

ADSORPTION PROPERTIES OF ROXARSONE AND ARSENATE ON GOETHITE AND KAOLINITE

Mary C. Harvey

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Dr. Madeline Schreiber
Dr. Donald Rimstidt
Dr. Christopher Tadanier

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ABSTRACT

This study investigated the adsorption properties of roxarsone, an organoarsenic poultry feed additive, to goethite and kaolinite in order to determine what role mineral surfaces play in controlling the mobility of roxarsone in watersheds where poultry litter is applied. Adsorption edge experiments for goethite and kaolinite showed a dependence on pH for both As(V) and roxarsone. This pattern can be explained by the pH-dependent changes in the mineral surface charge and protonation of the aqueous arsenic species. Isotherms for As(V) and roxarsone on goethite and kaolinite show surface saturation for As(V), but not for roxarsone. The overall adsorption patterns show that As(V) and roxarsone adsorption is similar, suggesting that the arsenate functional group is the dominant control on roxarsone adsorption. However, there are some subtle differences between adsorption of As(V) and roxarsone, which can be explained by the relative sizes of the molecules, the presence of functional groups, differences in solubility, and differences in the type of adsorption (monolayer versus multilayer). Comparison of roxarsone adsorption to goethite and kaolinite reveals that at the low concentrations of roxarsone that are expected to leach from poultry litter into soil water, goethite adsorbs roxarsone more strongly than kaolinite. However, due to the abundance of kaolinite, both are important controls on roxarsone mobility.

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1. Introduction

Arsenic is a naturally-occurring toxin that damages neurological and cardiovascular systems and has been linked to cancer (NRC 1999). Anthropogenic and natural sources of arsenic contribute to the release of arsenic into the environment. Naturally occurring arsenic is contained in minerals including arsenopyrite (FeAsS), realgar (AsS), orpiment (As_2S_3), and scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). Examples of anthropogenic sources of arsenic are wood preservatives, glass production, pesticides, and animal feed additives (Welch et al. 2000). Because of the toxicity of As, the maximum contaminant level for arsenic in drinking water is currently set at $10 \mu\text{g/L}$ by the US Environmental Protection Agency. This is consistent with the current arsenic recommendation from the World Health Organization.

Roxarsone (3-nitro-4-hydroxyphenylarsonic acid) (Figure 1) is used as a poultry feed additive spiked in feed at concentrations of 20.6-41.3 mg/kg in order to increase growth, aid with pigmentation, increase egg production, and allow for better feathering of the chickens (Anderson 1983). According to previous research, arsenic is not retained in significant concentrations in the chicken tissue and is primarily excreted in the poultry manure (Anderson and Chamblee 2001). The manure containing this excreted arsenic is mixed with bedding material and used as a fertilizer, termed poultry litter, which contains arsenic in concentrations ranging from 10-50 mg/kg (Brown et al. 2005). With large quantities of litter spread over agricultural fields each year ($>33 \times 10^7$ kg/year in Virginia), the environmental fate of roxarsone is of a growing concern. Previous studies have shown that roxarsone leaches easily from poultry litter with 70-75% soluble in water (Jackson and Miller 1999; Hancock et al. 2002; Rutherford et al. 2003). Leachate containing roxarsone can infiltrate soil and into groundwater. Brown et al. (2005) found As(V), the biotransformation product of roxarsone, in soil water underlying a field to which poultry litter had been applied.

Adsorption of arsenic on mineral surfaces is an important process that affects arsenic's mobility in the subsurface (Stollenwerk 2003). Arsenic adsorption to Mn, Fe, and Al oxides as well as clay minerals has been well documented (Manning and Goldberg 1996; Manning and Goldberg 1996; Manning and Goldberg 1997; Grafe et al. 2001; Cornu et al. 2003; Saada et al. 2003). Mineral surface charge and aqueous speciation are controlled by pH, thus making pH an important control on adsorption (Stollenwerk 2003). Several ions have been discovered to compete with arsenic for adsorption sites, including phosphate, sulfate, molybdate, carbonate,

silica and organic acids (Hingston et al. 1971; Manning and Goldberg 1996; Manning and Goldberg 1996; Grafe et al. 2001; Goldberg 2002).

Because As(V) has a strong affinity for iron hydroxides (e.g. goethite and ferrihydrite) and because of the natural abundance of iron hydroxides, many studies have examined this adsorption system (Pierce and Moore 1982; Wilkie and Hering 1996; Ladeira and Ciminelli 2004). The pattern of increasing As(V) adsorption as pH decreases has been observed for both goethite and ferrihydrite (Grossl and Sparks 1995; Manning et al. 1998; Sun and Doner 1998). When adsorption to goethite is compared to gibbsite ($\text{Al}(\text{OH})_3$) studies have shown that more As(V) adsorbs to goethite (Hingston et al. 1971; Gullledge and O'Conner 1973; Manning and Goldberg 1996; Ladeira and Ciminelli 2004).

Arsenic adsorption on common clay minerals, including kaolinite, is also an important process for controls arsenic mobility in the environment. Goldberg (1986), Stollenwerk, (2003) and Manning and Goldberg (1996) found that maximum adsorption of As(V) on kaolinite occurs between pH 3 and pH 5. In addition to adsorption, Lin and Puls (2000) suggested that high concentrations of As(V) can result in precipitation of a hydroxyl-arsenate interlayer in clay minerals.

Understanding the adsorption mechanism and other processes affecting the interactions of arsenic with mineral surfaces is vital to predicting the mobility of As in the environment. As(V) adsorption to goethite and kaolinite has been well studied, but the mechanisms of roxarsone adsorption to these minerals have not. Brown et al.(2005) investigated adsorption of roxarsone onto the Ap and Bt horizons of one soil type from a watershed where poultry litter is applied, but to date, no studies have addressed roxarsone adsorption to specific minerals. The objective of this study is to evaluate and compare the adsorption properties of As(V) and roxarsone to common soil minerals (goethite and kaolinite) in order to better predict the mobility of roxarsone in agricultural watersheds.

2. Methods

Adsorption edge and isotherm experiments were conducted to determine the adsorption properties of roxarsone and As(V) to goethite and kaolinite. The experiments were conducted in a Brinkmann Methrohm 719 Stat Titrino using a teflon beaker inside a glass chamber to house

the slurry. A trial was conducted to determine the potential for roxarsone or As(V) to adsorb to teflon. Results showed no loss of As(V) or roxarsone due to adsorption to reactor or other equipment's surfaces. To examine the potential for photodegradation of roxarsone, which had been reported by Bednar et al. (2003), samples collected during the experiments and from roxarsone stock left in direct light for 24 hours were analyzed by spectroscopic (UV-Vis; 334 nm wavelength) analysis. Although results showed no signs of degradation, all vessels and samples for the experiments described below were wrapped in aluminum foil to ensure no photodegradation would occur.

Goethite was prepared by precipitation of ferric chloride (Schwertmann and Cornell 2000). After precipitation, the concentrated slurry was centrifuged at 4000 rpm for 8 min. The sample was decanted, rinsed and dialyzed in Mill-Q water (<5 ppb total organic carbon; >18.2 M Ω). The goethite was then freeze dried and the mineralogy confirmed using x-ray diffraction (Scintag XDS2000 powder diffractometer) (Figure 2). The surface area of the goethite was determined to be 71.5 m²/g using the six point N₂-Brunauer, Emmett and Teller (BET) method (NOVA Quantochrome 1000). Kaolinite used in the experiments was reagent grade (Fisher). The surface area, 17.0 m²/g, was also determined by BET isotherm analysis. Our surface area is in the typical range for kaolinite (8.4 to 24.0 m²/g) (Bickmore et al. 2002). The kaolinite was examined using scanning electron microscope (SEM) (Figure 3A) and was analyzed quantitatively by energy dispersive spectral analysis (EDS) (Figure 3B). The analysis indicated a relatively clean kaolinite surface with minor Ti impurity.

The mineral slurries (1 g/L goethite or 4.1 g/L kaolinite) were prepared using a total mineral surface area of 72 m²/L. To do this, the appropriate amount of mineral was added to 80 mL of 0.01 M NaCl and sonicated at 50% intensity for five minutes. The slurry was then allowed to sit overnight to ensure that the mineral was fully hydrated. To avoid CO₂ interference with adsorption, N₂(g) was bubbled into the 0.01 M NaCl solution until the pH stabilized at 6.7 to drive out the CO₂(g). In addition to this initial sparge, the slurry was bubbled continuously with N₂(g) throughout the experiment.

To start the experiments, the slurry was adjusted to pH 11.2 with 0.1 M NaOH and then spiked with a known concentration of arsenic. The pH was subsequently adjusted downward with 0.1 M HCl and allowed to reach equilibrium. Equilibrium was considered to be the time at which the concentrations of arsenic in solution stabilized. This time was determined from

preliminary experiments to be 1.5 hours. Once equilibrium was reached, a 2.4 mL sample was collected and filtered (0.2 μm). Samples were stored temporarily in an anaerobic chamber and were subsequently ultracentrifuged (Beckmann TL-100 Ultracentrifuge) at 50,000 rpm and 25°C for 60 minutes to remove particles from the supernatant (Tadanier et al. 2005). One milliliter of the supernatant was preserved with 25 μL of concentrated HCl. Samples were diluted serially (10, 100, and 1000) and analyzed for arsenic using Graphite Furnace Atomic Adsorption Spectroscopy (Varian Spectra 220Z) with Zeeman background correction. The detection limit for arsenic was 3 $\mu\text{g/L}$. The arsenic adsorbed to the mineral was calculated as the difference between the spike concentration and the aqueous concentration in supernatant.

To confirm the concentration of As added to the goethite experiments, slurry samples were collected at the end of the experiment and were digested (0.158 M oxalic acid) for 3 days. Digested samples were analyzed for Fe and As using inductively coupled plasma atomic emission spectroscopy, ICP-AES (Spectra Flame Modula Tabletop). The detection limits for Fe and As were 25 $\mu\text{g/L}$. Due to the difficulty in digesting kaolinite, a different approach was used to confirm the concentration of As added to the kaolinite experiments; replicate spikes (one in kaolinite slurry and the other in 0.01M NaCl) were completed for each experiment. The arsenic concentration from the spike in 0.01M NaCl was analyzed to determine the spike concentration. The accuracy of the spike method used for kaolinite was tested on a goethite experiment by comparing the digested sample against a replicate spike. For both methods, the actual spike concentration was within 5% of the expected concentration.

Zeta potential was measured on kaolinite slurries at pH 3 and 11 with varying adsorbed As(V) and roxarsone concentrations. These measurements were made by Laser Doppler Velicometry (Malvern Zetasizer 3000HS). All samples were diluted by a factor of six in 0.01M NaCl in order to be in an ideal range for measurements. Measured pH values after dilutions were 3.5 for the slurry initially at pH 3 and 10.7 for the pH 11 slurry.

3. Results

3.1 As(V) and Roxarsone Adsorption on Goethite

3.1.1 Adsorption Edges

Adsorption edges were constructed to examine the pH dependence of As(V) and roxarsone adsorption to goethite (Appendix A and Figure 4). At each pH, increasing the loading concentration of either arsenic type resulted in increasing amounts of arsenic adsorbed to goethite. Also shown in the adsorption edges is the pH dependence of arsenic adsorption; adsorption increased as pH decreased with maximum adsorption occurring at the minimum pH measured (pH 3), near the pK_{a1} of As(V) (2.3). A slight slope change can be seen at the pzc for goethite (8.4) (Kosmulski et al. 2003). Due to surface site availability, the various loading concentrations result in different pH dependence of As(V) adsorption to goethite. There is no increase in As(V) adsorption at low pH at the 38 μM loading, because there are enough surface sites to accommodate all of the As(V). For example, at pH 3, 100% of the 38 μM loading As(V) adsorbed to the goethite surface. This is also observed at several lower pH values for other loading concentrations. However, at higher loadings (e.g. 500 μM) not all of the As(V) is adsorbed to the surface for any pH; only 55% of As(V) is adsorbed at pH 3. Since there is still arsenic in solution at this concentration, adsorption does not plateau at low pH but instead continues to increase as pH is lowered.

The roxarsone edges have similar overall trends as the As(V) edges. As pH decreases, roxarsone adsorption increases. The roxarsone data show a similar pH dependence as As(V) (Figure 4B). The slope change at 8.4 is more pronounced in these data.

