

**Sorption Kinetics and Mechanisms of Hydrophobic Ionizable Organic
Compounds on Surfactant-Modified Clays**

by

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ABSTRACT

We investigated the kinetic and equilibrium sorption of pentachlorophenol (PCP) to a surfactant-modified clay and the solubility of PCP, as a function of pH and ionic strength. Pentachlorophenol is a hydrophobic ionizable organic compound (HIOC). Therefore, it can exist either as a protonated or deprotonated species. The objectives of this study were to determine differences in the sorption and solubility of the two species, and to model these properties as a function of pH.

The modifying surfactant was hexadecyltrimethylammonium cations (HDTMA). Large stable structures were observed on the external surface of the washed HDTMA-clay. Based on scanning force microscopy images and zeta potential measurements, we proposed that these structures were hemimicelles. They appeared to form when HDTMA replaces $\geq 70\%$ of the clay's cation exchange capacity.

The PCP sorption was rapid and reversible, with equilibrium reached within 10 minutes. The sorption kinetics were characterized by a pseudo first-order model; there was not a significant difference in the rate of sorption between the two PCP species. Equilibrium sorption of the protonated species was significantly greater than the deprotonated species. The proposed model, represented by the summation of the sorption for the deprotonated species by a Langmuir isotherm and the protonated

species by a linear isotherm, described the experimental data well. The solubility was strongly dependent upon the PCP speciation. A model for the maximum aqueous phase concentration of PCP, as a function of pH, was proposed. This model shows an exponential increase in the maximum PCP aqueous concentration, above the pK_a .

We concluded that the sorption and solubility of the two PCP species are significantly different. We believe that, to a varying degree, this is true for all HIOC. Therefore, when considering the environmental transport of HIOC speciation should be considered. We have presented a basic approach that may be used to estimate changes in the sorption and solubility of a HIOC as a function of pH.