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THE SORPTION OF HUMIC ACIDS TO MINERAL SURFACES AND THEIR ROLE IN CONTAMINANT BINDING

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Abstract

Humic substances dissolved in groundwater may adsorb to certain mineral surfaces, rendering hydrophilic surfaces hydrophobic and making them sorbents for hydrophobic organic compounds (HOC). The sorption of humic and fulvic acids (International Humic Substance Society, IHSS, reference samples) on hematite and kaolinite was investigated to determine how natural organic coatings influence HOC sorption. The sorption behavior of the humic substances was consistent with a ligand-exchange mechanism, and the amount of sorption depended on the concentration of hydroxylated surface sites on the mineral and the properties of the humic substance. The sorption of the humic substances to two solids was proportional to their aromatic carbon content and inversely proportional to the O/C ratio.

Increasing quantities of sorbed humic substances (f_{oc} 0.01 to 0.5%) increased the sorption of carbazole, dibenzothiophene, and anthracene. Peat humic acid, the most aromatic coating, showed the greatest sorption enhancement of HOC when sorbed to hematite. In addition, HOC sorption was greater on organic coatings formed at low ionic strength ($I = 0.005$) as compared to higher ionic strength ($I = 0.1$). We suggest that both the mineral surface and the ionic strength of the electrolyte affect the interfacial configuration of the sorbed humic substance, altering the size or accessibility of hydrophobic domains on the humic molecule to HOC.

Introduction

The sorption of hydrophobic organic compounds (HOC) to organic matter in soil, sediment, and aquifer material and the binding of HOC to dissolved and colloidal humic substances are dominant processes controlling the aqueous concentrations and transport of HOC in the environment. Although several studies have addressed the interaction of HOC with dissolved or colloidal humic substances in groundwater (McCarthy and Jimenez, 1985; Chiou et al., 1986, 1987; Gauthier et al. 1986, 1987), little is known about the chemical and physical properties of mineral-bound organic coatings and their potential influence on HOC sorption to low-carbon sediments. Information on organic coatings on aquifer sediments is scarce, but these coatings are expected to occur to varying degrees, depending on aquifer mineralogy, water chemistry, and the composition and nature of the DOC. Particle-associated humic substances may form mineral coatings, given that natural dissolved/colloidal organic material binds to a variety of oxide (Al and Fe) and layer silicate surfaces that are common in aquifers (Kummert and Stumm 1980; Davis and Gloor 1981; Tipping 1981; Davis 1982; Tipping and Cooke 1982; Tipping and Heaton 1983; Morse 1986). These organic coatings may render the hydrophilic mineral surfaces hydrophobic, and more capable of sorbing organic compounds.

The structural and bulk chemical properties of organic matter in soils and subsoils varies between different climatic and geochemical environments (Lobartini and Tan 1988), and these variations influence HOC sorption (Chiou et al. 1983; Ainsworth et al. 1989). For different soils, the carbon normalized binding constant of a single HOC may range over an order of magnitude, and such variations may be attributed to compositional differences in the organic matter, such as polarity and aromaticity (Karickoff 1984; Garbarini and Lion 1986; Mingelgrin and Gerstl 1983).

In addition to the chemical properties of the humic material, the sorption of HOC to bound organic matter may also be influenced by the structural orientation of the humic coating on the mineral surface (Murphy et al. 1990). Karickhoff (1984) suggested that the availability of organic carbon to pollutant sorption is reduced when it is incorporated or bound to sediment particles. The structure of dissolved humic substances is largely determined by the groundwater pH, ionic strength, and the presence of divalent cations (Ghosh and Schnitzer, 1980; Tsutsuki and Kuwatsuka, 1984; Davis, 1982; Tipping and Cooke, 1982). These same properties may influence the structure and orientation of the humic material sorbed to the mineral surface, similar to the sorption of polyelectrolytes to surfaces (Hesselink, 1983; Lyklema, 1985).

