Sorption of Pentachlorophenol to HDTMA–Clay as a Function of Ionic Strength and pH

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We investigated the 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; therefore, it can exist as either a protonated or a deprotonated species. The objectives of this study were to determine differences in the sorption and solubility of the two species and to model the sorption as a function of pH. We developed a model that described the sorption across the experimental pH range (4–8.5). The model represented the sorption of the deprotonated species by a Langmuir-type isotherm and the sorption of the protonated species by a linear isotherm. Between pH 4 and pH 8.5, the sorption decreases by three times and the solubility increases by 3 orders of magnitude as the dominant aqueous species changes from the protonated to the deprotonated form.

Introduction

The use of surfactant-modified clay as a sorbent for organic compounds from an aqueous phase has been an active area of research (1–19). Most of this research has involved the use of quaternary ammonium compounds (surfactants) to modify mainly smectitic clays. The addition of the surfactant to the clay, via an ion-exchange reaction, produces a sorbent with an increased sorption capacity for organic compounds. The selectivity of the sorbent can be controlled, to a degree, by the surfactant that is used to modify the clay. Therefore, it is possible to produce a sorbent that can maximize the sorption of a specific class of compounds. Background information on the modification process is well documented (see above references) and will not be discussed here.

The majority of the research in this area has focused on the sorption of nonionic organic compounds (NOCs), while a few studies (7) have investigated the sorption of ionizable organic compounds (IOCs). Ionizable organic compounds, in the aqueous phase, can exist either as a protonated or a deprotonated species. They can be represented by organic acids and bases as shown in the following equilibrium relationship:

\[
HA^+ = A^- + H^+ \quad (1)
\]

\[
BH^+ = B^- + H^+ \quad (2)
\]

where \(HA^+\) is the organic acid, protonated species; \(A^-\) is the conjugate base of the organic acid, deprotonated species; \(B^-\) is the organic base, deprotonated species; and \(BH^+\) is the conjugate acid of the organic base, protonated species.

The occurrence of the protonated and deprotonated species depends on the solution pH in relation to the dissociation constant \((pK_a)\) of the compound. The protonated species are dominant when the \(pH < pK_a\); the deprotonated species are dominant when the \(pH > pK_a\). However, both of the protonated and deprotonated species are significant when the \(pH \approx pK_a\).

One might anticipate that the chemical properties of the two species would be different. Therefore, it is important to consider differences in the chemical properties of the species when describing sorptive behavior. However, the sorption of an IOC on a surfactant-modified clay, over a pH range that would include both species, has not been systematically investigated to date. The pH range of surface and groundwater is approximately from 4 to 9. Therefore, IOCs with a \(pK_a\) in the same range are of special interest because both the protonated and deprotonated species may be found in the aqueous phase. Several priority pollutants are IOCs and have \(pK_a\)'s that fall within the above range, such as chlorinated phenols, nitrophenols, and dinitrophenols. Most notable is the organic acid pentachlorophenol (PCP), with a \(pK_a\) of 4.75 (20).

Solubility and distribution ratios are two general properties of IOCs that can differ significantly with pH. For PCP, Valsaraj et al. (21) reported the solubility to range from 30 to >15 000 \(\mu\)M as the pH increased from 2.5 to 8. Kaiser and Valdmanis (22) found that the logarithm of the distribution ratio (log \(D\)) between octanol and water decreased from 4.8 to 1.3 when the pH increased from 4 to 10. Jafvert et al. (23) also reported an increase in the distribution ratio with a decrease in pH. In addition, the ionic strength and the background electrolyte have been shown to influence the distribution ratio of PCP between octanol and water at \(pH > 8\) (23).

It is important to differentiate between two terms to avoid confusion when discussing IOCs: a partition coefficient \((K_p)\) is the concentration ratio for a particular species (protonated or deprotonated) between two phases, and a distribution ratio \((D)\) is the ratio of the total analytical concentration (protonated and deprotonated) between these two phases. Westall and co-workers (23–26) determined distribution ratios of hydrophobic ionizable organic compounds (HIOCs) between octanol and water as a function of solution pH and the nature and concentration of the background electrolyte. For such hydrophobic substances, these papers convincingly show that the sizes of the species of organic acids and bases enter the octanol phase. Four mechanisms for the distribution of an IOC between two phases were proposed (23–26) based on the organic acid (HA):

(I) Hydrophobic sorption of the protonated species:

\[
HA^+ = HA^+ \quad (3)
\]

(II) Transfer of the deprotonated species, as an ion pair \((A^- + M^+)\) or a free ion \((A^-)\), between two phases:
(III) Sorption of the deprotonated species to a lipophilic surface with the counterion retained in the electric double layer:

$$\text{A}^- + \text{M}^+ = \text{A}^- \text{M}^+ (\text{A}^- + \text{M}^+)$$ (4)

(IV) Ion exchange of the deprotonated species with a surface group, such as hydroxide:

$$\text{XOH} + \text{A}^- = \text{X}^+ + \text{OH}^-$$ (6)

where \(\text{M}^+\) is the background cation, \(\text{Y}\) is the uncharged (lipophilic) surface site, and \(\text{X}\) is the positively charged (hydrophilic) surface site. The overbar indicates a non-aqueous phase.

