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ADSORPTION OF ARSENITE AND ARSENATE ON AMORPHOUS IRON HYDROXIDE

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Abstract—Adsorption isotherms in solutions with ionic strengths of 0.01 at 25°C were measured over the arsenite and arsenate concentration range 10^{-7}–10^{-3} M and the pH range 4–10. At low concentrations, these isotherms obeyed equations of the Langmuir type. At higher concentrations the adsorption isotherms were linear, indicating the existence of more than one type of surface site on the amorphous iron hydroxide adsorbent. Removal of arsenite and arsenate by amorphous iron hydroxide throughout the concentration range were determined as a function of pH. By careful selection of the relative concentration of arsenic and amorphous iron hydroxide and pH, removals on the order of 92% can be achieved.

INTRODUCTION

Arsenic, a toxic and possible carcinogenic element, is entering the oceans and surface waters in increasing amounts through the use of arsenical pesticides, mining and processing sulfide ores, and burning of fossil fuels. One of the main factors controlling arsenic in natural aquatic systems is adsorption on the sediments. It is important to acquire the capability of modeling adsorption by amorphous iron hydroxide [am-$Fe(OH)_3$] because of its universal presence in clays, soils, and sediments, both as partial coatings on other minerals and as discrete oxide particles, as well as its significant adsorptive properties (Jenne, 1968). This study investigates the interaction of arsenite and arsenate, the primary forms of arsenic in aqueous systems, with amorphous iron hydroxide.

Certain bacteria have been found not only to have oxidizing and reducing powers but also to be able to methylate organic and inorganic arsenic compounds. Biological methylation is not thermodynamically favorable in water and thus contributes little to the overall arsenic cycle in most aquatic systems (Braman & Foreback, 1973; Chau & Wong, 1978).

At the high *Eh* values encountered in oxygenated waters arsenic acid species (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}) are stable. At *Eh* values characteristic of mildly reducing conditions, arsenous acid species (H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{2-}$) become stable (Ferguson & Gavis, 1972). Removal of arsenic depends not only on the concentration of arsenic in solution, amount of sorptive oxides, and pH, but also on the oxidation state.

Typical adsorption studies have been carried out at relatively high concentrations (10^{-4}–10^{-2} M) compared to that found in natural waters (10^{-7}–10^{-5} M) or even most waste waters and geothermal waters (10^{-5}–10^{-4} M) and very little at high concentrations ($>10^{-5}$ M).

Ferguson & Anderson (1974) studied adsorption characteristics of arsenite and arsenate on iron hydroxide and aluminum hydroxide at the 10^{-5}–10^{-3} M initial arsenic concentration in the pH range 6.0–7.5. They found Langmuir isotherm was obeyed. They later studied arsenate adsorption on amorphous aluminum hydroxide (Anderson *et al.*, 1976). Langmuir isotherms were followed at the 10^{-3}–10^{-5} M initial arsenic concentration and initial pH values of 3.5–10.5. Gupta & Chen (1978) found adherence to the Langmuir equation when arsenite or arsenate adsorbed on alumina and bauxite. The pH range was 6.5–8.5 and the initial arsenic concentration was 5–130 μM in both cases. Holm *et al.* (1979) found that adsorption of arsenite on river sediments was linearly dependent on concentration where as arsenate adsorption followed a Langmuir isotherm. The initial level of arsenic was 10^{-5}–10^{-4} M, and the pH at which the single isotherm was generated was not mentioned.

Some anions and cations have a specific affinity for surface metal atoms and adsorb out of all proportion to their concentration in solution. Adsorption under the combined influence of ionic and non-ionic bonding is called specific adsorption and can occur even when the surface is uncharged. Specific adsorption of anions should lower the pH of the isoelectric point (pH_{iep}). The amount of shift in the pH_{iep} depends on the particular ion and its concentration, as well as the particular solid surface. The isoelectric point is the pH at which the solid surface charge from all sources is zero.

Thus the present study was undertaken to establish quantitatively the isotherms of arsenite and arsenate adsorption on am-$Fe(OH)_3$ at concentrations which range over four orders of magnitude and a wide range of pH.

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This work should not only be of interest to environmental scientists but also to engineers concerned with water and wastewater treatment as well as soil scientists concerned with nutrient retention.