At high ionic strength, low pH, or in the presence of cations, the charge repulsion between adjacent carboxyl or hydroxyl groups on the humic substance is neutralized resulting in a coiled configuration (Ghosh and Schnitzer, 1980; Tsutsuki and Kuwatsuka, 1984; Tipping and Cooke, 1982). At the mineral/solution interface the coiled configuration could result in fewer attachment points between the humic carboxyl and mineral surface hydroxyl groups and an extension of the shear plane outward from the mineral surface (Tipping and Cooke, 1982). At the other extreme, low ionic strength, high pH, and in the absence of cations, the humic substance may adopt a more open configuration in solution, resulting in more attachment points upon sorption to the mineral surface. The focus of this study was to 1) investigate the sorption of reference humic substances on typical aquifer sediments, and 2) determine if the ionic strength of the medium imparted a different structure to the adsorbed humic substance that in turn affected HOC sorption.

Experimental Procedures

Materials. A well-crystallized kaolinite (KGa-1, Clay Minerals Society Source Clay) and hematite were prepared as outlined in Murphy et al. (1990). The surface areas were 15.6 m^2/g and 5.4 m^2/g for kaolinite and hematite respectively. Well-characterized humic substances were obtained from the International Humic Substances Society (IHSS). The distribution of carbon functional groups of the humic and fulvic acids can be found in Thorn et al. (1990) and the elemental analyses are available from IHSS (R. L. Malcolm, personal communication). ^{14}C-ring-labeled compounds, carbazole, dibenzothiophene, and anthracene, were custom-synthesized by Sigma and used to quantify sorption.

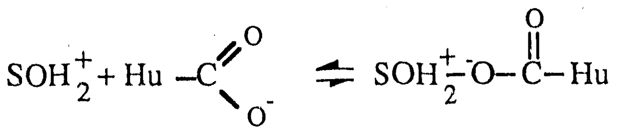
Sorption Experiments. The sorption of humic substances was measured on kaolinite and hematite over a pH range of 4 to 7.5 in a 250-ml jacketed glass flask maintained at 25°C under a nitrogen atmosphere. A surface area of 55 m^2/L was used in the kaolinite experiments; a surface area of 25 m^2/L was used for hematite. The initial concentration of humic substance was ~10 mg C/L. Additional details of these experiments can be found in Murphy et al. (1990).

The sorption of HOC was evaluated on kaolinite or hematite that were coated to different degrees with peat humic acid. Varying amounts of dissolved humic substances were equilibrated with the sorbents in either 0.1 M or 0.005 M $NaClO_4$ at pH 4.5. The coated minerals were washed twice in DOC-free electrolyte; previous experiments showed that this washing did not induce desorption of the sorbed humic substance. The f_{oc} (mass fraction organic carbon) contributed by the sorbed humic substances ranged from ~0.01 to 0.5% for hematite and kaolinite. Radiolabeled HOC solutions were added to the sorbent suspensions to reach a final working concentration of 25% of the compound's water solubility. The suspensions were equilibrated with slow end-over-end mixing for 20 h at 25°C. The fraction of HOC sorbed in these batch experiments was calculated by difference based on the ^{14}C activity remaining in solution. Desorption of the humic coating was not measurable over the course of these experiments. Additional experimental details can be found in Murphy et al. (1990).

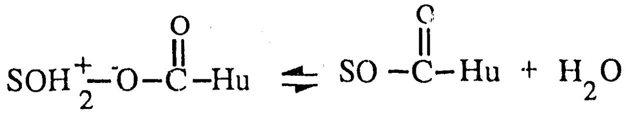
Results and Discussion

The sorption characteristics of humic substances were investigated on kaolinite (Figure 1) and hematite. Humic acids were invariably more strongly sorbed than fulvic acids. In addition, the sorption of humic substances was directly proportional to the aromaticity and inversely proportional to the polarity as approximated by the elemental O/C ratio. The sorption of humic substances increased with decreasing pH in response to positive charge development on the sorbents. This pattern was consistent with a ligand exchange mechanism, as previously suggested by Parfitt et. al. (1977), Tipping (1981), Tipping and Cooke (1982), and Davis (1982). Sorption of humic substances by ligand exchange is believed to occur in the following sequence (Sposito 1984; Zhang and Sparks 1989):

$$\mathrm{SOH + H^+ \rightleftharpoons SOH_2^+} \qquad (1)$$



$$\mathrm{SOH_2^+ + Hu{-}C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O^-} \rightleftharpoons SOH_2^{+}{-}{}^{-}O{-}\overset{\overset{O}{\|}}{C}{-}Hu} \qquad (2)$$