These mechanisms have been used to describe the distribution of PCP between octanol and water and between a solid phase and water and were considered for application to a water–PCP organoclay system in the present study.

In this paper, we report on equilibrium batch isotherms conducted in order to investigate the sorption of PCP to a hexadecyltrimethylammonium–montmorillonite (HDTMA–clay) as a function of pH and ionic strength. The objectives were to describe the sorption mechanism(s) of an HIOC on a HDTMA–clay as a function of pH and ionic strength and to present a model for the sorption of PCP on HDTMA–clay capable of describing data over a wide pH range.

**Experimental Methods**

**Preparation of Base Clay.** Sodium–montmorillonite (SWy-1) from Crook County, Wyoming, was obtained from the Source Clays Repository at the University of Missouri. The clay was fractionated by adding approximately 100 g of SWy-1 to 1 kg of deionized water (DI). Particles >2 \(\mu\)m in diameter were removed by sedimentation. The pH of the suspension was then reduced to 5 with dilute HCl, and the temperature of the suspension was increased to 333 K and maintained for 3 h to remove any carbonates from the mineral surface. After cooling to room temperature, the clay was Na-saturated by increasing the Na+ concentration, in the suspension, to 1 M (using NaCl) and allowing equilibration for 24 h. The suspension was then washed with DI, dialyzed, and freeze-dried. The pre-treated clay, termed the base clay, was used for subsequent preparation of HDTMA-modified clay.

The cation-exchange capacity (CEC) of the base clay, as measured by Ca–Mg exchange, was 90 cmol kg\(^{-1}\). X-ray diffraction analysis of the clay did not reveal the presence of other minerals.

**Preparation of Modified Clay.** The modified clay was prepared by the addition of hexadecyltrimethylammonium bromide (also referred to as cetrimonium bromide) (Aldrich) to a 750 mg kg\(^{-1}\) base clay suspension in a 1:1 molar ratio to the CEC. The HDTMA\(^+\) was anticipated to replace =100% of the Na\(^+\) on the clay. Since the suspension flocculated instantly upon addition of the HDTMA\(^+\), it was mixed by hand until the floc was broken down sufficiently to allow mixing with a magnetic stir bar. The suspension was mixed for 24 h, washed four times to remove excess ions, and freeze-dried. The wash water was analyzed for HDTMA\(^+\) using the methodology of Furlong and Elliker (27). The analysis did not detect any HDTMA\(^+\), indicating that the HDTMA cations were quantitatively taken up at exchange positions. This assumption is consistent with the data of Zhang et al. (28), who showed that HDTMA\(^+\) replaced >98% of the Na\(^+\) on the SWy-1 clay. This solid will be called the modified clay.

**Determination of PCP Solubility.** When conducting sorption experiments, it is important to consider the solubility of the sorbate. The solubilities of IOCs are pH dependent, and for hydrophobic compounds they can be very low. However, there is a limited amount of information on PCP solubility in the literature, with considerable disagreement between reported values. Valsaraj et al. (21) suggested that the discrepancies could have resulted from inappropriate control of pH and temperature during the experiments. We therefore determined the solubility under our experimental conditions in the pH range 4–5.5 and at a temperature of 298 K. Experiments could then be designed to avoid the formation of a precipitate in the aqueous phase.

The solubility of PCP was determined at the above pH range at ionic strengths of 0.001 and 0.1 M with NaCl as the background electrolyte. A concentrated PCP solution (0.01 M) was added to the aqueous phase until precipitation occurred. The samples were placed on an orbital shaker and allowed to equilibrate for several weeks in an environmental chamber at 298 K until a constant aqueous-phase concentration was achieved. The pH was manually adjusted with dilute NaOH or HCl as needed during this period.

