Arsenite and Arsenate Adsorption on Hydrous Ceric Oxide and H+/OH- Release Stoichiometry
Abstract: Arsenite and Arsenate Adsorption on Hydrous Ceric Oxide and H+/OH- Release Stoichiometry.

Arsenite [As(III)] and arsenate [As(V)] are highly toxic inorganic arsenic species that represent a potential threat to the environment and human health. This study is to determine how the arsenic removal and how the H⁺/OH⁻ release amount is changed when arsenic species is adsorbed on the hydrous ceric oxide. Under initial concentration of 200 mg/L arsenic, the experiments were conducted with 2 g/L hydrous ceric oxide prepared in a 0.01M NaNO₃ solution and at pH 4 and 9, respectively. The experiments lasted for 6 hours and the solutions reached an equilibrium within 2 hours for arsenite and after 4 hours for arsenate, respectively. The removal rate was overall greater for arsenite than for arsenate, and arsenite showed a greater reduction at pH 9 whereas arsenate showed a greater reduction at pH 4. The total removal quantity was as high as 80 mg/g for arsenite and 50 mg/g for arsenate. The adsorption process followed a pseudo-second order kinetic model, where the model fitted arsenite better than it fitted arsenate. A particulate inner diffusion model is adopted to find out the limiting factors. The pH was measured during the study and the data was used to calculate the H⁺/OH⁻ release. Arsenate adsorption resulted in the release of OH⁻ at pH 4 and 9, while arsenite adsorption resulted in the release of OH⁻ at first and then started to release H⁺. With continuous adsorption, a main trend is that the OH⁻ release rate (mole OH⁻ release per mole As adsorbed) decreases and for arsenite the H⁺ release rate is increased with time. The result of this study indicate the bonding mechanism of As adsorption on hydrous ceric oxide at pH 4 and 9, however more work is needed to obtain valid evidence of these mechanisms.

Key words: Arsenic removal, adsorption, hydrous ceric oxide, H⁺/OH⁻ release.
1 Introduction

Arsenic is a natural part of the earth’s environment, but the concentration in the groundwater is increasing due to anthropogenic activity such as mining, pesticides and burning of fossil fuels (M L Pierce, 1982). There are two common inorganic arsenic species in natural waters; arsenite [As(III)] and arsenate [As(V)]. Both species are highly toxic and represent a potential threat to the environment and human health. About 14.6 million people in China are exposed to arsenic contaminated drinking water with a concentration higher than 0.03 mg l\(^{-1}\) (Zhang, 2003), which is greater than the level of 0.01 mg l\(^{-1}\) adopted by WHO, the European Union and the United States (Dutta, 2004; Zhang, 2003). Long term exposure of contaminated drinking water containing arsenic can lead to several diseases such as cerebrovascular disease and several forms of cancer (Zhang et al., 2005). Therefore it is of great importance to develop an effective technology to treat arsenic contaminated drinking water to a low cost.

There are two common ways of separating arsenic from water and those are coagulation and adsorption. Adsorption is however a more promising method because it is more efficient, is easy to handle and is possible to regenerate (Y Zhang, 2003; Y Zhang, 2005). Reports state that hydrous oxides of rare earth elements have a high affinity for adsorbing hazardous anions like arsenite and arsenate. They have a relatively strong basicity and a small ionic potential and they can therefore dissociate OH-groups into hydroxyl ions. Hydrous ceric oxide has been proved to have a strong affinity for both arsenite and arsenate (Y Zhang, 2005).

A study was made to investigate the adsorption mechanism of arsenite and arsenate on hydrous ceric oxides. The study was also to try to understand the H\(^+\)/OH\(^-\) Release Stoichiometry

2 Methods and material

2.1 Material

Following reagents were used in the experiments: hydros ceric oxide powder, 0.01 M NaNO\(_3\), HCl (0.1 M, 0.05 M, 0.025 M, concentrated), NaOH (0.5M, 0.025M, 0.01M, concentrated), 20 g/L As (III) solution, 17.5 g/L AS(V) solution 10.0 ml/L standard As(III) solution, 5% thiourea, 3% ascorbic acid and 10% potassium borohydride.

2.2 Preparing the samples

0.2 g of hydrous ceric oxide was scaled and mixed with 50 mL of 0.01 M NaNO\(_3\) in a 200 mL plastic bottle. The prepared samples were then set in a rocking incubator at 25 °C, 150 rpm for about 12 hours. Two samples was prepared for every species, one for each pH-value.
2.3 Titration
Before adding the arsenic specie the pH was changed to 4 or 9 with NaOH and the amount of base was recorded. This was done with an atomic titration device, Titroline Easy, Schott Instruments. 100 mL of the arsenic [As(III) or As(V)] solution was then added at a recorded time and after 5 minutes the pH was yet again changed to pH 4 or 9. The amount of reagent added was recorded, as was the pH before and after the titration. A 250 μL sample of the arsenic solution was taken and filtrated with a 0.45 μm membrane. The supernate was then put in a testtube that was filled up with ionized water to 50 mL (diluting it 200 times). The procedure was then redone after 15, 20, 40, 60, 120, 180, 240, 300 and 360 minutes resulting in a data range of 10 measures points over 6 hours for each As-specie at pH 4 and 9.

