

INFLUENCE OF HUMIC SUBSTANCE (HS) ADSORPTIVE FRACTIONATION ON PYRENE PARTITIONING TO DISSOLVED AND MINERAL-ASSOCIATED HS

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Abstract

Changes in pyrene partitioning due to mineral surface adsorptive fractionation processes of humic substances (HS) were examined in model environmental systems. For purified Aldrich humic acid (PAHA), carbon-normalized pyrene binding coefficients (K_{oc}) for the residual (i.e., nonadsorbed and dissolved) PAHA components were different from the original dissolved PAHA K_{oc} value prior to contact with mineral suspensions. A positive correlation between the extent of pyrene binding and weight-average molecular weight (MW_w) of residual PAHA components was observed, which appeared to be unaffected by the specific mineral adsorbents use and fractionation mechanisms. A similar positive correlation was not observed with the adsorbed PAHA components, suggesting that conformational changes occurred for the mineral-associated components upon adsorption. Nonlinear pyrene sorption to mineral-associated PAHA was observed, and the degree of nonlinearity is hypothesized to be dependent on adsorptive fractionation effects and/or structural rearrangement of the adsorbed PAHA components.

Key words: humic substances (HS), K_{oc} , adsorption, fractionation, minerals, molecular weight

1. Introduction

Partitioning of hydrophobic organic contaminants (HOCs) to dissolved and/or mineral-associated humic substances (HS) often governs their transport, fate and environmental effects in soil and groundwater systems (1). In many of these systems, organic carbon-normalized partition coefficients (K_{oc}) are critical factors in determining HOC distributions. Molecular weight fractionation of HS caused by selective adsorption to minerals can be quantified by size exclusion chromatography (SEC) (2). A number of studies using SEC have clearly shown deviations in the average molecular weights (MW) of residual HS remaining in solution after adsorption versus the original average HS MW.

Several of these studies have also demonstrated experimental K_{oc} values that were different among the various HS fractions, such as $K_{oc(ads)}$ derived from mineral-associated HS, $K_{oc(bulk)}$ for the original, dissolved HS, and $K_{oc(res)}$ for the residual HS left in solution after sorption. Possible explanations for these different K_{oc} values include HS adsorptive fractionation and structural changes of the HS components upon adsorption (1,3). However, little to no studies have quantitatively investigated the impacts of HS adsorptive fractionation on HOC partitioning in HOC-HS-mineral systems. The overall objective of this study was to 1) investigate possible correlations between pyrene K_{oc} values for sorption-fractionated dissolved and mineral-associated HS and the corresponding HS MWs, and 2) evaluate isotherm linearity for pyrene sorption onto HS-coated minerals in terms of HS adsorptive fractionation.

2. Experimental Methods

Purified Aldrich humic acid (PAHA) and Suwannee River fulvic acid (SRFA) were used as representative HS. Pyrene was selected as a model HOC. Commercially-available kaolinite (Sigma) and hematite (Alfa) were used without further treatment. After sorption equilibration, mineral solids were separated from the aqueous phase by centrifugation at 3000 rpm for 1 hour. Organic carbon was measured to quantify HS concentrations. UV absorbance was recorded for every sample to make fluorescence corrections. Size exclusion chromatography (SEC) with UV detection was used to determine weight-average molecular weights (MW_w) of residual HS samples. A modified fluorescence quenching technique was conducted to determine $K_{oc(res)}$ values. The intensity of fluorescence is proportional to the concentration of pyrene that is not associated with HS (i.e., $[pyrene]_{free}$) if dynamic quenching can be neglected. Based on this assumption, the concentrations of freely dissolved pyrene in HS samples were determined by fluorescence using external standards. The concentrations of pyrene associated with HS were calculated by difference from the initial known concentrations and the freely dissolved pyrene concentrations. For $K_{oc(ads)}$ and pyrene sorption isotherms, pyrene stock solutions were spiked into centrifuge tubes containing equilibrated HS and mineral suspensions. After equilibration and removal of the solid phase, the total concentration of unadsorbed pyrene in solution was quantified by hexane extraction and fluorescence. Adsorbed pyrene concentrations were then determined by mass balance. Independent experiments of pyrene sorption to bare minerals without HS were also conducted to account for potential mineral contributions to pyrene sorption. To estimate $K_{oc(ads)}$ values, it was assumed that adsorbed HS were limited to the surface edge sites on kaolinite whereas for hematite, adsorbed HS were assumed to be uniformly distributed across the surface.