$$\mathrm{SOH_2^{+}{-}{}^{-}O{-}\overset{\overset{O}{\|}}{C}{-}Hu \rightleftharpoons SO{-}\overset{\overset{O}{\|}}{C}{-}Hu + H_2O} \qquad (3)$$

where SOH represents the surface hydroxyl group on the sorbent, and $\mathrm{Hu\text{-}COO^-}$ represents the humic carboxyl group. The first step of this process is protonation (eq 1), which is believed to render the surface hydroxyl group more exchangeable (Sposito 1984). The protonation step is responsible, in part, for the pH dependence of the fractional sorption. The humic carboxyl groups may then form an outer-sphere surface complex with the protonated hydroxyl group (eq 2). Ligand exchange (OH_2 for $\mathrm{Hu\text{-}COO^-}$) is postulated to occur in the final step (eq 3), yielding an inner-sphere complex. In these experiments, the desorption of the humic substances from the sorbents was insignificant after 7 days, evidence for the formation of stable inner-sphere complexes between multiple carboxyl groups on the humic substance polyelectrolyte and surface hydroxyl sites on the sorbents.

Although it is believed that protonation of the surface hydroxyl initiates the ligand exchange reaction, additional reaction of the humic carboxyl groups and unprotonated surface hydroxyl groups results in the release of hydroxyl ion in addition to water during ligand exchange. The release of hydroxyl ion during the sorption of peat humic acid to hematite is shown in Figure 2. Hematite was equilibrated in a stir cell under nitrogen at pH 5.5 overnight. Peat humic acid, adjusted to pH 5.5, was added at successive intervals. A blank, containing only peat humic acid, is also shown in Figure 2. The release of hydroxyl was measured as the amount of H^+ added to the stir cell to maintain the pH at 5.5.

Isotherms for the sorption of peat humic acid on kaolinite (Figure 3) followed a Langmuir-type curve and are similar to previously reported isotherms for humic substance sorption on mineral surfaces (Tipping 1981; Parfitt et al. 1977). Such isotherms showed high affinity sorption at low surface coverage that rapidly reached sorption maxima. The Langmuir method has previously been applied to determine the maximum sorption density by assuming that the plateau or sorption maximum of the Langmuir curve represents monolayer coverage of the solid by the polymer (Bohn et al. 1979; Kummert and Stumm 1980; Liang 1988). Monolayer coverage does not necessarily represent saturation of surface hydroxyl sites by direct coordination with carboxyl groups on the polyelectrolyte.

At low ionic strength (I = 0.005) the sorption maxima of peat humic acid on kaolinite occurs at approximately 6.5 μmol C/m^2 as opposed to almost 13 μmol C/m^2 at high ionic strength (I = 0.1). These results suggest that the humic acids adopt a more linear or open configuration at low ionic strength and on a mole carbon basis occupy a greater amount of mineral surface area than humic acids at high ionic strength. This observation is consistent with the effect of ionic strength on the configuration of humic substances in solution (Ghosh and Schnitzer 1980; Tsutsuki and Kuwatsuka 1984), and suggests that the solution configuration can impact the configuration of the sorbed humic substance.