**Batch Studies.** Batch studies were conducted over an aqueous concentration range of 3–200 \(\mu\)M (or up to the solubility limit at lower pH values), at background ionic strengths of 0.001 and 0.1 M (NaCl), and over a pH range of 4–8.5. The PCP sorption experiments, except those at pH greater than 7.5, were conducted in 25-mL Corex centrifuge tubes with Teflon cap liners or in 125-mL Erlenmeyer flasks. Initially, the ionic strength of the DI was adjusted, the modified clay was added, and then the pH of the suspension was adjusted to the desired value. The solid/solution ratio was 100 mg of modified clay/kg solvent for all experiments. The suspension was mixed on either an orbital or reciprocating shaker for 24 h. Then the PCP was added, as a concentrated solution (0.01 M), to obtain the desired initial PCP concentration. The pH was automatically adjusted during the addition of the PCP using an autoburette with either dilute HCl or NaOH solutions. Once the pH was stabilized, the samples were placed in an environmental chamber (298 K) and gently mixed for 24 h. Long-term equilibrium studies (data not presented) have not shown a significant change in the sorption equilibrium between a 24-h and a 6-month period. The pH was determined at the beginning and end of each experiment; pH variation was less than 0.2 unit. The equilibrium pH is reported in all tests. At the end of the equilibrium period, the samples were removed from the shaker and allowed to settle for a minimum of 2 h. Samples (5–10 mL) of the clear supernatant were removed with a glass pipet for analysis. Analysis of the blanks in the experiment indicated that the loss of PCP from the aqueous phase was only due to the HDTMA-clay. The sorbed PCP concentration was determined based on the change in the aqueous-phase PCP concentration over the test period.
Absorption of CO₂(g) by the aqueous phase made the pH difficult to maintain above 7.5. Atmospheric CO₂ could not be successfully excluded from the headspace of the centrifuge tubes or Erlenmeyer flasks that were used. Therefore, the isotherms were conducted in a single, 500-mL three-neck flask with multiple additions of PCP. The system was closed to the atmosphere, with N₂ continually purged through the system, and the pH was automatically adjusted using an autoburette. This allowed for continual monitoring of the pH and automatic addition of titrant, maintaining the pH at the desired value. The PCP was added in six separate additions. After addition of a PCP aliquot, the system was allowed to equilibrate for a minimum of 2 h before it was sampled and then the next aliquot of PCP was added to the system. Kinetic studies showed that the system was at equilibrium within 2 h. All additions were made over a 24-h period. During sampling, a 15–20-mL sample of the suspension was withdrawn. This sample was allowed to settle or was filtered, and a subsample of the clear solution was analyzed to determine the PCP concentration.

Analysis. Pentachlorophenol was quantified by its absorbance at 214 nm using a Hewlett-Packard HP 8452A diode array UV-visible spectrophotometer. Five to ten milliliter samples of the clear supernatant were acidified with 0.1–0.2 mL of 0.5 M H₂SO₄. The addition of the acid ensured that the PCP was quantified as the protonated species. A five-point calibration curve (2–30 μM) was run before and after each set of analyses. In this absorbance region, the standard curve was linear. Samples were diluted, prior to acidification, to keep absorbance within the standard’s range. No interferences were observed in the analyses.

Results

Solubility Determination. The solubility of the PCP increased with pH (Figure 1). There was no difference in the solubility between the two ionic strengths at pH 4. However, as the pH increased above the pKₐ, the solubility increased with ionic strength.

Sorption Isotherms. Sorption of PCP on the HDTMA-clay was inversely related to the pH of the solution. At pH = 4, the isotherms were linear and there was no difference in sorption between the two ionic strengths (Figure 2). There was a rapid decrease in the sorption as the pH increased from 5 to 6 (Figure 3) and the isotherms became distinctly nonlinear. However, the data could not be represented by a simple isotherm equation in this region. As the pH increased above 6, the nonlinear isotherms could be represented by a Langmuir equation. Sorption between pH 7 and pH 8.5 (Figure 4) was also described well by the Langmuir equation. There was a significant increase in the extent of sorption, with ionic strength, when the pH was greater than 8.

Discussion

Solubility Determination. The maximum aqueous-phase PCP concentration (SWPCP), the sum of the protonated (PCP⁺) and deprotonated (PCP⁻) species, as a function of the solution pH is directly related to the solubility of PCP⁺ (SWPCP⁺). The following mass balance is based on the equilibrium relationship for the dissociation of the proton:

\[
\text{SW}_{\text{PCP}} = \text{SW}_{\text{PCP}^+} + 10^{\text{pH}-pK_a}
\]
PCP⁻ is predominant, since the extent of sorption is limited by the area of exposed nonpolar surface. Similarity of the to yield the nonlinear isotherm observed at high pH where double layer. The latter of these would seem most likely these would be sorption in the three-dimensional lipophilic proposed by Westall and co-workers (23-26). Respectively, this reaction.