EXPERIMENTAL

Amorphous iron hydroxide was prepared by the addition of 25 ml of 1 M NaOH to 1.665 g of analytical grade $Fe_2(SO_4)_3$ dissolved in 200 ml of doubly distilled water. The suspension was filtered, washed several times with doubly distilled water, and diluted up to 200 ml, so that the final suspension concentration was 4.45 g l^{-1} $Fe(OH)_3$. The flask was then immersed for 5 min in an ultrasonic bath. The suspension was soluble in acid ammonium oxalate (pH 3) and 1 M HCl, indicating that there had been little or no crystallization. This was confirmed by X-ray diffraction. A batch of fresh suspension was prepared for each experiment. Reproducible characteristics were obtained using this method.

The adsorption studies were run at a constant am-$Fe(OH)_3$ concentration of 0.00445 g l^{-1} and ionic strength of 0.01 adjusted with 1 M $NaNO_3$. Ten initial arsenite and arsenate concentrations in the form of $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$ were 0.667, 1.33, 3.34, 6.67, 13.3, 33.4, 66.7, 133, 334, 667 μm l^{-1} As. Eight 200-ml volumetric flasks were used in each of the 10 studies, whereupon the contents containing $NaNO_3$, iron hydroxide, arsenite or arsenate, and water were transferred to Erlenmeyer flasks. The initial pH value of each of the 8 solutions was adjusted to give the desired final equilibrium pH between 4 and 10. The initial pH values were adjusted using either 1 M HNO_3 or 1 M NaOH to give the same final pH ($\pm$0.1 pH unit) for each of the 10 different initial arsenite or arsenate concentrations. The suspensions were mixed continuously by magnetic stirrers in stoppered 250-ml Erlenmeyer flasks for 24 h.

At the end of the reaction period, the final pH was measured, 10 ml of the mixture was centrifuged, and the supernatant analyzed for arsenic. Arsenic was determined using a Perkin–Elmer 403 atomic absorption spectrophotometer equipped with a deuterium arc background corrector, HGA 2100 graphite furnace, and electrodeless discharge lamp. Standards were diluted from a 1000-ppm arsenic stock solution, which was prepared from primary standard arsenic trioxide. A blank experiment was run without the iron hydroxide to see if arsenite or arsenate adsorbed onto the walls of the flask or magnetic stirbar.

Kinetic studies were also performed at the 0.667 and 13.3 μm l^{-1} As initial concentration of arsenite and arsenate in order to see when equilibrium was achieved. The same procedure was used in the adsorption experiment except 3-ml aliquots were removed at 0.05, 0.5, 1, 2, 4, 8, 16, 24 h and analyzed for arsenic. Three experiments were run with arsenite involving a final pH of 4.0, 6.1, and 9.8. Three experiments were also run with arsenate involving a final pH of 4.0, 8.0, and 9.9.

RESULTS AND DISCUSSION

Conversion of arsenite to arsenate takes weeks (in basic solution) before measurable air oxidation occurs. Thus errors due to the presence of arsenate did not become a factor in this investigation. Also, Gulens *et al.* (1979) stated that a redox reaction between Fe(III) and As(III) has not been observed, as well as heterogeneous oxidation, despite its thermodynamic favorability.

The blank experiments showed no detectable ($<10^{-8}$ M As) arsenite or arsenate adsorbed on the walls of the flask or magnetic stirbar.

The rate of adsorption of arsenite on amorphous iron hydroxide was fast with 90% completion after 2 h of stirring at each of the three final pH values (4.0, 6.1, and 9.8). The rates at the 13.3 μm l^{-1} As initial concentration were noticeably faster than at the 0.667 μm l^{-1} As.

The rate of adsorption of arsenate was much faster than that of arsenite with 90% completion after only 1 h of stirring at each of the three final pH values (4.0, 8.0, and 9.9). The rates at the 13.3 μm l^{-1} As initial arsenate concentration were somewhat faster than at the 0.667 μm l^{-1} As.

After 4 h, 99% of the maximum adsorption had taken place with both arsenite and arsenate. Thus 24 h was adequate time for equilibration to occur. Adsorption solely due to electrostatic processes is usually very rapid on the order of seconds. The adsorption of arsenic is on the order of hours which indicates a specific adsorption or formation of a chemical bond between the arsenic species and the adsorbent.