2.4 Analyzing the As-samples
The arsenic amount in the samples taken during titration was determined with Atomic Fluorescence Spectrometer (AFS). The determination was done according to the instrument instructions.

3 Results and discussion

3.1 As adsorption at pH 4 and 9
In figures 1 and 2 the amount of arsenite and arsenate adsorbed (per cent of start amount) is displayed over the experiment time of six hours. For arsenite (Figure 1) the result shows a greater removal at pH 9 then at pH 4 and it reaches an equilibrium after 2 hours. The removal rate is a bit slower at pH 4 and it does not reach the same removal percentage as for pH 9. In the case of arsenate (Figure 2) the removal is not equally efficient and the removal rate is much slower. Arsenate showed greater removal at pH 4 which confirms the findings of Amita, J. et. al. (1999) and others. The adsorption of arsenate reach an equilibrium after about four hours. The total amount of arsenic adsorbed is presented in Figure 3.

The difference in adsorption between arsenite and arsenate can probably be explained with the fact that have different adsorption mechanisms, which will be discussed later.
3.2 Kinetic model

The adsorption follows a pseudo-second order reaction as shown in figures 4 and 5.

First and second order kinetic functions is not always suitable for solid-fluide adsorption, so a pseudo-first, or second, order kinetic function is adopted. The data did not fit a pseudo-first order
kinetic model (se appendix) so a pseudo-second order kinetic model was applied with success. The pseudo-second order kinetic function is:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad \text{Eq. 1.}$$

where $q_e$ and $q_t$ is the amount of arsenate and arsenite adsorbed (mg g$^{-1}$) at the equilibrium time and time $t$ (min), respectively, and $k_2$ is a rate constant of adsorption (min$^{-1}$). With the knowledge that $t=0$, $q_t=0$ and $t=t$, $q_e = q_t$, it’s possible to rewrite the equation as follows, which was the equation used to produce the figures:

$$t = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Eq. 2.}$$

The $k_2$-value was calculated from the trend lines in figures 4 and 5 resulting in four $k_2$-values presented in Table 1.

<table>
<thead>
<tr>
<th>pH</th>
<th>$k_2$-value for pseudo-second order kinetic model of arsenate and arsenite adsorption at pH 4 and 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>As(V)</td>
</tr>
<tr>
<td></td>
<td>q_e=0.001037</td>
</tr>
<tr>
<td>9</td>
<td>q_e=5.77E-04</td>
</tr>
<tr>
<td>4</td>
<td>As(III)</td>
</tr>
<tr>
<td></td>
<td>pH=9 q_e=9.72E-04</td>
</tr>
<tr>
<td></td>
<td>pH=9 q_e=0.0034</td>
</tr>
</tbody>
</table>

### 3.3 Release of OH$^-$ / H$^+$

When arsenic is adsorbed OH$^-$ and H$^+$ is released. The amount released during the experiment is shown in figure 6 and 7.

In figure 6 adsorption of arsenite is shown and one can see that the level of OH$^-$ in the solution is decreased at pH 4 and is stable at pH 9. The decrease of OH$^-$ is due to the release of H$^+$ and this is an
indication on how arsenite the adsorption mechanism works. In the beginning of the experiment it was a release of OH\(^-\) which increased the pH. Then is changed to a release of H\(^+\) which lowered the pH again. It’s difficult to say exactly what caused this change in release and further studied is needed to do so, but it present an indication on how arsenite is adsorbed.

The release of OH\(^-\) and H\(^+\) when arsenate is adsorbed is presented in figure 7 and at pH 4 there is an obvious release of OH\(^-\). Similar to arsenite the release at pH 9 is stable throughout the experiment.

![Figure 8](image1.png)  
**Figure 8.** Total release amount of OH\(^-\) after 6 hours at pH 4 and 9 in 10\(^{-5}\) mol/L

![Figure 9](image2.png)  
**Figure 9.** Total release amount of H\(^+\) after 6 hours at pH 4 and 9 in 10\(^{-5}\) mol/L

After six hours of experiment the total amount of released OH\(^-\) and H\(^+\) was calculated and the result is presented in figures 8 and 9. They show the big release of OH\(^-\) when arsenate is adsorbed and the somewhat outstanding release of H\(^+\) that occurs when arsenite is adsorbed.
4 Conclusions

This study have contributed to the understanding of the complex adsorption of arsenic. It have provided more evidence that hydrous ceric oxide is a good arsenic adsorbant and that it is of great importance to continue the research on this substance. The finding that arsenate is better adsorbed at pH 4 and arsenite is better adsorbed at pH 9 is of usefull help to improve the effictveness of adsorption. This study also found that the adsorption isotherms of both arsenic species fit well the pseudo-second order kinetic model. The OH release was greater for arsenate and the H’ release was greater for arsenite. These findings can help to map the release stoichiometry. But futher studies is needed and other methods need to be used to get a full picture of the mechanisms of arsenic adsorption.
5 References


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