ARSENIC ADSORPTION FROM GEOTHERMAL BORE WATER: THEORY AND PRACTICE

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SUMMARY

Arsenic adsorption onto hydrous iron oxide **(HFO)** is viewed as a viable option for the removal of arsenic from geothermal bore waters. On the basis of published experimental data and model predictions using MINTEQM, complete arsenic removal may be expected under optimum pH and HFO concentrations. However, previous studies of arsenic in natural freshwater and saline waters have indicated an often large discrepancy between observed and theoretically predicted arsenic behaviour; a discrepancy which also occurs in geothermal bore waters. Experimental adsorption of both As^{III} and As^V from the bore water of Wairakei Flashplant 10 showed that, while both As^{III} and As^V were rapidly adsorbed onto HFO, only As^V at pH < 5 approached the 90% adsorption predicted by MINTEQA2. At pH < 9, As^{III} adsorption was consistently < 50% of the predicted value, while **As"** adsorption ranged from 33-95% of the predicted adsorption. It is tentatively concluded that theoretically calculated As adsorption fails to correctly account for either the changes in HFO surface potential and/or bonding site competition which arises through the adsorption of major ions, or for the effect of dissolved arsenic complex formation.

INTRODUCTION

Bore water discharge from the Wairakei Geothermal field routinely carries arsenic concentrations of ca. 4 mg/kg. This bore water is discharged into the Waikato River and, at a time when international limits for arsenic concentrations in drinking water are being steadily lowered (eg., WHO, 1993), arsenic removal prior to discharge is desirable. Arsenic removal by adsorption onto hydrous iron oxide (HFO) is an option which has previously been investigated in field trials by Buisson et al (1979) and Finlayson & Webster (1989) and is currently being re-examined. As part of this project, ESR was requested to undertake an experimental study of the oxidation and adsorption rates of arsenic in Wairakei bore effluent. This provided an opportunity to compare theoretically-predicted with observed arsenic adsorption behaviour in an arsenic-rich system.

In theory, many aspects of arsenic chemistry and adsorption characteristics are relatively straightforward. In most natural aqueous systems, arsenic occurs predominantly in either an As^{III} or As^V oxidation state and, with the exception of an uncharged As^{III} species $(H_3AsO_3^0)$, as negatively charged ion species $(H_2AsO_3^-, H_2AsO_4^-, HAsO_4^{-2})$. The oxidation of **As"** to As^V is slow in near-neutral pH waters unless catalyzed by bacteria, but the adsorption chemistry of both oxidation states is similar (eg., Pierce & Moore, 1982). Both As^{III} and **As"** are readily adsorbed onto hydrous oxides in natural waters and, as anions, adsorb more readily at acid pH. Arsenic can therefore be preferentially removed from effluents by adsorption under conditions which do not favour the adsorption of other metals, such as copper, lead and zinc, which occur as cationic species in natural waters.

The *MINTEQM* computer program (Allison et al., 1991) is one of the few chemical speciation models to include adsorption processes, and can be used to theoretically predict the degree of metal adsorption in natural systems. However, recent studies of arsenic partitioning between sediments and solution in New Zealand freshwaters and estuaries by the authors have demonstrated significant discrepancies between observed and theoretically predicted arsenic adsorption. Analytical results indicate that arsenic is occurring predominantly in dissolved forms, while theoretical predictions using MINTEQA2 suggest that, at near-neutral pH, most of the arsenic should be bound in the HFO-bearing particulate phase.

This paper reports the results of the recent experiments designed to test **As"** and As^V adsorption from bore water onto HFO. The results are compared with the degree of arsenic adsorption predicted using MINTEQA2, highlighting some of the problems which can occur when trying to reconcile observed and theoretically predicted arsenic behaviour.