Figure 1 shows the adsorption of arsenite per unit mass of am-$Fe(OH)_3$ plotted against final pH for the first five different initial concentrations from 0.667 to 13.3 μm l^{-1} As. The amount of arsenite taken up by the adsorbent reaches a maximum value at constant pH and this maximum value varies with pH. Adsorption increases to a maximum around pH 7, and then decreases as pH is increased with the first five of

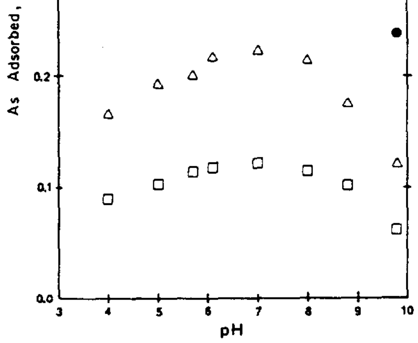

Fig. 1. Arsenite adsorption per unit mass adsorbent (Γ_A) as a function of the final pH for five different amounts of added arsenite, concentrations in μm l^{-1} As: 0.667 (□); 1.33 (△); 3.34 (●); 6.67 (■); 13.3 (▲). Concentration of am-$Fe(OH)_3$, 0.00445 g l^{-1}; ionic strength, 0.01; equilibration time, 24 h.

the arsenite concentrations studied. The adsorption maxima in Fig. 1 tend to be sharper as the initial arsenite concentration is increased, indicating a greater dependence on pH at higher concentration levels. At pH 7, the amount of arsenic removed is 81% at the 0.667 μm l^{-1} As initial concentration, 74% at 1.33 μm l^{-1} As, 53% at 3.34 μm l^{-1} As, 32% at 6.67 μm l^{-1} As, and 17% at 13.3 μm l^{-1} As.

Arsenous acid (H_3AsO_3) is a weak acid with the first pK at 9.2. The anion, $H_2AsO_3^-$, is capable of coordinating to the surface metal atom of the adsorbent and adsorption of the anion will occur provided the energy of adsorption is sufficiently large to dissociate the acid. The proton produced is used to remove the OH$^-$ from the coordinating layer of the surface and provide a site for the anion. In these circumstances anion adsorption in excess of the positive charge and even on negative surface is possible. The ease with which a proton can be removed from undissociated acid in solution will vary with the pH of the solution. The adsorption maxima at pH 7 can be explained by the fact that the difference between the energy released upon adsorption and the energy required to dissociate the acid is at a maximum.

Isotherms, plotted at constant pH, show that the amount of arsenite adsorbed increases until a condition of surface saturation is reached at some concentration. In the concentration range of 0.667–13.3 μm l^{-1} As, this was best represented by the Langmuir equation, $\Gamma_A = \Gamma_{A,\max} C_{\mathrm{equil}}/(K_L + C_{\mathrm{equil}})$ where Γ_A is the adsorption per unit mass adsorbent, $\Gamma_{A,\max}$ is the maximum adsorption per unit mass adsorbent, C_{equil} is the equilibrium concentration of arsenite in solution, and K_L is the Langmuir constant. Rearrangement of this equation yields: $C_{\mathrm{equil}}/\Gamma_A = K_L/\Gamma_{A,\max} + (1/\Gamma_{A,\max})C_{\mathrm{equil}}$. Since the Langmuir equation is obeyed, a plot of $C_{\mathrm{equil}}/\Gamma_A$ vs C_{equil} gives a straight line with a slope of $1/\Gamma_{A,\max}$ and an intercept of $K_L/\Gamma_{A,\max}$. This is shown in Fig. 2 for each of the eight equilibrium pH values employed. Table 1 lists the calculated Langmuir parameters, as well as correlation coefficients to a straight line at each pH. These isotherms indicate that the coverage is monolayer. By plotting the Langmuir constants against pH, one can determine the constants at any pH. Knowing the pH and the equilibrium arsenite concentration, the amount of adsorption on the adsorbent can be calculated using the Langmuir equation.

Table 1. Parameters in the Langmuir adsorption equation for arsenite

pH	$\Gamma_{A,\max}$ (μm g^{-1})	K_L (μm l^{-1})	Corr. coeff.*
4.0	457	1.03	0.999
5.0	463	0.657	1.000
5.7	490	0.544	0.999
6.1	503	0.457	1.000
7.0	513	0.431	1.000
8.0	488	0.493	0.999
8.8	417	0.646	0.999
9.8	417	1.82	0.989

*Correlation to a least-squares approximation of the best straight line through the points in Fig. 2.

The isoelectric points of am-Fe(OH)$_3$ and the first five different amounts of added arsenite were published earlier (Pierce & Moore, 1980). As predicted, the isoelectric point (pH$_{\mathrm{iep}}$) depends on the amount of arsenic adsorbed and decreases from 8.0 with no added arsenite to 7.3 with 13.3 μm l^{-1} As initial arsenite concentration. This shift in the pH$_{\mathrm{iep}}$ also indicates a specific adsorption process rather than a purely electrostatic adsorption process.

