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Sorption of 1-hydroxy-2-naphthoic acid to goethite, lepidocrocite and ferrihydrite: Batch experiments and infrared study

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Abstract

The adsorption of naphthoic acids to iron oxides and hydroxides influences strongly their mobility in soils and sediments. Sorption of 1-hydroxy-2-naphthoic acid (HNA) to three iron oxides was examined over a wide range of conditions (pH, ionic strength, sorbate and sorbent concentrations). In the examination of HNA sorption, Tempkin model was performed to fit sorption data of HNA onto all iron oxides. The adsorption in the Henry law range increases in the order: goethite < lepidocrocite < ferrihydrite, while at high sorbate equilibrium concentration, the trend is opposite. Structure of the HNA surface complexes was examined by infrared spectroscopy at different surface coverages and pH conditions. The variation of HNA sorption with solid-to-solution ratio (SSR) in batch experiments exhibited a solid effect for tested oxides except goethite. The role of hydrophobicity in HNA sorption and an eventual formation of solute aggregation on the solid surface have been particularly highlighted on goethite. These results indicate that the mineralogy of the iron oxides and pH value should be considered when predicting HNA sorption in iron oxides and its fate in soil and environment.

Keywords: Naphthoic acids; Sorption; Iron oxides; Surface complexes; Infrared spectroscopy

1. Introduction

The formation of naphthoic acids during the biodegradation of polycyclic aromatics hydrocarbons (PAH) under simulated and natural conditions was investigated in many contaminated soils (Ohlenbusch et al., 2002; Weigand et al., 2002). 1-Hydroxy-2-naphthoic acid (HNA), primary degradation product of phenanthrene, has been identified in previous soil degradation studies (Parikh et al., 2004; Burgos and Pisutpaisal, 2006). Therefore, it is important to consider the potential mobilization risks of groundwater pollution associated with these compounds and to investigate their interaction with soil constituents such as mineral oxides. Iron oxides and hydroxides are important soil components influencing the mobility of various inorganic and organic compounds (Dzombak and Morel, 1990; Schwertmann and Cornell, 2000). The role of the iron oxides in the mobility of aromatic acids has not been very well investigated relative to heavy metals, inorganic anions or simple organic acids which have been studied much more extensively (Nilsson et al., 1996; Filius et al., 1997). Novoszad et al. (2005) and Burgos and Pisutpaisal (2006) have examined the sorption of ionizable degradation products of PAH to natural soils and sediments. Previous studies involved one or several organic acids with one iron oxide such as goethite (Nilsson et al., 1996; Filius et al., 1997; Evanko and Dzombak, 1999). In this study, different iron oxides were chosen as sorbents to investigate the effect of their morphological properties on sorption behavior and to compare their sorption capacity when the results are normalized to specific surface area.

The spectroscopic techniques have been well used to provide information on the structure of sorbed species on mineral surfaces. Several authors studied the bonding

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mechanism of organic acids, such as benzoic, phthalic and salicylic acids with precipitated hydrous ferric oxide by infrared spectroscopic analysis (Yost et al., 1990; Tejedor-Tejedor et al., 1992; Biber and Stumm, 1994; Kubicki et al., 1999). Although the surface complexation modeling of naphthoic acids on goethite has been discussed by Evanko and Dzombak (1999), no infrared study has been developed concerning the sorption behavior of these compounds onto iron oxides.

In this work, the sorption of 1-hydroxy-2-naphthoic acid to three types of iron hydroxides (goethite, lepidocrocite and two-line ferrihydrite) was investigated at various chemical conditions (pH, ionic strength and sorbate and sorbent concentrations). In order to determine the role of hydrophobicity in HNA sorption, the effect of MeOH on HNA sorption/desorption from oxide surface was also evaluated. To identify the surfaces complexes, the diffuse-reflectance infrared Fourier transform (DRIFT) spectroscopy was applied to examine the sorption of HNA on iron oxides at three pH conditions and two sorbent concentrations.