The sorption of carbazole, dibenzothiophene, and anthracene was investigated on hematite and kaolinite that had been coated with Peat humic acid. In these experiments, f_{oc} values were varied over the range of 0.001 to 0.01 to encompass the organic carbon concentrations found in low-carbon groundwaters and aquifers. Sorption of the HOC was very low on the bare mineral surfaces because they had been pretreated to remove any small amounts of organic carbon that might be present. As shown in Figure 4a, increasing quantities of sorbed peat humic acid increased the fractional sorption of anthracene, dibenzothiophene, and carbazole. Anthracene (log K_{ow} = 4.45), the most hydrophobic HOC, showed the greatest sorption enhancement, followed by dibenzothiophene (log K_{ow} = 4.38), and carbazole (log K_{ow} = 3.29). Peat humic acid coatings associated with hematite showed greater sorption enhancement of the HOC than the same amount of Peat humic acid sorbed to kaolinite. However, the sorption enhancement was not linear. The HOC sorption increased most dramatically per unit of sorbed humic carbon at the lowest f_{oc}. This apparent nonlinear response to increasing surface carbon contrasted with the behavior of HOC sorption to humic substances in solution (Chiou et al. 1987), who reported a linear increase in the apparent solubility of HOC with increasing concentration of dissolved humic substances. As concentrations of humic substances bound to the mineral surface increase, they may progressively adopt configurations that limit carbon availability for HOC sorption (Karickoff 1984), or that limit the size and accessibility of hydrophobic domains on the sorbed macromolecule. We suggest that the mineral surface affects the interfacial configuration of the humic substance, possibly altering the size of the hydrophobic domain on the humic molecule or their accessibility to HOC. The more uniform distribution of hydroxyl sites over the entire hematite surface may allow the humic substances to adopt a more open structure on the surface, yielding a larger hydrophobic area than would occur under comparable f_{oc} on kaolinite. The conformation of the edge-adsorbed humic substances on kaolinite is apparently less conducive to HOC sorption.

The sorption of HOC at low ionic strength (Figure 4b) is enhanced over the sorption at high ionic strength, even when almost twice as much peat humic acid is adsorbed to the kaolinite surface. We suggest that a more open configuration of peat humic acid on the mineral surface enhances HOC sorption by facilitating the exposure of hydrophobic binding domains. Specific adsorption of the HOC on the organic phase, rather than partitioning, is indicated by the sorption isotherms shown in Figure 5. Sorption isotherms for HOC on kaolinite with bound peat humic acid were linear on a log-log basis and conformed to the Freundlich equation:

$$\log S = \log K_F + N \log C_e \qquad (4)$$

where K_F and N are constants specific to the coated sorbent, S = micromoles of HOC adsorbed per gram of solid, and C_e = micromoles of HOC per milliliter of solution. The best fit linear regressions to the data in Figure 5 did not exhibit a slope of 1 (ie. Freundlich $N \neq 1$). Slopes of non-unity were observed regardless of whether sorption was measured by aqueous phase difference or by direct analysis of the sorbent phase; in fact, the statistics of these two types of sorption measurements were comparable. Both humic-coated kaolinite and hematite (not shown) exhibited N values of less than unity. The slope of the high f_{oc} isotherms on kaolinite increased with sorbate K_{ow} or hydrophobicity resulting in isotherm slopes for anthracene, the most hydrophobic compound, close to unity.

Chiou et al. (1983) and Chiou and Shoup (1985) argue that a slope of one of the HOC isotherm (ie. often referred to as a "linerar isotherm" when not plotted on a log-log basis) is evidence for partitioning of HOC into an organic phase. The nonlinearity of the isotherms (i.e., $N \neq 1$) on the mineral-humate sorbents suggests that the sorbed humic substance is behaving as a hydrophobic surface rather than a hydrophobic phase. This observation is consistent with the lower sorption affinity of HOC at high ionic strength. Presumably the coiled configuration of the humic acid at high ionic strength limits the availability of sites for HOC sorption.

Conclusions

The sorption of humic substances on kaolinite and hematite was consistent with ligand-exchange between carboxylic acid groups on the humic substance and hydroxylated surface sites on the solids. The sorption of humic substances to both hematite and kaolinite was proportional to their aromatic carbon content and inversely proportional to their O/C ratio. Humic acids were invariably more strongly adsorbed than fulvic acids. Sorption isotherms of peat humic acid on kaolinite suggested that on a mole carbon basis, peat humic acid occupies a greater amount of mineral surface area at low ionic strength than at high ionic strength. Furthermore, the sorption of HOC on organic coatings formed at low ionic strength was greater than those formed at high ionic strength, again suggesting that at low ionic strength the humic acid adopts a more open configuration on the mineral surface which facilitates HOC sorption.

Sorbed humic substances greatly enhanced HOC sorption at low surface coverage and f_{oc}. The HOC sorption increased most dramatically per unit of sorbed humic carbon at the lowest f_{oc}, suggesting that as concentrations of humic substances increase, they adopt configurations that limit carbon availability for HOC sorption. Sorption isotherms of HOC on the humic coated mineral substrates were nonlinear implying that the sorption phenomena was adsorption onto rather than partitioning into the surface organic phase. Humic surface coatings may be an important sorbing phase for HOC in low-carbon substrates, which are typically found in aquifers.