The adsorption of arsenite per unit mass am-Fe(OH)$_3$ plotted against final pH for the last five different initial concentrations from 33.4 to

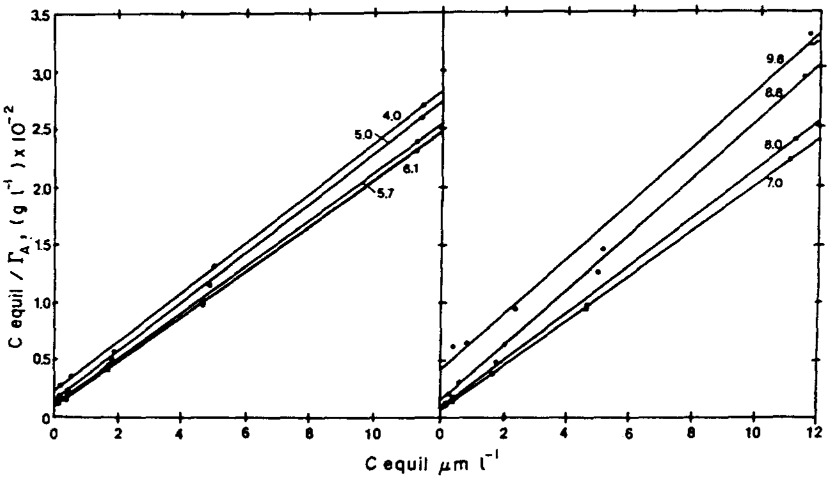

Fig. 2. Equilibrium arsenite concentration (C_{equil}) divided by the amount of arsenite adsorbed per unit mass adsorbent (Γ_A) as a function of the equilibrium arsenite concentration at various pH values indicated on the graph. Initial concentrations of arsenite, 0.667–13.3 μm l^{-1} As; am-Fe(OH)$_3$ concentration, 0.00445 g l^{-1}; equilibration time, 24 h.

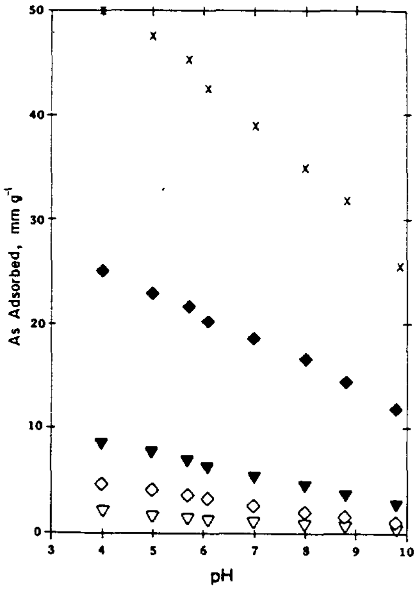

Fig. 3. Arsenite adsorption per unit mass adsorbent (Γ_A) vs final pH for five different amounts of added arsenite, concentrations in μm l^{-1} As: 33.4 (▽); 66.7 (◇); 133 (▼); 334 (◆); 667 (×). Concentration of am-Fe(OH)$_3$, 0.00445 g l^{-1}; ionic strength, 0.01; equilibration time, 24 h.

667 μm l^{-1} As is shown in Fig. 3. The amount of arsenite taken up by the adsorbent continually decreases with increasing pH with the higher concentrations showing a greater dependence on pH. This dependence on pH is clearly different from that at the lower concentrations of arsenite. This can be explained by the fact that the surface has primarily a net negative charge due to adsorption of anions. Thus adsorption of anions on a negatively charged surface should decrease as the pH is increased. At a pH of 4, removals on the order of 35% were found for all five of the initial concentrations. The eight final pH values were the same as in the earlier arsenite adsorption studies at the lower concentration range.

Figure 4 shows that the Langmuir equation is not obeyed in the arsenite initial concentration range of 33.4–667 μm l^{-1} As. Rather a linear isotherm is followed whereupon the amount of arsenite adsorbed (Γ_A) vs the equilibrium concentration of arsenite in solution (C_{equil}) is a linear relationship. That is $\Gamma_A = kC_{\text{equil}}$.