2. METHODS

2.1 Sample collection and analytical method

Six litres of bore water were collected from Flashplant 10 in February 1994. Three litres were collected into normal polyethylene sampling bottles to be used for experiments requiring As^V. Three litres were collected into air tight glass sampling bottles, excluding air and minimising air contact with the sample, for use in experiments requiring As^{III}. Bore water contained in the glass bottles was analyzed
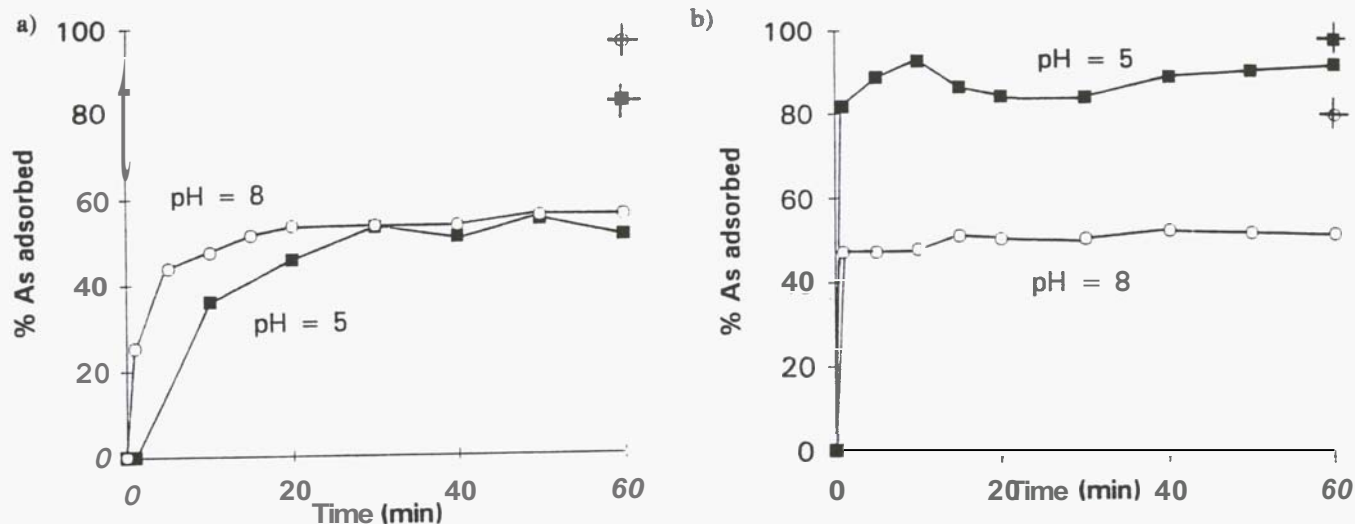
Figure 1. Experimental As^{III} (a) and As^V (b) adsorption onto amorphous HFO at pH = 5 and 8. Initial **As** concentrations were As^{III}: 3.74 mg/kg at pH = **5**, 3.57 mg/kg at pH = 8, and **As":** 3.88 mg/kg at pH = **5** and **3.11mg/kg** at pH = 8. The concentration of HFO = **1** x 10^{-3}m. Arsenic adsorption predicted hy MINTEQAZ is also shown as ┿ & ┿ .

immediately upon opening for both total arsenic and As'': total **As** concentrations ranged from **3.5** - 4.5 mg/kg **As,** of which more than **90%** was **As'''.** Bore water to be used in experiments requiring arsenic **as** As^V was oxidised by the addition of **2.5** ml **30%** H_2O_2 per 500 **mls** bore water, 7 days before use. For experiments using As^V, samples were analyzed for total inorganic arsenic. Samples were pre-reduced using KI and HCl then analyzed by hydride-generation atomic adsorption spectrophotometry **(HGAAS) ,** using a reaction vessel and reagents similar to those used by Aggett and Aspell **(1976)** to generate arsine gas (AsH_3). The gas passed through an electrically heated quartz **tube,** instead of a flame, placed in the optical path of the lamp.

For As'' analysis, the sample was not pre-reduced but was instead analyzed in a citrate buffer (pH = 6), **so** that only As^{III} reacted to form arsine gas. As'' concentrations were determined by difference. In the latter stages of the study, total **As** and As^{III} concentrations were determined using a continuous **flow** hydride generation system, with **a** flame-heated quartz tube.

2.2 Experimental methods

In a 500 ml round bottomed flask, a solution containing 0.202g $Fe(NO_3)_3.9H_2O$ was acidified with HNO, to pH **ca.** 2. The pH was then slowly raised to **7,** by the addition of 1m NaOH, to precipitate amorphous **HFO** at a concentration of **1** x 10^{-3}m. The precipitate was allowed to age and settle overnight, before removing the overlying solution from the **flask** and refilling the flask with the bore water.

Initially adsorption experiments were **run** for up to **60** minutes to determine the time taken to attain equilibrium between adsorbed and dissolved arsenic species. Separate **runs** were made at pH = 5 and pH = 8 **(see** Figure **1).**

In addition to the **runs** in which pH was controlled, two

further experiments were undertaken to show the relationship between arsenic adsorption and pH **(see** Figure 2). From a starting point of high pH **(9.1** for As^V and 11.9 for As'''), pH was gradually lowered with consecutive additions of HNO,. After each addition the solution was allowed **30** minutes to re-equilibrate with the oxide before the next aliquot **was** extracted for analysis.