To examine the adsorption differences between the arsenic types, the adsorption edges of As(V) and roxarsone on goethite with comparable loadings were plotted against each other (Figure 5). At low (40 μM) loading concentrations, As(V) and roxarsone adsorption to goethite is very similar to each other. However, at the moderate (150 μM) concentrations, roxarsone adsorbs less than As(V) but with a similar dependence on pH. At high loading (500 μM), roxarsone and As(V) adsorption is similar at low pH; at higher pH (>8), roxarsone adsorption is greater than As(V). However, it should be noted that the loading of roxarsone (562 μM) is higher than the As(V) loading (475 μM), thus the comparison at these loadings may not be accurate.

3.1.2 Isotherms

Equilibrium isotherms for As(V) and roxarsone were constructed by plotting adsorbed As versus aqueous As (Figure 6). The As(V) isotherm shows increasing adsorbed arsenic with increasing aqueous arsenic concentration. The adsorbed concentration approaches a limit; this is characteristic of a surface saturation. Roxarsone isotherm data display a similar trend as As(V) (Figure 6).

Two isotherm models are commonly used to fit to adsorption: Freundlich and Langmuir models. The Freundlich isotherm model is empirically-based and the parameters do not represent physicochemical information about the adsorption mechanism. Additionally, one assumption of the Freundlich model is that there is an infinite supply of available surface sites on the mineral (Langmuir 1916). The Langmuir model is also empirical. In contrast to the Freundlich model, the Langmuir model includes physicochemical parameters, specifically the adsorption maximum, C_{\max} (mmol/m²) (Equation 1) (Langmuir 1916).

$$C_{\text{sorbed}} = \frac{aC_{\text{soln}}C_{\text{max}}}{1 + aC_{\text{soln}}} \quad (1)$$

where a is a fitted constant parameter (Table 1), C_{soln} (mmol/L) is the aqueous arsenic concentration and C_{sorbed} (mmol/m²) is the concentration of arsenic adsorbed per surface area of the mineral. The assumptions of the Langmuir model are that surface sites are limited and that adsorption occurs as a single layer on the mineral surface. The Langmuir isotherm model was chosen to fit our experimental data. In order to fit the data more easily, the linearized Langmuir isotherm was used:

$$\frac{C_{\text{soln}}}{C_{\text{sorbed}}} = \frac{1}{a} + \frac{C_{\text{soln}}}{C_{\text{max}}} \quad (2)$$

$C_{\text{soln}}/C_{\text{sorbed}}$ was plotted against C_{soln} to obtain a fit (Figure 7). If the isotherm plotted for the linearized Langmuir equation do not follow a linear trend, then the Langmuir assumptions are not valid for the system. The regressions for the Langmuir model produced a good fit ($R^2 > 0.75$) (Table 1). However, as pH increases, the R^2 value for the roxarsone regressions decreases.

When C_{\max} values for As(V) (Table 1) are plotted against pH, they display a linear trend (Figure 8). Because the R^2 values for the linear Langmuir fit to the roxarsone data are less than 0.75 at pH > 7, the C_{\max} values for the high pH values are not shown. C_{\max} increases with decreasing pH As(V). Roxarsone's C_{\max} values also display a linear trend over the pH range. As

was seen for As(V), the C_{\max} for roxarsone also increases as pH decreases. Although As(V) has a slightly higher C_{\max} over the pH range 2-6, the differences in C_{\max} values are small (Figure 8).

3.2 As(V) and Roxarsone Adsorption on Kaolinite

3.2.1 Adsorption Edges

Results of the adsorption edge experiments showed a pH dependence of As(V) and roxarsone on kaolinite (Figure 9). Similar to goethite, adsorption to kaolinite increased with decreasing pH with a stronger pH dependence at higher loading. A slight slope change can be observed between pH 4 and 5, near the pzc of kaolinite (4.6) (Stumm and Morgan 1970).

When As(V) and roxarsone are compared, several differences are observed (Figure 10). At lower loading (40 μM), the amounts of As sorbed are equal except at low pH values (3-4), whereas at moderate loading (100 μM) and high loading (500 μM) roxarsone adsorbs less strongly than As(V). At low pH values (below the pzc of kaolinite), roxarsone appears to adsorb to a greater extent than As(V).

3.2.2 Kaolinite Isotherms

Isotherms for As(V) and roxarsone adsorption on kaolinite are shown in Figure 11. As discussed for adsorption to goethite, fitting a Langmuir isotherm equation requires monolayer adsorption and a finite number of surface sites. As(V) appears to reach saturation but roxarsone maintains a linear trend. Since roxarsone adsorption to kaolinite displays a linear trend and does not reach surface saturation, it is not appropriate to apply the Langmuir model to this system.

3.3 Surface charge results

The surface charge results for kaolinite are shown in Figure 12. The zeta potential of the kaolinite slurry was -29 mV. This is consistent with the values (-30 mV) reported in the literature (Yukselen and Kaya 2003). Kaolinite, which has a pzc of 4.6 (Stumm and Morgan 1970), should have an overall positive surface charge at pH values below the pzc. However, due to adsorption of arsenic species, the surface charge of kaolinite with adsorbed As(V) and roxarsone is negative. As is shown in Figure 12, the negative charge increases with increased loading of As(V) and roxarsone. At pH 11, the surface charge is more negative than at pH 3 and

becomes more negative as loading of arsenic increases. Although there are subtle differences for As(V) and roxarsone, they are likely within measurement error.

Only one surface charge measurement of goethite was made (pH 6). This measurement was made for a goethite slurry with no arsenic adsorbed. Results (not shown) show a surface charge of +27 mV at pH 6, which was expected, as the pzc of goethite is approximately 8.4 (Kosmulski et al. 2003). Luxton et al. (2006) published a value of +36 mV for goethite at pH 6.

4. Discussion

4.1 Adsorption to Goethite

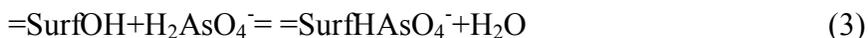
The edge data for As(V) and roxarsone adsorption on goethite show increasing adsorption as the concentration increases and pH decreases (Figure 4). The adsorption edges are in agreement with published results. Comparison of the As(V) adsorption data to the results of Manning et al. (1998), Manning and Goldberg (1997) and Grafe et al (2001) shows similar adsorption values and trends. For example, at pH 3 Manning and Goldberg (1997) reported As(V) adsorption of approximately 97 mmol/kg for As(V) adsorption to goethite, and our experiments produced an adsorption of 98 mmol/kg under the same conditions.

As(V) isotherms displayed a Langmuir (saturation) trend over all loading concentrations, which suggests monolayer specific adsorption even at higher concentrations (Langmuir 1997). As described previously, the linearized form of the Langmuir equation was fit to As(V) (Figure 7) to derive parameters for As(V) adsorption that could be compared with roxarsone. The fitted Langmuir isotherms for As(V) yielded C_{\max} values that increased as pH decreased (Figure 8) which agrees with the edge data.

Roxarsone displays a different isotherm pattern than As(V). The roxarsone isotherms only follow the Langmuir trend at low loading concentrations. As the loading concentration increases, the adsorption displays a linear trend (Figure 6), which suggests that at higher loadings, adsorption may not occur as a single layer but instead in multiple layers. The values of adsorption maximum, C_{\max} , for roxarsone adsorption to goethite derived from the Langmuir isotherm model are plotted against pH in Figure 8. Comparison of C_{\max} values for As(V) and roxarsone shows that the C_{\max} for As(V) is greater for pH 3 to 5; however, differences are small.

The protonation of the aqueous species is important to arsenic adsorption. As clearly shown in the adsorption edges and isotherms, As(V) to goethite adsorption is dependent on pH. As pH

increases above the pK_{a1} values of As(V) (2.3) and of roxarsone (3.49) (Qiang and Adams 2004), the arsenic species deprotonates, resulting in an overall negative charge on the species. Arsenic adsorbs via ligand exchange with OH and OH_2^+ surface functional groups and forms inner-sphere complexes with goethite (Stollenwerk 2003). This formation requires the arsenic species to be able to donate a proton in order to form an H_2O molecule. An example of this can be seen in Equation 3:



This binding can occur with a monodentate or bidentate bond. For the monodentate bond, an arsenate molecule is attached to an oxygen molecule on goethite with a single bond; however, for a bidentate bond the arsenic molecule is bonded to two separate oxygen molecules. A structure of high affinity inner-sphere bidentate surface complexes has been determined by other studies (Manning and Goldberg 1996; Grossl et al. 1997; Manning and Goldberg 1997; Manning et al. 1998; Grafe et al. 2001). It has been shown by Fendorf et al. (1997) that arsenate forms a monodentate bond at lower loading rates and a bidentate bond with goethite at high loading rates.

Understanding the bonding mechanism of As(V) to goethite allows us to compare and hypothesize the bonding mechanism for roxarsone. To gain a better understanding of whether roxarsone the bonding mechanisms are monodentate or bidentate, the potential amount of arsenic that could be adsorbed by the surface for each bonding type was calculated. Surface site calculations, using a surface site density of 3.52 sites/ m^2 on goethite (Barron and Torrent 1996), show that there are 5.8 μmol sites available for adsorption per m^2 of goethite. If there is a bidentate bond forming, a maximum of 2.8 $\mu\text{mol}/\text{m}^2$ of As should be able to be adsorbed. For a monodentate bond, 5.8 $\mu\text{mol}/\text{m}^2$ of As(V) can be adsorbed. The maximum amount of As(V) to goethite adsorption observed in our study was 3.2 $\mu\text{mol}/\text{m}^2$ at pH 3 (1000 μM spike, Appendix A). In contrast, the maximum amount of roxarsone adsorbed to goethite was 3.8 $\mu\text{mol}/\text{m}^2$ at pH 3. Because these maximums fall between the expected adsorption for monodentate and bidentate bonding, it is difficult to determine if one of these bonds is forming preferentially to the other. However, because more As(V) and roxarsone adsorbed than can be explained by only monodentate bonding, it suggests that a combination of monodentate and bidentate bonds formed during our adsorption experiments.

There are several possible explanations for the differences and similarities between As(V) and roxarsone adsorption to goethite (Figure 5). As explained previously, As(V) and roxarsone

show an overall similar pH dependent adsorption behavior on goethite. However, there are some observable concentration-dependent differences. At low concentrations (40 μM), roxarsone and As(V) show similar adsorption to goethite. At the low concentrations, there may be an abundance of surface sites so that differences in size, solubility, and electrostatic interactions between functional groups may not impact adsorption. At moderate loading concentrations, As(V) adsorbs more strongly than roxarsone at high loadings; an accurate comparison is difficult to make because the loading concentrations are different (475 μM for As(V); 562 μM for roxarsone). Adsorption differences may be related to the size of the roxarsone molecule, which is much larger than the As(V) molecule, and to electrostatic interactions between the different functional groups of roxarsone. Other possible explanations for differences between As(V) and roxarsone adsorption could be the type of bonding (monodentate versus bidentate), the type of layering (monolayer versus multilayer) or the solubility of roxarsone. In the pH range of 6 to 10, roxarsone is reported as “very soluble” (ACS 2005). Figure 6B shows that the isotherms for these higher pH values show a trend that almost appears to reach surface saturation. However, at lower pH values, roxarsone solubility decreases and is reported as “slightly soluble” at pH 3 to 4 and “soluble” at pH 5 (ACS 2005). There may be enhanced multilayer adsorption as the loading concentration approaches the solubility. However, because our range of loading concentrations is not large enough to determine if the trend of adsorbed roxarsone continues to follow this shape, this theory is difficult to test.

4.2 Adsorption to Kaolinite

The trends of increasing adsorption of As(V) to kaolinite with increasing pH are similar to those reported by Goldberg (2002), but the amount of arsenic adsorption per unit surface area was consistently higher in our experiments (Figure 9) than shown by Goldberg (2002). Adsorption values from our study and Goldberg’s 2002 study can not be directly compared due to differences in our loading concentrations. However, our adsorption data are within an order of magnitude of Manning and Goldberg (1997) for the one loading concentration that our experiments are comparable (approximately 40 μM) and within two orders of magnitude from Lin et al. (2000) who reported 2.5 $\mu\text{g/g}$ at pH 5 compared to 227 $\mu\text{g/g}$ from this study under approximately the same conditions.