The slopes of the Γ_A vs C_{equil} plots at each pH and correlation coefficients to a straight line can be found in Table 3. Knowing the pH and equilibrium concentrations of arsenite, the adsorption can be calculated as long as the equilibrium concentration is greater than 14 μm l^{-1}. Below 14 μm l^{-1} As, the Langmuir equation and constants would have to be used.

This adsorption dependence on two different isotherms may be explained partially by assuming that oxide surfaces have different types of surface sites, with different affinities for adsorbate ions. The surface density of the strong binding sites would be much less than the weaker binding sites. So adsorption proceeds until all the strong binding sites are occupied, which would follow a Langmuir isotherm. Then the anions would start to adsorb on the weaker binding sites. The linear isotherm at the high concentrations indicates that either the number of weaker adsorption sites remains constant even though the amount of anions adsorbed increases, or that the number of weaker sites is very large compared with the amount adsorbed. If the former is the case, it suggests that the adsorbate can penetrate into the oxide surface which is theoretically possible with an amorphous solid. That is, an open permeable structure exists for am-Fe(OH)$_3$.

This multisite adsorption due to heterogeneity of the surface is consistent with that proposed by Benjamin & Leckie (1981) and Davis *et al.* (1978).

Figure 5 shows the adsorption of arsenate per unit mass of am-Fe(OH)$_3$ plotted against final pH for the first five different initial concentrations from 0.667 to 13.3 μm l^{-1} As. At the lower concentrations and at lower pH arsenate adsorption is independent of pH. But as pH increases there is a "point" where adsorption begins to decrease. This "point" shifts to lower pH values as the initial arsenate concentration is increased. At pH 4, the amount of arsenate removed is 81% at the 0.667 μm l^{-1} As initial concentration, 92% at 1.33 μm l^{-1} As, 78% at 3.34 μm l^{-1} As, 80% at 6.67 μm l^{-1} As; and 47% at 13.3 μm l^{-1} As.

Arsenic acid (H_3AsO_4) has p*K* values of 3.6, 7.3, and 12.5, thus $H_2AsO_4^{-}$ and $HAsO_4^{2-}$ are the predominant anions in the pH range studied which would have a greater effect on the surface charge than the singly-charged anion of arsenous acid. This accounts for the "point" in the adsorption vs pH plots where the adsorption begins to decrease and the shift in that "point" to lower pH values. The pH$_{\text{iep}}$ decreases much more rapidly as compared with arsenite

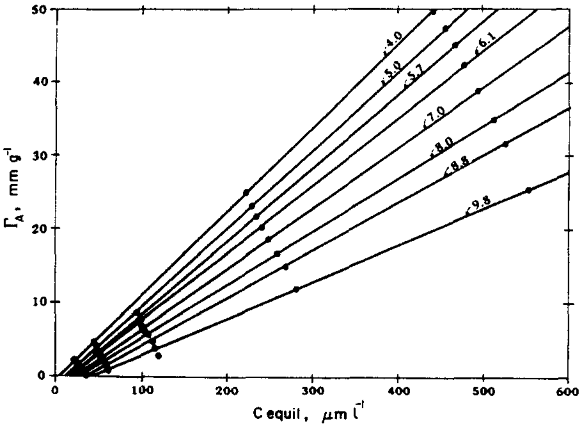

Fig. 4. The amount of arsenite adsorbed per unit mass adsorbent (Γ_A) as a function of the equilibrium arsenite concentration (C_{equil}) at various final pH values indicated on the graph. Initial concentrations of arsenite, 33.4–667 μm l^{-1} As; am-Fe(OH)$_3$ concentration, 0.00445 g l^{-1}; equilibration time, 24 h.

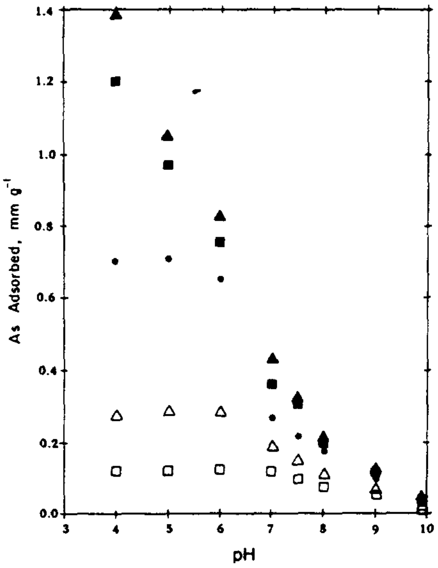

Fig. 5. Arsenate adsorption per unit mass adsorbent (Γ_A) as a function of the final pH for five different amounts of added arsenate, concentrations in μm l^{-1} As: 0.667 (□); 1.33 (△); 3.34 (●); 6.67 (■); 13.3 (▲). Concentration of am-Fe(OH)$_3$, 0.0045 g l^{-1}; ionic strength, 0.01; equilibration time, 24 h.

from 8.0 with no added arsenate to 4.7 with 13.3 μm l^{-1} As initial arsenate concentration (Pierce, 1981).