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Figures

1) Fractional adsorption of IHSS humic and fulvic acids on kaolinite at varying pH. The initial humic substance concentration was 10 mg C/L.

2) The release of hydroxyl ion during successive additions of peat humic acid to hematite. The lower curve shows the equilibration of a blank containing only peat humic acid.

3) Sorption isotherms of peat humic acid on kaolinite at high and low ionic strength. Dashed line defines approximate sorption maxima (monolayer coverage).

4) The fractional adsorption of HOC on peat humic acid coatings. (a) a comparison of the fractional adsorption of HOC on hematite and kaolinite coated with peat humic acid. (b) the effect of ionic strength on the fractional adsorption of HOC to kaolinite coated with peat humic acid.

5) Sorption isotherms of HOC on kaolinite coated with high and low concentrations of peat humic acid.

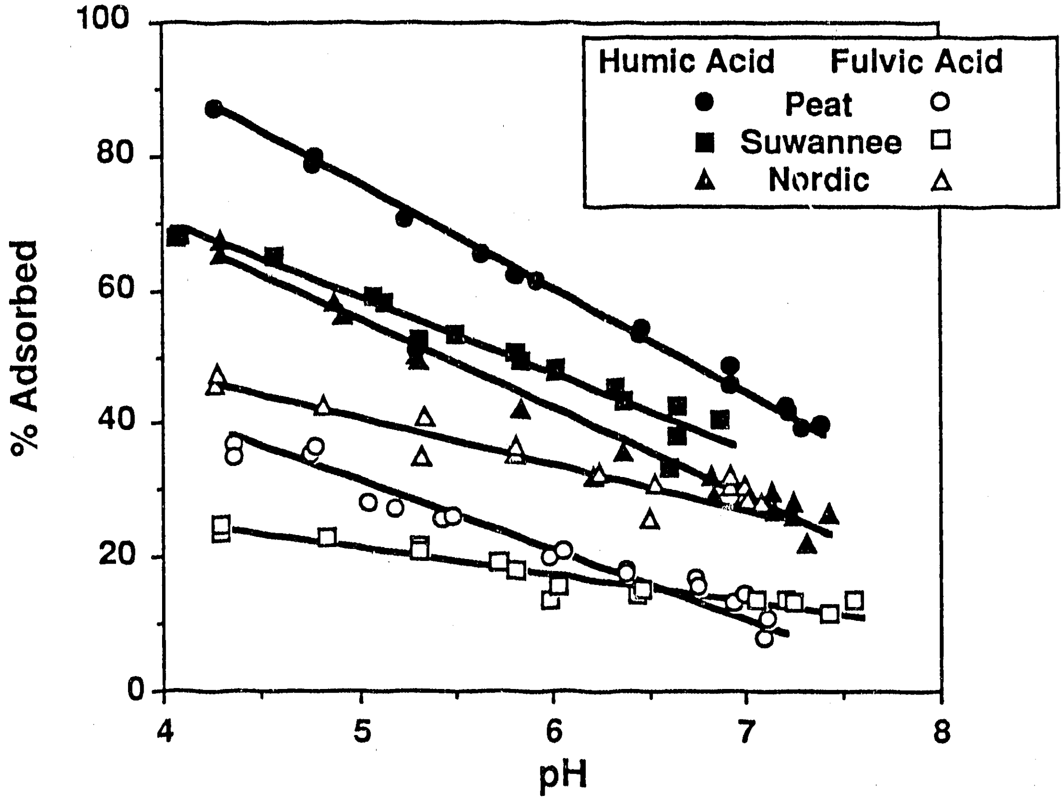
100
80
60
40
20
0
% Adsorbed
4
5
6
7
8
pH
Humic Acid
Fulvic Acid
● Peat ○
■ Suwannee □
▲ Nordic △