Although there is considerable variation (an order of magnitude) within the published adsorption values, there is a greater amount of adsorption observed in our study than in previous studies. A possible reason for the variation may be the physical nature of the surface area. As can be seen in the SEM image (Figure 3A), the kaolinite used in this study has a large portion of exposed layer edges which contain the Al-based functional groups to which the most adsorption is expected to occur (Heidmann et al. 2005).

The isotherm for As(V) adsorption to kaolinite is shown in Figure 11A. As pH decreases, the data show increasing adsorbed arsenic. The data appear to be approaching saturation. Langmuir type isotherms were used by Ladeira and Ciminelli (2004) to describe As(V) adsorption on kaolinite. Our isotherm plot for As(V) on kaolinite can be fit to a Langmuir isotherm with acceptable R^2 values (>0.75), which suggests monolayer specific adsorption.

As was the case for goethite, roxarsone adsorption on kaolinite does not produce the same fit as As(V). As shown in Figure 11B, the roxarsone isotherm has an overall linear trend. Adsorption does not reach a maximum saturation value within the range of loading concentrations used in the experiment. It appears that roxarsone adsorption is independent of surface area. This may be explained by possible layering of roxarsone molecules on the mineral surface. For example, the phenol or nitro group of the roxarsone molecule could be interacting with functional groups on an adsorbed roxarsone molecule. More roxarsone could be adsorbed in this stacking manner than in a monolayer distribution.

Both As(V) and roxarsone adsorption on kaolinite displays pH dependence. As described for goethite, the pH dependence of As(V) and roxarsone adsorption is controlled by the surface charge of the mineral and the charge of the aqueous arsenic species present. As pH increases past the pK_a values (2.3, 6.9, 11.5 for As(V) and 3.5, 5.7, and 9.1 for roxarsone), the negative charge of the arsenic species will increase. Below its pzc (4.6), kaolinite will have a positive charge. Thus, the pH will influence the attraction of the negatively charged arsenic species to the mineral surface. It should be mentioned that adsorption of arsenate is controlled by both electrostatic (outer-sphere) and inner-sphere complexation. Thus, even at pH values above the pzc, arsenate, which is negatively charged, can adsorb to a negatively charged mineral surface.

Comparison of adsorption of As(V) and roxarsone to kaolinite at low and moderate loadings (Figure 10) shows several differences that are similar to the differences described for goethite. At lower loading concentrations, roxarsone and As(V) adsorb at similar concentrations. At these

loadings, excess surface sites are available on the mineral surface and size, solubility, and electrostatic interactions do not play an important role in controlling adsorption. At moderate concentrations, roxarsone adsorbs less strongly than arsenate. Two possible explanations for these trends are size differences and electrostatic interactions between functional groups on roxarsone. As the concentration of roxarsone increases, the functional group with the highest affinity for the surface may out compete the other functional groups for surface sites. This competition could force a uniform orientation of molecules with the functional group with the strongest affinity attaching to the mineral surface.

While the binding mechanisms of As(V) adsorption to kaolinite have not been well studied, it has been suggested that arsenic adsorbs on the edges of clay particles. At these edges, Al ions with OH groups are exposed where As(V) can adsorb via ligand exchange (Stollenwerk 2003), which is similar to the binding mechanisms discussed for goethite. Although arsenic binding to kaolinite has not been previously described as monodentate or bidentate, surface site calculations were conducted to provide insight on the binding mechanism. Similar to the calculations conducted for goethite, the concentration of available surface sites for adsorption to kaolinite was calculated. Assuming a site density for kaolinite of 3.40 sites/nm^2 (Langmuir 1997), the concentration of sites available for adsorption to kaolinite is $5.6 \text{ } \mu\text{mol of sites/m}^2$. Thus, it would be expected for $5.6 \text{ } \mu\text{mol/m}^2$ of arsenic to be adsorbed to the surface for a monodentate bonding mechanism and $2.8 \text{ } \mu\text{mol/m}^2$ of arsenic to be adsorbed for a bidentate bonding mechanism. The maximum observed value of adsorption for As(V) at pH 3 was $2.9 \text{ } \mu\text{mol/m}^2$ (1000 μM spike; Appendix C). This suggests that there may be bidentate bonding between As(V) and kaolinite. For roxarsone $3.9 \text{ } \mu\text{mol/m}^2$ is the highest adsorbed amount observed (1000 μM spike; Appendix D), which perhaps suggests a mixture of binding mechanisms. The assumption that the arsenate functional group of the roxarsone molecule controlling adsorption must be made for these calculations.

4.3 Implications for Roxarsone Mobility in Watersheds

While many factors play a role in roxarsone adsorption, soil mineralogy and pH are dominant controls. Although litter derived from poultry that are fed roxarsone contains arsenic from 10 to 50 mg/kg (Garbarino et al. 2003), the concentrations of As measured in soil water under litter applied fields is relatively low. For example, Brown et al (2005) found arsenic <10

$\mu\text{g/L}$ in soil water to which poultry litter had been applied. Thus, it is relevant from an environmental perspective to examine the mobility of roxarsone at low loading concentrations. Figure 13 shows a plot of roxarsone adsorption onto goethite and kaolinite at the lower loading concentrations that may be found in the environment. At these low loading concentrations, goethite adsorbs more roxarsone than kaolinite at pH values expected in natural waters. However, clay minerals are often more abundant in soils than iron oxides. For example, in the Shenandoah Valley where poultry litter is extensively spread on cornfields, soils contain 30% clay minerals and 1-3% total iron (Kauffman 1994). Therefore, both minerals are important in controlling the mobility of roxarsone.

4.4 Suggestions for Future Work

Very little work on the mobility of roxarsone has been reported in the literature. Quantifying the solubility of roxarsone and its relationship to pH will be important in order to better understand adsorption. Future work needs to be focused on determining the interaction of the various roxarsone functional groups with the mineral surfaces as well as the type of binding mechanisms. Extended X-ray adsorption fine structure (EXAFS) spectroscopy or infrared radiation (IR) studies may provide insight to the type of adsorption (monolayer versus multilayer) of roxarsone.

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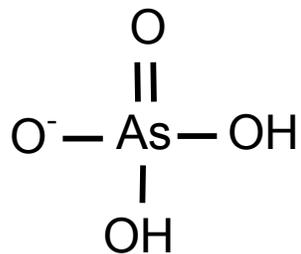
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Figure 1. Structure and pKa values of arsenate (Stollenwerk 2003) and roxarsone (Qiang and Adams 2003).

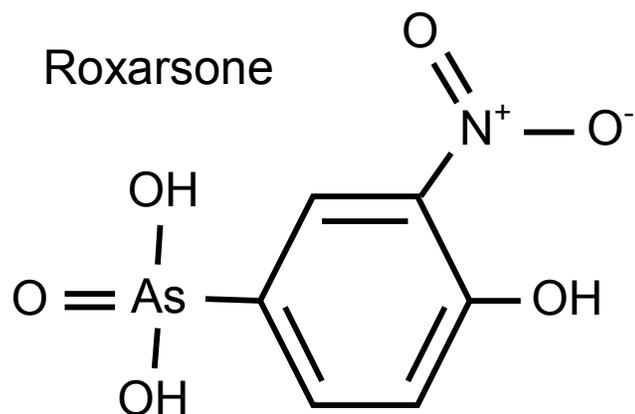
Arsenate



pKa values:

2.25
6.96
11.50

Roxarsone



pKa values:

3.49
5.74
9.13

Figure 2. X-ray diffraction pattern of synthesized goethite.

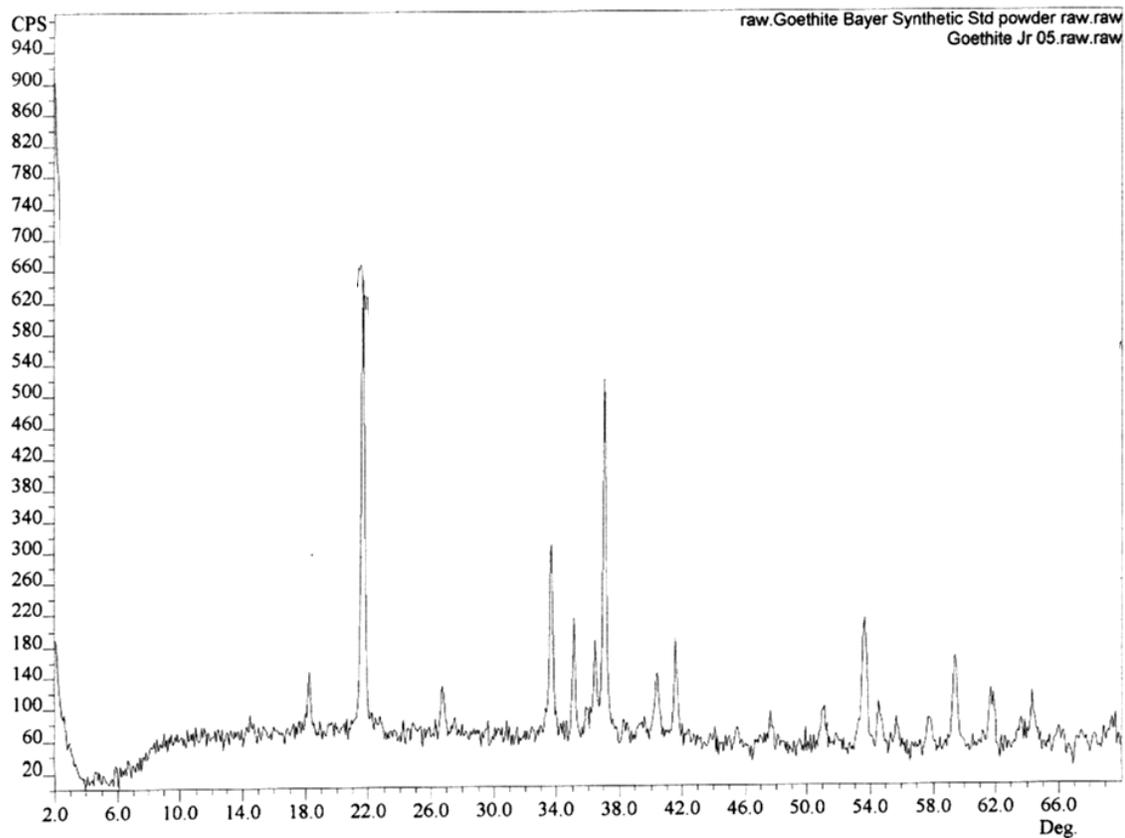


Figure 3. A. Scanning electron microscope image of the kaolinite grains (SEM) scan of the surface elements on a representative kaolinite grain. From Chermak and Rimstidt (1990) B. Representative surface scan using energy dispersive spectral analysis (EDS) of the kaolinite sample.

A.



B.