Arsenate also showed an adherence to the Langmuir adsorption isotherm in the concentration range 0.667–13.3 μm l^{-1} As. Plots of C_{equil}/Γ_A vs C_{equil} shown in Figure 6 yield straight lines for each of the eight equilibrium values of pH. Table 2 lists the calculated Langmuir parameter as well as correlation coefficients to a straight line. As with arsenite, the amount of adsorption can be calculated using the Langmuir equation and knowing the pH and equilibrium arsenate concentration.

The adsorption of arsenate per unit mass of iron hydroxide plotted against final pH for five different initial concentrations from 33.4 to 667 μm l^{-1} As is shown in Fig. 7. The amount of arsenate taken up by the adsorbent continually decreases with increasing pH with the higher concentrations showing a greater dependence on pH. At a pH of 4, removals on the order of 35% were found for all five of the initial concentrations similar to arsenite. The eight equilibrium pH values were the same as in the earlier arsenate adsorption studies at the lower concentration range of 0.667–13.3 μm l^{-1} As.

Table 2. Parameters in the Langmuir adsorption equation for arsenate

pH	$\Gamma_{A,max}$ (μm g^{-1})	K_L (μm l^{-1})	Corr. coeff.*
4.0	1530	0.683	0.974
5.0	1100	0.396	0.993
6.0	850	0.309	0.998
7.0	454	0.872	0.989
7.5	344	0.839	0.995
8.0	226	0.719	0.999
9.0	136	0.868	0.998
9.9	482	1.51	0.986

*Correlation to a least-squares approximation of the best straight line through the points in Fig. 6.

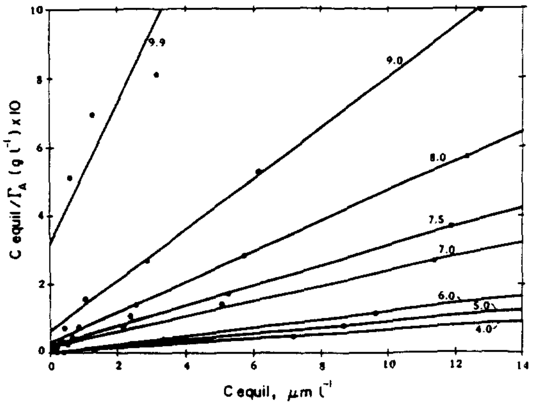

Fig. 6. Equilibrium arsenate concentration (C_{equil}) divided by the amount of arsenite adsorbed per unit mass adsorbent (Γ_A) as a function of the equilibrium arsenate concentration at the various pH values indicated. Initial concentrations of arsenate; 0.667–13.3 μm l^{-1} As; am-Fe(OH)$_3$ concentration, 0.0045 g l^{-1}; equilibration time, 24 h.

Figure 8 shows that the Langmuir equation is not followed in the arsenate initial concentration range of 33.4–667 μm l^{-1} As. A linear isotherm is followed whereupon the amount of arsenate adsorbed (Γ_A) vs

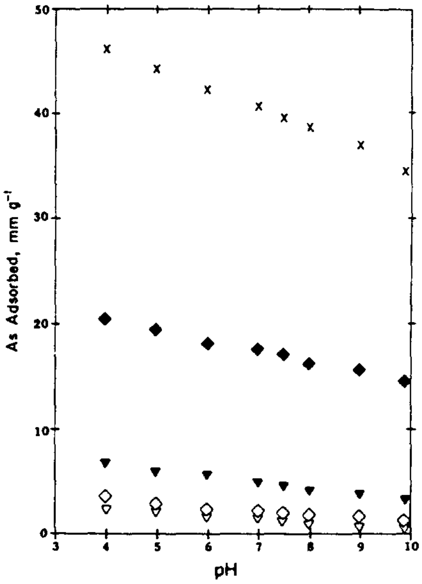

Fig. 7. Arsenate adsorption per unit mass adsorbent (Γ_A) as a function of the final pH for five different amounts of added arsenate, concentrations in μm l^{-1} As: 33.4 (▽); 66.7 (◇); 133 (▼); 334 (◆); 667 (×). Concentration of am-Fe(OH)$_3$, 0.00445 g l^{-1}; ionic strength, 0.01; equilibration time, 24 h.