Sorption Isotherms. The significant change in the isotherm shape between pH 4 and pH 8 suggests that there are at least two sorption mechanisms. We hypothesize that the main difference in the isotherms is related to the sorption of the protonated vs deprotonated PCP species. Although all data are not shown, this trend was found in all experimental tests in this research.

The change in the sorption near the pKₐ is consistent with research reported by Schellenberg et al. (20) and Lee et al. (32) for the sorption of PCP by soil and sediments. Lee et al. (32) compiled data from the literature that shows a similar sorption trend as a function of the pH. However, a linear isotherm was used to describe the sorption of both the protonated and deprotonated species. The data presented in our paper differ from these previous results in showing a distinctly nonlinear isotherm near and above the pKₐ. We believe the differences in our data compared to those of Schellenberg et al. (20) and Lee et al. (32) result either from the smaller aqueous equilibrium range in their studies (with data representing only the linear section of a nonlinear isotherm) or from different operative sorption mechanisms with organoclays than with solids and sediments. Boyd et al. (3) reported a nonlinear sorption isotherm for the sorption of PCP to a HDTMA–clay for two pH's, 5.5 and 10. The authors did not indicate that there was a difference in the sorption between the two pH's. However, the range for the aqueous concentration was only 0-15 μM, and a difference in the sorption may not be apparent in this range.

We believe the sorption mechanism for PCP⁺ is partitioning between the hydrophobic section of the modified clay and the aqueous phase. This conclusion is based on a linear isotherm over at least 90% of the compound's solubility and similarity between the Kₑ and the distribution coefficient normalized for the organic carbon content. This is consistent with a partition process (31). The first of the proposed mechanisms by Westall and co-workers (23-26), presented earlier, would represent this reaction.

The sorption mechanism for the phenolate species could be represented by either the second or the third mechanism proposed by Westall and co-workers (23-26). Respectively, these would be sorption in the three-dimensional lipophilic space (either as a neutral ion pair or as a free ion with a counterion to balance the charge) or sorption to the two-dimensional lipophilic surface with a counterion in the double layer. The latter of these would seem most likely to yield the nonlinear isotherm observed at high pH where PCP⁻ is predominant, since the extent of sorption is limited by the area of exposed nonpolar surface. Similarity of the initial slopes of the PCP⁻ and PCP⁺ isotherms may then be explained by similar affinities of the nonpolar portions of the respective molecules for the nonpolar phase.

The experimental results also suggest that there may be a modification in the sorption mechanism above pH 8 as ionic strength increases. These findings are similar to Westall et al. (25), who suggested the relationship between the ionic strength and log D as related to the shift in the main species, in the octanol phase, from the protonated to deprotonated form. However in our system, the shift from the protonated to the deprotonated sorbed species occurred at a pH <6 in the equilibrium range under study. The potential modification in the sorption mechanism of PCP⁻ may involve an increase in the affinity between PCP⁻ and a counterion.

Based on our experimental data, we propose a model that describes PCP sorption, in our system, as a function of pH at a background ionic strength of 0.001 M. The model consists of the summation of the isotherms representing the independent sorption of the deprotonated and protonated species. The sorption of the deprotonated species (qPCP⁻) has been represented by a nonlinear isotherm (eq 8a), and the sorption of the protonated species (qPCP⁺) has been represented by a linear isotherm (eq 8b). Thus, the total sorption of PCP on HDTMA-clay (qPCP), as a function of pH, can be represented by the following set of equations:

\[
q_{PCP} = \frac{PCP^- K_{PCP^-} M_{PCP^-}}{1 + PCP^- K_{PCP^-}} \quad (8a)
\]

\[
q_{PCP} = PCP^+ M_{PCP^+} \quad (8b)
\]

\[
q_{PCP} = q_{PCP^-} + q_{PCP^+} \quad (8c)
\]

where \(K_{PCP^-}\) is the Langmuir equation constant for the sorption of the deprotonated species, \(M_{PCP^-}\) is the Langmuir equation constant for the sorption of the deprotonated species, and \(m_{PCP^-}\) is the slope of the linear isotherm for the sorption of the protonated species.

The two PCP species were found from the basic equilibrium relationship between the solution pH and pKₐ of PCP⁻:

\[
PCP^- = \frac{C_i}{1 + 10^{pK_a pH}} \quad (9a)
\]

\[
PCP^+ = C_i - PCP^- \quad (9b)
\]

where \(C_i\) is the total pentachlorophenol concentration in solution (where no solubility limit applies).