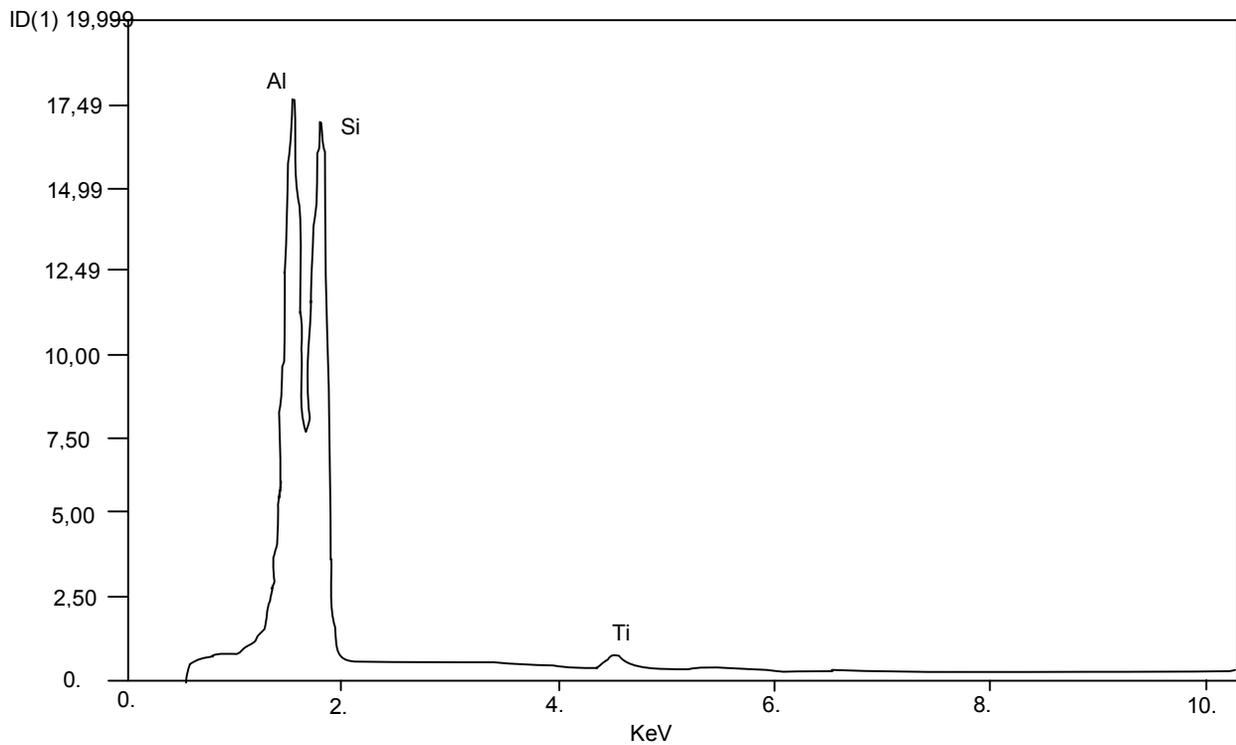


Figure 4. Experimental adsorption edges on goethite. As(V) is shown in A; roxarsone is shown in B.

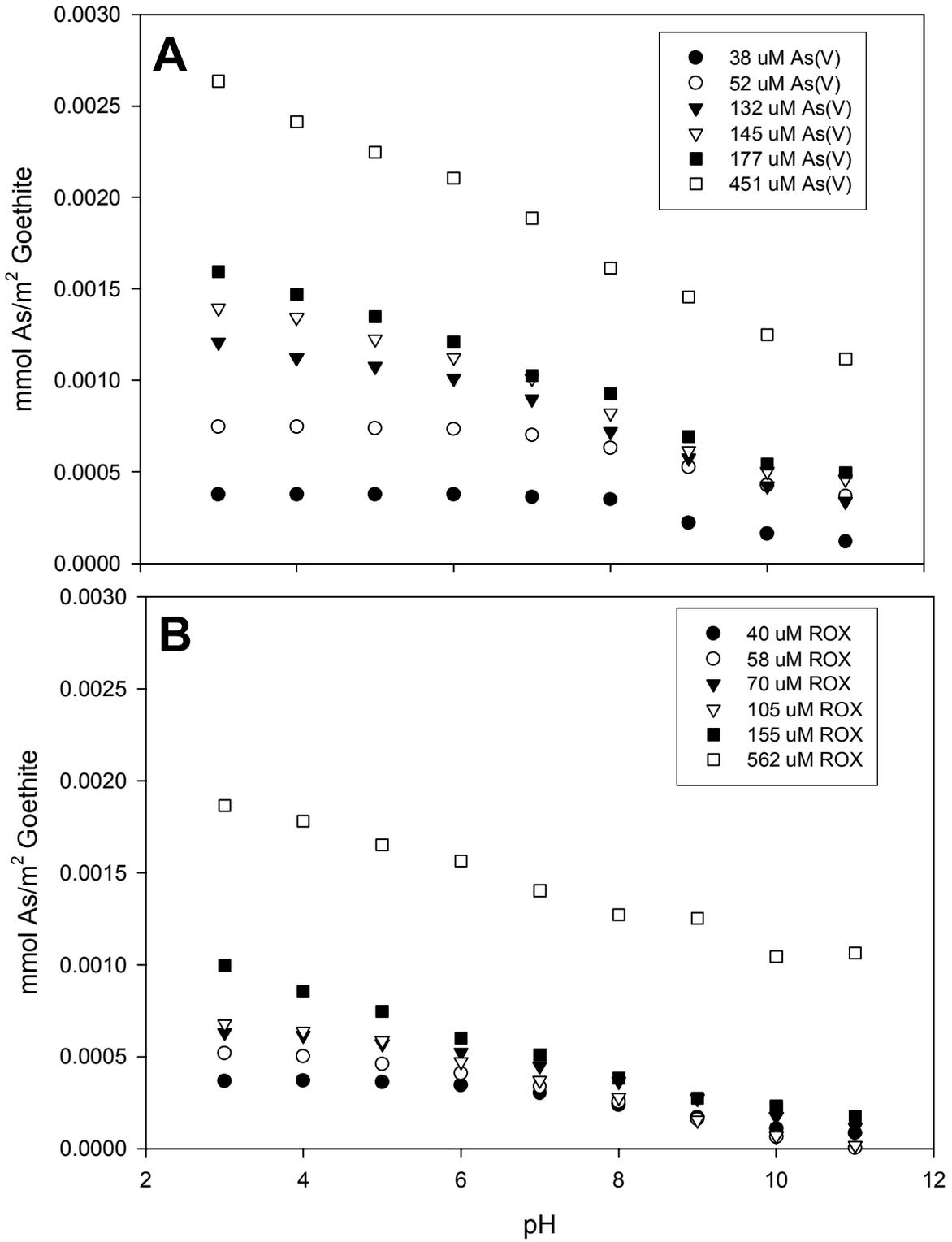


Figure 5. Comparison of As(V) (closed shapes) and roxarsone (open shapes) adsorption on goethite for similar loading concentrations.

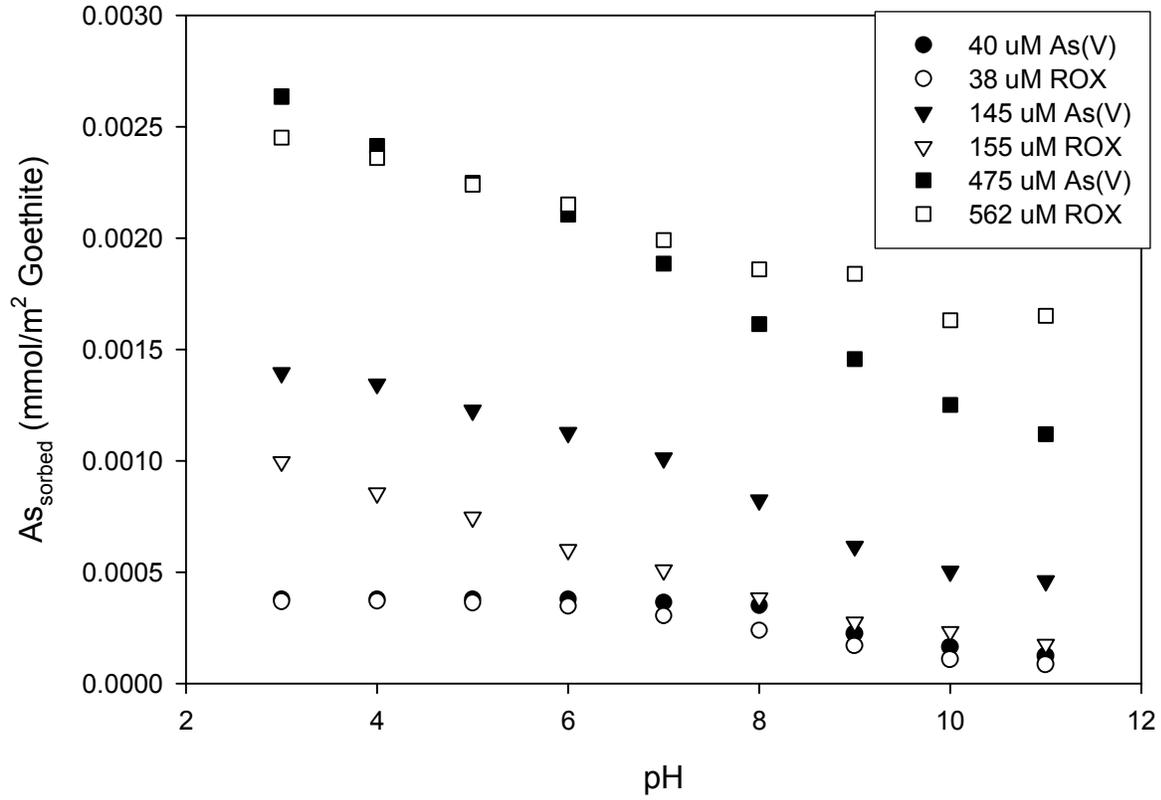


Figure 6. Isotherm plots for A. As(V) on goethite and B. roxarsone on goethite

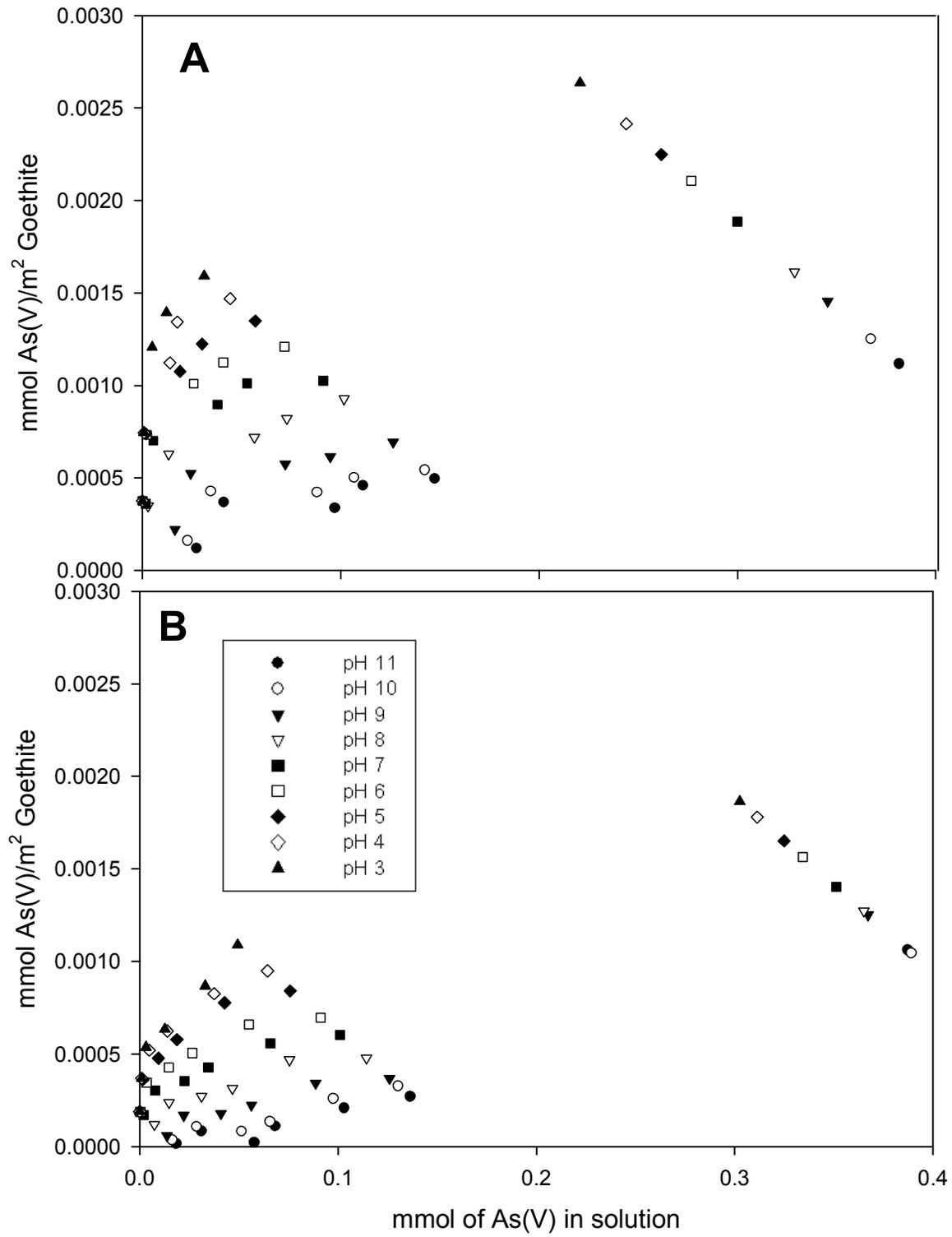


Figure 7. Linearized Langmuir Isotherm plots with fitted regression lines shown (open shapes are As(V) and closed shapes are ROX).

