

The Sorption of Anthracene onto Goethite and Kaolinite in the Presence of Some Benzene Carboxylic Acids

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The uptake of anthracene from dilute aqueous solutions onto goethite and kaolinite was investigated at 25°C, first in the absence and then in the presence of three benzene carboxylic acids: phthalic acid (benzene-1,2-dicarboxylic acid), trimesic acid (–1,3,5–), and mellitic acid (–1,2,3,4,5,6–). Carboxylic acid concentrations were 0.20, 0.10, and 0.05 mM. Anthracene (0.20 μM) did not adsorb strongly onto the pure mineral surfaces, but in the presence of phthalic acid a substantial increase in anthracene uptake was observed, particularly for the goethite systems. Trimesic and mellitic acids did not enhance anthracene uptake. Phthalate and proton adsorption data have been used to model phthalate adsorption onto the mineral surfaces using an extended constant capacitance surface complexation model. This model was then successfully adapted to account for the observed increase in anthracene uptake, where anthracene molecules were assumed to interact with adsorbed phthalate. We propose that the enhancement of anthracene adsorption in the presence of phthalic acid is due to an increase in the hydrophobicity of the mineral surface once phthalic acid molecules adsorb. The same effect was not observed for the other benzene carboxylates because of their greater polarity. © 2002 Elsevier Science (USA)

Key Words: adsorption; anthracene; PAH; kaolinite; goethite; carboxylic acid; surface complexation; clays.

1. INTRODUCTION

The hydrophobic nature of pollutants such as polycyclic aromatic hydrocarbons (PAHs) plays a key role in their persistence in aquatic systems (1). Because they are relatively nonpolar, their transport and fate is largely controlled through association with particles. This particulate association is driven by hydrophobic uptake into the organic fraction of catchment soils and sediments, as interactions with polar mineral fractions are weak in comparison (2). Although several studies have shown an increase in sorption of PAHs with the amount of soil/sediment organic matter (SOM) (3, 4), the underlying mechanisms responsible for interactions are not well understood. In particular, little is known about the molecular-scale forces that determine sorption and hence about the effects of SOM composition. The

decrease in the content of polar groups from soil to sediment OM, for example, has been related to a higher partition of nonpolar solutes in the latter (5).

Since humic substances generally comprise more than 70% of SOM (6), many studies have dealt with their effects on organic pollutant sequestration (7, 8). Humic substances strongly associate with soil minerals (9, 10) to form an organic coating that allows widely differing chemical interactions with nonpolar compounds (11). However, the composition of particulate humus can vary considerably between distinct geographical locations (12), therefore affecting sorption and accumulation in the solid phase. In order to understand and predict molecular interactions in these systems, it is important to know the role played by individual building blocks of these large macromolecular substances. Aromatic structures substituted by COOH and OH groups comprise more than half of the mass of humic substances (6). Benzenecarboxylic structures, in particular, are recognized as major degradation products of humic acids. Among these, di-, tri-, tetra-, penta-, and hexacarboxylic acids are prominent (6).

To obtain information on the nature of the interactions between humic substances and mineral surfaces, we investigated the sorption of benzene di-, tri-, and hexacarboxylic acids on the common soil minerals kaolinite and goethite. To establish the effect of humic-like coatings on nonpolar pollutant uptake, we further investigated the sorption of a three-ring PAH, anthracene, on the same mineral substrates in both the presence and the absence of the benzene carboxylic acids.

2. EXPERIMENTAL

2.1. Preparation and Characterisation of Substrates

The kaolinite and goethite samples have been described previously (13, 14). The BET surface areas were 14.7 m² g⁻¹ (kaolinite) and 49.6 m² g⁻¹ (goethite). The XRD spectra for the goethite and kaolinite samples showed no detectable evidence of contamination by other minerals.

2.2. Adsorption Experiments

Adsorption experiments and potentiometric titrations were performed in a jacketed reaction vessel under an atmosphere of CO₂-free nitrogen. The reaction vessel and flat flange lid

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