity > 99%) were purchased from Sigma-Aldrich Chemical Company. The physicochemical properties of the chosen PAHs are summarized in Table 1.

Table 1.*Physicochemical properties of selected PAHs*[3]

Compounds	MW (g/mol)	$logK_{ow}$	S_w (mg/l)	V_i
Naphthalene	128.17	3.36	30	1.09
Phenanthrene	178.23	4.55	1.6	1.45

MW, molecular weight (g/mol); K_{OW}, octanol-water partition coefficient; S_W, water solubility (mg/l); V_i, McGowan volume in units of $(cm^3/mol)/100$.

Sorption-desorption isotherms

All sorption-desorption isotherms were run in duplicate at room temperature (20 ± 2ºC). The sorption isotherms were performed in conventional batch sorption experiments in 40 ml vials with Teflon lined septa. The background solution was 0.01 M $CaCl_2$ in deionized water with 100 mg/l NaN_3 as biocide. Initial concentrations of PAHs ranged from 0.005 to 1.0 mg/l. The solid/solution ratio was adjusted to result in 20-80% uptake of given organic compound. Head space in the vials was kept at a minimum in order to minimize the loss of compounds during the experiment due to evaporation. The procedure was as follows: in vials which contained premeasured sorbent and background solution, a certain volume of methanol stock solution of PAHs was spiked and equilibrated at room temperature by continuous shaking for 7 days. After the completion of sorption, vials were centrifuged at 3000 rpm for 15 minutes, and the aliquots of the clear supernatant were taken for PAHs analysis. Control vials, prepared similarly but with no sorbent, were run simultaneously for assessing the loss of sorbate due to processes other than sorption (evaporation, adsorption on the walls of the vials, degradation). The results showed that the total uncertainty was less than 5% of the initial concentrations. Desorption was conducted by sequential decant-refill steps, after the completion of the sorption experiments, which involves replacement of an aqueous solution that is in equilibrium with fresh background solution, which does not contain sorbate, after which the vials reach new equilibrium. Dilution factors were determined by measuring the mass of the vials before and after the addition of fresh portions of background solution. By calculating the mass balance based on the equilibrium sorbate concentrations, the masses removed of the supernatant solution and the portions added background solution, provided data on the amount of sorbate desorbed in the desorption, and data were collected to fit desorption isotherms.

PAHs in the supernatants were analyzed after liquid-liquid extraction with hexane (J.T.Baker, for organic residue analysis). PAHs were analyzed by gas chromatography with mass spectrometric detection (GC/MS, Agilent 7890A/5975C) on a HP-5MS column (J&W Scientific) with phenathrene-d10 as internal standard.

Data analysis

The sorption data were fitted with the Freundlich isotherm:

$$q_e = K_F \cdot C_e^n \qquad (1)$$

where q_e and C_e are the solid phase and aqueous phase equilibrium concentrations (in mg/kg and mg/l, respectively); K_F and the exponent n are the Freundlich sorption coefficient [expressed as $(mg/kg)/(mg/l)^n$].

Sorption-desorption hysteresis was explored using Hysteresis Index (*HI*) as proposed by Huang et al. [4]:

$$HI = \frac{q_e^d - q_e^s}{q_{es}} \bigg/_{T,c_e} \qquad (2)$$

where q_{es} and q_{ed} are solid-phase solute concentrations for the single cycle sorption and desorption experiments, respectively, and the subscripts T and C_e specify constant temperature and residual aqueous phase concentration, respectively.

Results and discussion

Characterization of Danube sediment

Danube sediment has average mesopore radius about 11.4 nm, while the results of t-test methods clearly show that sediment does not contain micropores. Additionally, the SSA and pore volume (PV) were 3.19 m^2/g and 0.018 cm^3/g, respectively. OC content of Danube sediment is 1.21%. Based on these results it can be concluded that the Danube sediment represents a typical sandy aquifer material with low OC content.

Sorption-desorption hysteresis

Sorption reversibility provides an additional insight into the sorption mechanisms, as well as structural properties of the sorbent governing the specific sorptive behaviour of the sorbate. The sorption-desorption hysteresis was quantified for each sorption and desorption isotherms using the hysteresis index (*HI*) (eq. 2). Hysteresis indices were calculated using Freundlich's parameters obtained from the sorption and desorption of the three sorbate equilibrium concentrations (C_e=1%, 5% i 50% of the solubility in water). The calculated *HI* values are represented in Table 2.

Table 2. Sorption-desorption hysteresis for investigated PAHs on the Danube sediment

Compounds	HI		
	$C_e(mg/l)$ S_W		
	0.01 S_W	*0.05 S_W*	*0.5 S_W*
Napthalene	0.65	1.02	1.70
Phenanthrene	0.45	0.31	0.11

The more pronounced sorption-desorption hysteresis was observed for naphthalene. Interestingly, Danube sediment showed a more pronounced hysteresis for naphthalene (*HI* = 1.70 to 0.65) than phenanthrene (*HI* = 0.45 to 0.11), which may indicate that the smaller naphthalene remains trapped after penetrating into the pores of the sorbent. In this case, hysteresis can be explained as follows: in low concentrations, sorption may be the result of surface interactions. Surface-bound molecules are probably desorbed much faster. However, as the concentration of sorbate increases, the increased concentration gradient causes molecules that penetrate deeper into the pores of sorbent and organic matter causing the creation of pores in which they are trapped, resulted in the pronounced hysteresis. Since the sediment has mesopores with average radius of about 114 Å, the pore volumes can be calculated and is equal to $6.20 \cdot 10^6$ A^3. Volume of one molecule of naphthalene is about 187 $Å^3$ which means that "irreversible entrapment" can be the cause of the observed sorption-desorption hysteresis.

For phenanthrene, desorption increased with increasing concentration. Hysteresis can be explained as follows: at lower concentration of phenanthrene sorption is results interaction between molecules of phenanthrene with condensed domain of SOM, while at higher concentrations molecules of phenanthrene can interact with soft domain of SOM.

Additionally, Sander et al. [5] point out that desorption hysteresis was widely reported for organic contaminants from soils/sediments, and was attributed to irreversible pore deformation of the sorbent by the sorbate and the formation of meta-stable states of sorbate in fixed mesopores.

Conclusion

In this study, the sorption-desorption behaviour of two compounds from the group of the PAHs on Danube sediment was investigated. Sorption-desorption hysteresis exists for both PAHs. The more pronounced sorption-desorption hysteresis was observed for naphthalene on the Danube sediment which may be due to irreversible pore deformation of the sediment which causes the formation of meta-stable states in the sorbate mesopores. Further research should be focused on a more detailed characterization of the organic matter in the sediment to better define the sorption behaviour. Understanding these results will be useful for exposure and risk assessment of investigated PAHs in aquifer materials and groundwater.

Acknowledgements

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