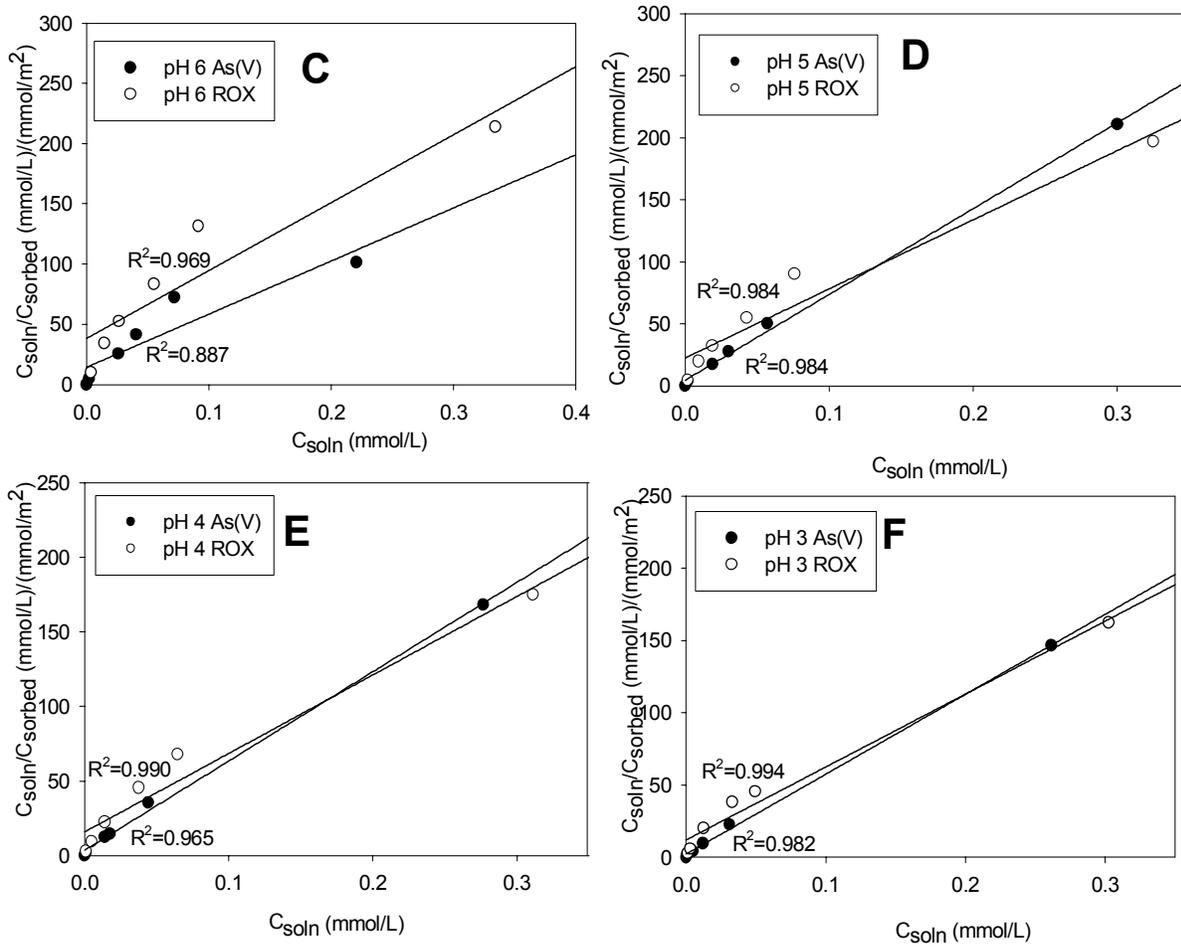


Figure 8. Adsorption maximums (C_{\max}) of roxarsone and As(V) on goethite as calculated from the linearized Langmuir isotherm equation.

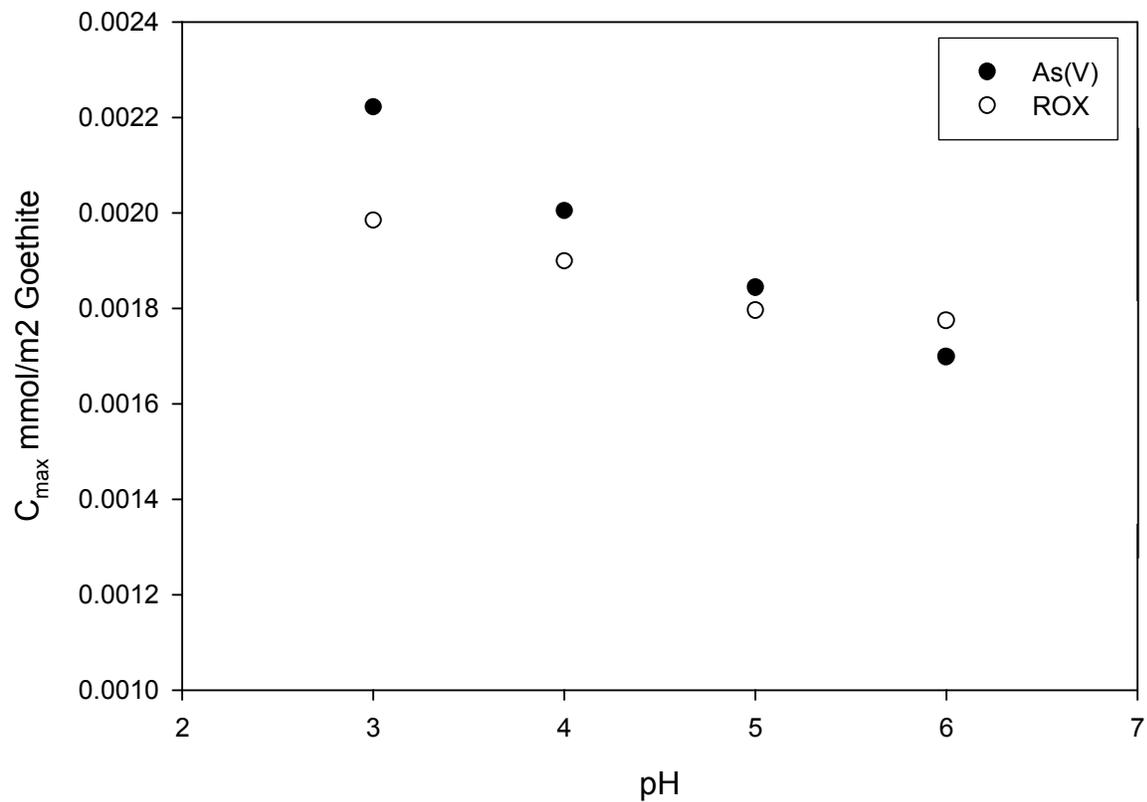


Figure 9. Adsorption edges for As(V) and roxarsone on kaolinite from experimental data.

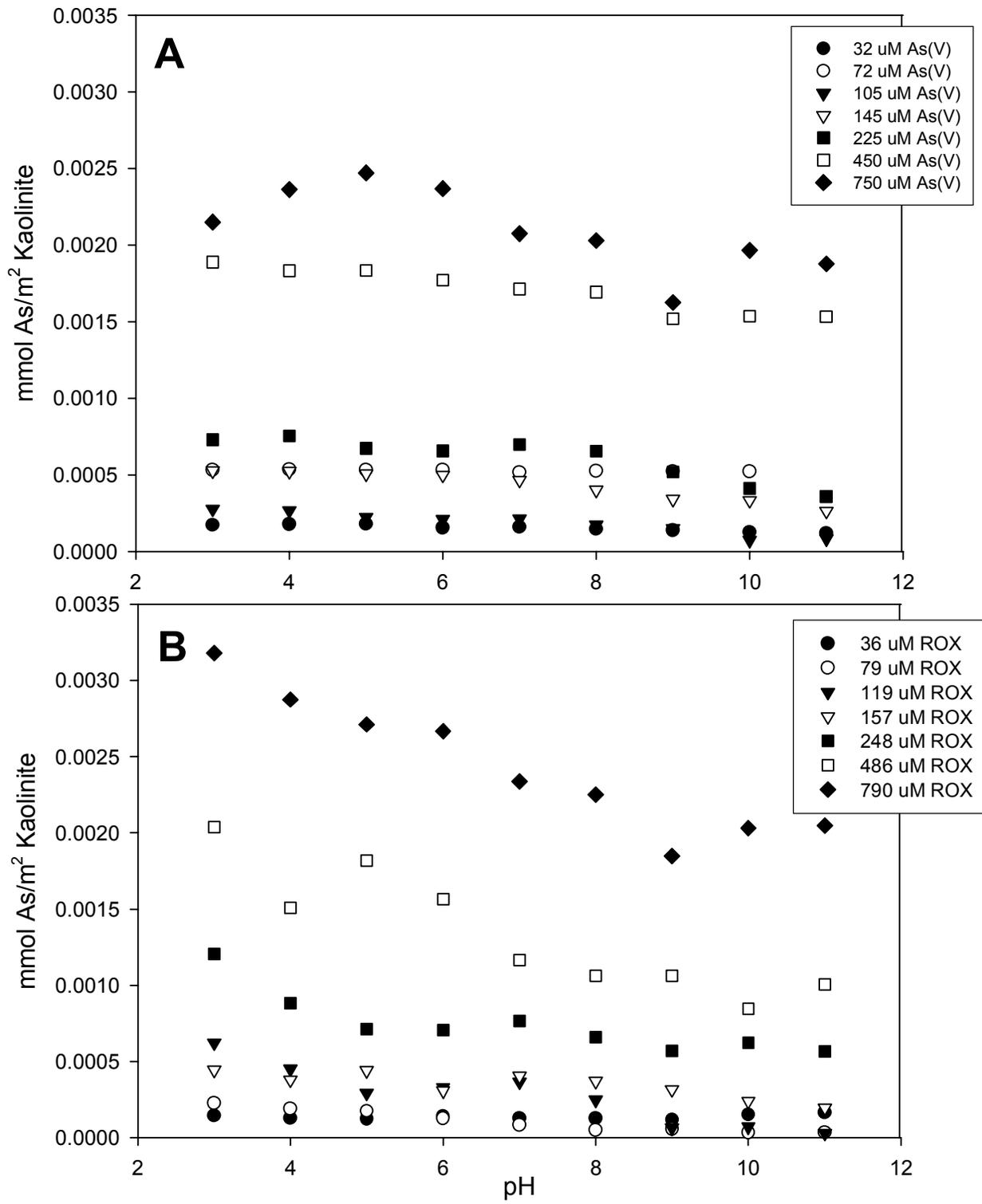


Figure 10. Comparison of As(V) (closed shapes) and roxarsone (open shapes) adsorption on kaolinite for similar loading concentrations.