3. Results and Discussion

HS sorption isotherms generally exhibited Langmuir-type behaviors (Figure 1). The greater HS adsorption observed for hematite versus kaolinite can likely be attributed to 1) the different mineral surface charge characteristics and/or 2) the different distributions and concentrations of surface hydroxyl groups on the two minerals.

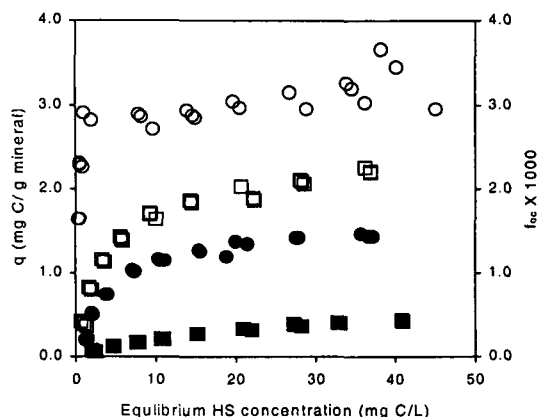


Figure 1. Adsorption isotherms of PAHA and SRFA on kaolinite (50 g/L) and hematite (10 g/L) at pH 7 and 0.1 M NaCl. O: PAHA and hematite. ●: PAHA and kaolinite. □: SRFA and hematite. ■: SRFA and kaolinite.

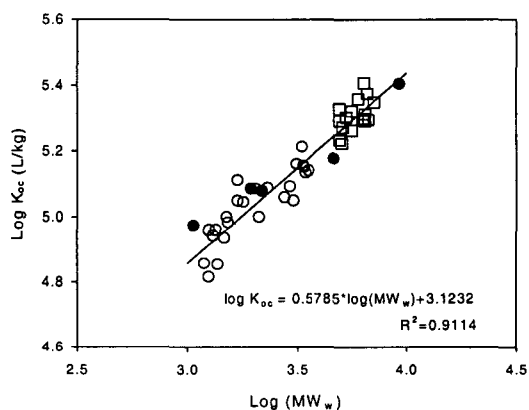


Figure 2. Relationship between $\log K_{oc}$ and $\log MW_w$ of nonadsorbed PAHA fractions (□: PAHA+hematite, O: PAHA+kaolinite) and PAHA fractions resulting from ultrafiltration (UF) (●). The UF data is from (4).

A $\log K_{oc}$ - $\log MW_w$ relationship was observed for the nonadsorbed, residual PAHA components (Figure 2). The similar relationship found between K_{oc} and MW_w for both minerals suggests that 1) MW_w may be a good descriptor for predicting K_{oc} even when dissolved HS are lacking certain size fractions due to adsorptive fractionation, and 2) the $\log K_{oc}$ - $\log MW_w$ relationship for residual HS is insensitive to the specific fractionation process. For example, Figure 2 shows that the data points for ultrafiltered size fractions are not significantly different from the trend established for the sorption-fractionated PAHA components.

Adsorbed HS MW_w s were estimated from the original MW_w and the MW_w of residual HS components based on an ideal mixture approach (4). Generally, MW_w values for the adsorbed HS components increased with fractional carbon coverage on the mineral surfaces ($f_{oc} = 0$ to 0.002) (Figure 3), which was opposite from the trend expected based on the residual HS results (i.e., higher degree of preferential adsorption of higher MW_w fractions at lower f_{oc}) (2). This indicates that the fraction of mass removal (UV removal for this study) of HS by adsorption to minerals contributed more to the estimate of adsorbed HS MW_w than did the degree of apparent preferential adsorption.

In contrast to PAHA, no correlation between K_{oc} and MW_w was observed for adsorbed or residual SRFA (data not shown).