Figure 1

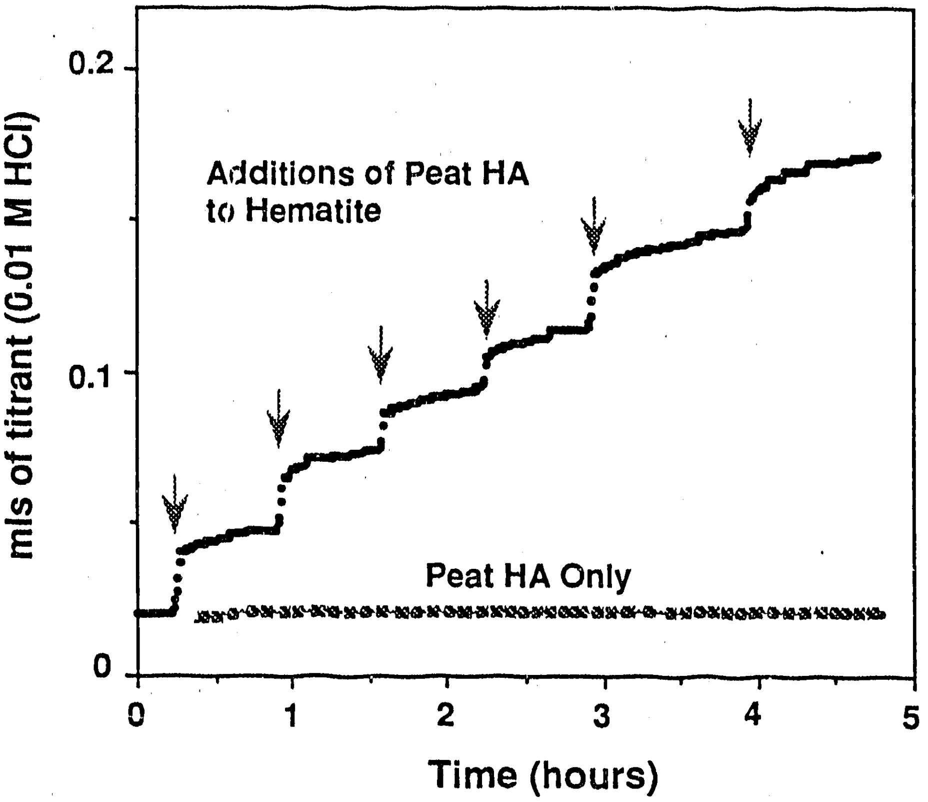
Additions of Peat HA to Hematite
Peat HA Only
mls of titrant (0.01 M HCl)
0.2
0.1
0
0
1
2
3
4
5
Time (hours)

Figure 2

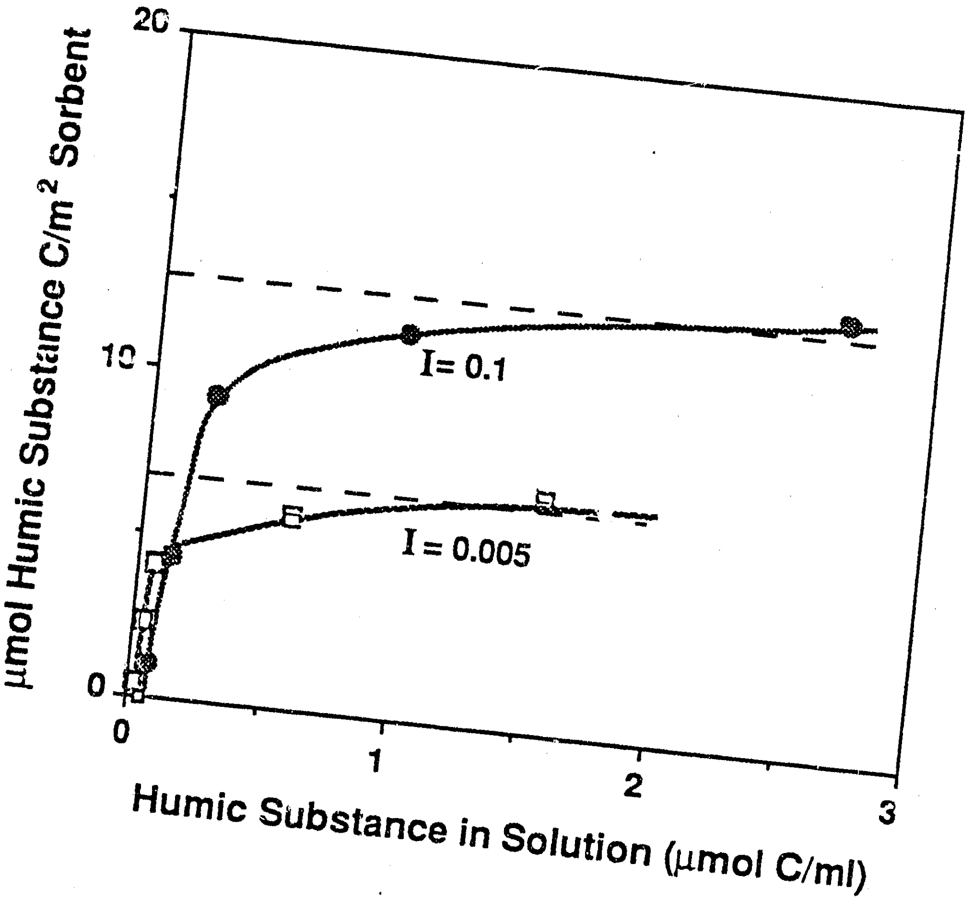
20
10
0
0
1
2
3
I= 0.1
I = 0.005
µmol Humic Substance C/m^2 Sorbent
Humic Substance in Solution (µmol C/ml)