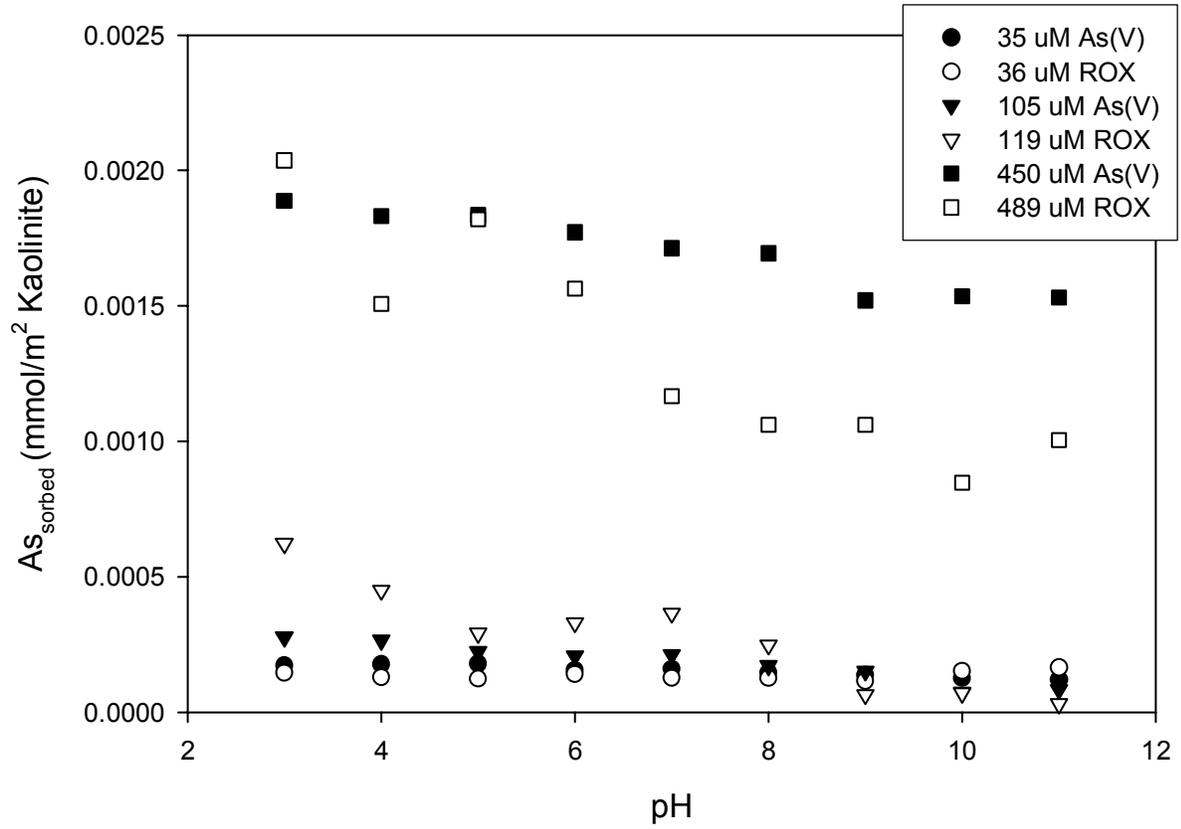


Figure 11. Isotherm plots for A. As(V) on kaolinite and B. roxarsone on kaolinite

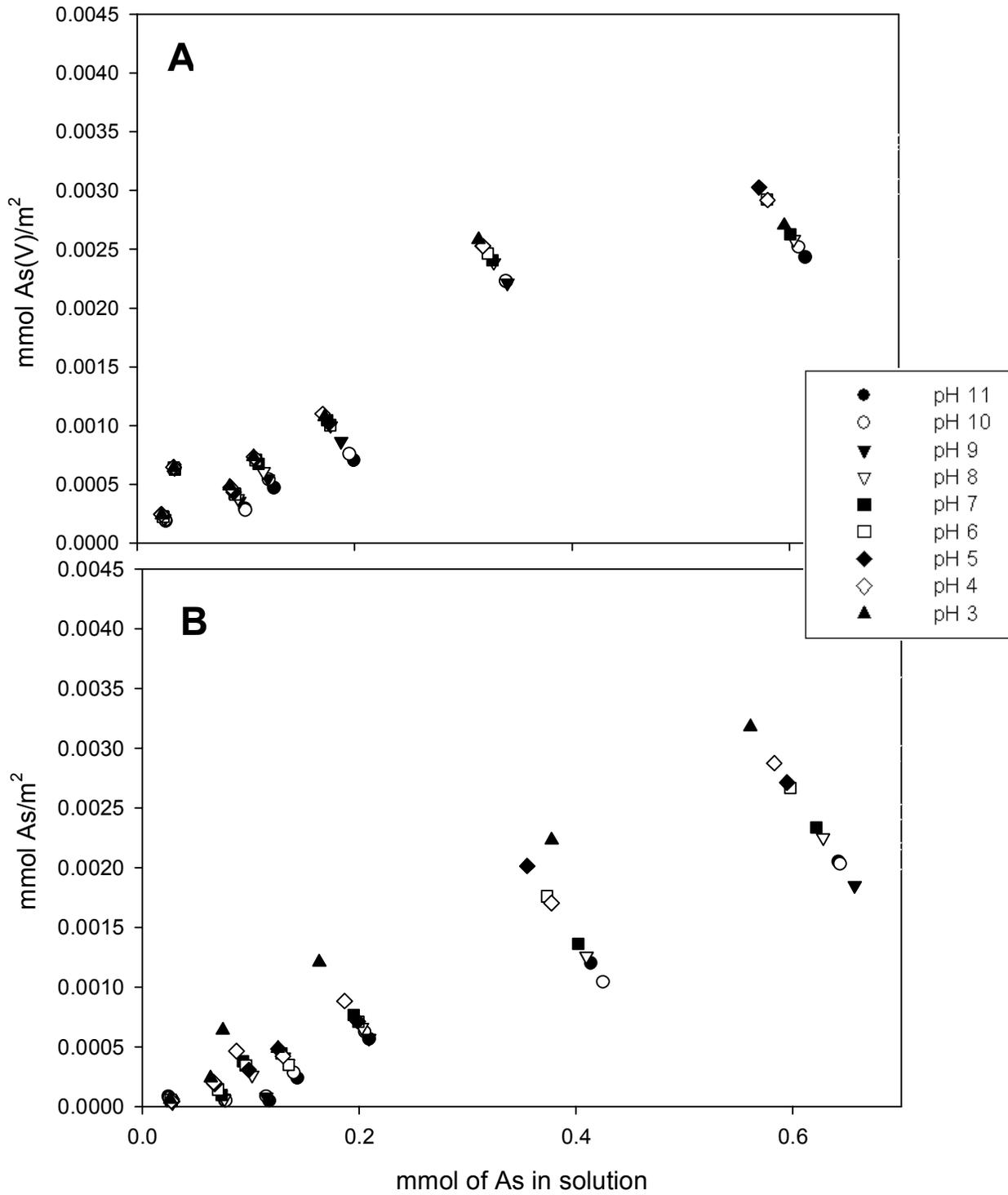


Figure 12. Zeta Potential measurements on Kaolinite using a voltage of 50 mv.

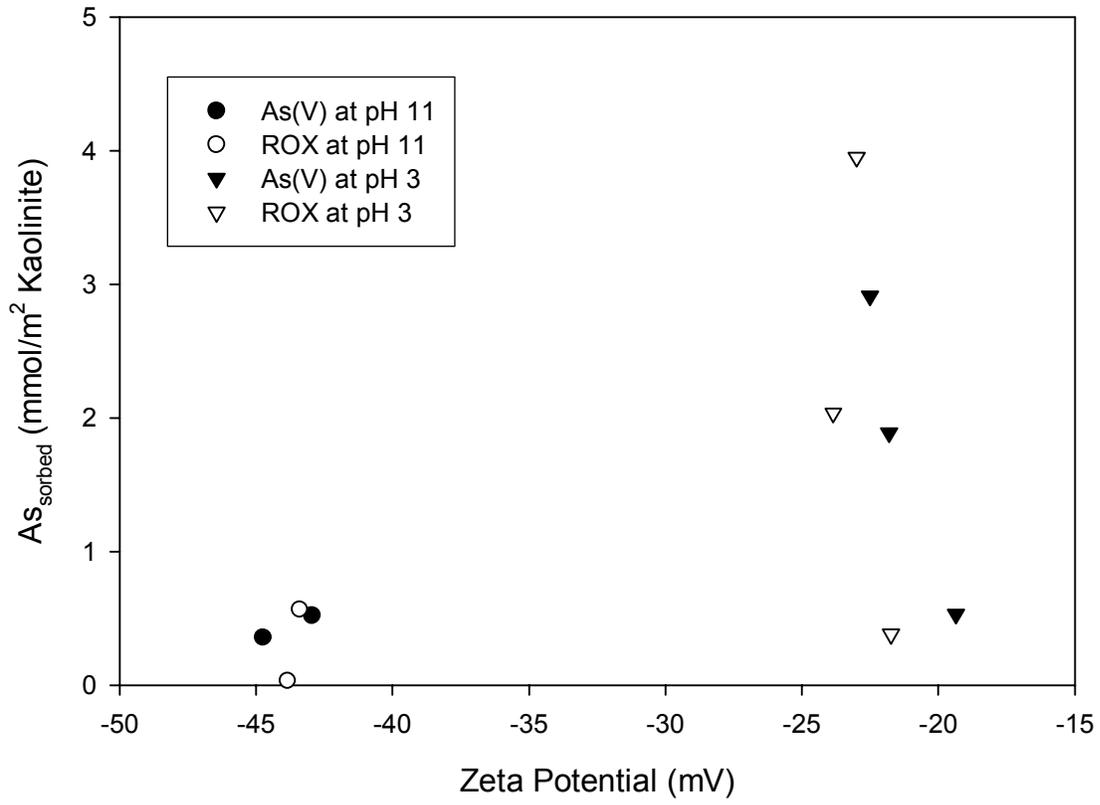


Figure 13. A comparison of roxarsone adsorption to kaolinite (open shapes) and goethite (closed shapes).

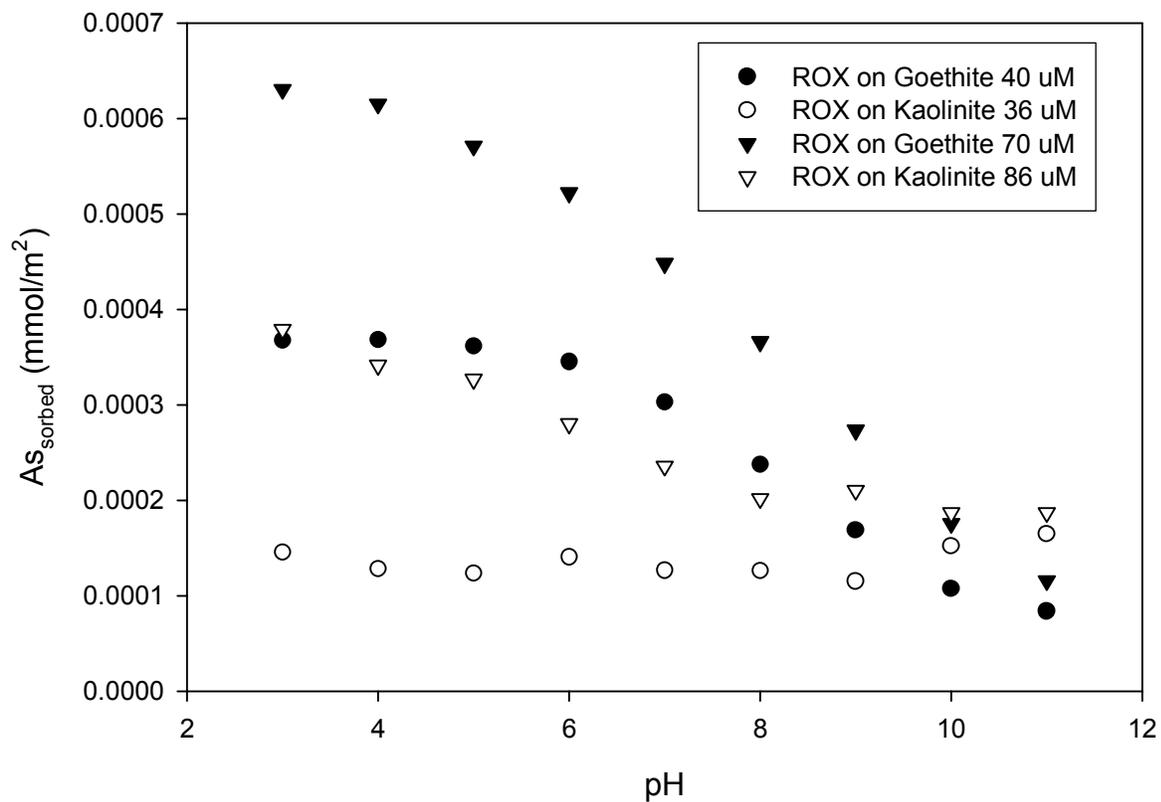


Table 1. Langmuir Parameters for the linear form on goethite. (See equation 2 for description of parameters)

As(V)			
pH	C _{max} umol/m ²	1/a	R ²
		(mmol/L) (mmol/m ²)	
11	1.316	315.64	0.701
10	1.156	185.58	0.724
9	1.239	93.87	0.855
8	1.242	32.51	0.960
7	1.486	19.08	0.949
6	1.698	11.07	0.969
5	1.844	7.56	0.984
4	2.004	4.86	0.990
3	2.222	3.03	0.994