In all experiments, the 10 **ml** aliquots extracted from the bulk solution were immediately filtered through a **0.45** μm Millipore filter to remove any particulate iron, and were analyzed for arsenic. The bore water **used** to test As^{III} adsorption was re-analyzed for total arsenic at the **end** of the experiment to confirm that oxidation to As^V had not occurred.

3. RESULTS

3.1 As''' and As^V adsorption rates

The results of the As'' adsorption rate experiments are shown in Figure 1a. At both pH = 5 and 8, As''' was adsorbed quickly but incompletely. At pH = **5,** As^{III} adsorption increased to **36%** in the first **10** minutes, settling at **50%** after **30** minutes. There appeared to be no further adsorption **as** the solution still **contained 1.85** mg/kg arsenic after 1 hour in contact with amorphous Fe oxide. At pH = 8, As^{III} adsorption increased to **44%** in **5** minutes and to **53%** after **20** minutes. Again there appeared to be a no further adsorption, with **1.59** mg/kg arsenic remaining in solution after 1 hour.

The results of the As^V adsorption rate experiments are shown in Figure 1b. At pH = **5** and **8** As'' was, like **As''',** adsorbed very quickly. **A** sample taken after only one minute of contact with the oxide showed that 47% of As^V at pH = 8 and 89% of As^V at pH = **5** had **been** adsorbed. At both pH = **5** and 8, As^V concentrations in solution
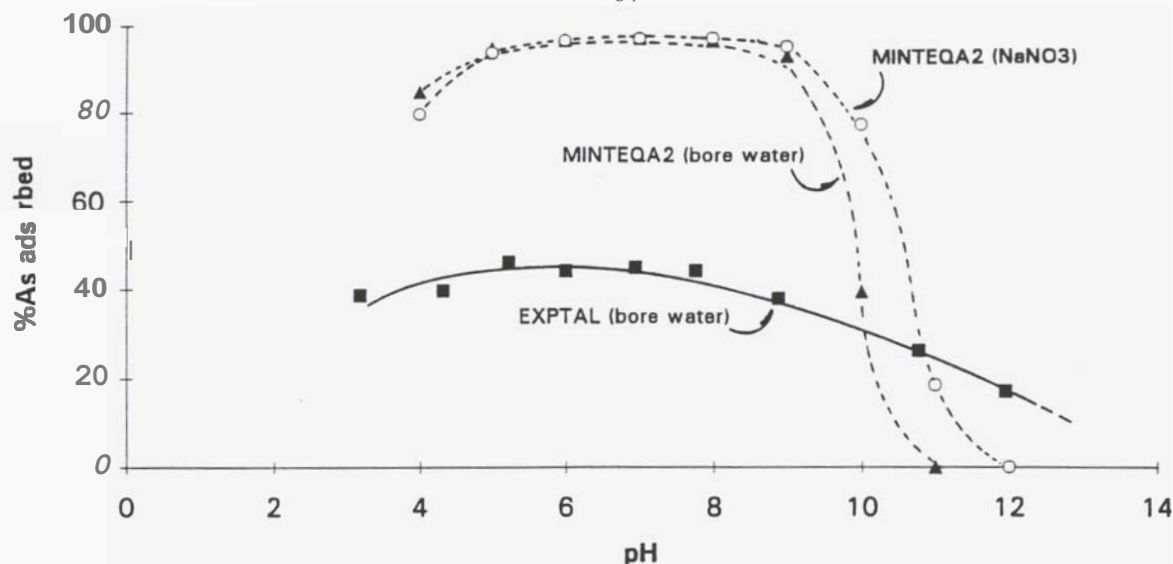
Figure 2.   As^{III} adsorption on HFO as function of pH in bore waters, as determined experimentally and as predicted by MINTEQA2. The adsorption of As^{III} from 0.1m NaNO$_3$ as predicted by MINTEQA2 is also shown. Initial As^V concentrations = 2.40 mg/kg and HFO concentrations = 1 x 10^{-3}m.
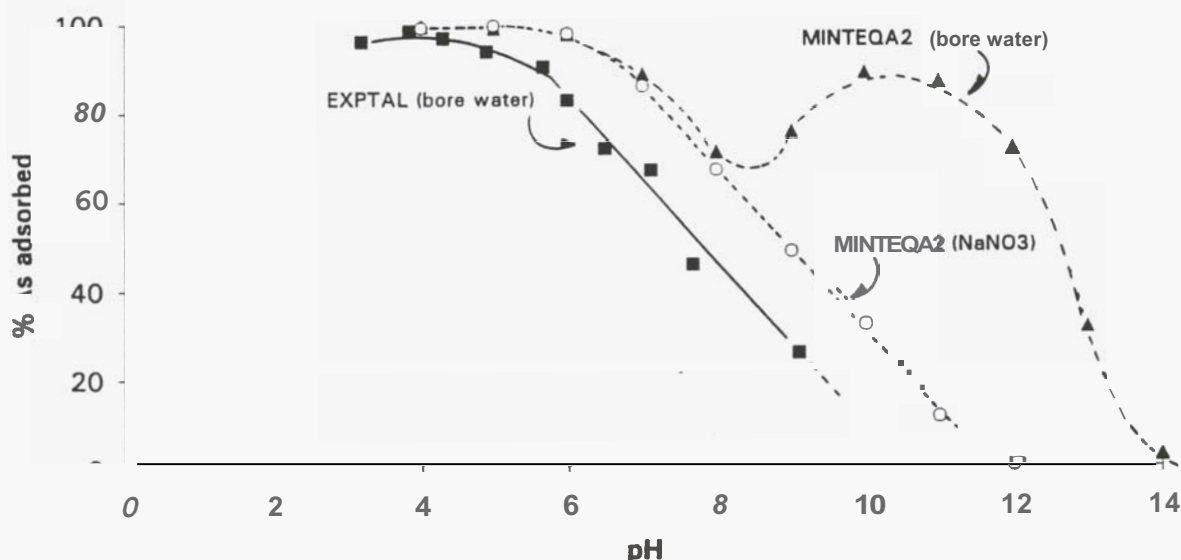