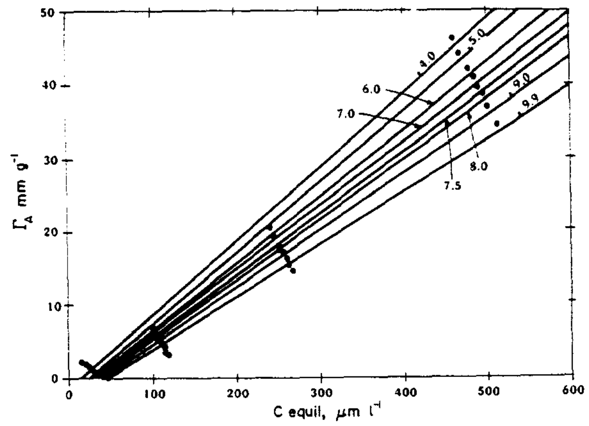

Fig. 8. The amount of arsenate adsorbed per unit mass adsorbent (Γ_A) as a function of the equilibrium arsenate concentration (C_{equil}) at various final pH values indicated on the graph. Initial concentrations of arsenate, 33.4–667 μm l^{-1} As; am-Fe(OH)$_3$ concentration, 0.00445 g l^{-1}; equilibration time, 24 h.

the equilibrium concentration of arsenate in solution (C_{equil}) is a linear relationship. The slopes of the Γ_A vs C_{equil} plots at each pH and correlation coefficients to a straight line can be found in Table 3. Above an equilibrium concentration of 14 μm l^{-1}the amount of adsorption taking place can be calculated knowing the pH and the equilibrium concentration and using the linear isotherm equation. In Fig. 8, the set of points at 66.7 μm l^{-1} As initial concentration are not shown due to some overlap with the points at 33.4 μm l^{-1} As.

CONCLUSIONS

The adsorptive capacity of am-Fe(OH)$_3$ is extremely high for arsenic. Adsorption continued to take place even at the highest concentrations of arsenic studied. Up to 667 μm l^{-1} (50 ppm) As initial concentration of arsenite or arsenate, removals on the order of 35% (at pH 4) were found, which amounted to an adsorption of 50 mm g^{-1} at pH 4. This adsorption is in the linear isotherm region where doubling the initial concentration would approximately double the amount adsorbed. The extremely high adsorptive capacity of amorphous iron hydroxide for arsenic can be explained by visualizing a loose, highly hydrated structure which is permeable to hydrated ions. The ions are free to diffuse throughout the structure and are not restricted to external surface sites such as the case with more crystalline solids.

Anderson *et al.* (1976) studied the adsorption of arsenate on amorphous aluminum hydroxide only up to 1.5 mm g^{-1} of arsenic adsorbed. They found adherence to a Langmuir isotherm at all equilibrium pH's studied. The extents of adsorption as well as the general dependence of adsorption on pH are similar to that found in this study of arsenate up to approx. 1.5 mm g^{-1} of arsenic adsorbed. In the adsorption vs pH plot, the "points" at which the adsorption begins to decrease are not the same as in this study because of the difference in the isoelectric points of am-Fe(OH)$_3$ and am-Al(OH)$_3$.

Competition from adsorption of other ions is important when considering natural aquatic systems or wastewater treatment. Phosphate is known to be very adsorptive on iron and aluminum oxide surfaces and indeed is very close to that or arsenate (Pierce, 1981). Addition of phosphate or sulfate after arsenate or arsenite had been adsorbed, has very little affect on the adsorption of arsenic. A significant effect on the

Table 3. Parameters in the linear adsorption equation for arsenite and arsenate

	Arsenite			Arsenate	
pH	*k*(1000 l g^{-1})	Corr. coeff.*	pH	*k* (1000 l g^{-1})	Corr. coeff.†
4.0	0.116	0.998	4.0	0.101	0.988
5.0	0.107	0.998	5.0	0.097	0.989
5.7	0.101	0.998	6.0	0.092	0.989
6.1	0.093	0.998	7.0	0.087	0.989
7.0	0.084	0.997	7.5	0.085	0.990
8.0	0.073	0.996	8.0	0.083	0.989
8.8	0.065	0.985	9.0	0.079	0.989
9.8	0.050	0.995	9.9	0.073	0.989

*Correlation to a least-squares approximation of the best straight line through the points in Fig. 4.