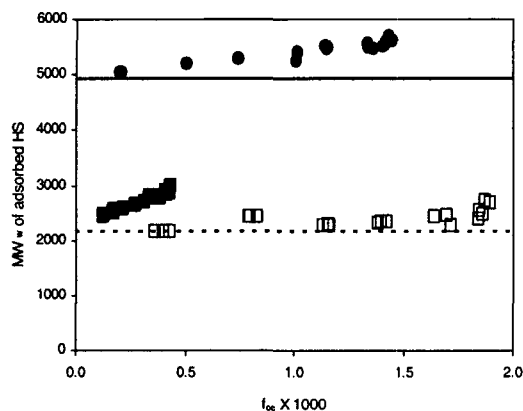


Figure 3. Relationship between adsorbed HS MW_w and the fractional coverage. Symbols used correspond to those in Figure 1. Solid line represents PAHA adsorbed on hematite.

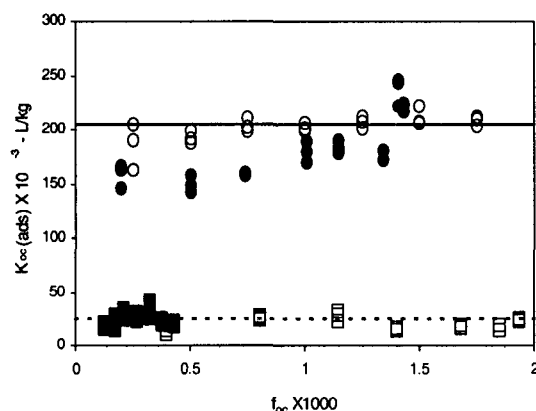


Figure 4. Relationship between pyrene $K_{oc(ads)}$ (L/kg) and f_{oc} . O: PAHA and hematite. ●: PAHA and kaolinite. ○: SRFA and hematite. ■: SRFA and kaolinite.

Compared to original K_{oc} values, the extent of pyrene partitioning to HS adsorbed on kaolinite was consistently lower except for the highest f_{oc} value (~ 0.0014) examined (Figure 4). This observation suggests that HS components undergo structural changes upon adsorption to kaolinite such that resulting conformations provide lower pyrene binding affinities. The lower $K_{oc(ads)}$ values versus $K_{oc(bulk)}$ are in contrast to the higher MW_w values of the corresponding residual PAHA versus the original MW_w values observed in Figure 4, indicating that the HS conformational changes upon adsorption may be more important in determining the extent of pyrene binding with adsorbed HS than is adsorptive fractionation.

More nonlinear sorption behavior was observed with adsorbed PAHA for hematite versus kaolinite (Table 1). This may relate to the different locations and arrangements of adsorbed HS on these two minerals. For this study, adsorbed PAHA in the hematite systems did not undergo fractionation whereas preferential adsorption of higher MW components occurred with kaolinite. Recent studies

suggest that nonpolar aliphatic or carbohydrate structures of HS, which are abundant in the higher MW_w fractions of PAHA, are associated with linear HOC isotherms whereas aromatic structures are associated with nonlinear HOC sorption behavior (5,6).

Table 1. Pyrene sorption isotherm parameters.

	f _{oc}	Freundlich model			Linear model	
		K _{DF} ^a	n	R ²	K _{DL} ^b	R ²
PAHA + kaolinite	0.0003	0.0636 ±0.0082	0.9081 ±0.0369	0.9837	0.0431 ±0.0006	0.9760
	0.0011	0.2094 ±0.0208	0.9569 ±0.0454	0.9818	0.1906 ±0.0025	0.9778
PAHA + hematite	0.0002	0.2140 ±0.0131	0.8497 ±0.0169	0.9969	0.1243 ±0.0019	0.9802
	0.0025	0.9965 ±0.0488	0.7927 ±0.0197	0.9815	0.5933 ±0.0129	0.9624
SRFA + kaolinite	0.0006	0.0208 ±0.0024	0.9638 ±0.0314	0.9912	0.0182 ±0.0002	0.9914
	0.0042	0.0477 ±0.0065	0.9242 ±0.0443	0.9826	0.0378 ±0.0006	0.9788

^a Units in (μg/g)/(μg/L)ⁿ. ^b Units in (L/g).

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