Figure 3.   As^V adsorption on HFO as function of pH in bore waters, as determined experimentally and as predicted by MINTEQA2. The adsorption of As^V from 0.1m NaNO, as predicted by MINTEQA2 is also shown. Initial As^V concentrations = 3.73 mg/kg and HFO concentrations = 1 x 10^{-3}m.

remained mainly unchanged after the first minute, although small fluctuations were observed with time for As^V adsorption at pH = 5. As^V concentrations vary between 0.23 mg/kg and 0.57 mg/kg over the period 1 minute to 1 hour, perhaps oscillating as equilibrium between the dissolved and adsorbed As^V is established.

3.2 As^{III} and As^V adsorption as a function of pH

The results of As^{III} adsorption from bore water onto HFO, as a function of pH, are shown in Figure 2, identifying optimum conditions for adsorption between pH = 4 and 8. At pH > 8, As^V adsorption decreases from ca. 45% to 17% at pH = 12 and, by extrapolation, to 0% at or near pH = 14.

The results of As^V adsorption as a function of pH are shown in Figure 3, demonstrating a similar but more exaggerated trend. Optimum conditions for As^V adsorption are between pH = 3 and 5.5, limited at low pH by the stability of HFO which dissolves at pH < 3. As^V adsorption shows a linear decrease from > 90% at pH = 5.5, to 25% at pH = 9. If the trend continues above pH = 9, 0 % adsorption might be expected at pH = 11.

These results confirm those of the previous adsorption rate experiments in which a high degree of arsenic adsorption was observed only for As^V at pH = 5. Although As^V adsorption occurs more rapidly and to a greater degree than As^V under optimum pH conditions, these pH conditions evidently occur over a narrow range. Therefore, for arsenic removal from bore water, to maintain any advantage gained by oxidising arsenic to As^V, prior to removal by adsorption onto HFO, the pH of adsorption would need to be maintained at pH < 7.

4. DISCUSSION

In Figures 1 - 3 reporting experimentally determined arsenic adsorption, the degree of arsenic adsorption predicted using MINTEQAZ is also shown. With the exception of As^V adsorption at low pH, MINTEQA2 predicts higher arsenic adsorption than observed. Neither previous experimental studies (eg., Leckie et al., 1980) nor MINTEQA2 calculations support the possible argument that the incomplete adsorption of arsenic is due to a shortage of available binding sites on the HFO, i.e., that the adsorption capacity of HFO has been exceeded. Furthermore, this difference has been repeatedly noted during the authors' previous attempts to model arsenic behaviour in freshwater and estuarine systems, where HFO is often readily available in excess of the amount required to adsorb the low levels of metals present.