2. Materials and methods

2.1. Chemicals

1-Hydroxy-2-naphthoic acid (HNA) was obtained from Sigma Chemical with purity greater than 99%. 1-Hydroxy-2-naphthoic acid has two ionizable hydrogen ions (H_2L), which are the protons of the hydroxyl and carboxyl groups. pK_1 (2.71) and pK_2 (12.8) are the corresponding acidity constants of the carboxylate and phenolate groups, respectively (Parikh et al., 2004).

2.2. Iron oxides sorbents

Sorption experiments were conducted with synthetic iron (oxyhydr)oxides: two-line ferrihydrite (F), goethite (G) and lepidocrocite (L). They were chosen as prototypes because of their widespread abundance in soils and sediments.

The two-line ferrihydrite (F) sample studied was synthesized according to the method of Schwertmann and Cornell (2000). The ferrihydrite sample ($Fe_2(OH)_6$) was prepared by neutralizing a 0.2 M ferric chloride solution with 1 M NaOH to a pH of 7–8. The goethite (G) sample was prepared by neutralizing 500 ml of a 0.5 M ferric nitrate solution ($Fe(NO_3)_3 \cdot 9H_2O$) with 400 ml of 2.5 M sodium hydroxide solution, as described by Villalobos and Leckie (2000), in which the sodium hydroxide solution is added quickly. The solution was stirred vigorously during the addition of the sodium hydroxide, which was added in a nitrogen atmosphere in a glove box. The precipitate obtained was aged in an oven for 24 h at 60 °C. The lepidocrocite (L) sample (γ-FeOOH) was synthesized by oxidation of mixture (ferrous chloride + NaOH) following a procedure drawn from Schwertmann and Cornell (2000). All the precipitates were dialyzed to remove salts. All the solids were washed and then freeze dried and stored as solid.

2.2.1. Sample characterization

X-ray powder diffraction (XRD) experiments were performed to determine the crystal structure of minerals. XRD data were collected with a Philips PW1710 diffractometer using Co Kα radiation (35 kV, 30 mA). The diffractogramms were characteristic of the expected oxides. We also used Mössbauer spectroscopy to confirm the nature of all precipitates. The specific surface area of the iron oxides was determined by multipoint N_2–BET analysis using a Coulter (SA113) surface area analyzer. The point of zero charge (PZC) of minerals was determined at 293 K in 0.01, 0.1 and 1 M NaCl solutions by the potentiometric method of Parks and de Bruyn (1962). The potentiometric titrations were performed in a 200 ml jacketed reaction vessel under an atmosphere of CO_2-free nitrogen. The values of surface area and PZC are ($50\ m^2\ g^{-1}$; 8.4), ($59\ m^2\ g^{-1}$; 7.8) and ($327\ m^2\ g^{-1}$; 8.7) for goethite, lepidocrocite and ferrihydrite, respectively. These values are consistent with those reported in the literature (Schwertmann and Cornell, 2000).

2.3. Batch experiments

Batch sorption experiments were conducted for 1-hydroxy-naphthoic acid (HNA) across a range of total sorbate concentrations, pH and salt concentrations conditions as explained in Hanna et al. (2002, 2004). It should be noted that two species of HNA co-exists around pH 3 (near pK_1), the neutral species and the first ionized species. After pH 4 ($>pK_1 + 1$), the ionized species becomes predominant. Kinetic experiments were conducted for five days to determine the period required for adsorption to reach equilibrium. The sorption rate of HNA was relatively rapid during the sorption processes. Results of kinetic experiments indicated that more than 95% of HNA sorption was achieved within 100 min. However, a large incubation period (24 h) was chosen for the equilibrium sorption experiments.

2.3.1. Equilibrium sorption experiments

All equilibrium sorption experiments were conducted at 20 °C in triplicates, in 60 ml glass vials. NaCl (10 mM) was used as supporting electrolyte. The range of initial isotherm concentrations was chosen according the solubility limit of HNA. The solids samples were mixed with variable HNA concentrations and the vials were agitated for 24 h in the dark, at constant temperature (20 °C). The pH value of the suspension was recorded with the Orion pH meter model 710A having combination glass electrode. For each batch experiment, blank samples were prepared and monitored (i.e. HNA solutions without solid). The blank samples did not indicate any significant HNA degradation or sorptive losses on the glassware during the course of the