Figure 3

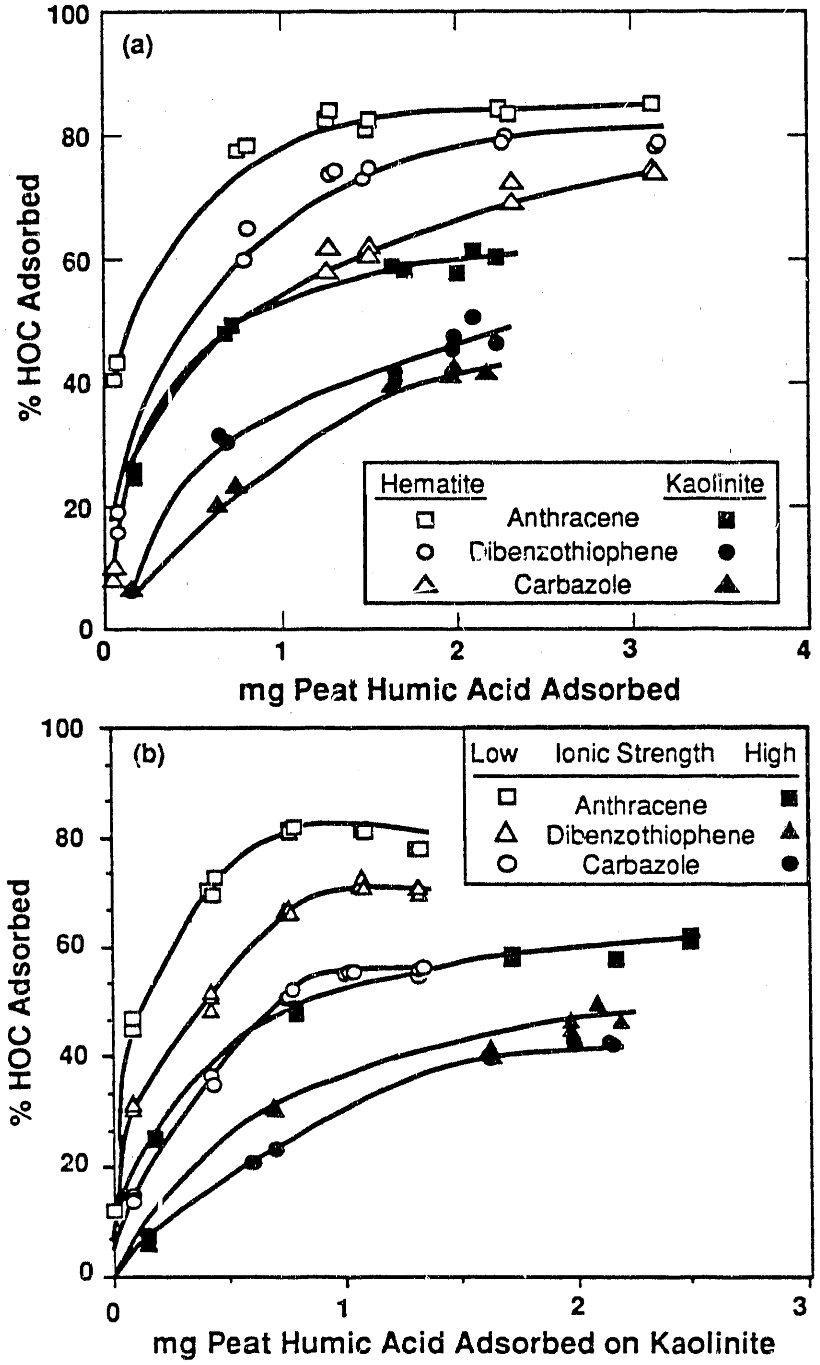
(a)
% HOC Adsorbed
100
80
60
40
20
0
0
1
2
3
4
mg Peat Humic Acid Adsorbed
Hematite
Kaolinite
□ Anthracene ■
○ Dibenzothiophene ●
△ Carbazole ▲
(b)
% HOC Adsorbed
100
80
60
40
20
0
0
1
2
3
mg Peat Humic Acid Adsorbed on Kaolinite
Low
Ionic Strength
High
□ Anthracene ■
△ Dibenzothiophene ▲
○ Carbazole ●