Roxarsone			
pH	C _{max} umol/m ²	1/a	R ²
		(mmol/L) (mmol/m ²)	
11	N/A	522.96	0.206
10	N/A	445.13	0.038
9	3.396	216.85	0.283
8	1.848	110.46	0.748
7	1.713	61.01	0.862
6	1.774	38.22	0.887
5	1.796	22.56	0.952
4	1.899	15.76	0.965
3	1.984	11.96	0.982

*N/A means negative values were derived

Appendix A. Experimental Data for As(V) on Goethite

Experiment Label: 01-V-40-A

Arsenic Type: As(V)
 Mineral Type: Goethite
 Spike Concentration: 38 μM As(V)
 Slurry contained of 0.08 g of goethite to 80 mls of NaCl
 Added 2.2 mls of 0.1 NaOH to bring pH to 11.21

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.99	1.014	2.10	0.02718	0.000102
10.00	1.461	2.10	0.02278	0.000144
9.00	0.579	2.10	0.01644	0.000203
7.99	1.480	2.10	0.00293	0.000331
7.00	1.536	2.10	0.00163	0.000343
5.99	0.426	2.10	0.00000	0.000358
4.99	1.007	2.10	0.00000	0.000358
4.00	1.200	2.10	0.00000	0.000358
3.00	3.412	2.10	0.00000	0.000358

Adsorption Edge Experiment
Experiment Label: 01-V-140-A

Arsenic Type: As(V)
 Mineral Type: Goethite
 Spike Concentration: 133 μM As(V)
 Slurry contained of 0.08 g of goethite to 80 mls of NaCl
 Added 2.2 mls of 0.1 NaOH to bring pH to 11.21

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.99	1.797	2.10	0.09705	0.00034
10.00	3.190	2.10	0.08811	0.00042
9.00	0.951	2.10	0.07200	0.00057
7.99	2.110	2.10	0.05652	0.00072
8.00	2.586	2.10	0.03782	0.00090
5.99	1.394	2.10	0.02582	0.00101
4.99	0.305	2.10	0.01891	0.00108
4.00	1.137	2.10	0.01391	0.00112
3.00	2.907	2.10	0.00488	0.00121

Adsorption Edge Experiment
Experiment Label: 01-V-80-A

Arsenic Type: As(V)
 Mineral Type: Goethite
 Spike Concentration: 52 μM As(V)
 Slurry contained of 0.08 g of goethite to 80 mls of NaCl
 Added 1.7 mls of 0.1 NaOH to bring pH to 11.12

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.99	0.737	2.10	0.01110	0.00010
9.99	1.245	2.10	0.01746	0.00016
9.00	0.861	2.10	0.02769	0.00026
7.99	1.440	2.10	0.03879	0.00037
7.00	2.780	2.10	0.04650	0.00044
6.00	0.552	2.10	0.04983	0.00047
4.99	0.422	2.10	0.05031	0.00047
4.00	0.712	2.10	0.05112	0.00048
3.00	1.713	2.10	0.05118	0.00048

Adsorption Edge Experiment
Experiment Label: 01-V-160-A

Arsenic Type: As(V)
 Mineral Type: Goethite
 Spike Concentration: 145 μM As(V)
 Slurry contained of 0.08 g of goethite to 80 mls of NaCl
 Added 1.3 mls of 0.1 NaOH to bring pH to 11.09

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
11.00	0.448	2.10	0.11121	0.00032
10.00	1.077	2.10	0.10670	0.00036
9.00	0.647	2.10	0.09467	0.00047
7.99	1.530	2.10	0.07284	0.00068
7.00	2.800	2.10	0.05274	0.00087
6.00	0.518	2.10	0.04070	0.00098
4.99	0.372	2.10	0.03007	0.00108
4.00	0.874	2.10	0.01754	0.00120
3.00	2.966	2.10	0.01215	0.00125

Adsorption Edge Experiment
Experiment Label: 01-V-200-A

Arsenic Type: As(V)
 Mineral Type: Goethite
 Spike Concentration: 177 μM As(V)
 Slurry contained of 0.08 g of goethite to 80 mls of NaCl
 Added 2.1 mls of 0.1 NaOH to bring pH to 11.20

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
11.00	1.581	2.10	0.14742	0.00050
10.00	1.301	2.10	0.14229	0.00054
9.00	0.633	2.10	0.12644	0.00069
7.99	0.793	2.10	0.10165	0.00093
7.00	3.25	2.10	0.09124	0.00103
6.00	0.648	2.10	0.07166	0.00121
4.99	0.331	2.10	0.05695	0.00135
4.00	0.505	2.10	0.04418	0.00147
3.00	1.825	2.10	0.03107	0.00159

Adsorption Edge Experiment
Experiment Label: 01-V-1000-A

Arsenic Type: As(V)
 Mineral Type: Goethite
 Spike Concentration: 950 μM As(V)
 Slurry contained of 0.08 g of goethite to 80 mls of NaCl
 Added 2.1 mls of 0.1 NaOH to bring pH to 11.21

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.97	1.581	2.10	0.85727	0.00135
9.99	1.301	2.10	0.84673	0.00145
9.00	0.633	2.10	0.81171	0.00178
8.00	0.793	2.10	0.78859	0.00199
7.00	3.250	2.10	0.75986	0.00226
6.00	0.648	2.10	0.72292	0.00261
5.00	0.331	2.10	0.68146	0.00300
4.00	0.505	2.10	0.67476	0.00307
3.00	1.825	2.10	0.66436	0.00317

Adsorption Edge Experiment
Experiment Label: 01-V-500-B

Arsenic Type: As(V)
 Mineral Type: Goethite
 Spike Concentration: 475 μM As(V)
 Slurry contained of 0.08 g of goethite to 80 mls of NaCl
 Added 1.2 mls of 0.1 NaOH to bring pH to 11.20

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.98	0.339	2.10	0.36856	0.00083
10.00	1.120	2.10	0.37172	0.00080
9.00	0.606	2.10	0.35109	0.00100
7.98	1.087	2.10	0.33397	0.00116
6.99	2.882	2.10	0.31296	0.00136
6.00	1.042	2.10	0.29788	0.00150
4.98	0.434	2.10	0.28219	0.00165
4.00	0.622	2.10	0.27451	0.00172
3.00	1.452	2.10	0.25483	0.00191

Appendix B. Experimental Data for Roxarsone on Goethite

Adsorption Edge Experiment

Experiment Label: 01-RX-40-A

Arsenic Type: ROX

Mineral Type: Goethite

Spike Concentration: 39 μM ROX

Slurry contained of 0.08 g of goethite to 80 mls of NaCl

Added 1.8 mls of 0.1 NaOH to bring pH to 11.09

pH	Volume added to slurry	Volume sampled	As_{soln}	$\text{As}_{\text{sorbed}}$
	ml	ml	mM	mmol/m ²
10.97	0.305	2.10	0.03112	0.00008
10.00	1.069	2.10	0.02859	0.00011
9.00	0.928	2.10	0.02211	0.00017
7.98	1.289	2.10	0.01484	0.00024
7.00	1.762	2.10	0.00791	0.00030
6.00	0.447	2.10	0.00343	0.00034
4.99	0.503	2.10	0.00166	0.00036
4.00	0.301	2.10	0.00097	0.00037
3.00	1.055	2.10	0.00103	0.00037

Adsorption Edge Experiment

Experiment Label: 01-RX-80-A

Arsenic Type: ROX

Mineral Type: Goethite

Spike Concentration: 70 μM ROX

Slurry contained of 0.08 g of goethite to 80 mls of NaCl

Added 1.8 mls of 0.1 NaOH to bring pH to 11.09

pH	Volume added to slurry	Volume sampled	As_{soln}	$\text{As}_{\text{sorbed}}$
	ml	ml	mM	mmol/m ²
10.98	0.222	2.10	0.05772	0.00012
9.99	0.812	2.10	0.05136	0.00018
9.00	0.663	2.10	0.04103	0.00027
8.00	1.387	2.10	0.03118	0.00037
7.00	2.042	2.10	0.02249	0.00045
6.00	0.645	2.10	0.01467	0.00052
5.00	0.562	2.10	0.00944	0.00057
4.00	1.021	2.10	0.00482	0.00061
3.00	2.156	2.10	0.00315	0.00063

Adsorption Edge Experiment

Experiment Label: 01-RX-60-A

Arsenic Type: ROX

Mineral Type: Goethite

Spike Concentration: 58 μM ROX

Slurry contained of 0.08 g of goethite to 80 mls of NaCl

Added 1.5 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As_{soln}	$\text{As}_{\text{sorbed}}$
	ml	ml	mM	mmol/m ²
10.96	0.311	2.10	0.00000	0.00000
9.99	1.069	2.10	0.00006	0.00006
9.00	0.823	2.10	0.00016	0.00016
7.99	1.613	2.10	0.00025	0.00025
6.99	2.544	2.10	0.00033	0.00033
5.99	1.002	2.10	0.00041	0.00041
4.98	1.164	2.10	0.00046	0.00046
4.00	1.136	2.10	0.00050	0.00050
3.00	1.828	2.10	0.00052	0.00052

Adsorption Edge Experiment

Experiment Label: 01-RX-130-A

Arsenic Type: ROX

Mineral Type: Goethite

Spike Concentration: 105 μM ROX

Slurry contained of 0.08 g of goethite to 80 mls of NaCl

Added 2.11 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As_{soln}	$\text{As}_{\text{sorbed}}$
	ml	ml	mM	mmol/m ²
10.98	0.154	2.10	0.10306	0.00002
9.99	1.358	2.10	0.09759	0.00007
8.99	0.674	2.10	0.08865	0.00015
7.99	1.201	2.10	0.07540	0.00028
6.98	2.287	2.10	0.06581	0.00037
5.99	0.798	2.10	0.05505	0.00047
5.00	0.691	2.10	0.04274	0.00059
4.00	0.605	2.10	0.03751	0.00064
3.00	1.988	2.10	0.03311	0.00068

Adsorption Edge Experiment
Experiment Label: 01-RX-160-A

Arsenic Type: ROX
 Mineral Type: Goethite
 Spike Concentration: 155 µM ROX
 Slurry contained of 0.08 g of goethite to 80 mls of NaCl
 Added 5.25 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.97	0.117	4.20	0.13646	0.000175
9.99	1.579	2.10	0.13029	0.000233
9.00	1.024	2.10	0.12599	0.000274
8.00	1.495	2.10	0.11428	0.000384
7.00	3.574	2.10	0.10106	0.000509
6.00	1.075	2.10	0.09131	0.000601
5.00	0.922	2.10	0.07585	0.000747
4.00	0.568	2.10	0.06441	0.000854
3.00	1.858	2.10	0.04947	0.000995

Adsorption Edge Experiment
Experiment Label: 01-RX-500-A

Arsenic Type: ROX
 Mineral Type: Goethite
 Spike Concentration: 562 µM ROX
 Slurry contained of 0.08 g of goethite to 80 mls of NaCl
 Added 4.2 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.99	0.158	4.20	0.38733	0.00165
10.00	1.528	2.10	0.38918	0.00163
9.00	1.229	2.10	0.36726	0.00184
7.99	2.197	2.10	0.36511	0.00186
7.00	3.679	2.10	0.35135	0.00199
6.00	1.344	2.10	0.33425	0.00215
5.00	1.005	2.10	0.32494	0.00224
4.00	0.848	2.10	0.31137	0.00236
3.00	2.518	2.10	0.30242	0.00245

Adsorption Edge Experiment
Experiment Label: 01-RX-800-A

Arsenic Type: ROX
 Mineral Type: Goethite
 Spike Concentration: 898 µM ROX
 Slurry contained of 0.08 g of goethite to 80 mls of NaCl
 Added 5.0 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.99	0.380	2.10	0.89749	0.00097
10.00	0.396	2.10	0.84290	0.00148
9.00	1.259	2.10	0.84824	0.00143
7.99	1.855	2.10	0.77450	0.00213
7.00	3.408	2.10	0.74399	0.00241
6.00	0.921	2.10	0.72921	0.00255
5.00	0.835	2.10	0.71102	0.00273
4.00	0.575	2.10	0.68010	0.00302
3.00	2.331	2.10	0.64151	0.00338