To begin to solve this problem, the way in which MINTEQAZ calculates arsenic adsorption must be more closely examined.

4.1 Modelling arsenic adsorption

As previously discussed, As^{III} and As^V exist predominantly as uncharged or negatively charged ions in solution. As'' occurs as H_3AsO_3 (arsenious acid) which dissociates at pH = 9.3 to form $H_2AsO_3^-$. As^V occurs as $H_2AsO_4^-$ which dissociates at pH = 6.9 to form $HAsO_4^{-2}$, which further dissociates to form AsO_4^{-3} at pH = 11.5. Each of the negatively charged arsenic species can potentially bind to the HFO surface if the surface maintains a positive charge. In most freshwaters, the surface of HFO has a positive charge at pH < 7.

Experimental studies of arsenic adsorption from 0.01 and 0.1m NaNO, onto HFO by Pierce & Moore (1982) and Leckie et al. (1980) have been used by Dzombak & Morell (1990) to derive the data which is used as the database for MINTEQA2. Dzombak and Morell (1990) list, and give surface complexation constants for, the following reactions which govern arsenic adsorption at the HFO surface (represented here as $\equiv FeOH°$):

For As^{III} ...

$$\equiv FeOH° + H_3AsO_3° = \equiv FeH_2AsO_3° + H_2O \qquad (1)$$

For As^V ..

$$\equiv FeOH° + H_3AsO_4° = \equiv FeH_2AsO_4° + H_2O \qquad (2)$$

$$\equiv FeOH° + H_2AsO_4^- = \equiv FeHAsO_4^- + H_2O \qquad (3)$$

$$\equiv FeOH° + HAsO_4^{-2} = \equiv FeAsO_4^{-2} + H_2O \qquad (4)$$

$$\equiv FeOH° + AsO_4^{-3} = \equiv FeOHAsO_4^{-3} \qquad (5)$$

MINTEQA2 partitions arsenic between these HFO-bound and dissolved arsenic species on the basis of surface-complex and complex equilibrium constants, using the HFO-bound species to derive the total proportion of adsorbed arsenic. The activity of individual HFO-bound arsenic species in 0.1m NaNO, is shown in Figure 4 as a function of pH. Because neither Na or NO, ions affect arsenic adsorption, this can be considered to represent arsenic adsorption in the absence of interfering ions. The presence of other ions can adversely affect arsenic adsorption in at least three ways: by complexing arsenic in solution, hy competing for binding sites on HFO, and by altering the surface charge of the HFO. In bore waters of the Wairakei geothermal field, Ca appears to be the only ion which can affect arsenic adsorption in this way. Comparing the predicted curves for arsenic adsorption from a typical bore water (composition = Wairakei drill hole 24; Ellis & Mahon (1977)) and 0.1m NaNO, shown in Figure 2 & 3, suggests that:

(a) Although SO, adsorption appears to adversely affect As'" adsorption at low pH (see Figure 2), SO, concentrations are too low in the bore water for this to be a major affect.

(b) Ca adsorption should increase As^V adsorption at pH > 8.

As shown in Figure 4, the predominant surface As^V species at pH > 6 is $\equiv FeOHAsO_4^{-3}$, and it is the formation of this species which is enhanced by the eo-adsorption of Ca. Ca adsorption alters HFO surface potential, creating a more positively charged surface to bind arsenic ions. As^{III} adsorption, on the other hand, does not appear to increase in the presence of Ca adsorbed onto the HFO surface.

4.2 Theory and practice

Evidently, although MINTEQA2 does allow for the effect of eo-adsorption of SO, and Ca on As^{III} and As^V adsorption respectively, the difference between observed and predicted adsorption shown in Figures 1 - 3, remains a problem. Either this difference is due to co-adsorption of Ca and SO,, but is incorrectly modelled, or is due to some other factors inherent in natural systems which are not correctly taken into account by MINTEQA2. For example, are the data used in the arsenic database of MINTEQA2 appropriate for application to natural systems? Are there strong complexes of arsenic which are not considered? Arsenic can form covalent bonds with carbon, creating a variety of stable organic compounds and complexes, such as dimethyl arsenic. These species are not included in the MINTEQA2 database, but are also unlikely to be of importance in bore waters. Thiocomplexes of As^{III} can occur in sulphide-bearing fluids such as the bore waters, although relative high sulphide concentrations would be required before $H_3AsO_3°$ would cease to be the predominant arsenic species for the pH conditions of interest (Webster, 1990).