†Correlation to a least-squares approximation of the best straight line through the points in Fig. 8.

adsorption of arsenic at low concentrations is evident after phosphate or sulfate had already been adsorbed.

In the rates of adsorption experiments, more than 50% of the arsenic was adsorbed before a sample could be taken. Thus, even in fast flowing rivers, a significant amount of arsenic would be adsorbed, as soon as the arsenic species came in contact with the surface of the oxide.

Adsorption of arsenic onto am-Fe(OH)$_3$ generally is inconsistent with a homogeneous surface site model except at very low adsorption density. Up to 0.5 mm g^{-1} As (+3) adsorbed (13.3 μm l^{-1} As initial concentration) at pH 7 and 1.5 mm g^{-1} As (+5) adsorbed (13.3 μm l^{-1} as initial concentration) at pH 4, the data can be fit using a Langmuir isotherm. At greater adsorption densities, the data can be fit using a linear isotherm. The range of surface coverages where the isotherm type changes is well below that at which one would expect site limitation to be important. In none of the experiments studied is there an indication that adsorption density is approaching a maximum, limiting value.

A heterogeneous site model for the surface of am-Fe(OH)$_3$ is conceptually consistent with all the observations. Many adsorption studies of oxide surfaces presently available include the assumption that all surface sites are equivalent. Thus it is important to perform model experiments over wide ranges of concentration of adsorbate and adsorbent in order to predict the removal of ions in natural systems accurately.

Based on the experimental results of this work, the following conditions are necessary for maximum arsenic removal. Amorphous hydroxides with a high isoelectric point such as am-Fe(OH)$_3$ or am-Al(OH)$_3$ are extremely efficient adsorbers. The oxidation state of the arsenic species is another important factor with the +5 oxidation state adsorbing to a greater extent than the +3 oxidation state at concentrations normally found in natural water. One of the most critical parameters is the solution pH. At concentrations normally found in natural waters, a pH of 7 is optimum for arsenite and a pH of 4 is optimum for arsenate.

This study not only identifies the ideal conditions necessary for maximum removal of arsenic in aqueous systems but also helps to explain the differences in the adsorption dependence on pH.

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REFERENCES

Anderson M. A., Ferguson J. F. & Gavis J. (1976) Arsenate adsorption on amorphous aluminum hydroxide. *J. Colloid Interface Sci.* **54**, 391–399.

Benjamin M. M. & Leckie J. O. (1981) Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide. *J. Colloid Interface Sci.* **79**, 209–221.

Braman R. S. and Foreback C. C. (1973) Methylated forms of arsenic in the environment. *Science* **182**, 1247–1249.

Chau Y. K. & Wong P. T. S. (1978) Occurrence of biological methylation of elements in the environment. *Am. Chem. Soc. Symp. Ser.* **92**, 39–53.

Davis J. A., James R. O. & Leckie J. O. (1978) Surface ionization and complexation at the oxide/water interface. *J. Colloid Interface Sci.* **63**, 480–499.

Ferguson J. F. & Anderson M. A. (1974) Chemical form of arsenic in water supplies and their removal. In *Chemistry of Water Supply, Treatment, and Distribution* (Edited by Rubin, A. J.), pp. 137–158. Ann Arbor Science, Ann Arbor, MI.

Ferguson J. F. & Gavis J. (1972) A review of the arsenic cycle in natural waters. *Wat Res.* **6**, 1259–1274.

Gulens J., Champ D. R. & Jackson R. E. (1979) Influence of redox environments on the mobility of arsenic in ground water. *Am. Chem. Soc. Symp. Ser.* **83**, 81–95.

Gupta S. K. & Chen K. Y. (1978) Arsenic removal by adsorption. *J. Wat. Pollut. Control Fed.* **50**, 493–506.

Holm T. R., Anderson M. A., Iverson D. G. & Stanforth R. S. (1979) Heterogeneous of arsenic in aquatic systems. *Am. Chem. Soc. Symp. Ser.* **93**, 711–736.

Jenne E. A. (1968) Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. *Am. Chem. Soc. Adv. Chem. Ser.* **73**, 337–387.

Pierce M. L. (1981) Chemical modeling of arsenic in aqueous systems. Ph.D. Dissertation, Arizona State University.

Pierce M. L. & Moore C. B. (1980) Adsorption of arsenite on amorphous iron hydroxide from dilute aqueous solution. *Envir. Sci. Technol.* **14**, 214–216.