Appendix C. Experimental Data for As(V) on Kaolinite

Adsorption Edge Experiment Experiment Label: 02-V-40-A

Arsenic Type: As(V)
Mineral Type: Kaolinite
Spike Concentration: 35 μM As(V)
Slurry contained of 0.32 g of kaolinite to 80 mls of NaCl
Added 2.225 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.96	0.204	2.40	0.02651	0.000119
9.99	1.385	2.40	0.02605	0.000126
9.00	0.292	2.40	0.02521	0.000137
8.00	0.720	2.40	0.02464	0.000145
7.00	1.129	2.40	0.02362	0.000159
6.00	0.133	2.40	0.02398	0.000154
5.00	0.165	2.40	0.02220	0.000179
4.00	0.300	2.40	0.02238	0.000177
3.00	1.291	2.40	0.02268	0.000172

Adsorption Edge Experiment Experiment Label: 02-V-120-A

Arsenic Type: As(V)
Mineral Type: Kaolinite
Spike Concentration: 105 μM As(V)
Slurry contained of 0.32 g of kaolinite to 80 mls of NaCl
Added 1.90 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.97	0.320	4.80	0.09898	0.000084
9.98	1.245	2.40	0.09975	0.000073
9.00	0.410	2.40	0.09409	0.000151
8.00	0.678	2.40	0.09264	0.000171
7.00	0.980	2.40	0.08970	0.000212
5.94	0.318	2.40	0.09002	0.000208
5.00	0.233	2.40	0.08889	0.000223
4.00	0.303	2.40	0.08582	0.000266
3.00	0.795	2.40	0.08504	0.000277

Adsorption Edge Experiment Experiment Label: 02-V-80-A

Arsenic Type: As(V)
Mineral Type: Kaolinite
Spike Concentration: 72 μM As(V)
Slurry contained of 0.32 g of kaolinite to 80 mls of NaCl
Added 1.8 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
11.00	0.130	4.80		
9.98	0.968	2.40	0.03438	0.000522
9.00	0.424	2.40	0.03425	0.000524
7.99	0.789	2.40	0.03412	0.000526
7.20	1.694	2.40	0.03476	0.000517
5.98	0.242	2.40	0.03360	0.000533
5.00	0.168	2.40	0.03359	0.000533
4.00	0.324	2.40	0.03342	0.000535
3.00	0.832	2.40	0.03374	0.000531

Adsorption Edge Experiment Experiment Label: 02-V-160-A

Arsenic Type: As(V)
Mineral Type: Kaolinite
Spike Concentration: 145 μM As(V)
Slurry contained of 0.32 g of kaolinite to 80 mls of NaCl
Added 2.0 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.98	0.127	4.80	0.12603	0.000263
9.98	1.084	2.40	0.12098	0.000333
9.00	0.338	2.40	0.12038	0.000342
8.00	0.868	2.40	0.11614	0.000400
7.10	1.728	2.40	0.11147	0.000465
6.00	0.103	2.40	0.10905	0.000499
5.00	0.220	2.40	0.10841	0.000508
4.00	0.257	2.40	0.10719	0.000525
3.00	0.784	2.40	0.10710	0.000526

Adsorption Edge Experiment
Experiment Label: 02-V-250-A

Arsenic Type: As(V)
 Mineral Type: Kaolinite
 Spike Concentration: 225 µM As(V)
 Slurry contained of 0.32 g of kaolinite to 80 mls of NaCl
 Added 2.55 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
11.00	0.320	4.80	0.02577	0.000358
9.97	0.162	2.40	0.02967	0.000412
8.99	0.452	2.40	0.03740	0.000519
8.00	1.260	2.40	0.04714	0.000654
7.00	0.215	2.40	0.05033	0.000698
6.00	0.330	2.40	0.04734	0.000657
5.00	0.127	2.40	0.04854	0.000673
4.00	0.224	2.40	0.05435	0.000754
3.00	0.832	2.40	0.05258	0.000729

Adsorption Edge Experiment
Experiment Label: 02-V-790-A

Arsenic Type: As(V)
 Mineral Type: Kaolinite
 Spike Concentration: 750 µM As(V)
 Slurry contained of 0.32 g of kaolinite to 80 mls of NaCl
 Added 2.55 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.99	0.481	4.80	0.61470	0.00188
9.98	1.291	2.40	0.60841	0.00196
9.00	0.470	2.40	0.63290	0.00162
8.00	0.698	2.40	0.60375	0.00203
7.00	0.636	2.40	0.60047	0.00207
6.00	0.572	2.40	0.57926	0.00237
5.00	0.220	2.40	0.57188	0.00247
4.00	0.321	2.40	0.57967	0.00236
3.00	0.961	2.40	0.59500	0.00215

Adsorption Edge Experiment
Experiment Label: 02-V-500-A

Arsenic Type: As(V)
 Mineral Type: Kaolinite
 Spike Concentration: 450 µM As(V)
 Slurry contained of 0.32 g of kaolinite to 80 mls of NaCl
 Added 2.3 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
11.00	0.000	2.40	0.33962	0.001531
9.97	1.250	2.40	0.33925	0.001537
9.01	0.325	2.40	0.34046	0.001520
8.00	0.742	2.40	0.32794	0.001694
7.00	1.380	2.40	0.32657	0.001713
6.00	0.766	2.40	0.32230	0.001772
5.00	0.204	2.40	0.31775	0.001835
4.00	0.331	2.40	0.31795	0.001832
3.00	0.805	2.40	0.31389	0.001888

Adsorption Edge Experiment
Experiment Label: 02-V-1000-A

Arsenic Type: As(V)
 Mineral Type: Kaolinite
 Spike Concentration: 950 µM As(V)
 Slurry contained of 0.32 g of kaolinite to 80 mls of NaCl
 Added 2.75 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.97	0.282	2.40	0.82744	0.001700
9.96	1.241	2.40	0.80145	0.002061
8.99	0.392	2.40	0.78489	0.002291
8.00	0.532	2.40	0.76642	0.002547
7.00	1.550	2.40	0.75712	0.002676
6.00	0.622	2.40	0.73756	0.002948
5.00	0.174	2.40	0.73934	0.002923
4.00	0.276	2.40	0.74330	0.002868
3.00	0.766	2.40	0.74029	0.002910

Appendix D. Experimental Data for Roxarsone on Kaolinite

Adsorption Edge Experiment Experiment Label: 02-RX-40-A

Arsenic Type: ROX
Mineral Type: Kaolinite
Spike Concentration: 36 μM ROX
Slurry contained of 0.32 g of kaolinite to 80 mls of 0.01M NaCl
Added 2.225 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.97	0.364	4.80	0.02413	0.000165
9.98	1.235	2.40	0.02505	0.000152
8.97	0.428	2.40	0.02771	0.000115
8.00	0.605	2.40	0.02693	0.000126
7.00	1.308	2.40	0.02690	0.000126
6.00	0.459	2.40	0.02589	0.000140
5.00	0.461	2.40	0.02712	0.000123
4.00	0.304	2.40	0.02677	0.000128
3.00	0.713	2.40	0.02553	0.000145

Adsorption Edge Experiment Experiment Label: 02-RX-120-A

Arsenic Type: ROX
Mineral Type: Kaolinite
Spike Concentration: 119 μM ROX
Slurry contained of 0.32 g of kaolinite to 80 mls of 0.01M NaCl
Added 2.55 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.98	0.173	4.80	0.11685	0.000030
9.97	0.172	2.40	0.11388	0.000071
8.99	0.518	2.40	0.11436	0.000064
8.00	0.714	2.40	0.10115	0.000248
7.00	1.117	2.40	0.09269	0.000365
6.00	0.311	2.40	0.09524	0.000330
5.00	0.201	2.40	0.09799	0.000292
4.00	0.224	2.40	0.08660	0.000450
3.02	0.868	2.40	0.07415	0.000622

Adsorption Edge Experiment Experiment Label: 02-RX-80-A

Arsenic Type: ROX
Mineral Type: Kaolinite
Spike Concentration: 79 μM ROX
Slurry contained of 0.32 g of kaolinite to 80 mls of 0.01M NaCl
Added 2.5 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.92	0.143	4.80	0.07652	0.008651
9.94	1.040	2.40	0.07656	0.008650
8.95	0.541	2.40	0.07484	0.008674
7.99	0.479	2.40	0.07548	0.008665
7.00	1.462	2.40	0.07303	0.008699
6.00	0.814	2.40	0.06982	0.008744
5.00	0.175	2.40	0.06645	0.008790
4.00	0.329	2.40	0.06540	0.008805
3.00	0.761	2.40	0.06269	0.008843

Experiment Label: 02-RX-160-A

Arsenic Type: ROX
Mineral Type: Kaolinite
Spike Concentration: 157 μM ROX
Slurry contained of 0.32 g of kaolinite to 80 mls of 0.01M NaCl
Added 2.80 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
10.98	0.564	4.80	0.14293	0.000195
9.99	1.492	2.40	0.13971	0.000240
8.99	0.950	2.40	0.13419	0.000317
8.00	1.505	2.40	0.13029	0.000371
7.00	1.794	2.40	0.12793	0.000403
6.00	0.613	2.40	0.13486	0.000307
5.00	0.541	2.40	0.12524	0.000441
4.00	0.430	2.40	0.12966	0.000379
3.00	1.317	2.40	0.12496	0.000444

Adsorption Edge Experiment
Experiment Label: 02-RX-250-A

Arsenic Type: ROX
 Mineral Type: Kaolinite
 Spike Concentration: 250 µM ROX
 Slurry contained of 0.32 g of kaolinite to 80 mls of 0.01M NaCl
 Added 3.1 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
11.00	0.378	4.80	0.20917	0.000566
9.99	1.221	2.40	0.20505	0.000624
9.00	0.597	2.40	0.20894	0.000570
8.00	0.877	2.40	0.20243	0.000660
7.00	1.244	2.40	0.19474	0.000767
6.00	0.321	2.40	0.19901	0.000708
5.00	0.257	2.40	0.19862	0.000713
4.00	0.329	2.40	0.18642	0.000882
3.00	1.000	2.40	0.16303	0.001207

Adsorption Edge Experiment
Experiment Label: 02-RX-790-A

Arsenic Type: ROX
 Mineral Type: Kaolinite
 Spike Concentration: 790 µM ROX
 Slurry contained of 0.32 g of kaolinite to 80 mls of NaCl
 Added 5.45 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
11.00	0.564	4.80	0.64234	0.002049
10.00	1.492	2.40	0.64370	0.002030
9.00	0.950	2.40	0.65684	0.001848
8.00	1.505	2.40	0.62783	0.002250
7.00	1.794	2.40	0.62154	0.002337
6.00	0.613	2.40	0.59773	0.002668
5.00	0.541	2.40	0.59459	0.002711
4.00	0.430	2.40	0.58282	0.002875
3.00	1.317	2.40	0.56079	0.003180

Adsorption Edge Experiment
Experiment Label: 02-RX-500-A

Arsenic Type: ROX
 Mineral Type: Kaolinite
 Spike Concentration: 486 µM ROX
 Slurry contained of 0.32 g of kaolinite to 80 mls of NaCl
 Added 4.25 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
11.00	0.568	4.80	0.41358	0.001005
9.98	1.744	2.40	0.42494	0.000847
9.00	0.773	2.40	0.40948	0.001062
8.00	1.246	2.40	0.40948	0.001062
7.00	1.497	2.40	0.40196	0.001166
6.00	0.571	2.40	0.37322	0.001565
5.00	0.357	2.40	0.35489	0.001819
4.00	0.464	2.40	0.37733	0.001508
3.00	1.091	2.40	0.33916	0.002037

Adsorption Edge Experiment
Experiment Label: 02-RX-1000-A

Arsenic Type: ROX
 Mineral Type: Kaolinite
 Spike Concentration: 985 µM ROX
 Slurry contained of 0.32 g of kaolinite to 80 mls of 0.01 NaCl
 Added 6.20 mls of 0.1 NaOH

pH	Volume added to slurry	Volume sampled	As _{soln}	As _{sorbed}
	ml	ml	mM	mmol/m ²
11.00	0.676	2.40	0.81787	0.002319
10.00	1.638	2.40	0.82498	0.002220
9.00	1.101	2.40	0.82758	0.002184
8.00	1.629	2.40	0.80966	0.002433
7.00	1.729	2.40	0.80008	0.002566
6.00	0.908	2.40	0.77874	0.002862
5.00	0.656	2.40	0.76807	0.003010
4.00	0.591	2.40	0.72825	0.003562
3.00	1.362	2.40	0.70034	0.003950