Further study will be required to identify the reason for the high degree of arsenic adsorption predicted by MINTEQA2, so that the model can be modified to more accurately predict arsenic behaviour. Particular attention should be paid to the effects of Ca co-adsorption on arsenic adsorption and to reanalysing the database used by MINTEQA2 to calculate arsenic speciation.
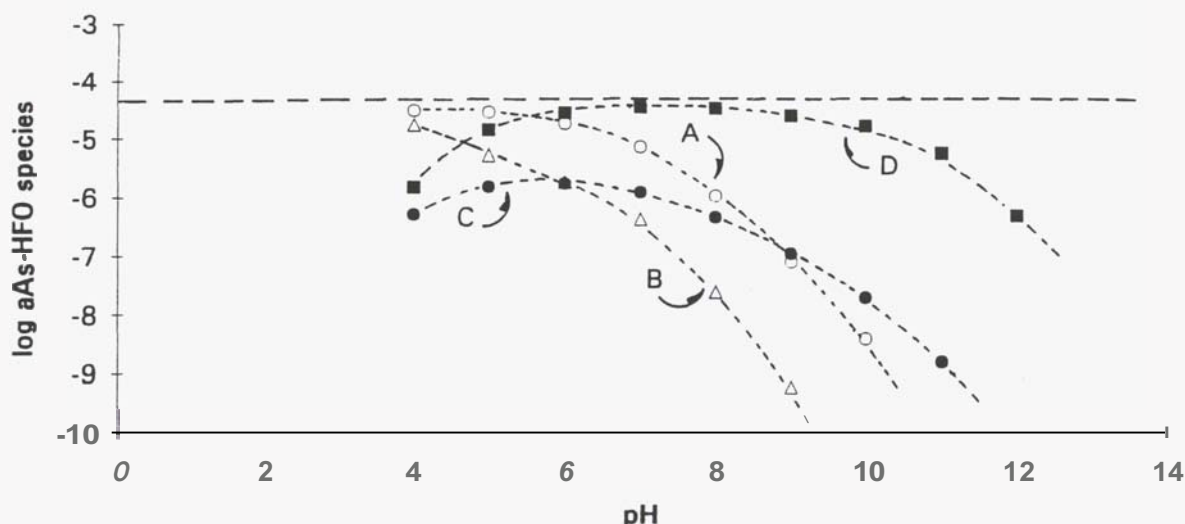
Figure **4.**   **The** log activity of As^V species **bound** at the HFO surface, **as** a function of pH in **0.**$1m$ $NaNO_$. A = $\equiv FeHAsO_4^{\cdot}$, B = $\equiv FeH_2AsO_4^{\circ}$, C = $\equiv FeAsO_4^{\cdot2}$ and D = $\equiv FeOHAsO_4^{\cdot3}$. The horizontal dashed line represents log activity of total arsenic.

5. CONCLUSIONS

(a) Both As^{III} and As^V are rapidly adsorbed onto HFO at $pH = 5$ and $pH = 8$, and equilibrium conditions appear to be established in less than **30** minutes. Adsorption is, however, incomplete at ca. 50% of the initial arsenic concentration for all except As^V adsorption at $pH = 5$.

(b) The degree of **As"** and As^V adsorption onto HFO decreases with increasing pH **as** expected for anion adsorption. Optimum conditions for **As"** adsorption are at a pH of between 3 and **9 (40 - 50%** adsorption) and for As^V are pH between 3 and **6** (80 - 100 % adsorption).

(c) Theoretical predictions made using MINTEQA2 significantly overestimate the degree of arsenic adsorption, particularly for **As^{III},** and for As^V at pH >8. This discrepancy has also been noted when modelling arsenic adsorption in freshwater and estuarine systems. It appears to be due to an error in the model predictions rather than in the analytical techniques used to determine, and to distinguish between, dissolved and particulate arsenic.

(d) It is tentatively concluded that the MINTEQA2 model is incorrectly assessing the effect of other ions on arsenic adsorption. Further study is required to identify the exact nature of this problem so that, if necessary, MINTEQAZ can be modified to more accurately predict particulate/ solution equilibria for arsenic in natural aquatic systems.

6. ACKNOWLEDGEMENTS

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