Figure 4

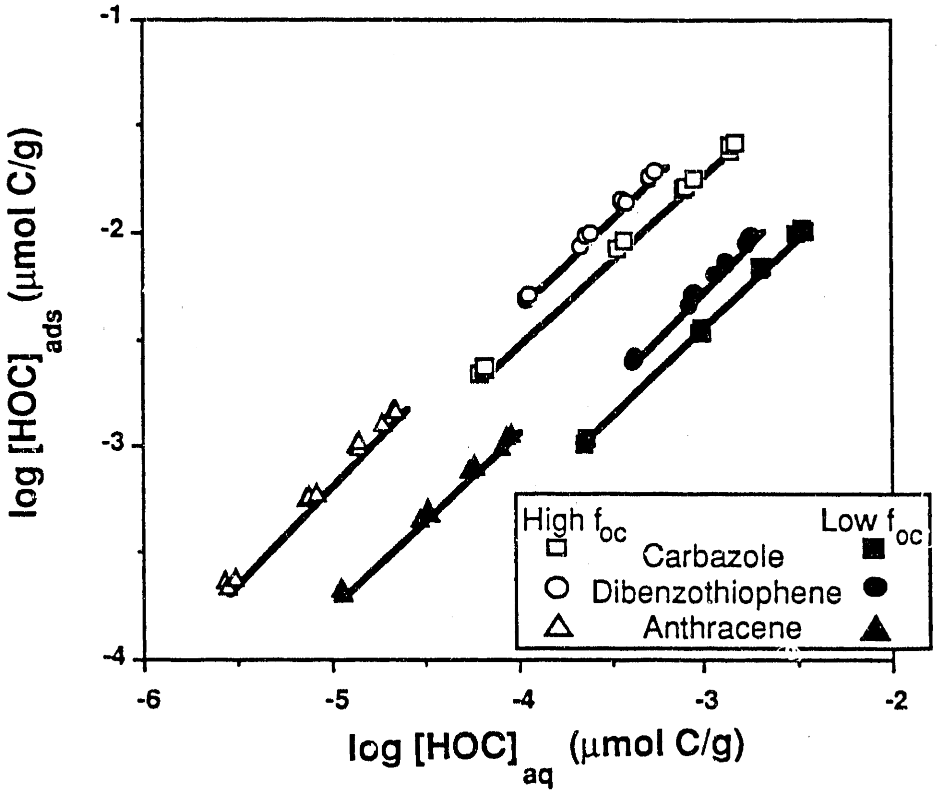
-1
-2
-3
-4
-6
-5
-4
-3
-2
log [HOC]$_{ads}$ (µmol C/g)
log [HOC]$_{aq}$ (µmol C/g)
High f_{oc}
Low f_{oc}
□ Carbazole ■
○ Dibenzothiophene ●
△ Anthracene ▲

Figure 5

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