To describe \(q_{PCP}\) using eq 8c, one must first determine \(K_{PCP^-}\), \(M_{PCP^-}\), and \(M_{PCP^+}\). To do this without solving for all three values simultaneously, experimental results may be used from a pH region where the aqueous and sorbed concentrations of one species are insignificant. For example at pH 8.5, the aqueous concentration of the deprotonated species is 4 orders of magnitude greater than the protonated species. Therefore, it may be assumed that the sorption of PCP⁺ is insignificant, allowing for the determination of \(K_{PCP^-}\) and \(M_{PCP^-}\). The 0.001 M data set, at pH 8.5, was therefore used to represent the sorption of PCP⁻. The two Langmuir constants in eq 8a were estimated using ISOTHERM, a nonlinear least square optimizing routine (33).
Table 1. Model Constants for Sorption of PCP on HDTMA-Clay, Eqs 8a and 8b

<table>
<thead>
<tr>
<th>Constant</th>
<th>Units</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{PCP}$</td>
<td>$\text{mol kg}^{-1} \mu\text{M}^{-1}$</td>
<td>0.918</td>
</tr>
<tr>
<td>$M_{PCP}$</td>
<td>$\text{mol kg}^{-1}$</td>
<td>0.899</td>
</tr>
</tbody>
</table>

Due to the potential dissolution of the mineral surface, the lowest pH used in these experiments was 4.0. At this pH, 15% of the total PCP in solution was PCP$^-$, contributing significantly to the total PCP sorption. This did not allow for a similar determination of $q_{PCP}$ while neglecting $q_{PCP^-}$. However, since the sorption of PCP$^-$ was already characterized (eq 8a), the sorption of PCP$^+$ could be determined by subtracting $q_{PCP^-}$ from the total sorption at lower pHs where PCP$^-$ sorption is least significant. Accordingly, data between pH 4 and pH 4.4 were used to model the sorption of PCP$^+$. These data, PCP$^+$ vs $q_{PCP}$, were subjected to a least square regression with a forced fit through the origin. Final values determined for the three adsorption parameters and the regression coefficient $r^2$ are presented in Table 1. Figure 5 contains plots of eqs 8a and 8b with experimental data for sorption of PCP$^+$ and PCP$^+$ species.

The model, eqs 8a–8c, successfully described the sorption as a function of pH for an ionic strength of 0.001 M (Figure 6). The experimental data plotted on the graph are consistent with the calculated isotherms, especially in the pH transition zone when the isotherms change from linear to nonlinear. The good fit of the data would indicate that the sorption of each species is independent of the other. The model does not predict the increase in sorption as a function of ionic strength that occurs in the experimental data when the pH is $>8$.

Using the model, one can also predict the sorption of both species as a function of the solution pH given a constant total PCP concentration in solution ($C_a$) (Figure 7). At low $C_a$ (1 $\mu$M), the sorption is uniform across the pH range. This results because the linear section of the Langmuir equation, for PCP$^+$, is similar to the linear isotherm, for PCP$^-$.

![Graph of sorption vs concentration for 0.001 M ionic strength (NaCl). Lines calculated for indicated pH values based on eqs 8a–8c. Experimental data points shown by measured equilibrium pH values: (--) pH = 4, (---) pH = 4.75, (-- --) pH = 5.25, (--- --) pH = 5.75, (----) pH = 6.25, (-----) pH = 8.](image)

![Graph of sorption vs concentration for a range of pH values.](image)
sorbed species shifts from $q_{PCP^{-}}$ to $q_{PCP}$+. The total PCP sorption is limited by the solubility of the protonated form at low pH and by the maximum sorption of the deprotonated form at high pH.

It is not known whether this model also applies to the sorption of IOCs to soils or sediments, but it would appear reasonable to expect limited sorption of ionized species on such surfaces, resulting in a nonlinear isotherm if characterized over a sufficient concentration range. The model would then predict that the environmental fates of ionized and nonionized species would be significantly different. We have shown that in a narrow pH range, pH $\approx pK_a$, both the sorption and the solubility of an IOC can change dramatically. When this pH range is within that found in the aqueous environment, both the protonated and the deprotonated species will be found. Therefore, it is important that one understand how the speciation of an IOC such as PCP will affect its environmental fate and transport since a minor change in pH will allow PCP to exist as either a sorbed, insoluble compound or a soluble, mobile ion. Additional research should be completed to confirm the application of the general form of eqs 8a–8c and to extend the results to solids and sediments based on organic carbon to better predict environmental transport of an IOC.

Literature Cited


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