MODELING ARSENIC(V) REMOVAL BY COAGULATION WITH FERRIC SALTS: EFFECTS OF pH AND DOSAGE

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ABSTRACT

In 2001 the U.S. Environmental Protection Agency (EPA) lowered the Maximum Contaminant Level for arsenic from 50 µg/L to 10 µg/L. Public water suppliers are required to comply with the lower standard by January of 2006 and several thousand water systems nationally are looking for efficient and inexpensive ways to remove arsenic. Ferric coagulation/filtration and ferric coagulation/microfiltration are two promising techniques for attaining the new arsenic water standard. Both processes remove arsenic by sorption to ferric hydroxides (and possibly co-precipitation as well). Models of arsenic removal by sorption to ferric hydroxide have been developed, but conflicting information has been given to practitioners about the relative importance of pH and iron dosage. Edwards (1994) modeled arsenic removal using an equilibrium chemistry approach and reported that pH effects were more important than coagulant dosage. However, a subsequent empirical approach (McNeill and Edwards 1997) ignored pH and initial arsenic concentration entirely and modeled removal percentage as depending on dose alone. While the more recent empirical approach has the advantage of being validated by observations at actual water treatment plants, understanding the equilibrium chemistry may help to define boundaries for the acceptable use of the empirical approach. In this study, the equilibrium chemistry approach of Edwards (1994) is followed and a model of arsenic(V) removal by ferric coagulation developed. This model runs in Microsoft Excel and is available free of charge upon request. Charts of arsenic removal as a function of pH, dosage, and ionic strength are developed to assist with the selection of appropriate initial conditions for pilot studies. Increasing ionic strength is found to modestly decrease arsenic removal. Above pH 8, arsenic removal is found to decrease rapidly with increasing pH. However, removals are relatively insensitive to changes in pH below pH 8. Similarly, at low coagulant doses, arsenic removal increases rapidly with increasing iron concentrations. However, further increases in dose produce diminishing additional removal. In the absence of competing anions, there is little benefit to increases in dose beyond 5 mg/L as iron. Initial arsenic concentration has little effect on removal percentage until initial concentrations exceed 200 µg/L, at which point the percentage removal decreases as initial arsenic concentration increases. This research indicates that equilibrium chemistry modeling generally supports the omission of pH and initial arsenic concentration from the empirical model of McNeill and Edwards (1997), but only if the pH is below 8 and the initial arsenic concentration is below 200 µg/l.
INTRODUCTION

Arsenic is a substance found in groundwater in both +3 and +5 oxidation states. If taken in sufficient quantities, arsenic can pose a threat to human health. Therefore, the Environmental Protection Agency (EPA) has set a drinking water standard or Maximum Contaminant Level (MCL) for arsenic. Previously the MCL for arsenic was set at 50 µg/L, but in 2001 it was lowered to 10 µg/L. The new standard will be enforced starting in January 2006. Public water suppliers, in order to comply, must look for efficient and inexpensive technologies available in the market to achieve the desired levels of arsenic concentration. The new standard has also put to work environmental researchers in an effort to develop improved processes to achieve the desired arsenic concentrations. Two of the most promising techniques in lowering arsenic concentrations are achieved by using ferric salts in processes known as ferric coagulation/filtration and ferric coagulation/microfiltration. Coagulation is achieved by adding ferric salts, such as ferric chloride to the contaminated water. The arsenic will then be adsorbed onto the surface of the ferric hydroxide that is formed. The ferric hydroxide, along with the adsorbed arsenic is then removed through filtration or micro-filtration. One advantage in using micro-filtration is that the size of the ferric hydroxide particles needs to be only slightly larger than the pore size of the micro-filter (which is 0.1-0.2 µm), as opposed to conventional filtration, which requires a larger size of particles.

PREVIOUS RESEARCH

While coagulation followed by filtration has proven successful for removing arsenic from water, there is still much research needed on how to optimize this process, such as determining the exact dose of iron to use and the optimum pH to set in order to achieve a specific arsenic concentration. Optimizing the process will not only save money for the water supplier, but it will also result in the production of less ferric hydroxide waste. In order to optimize the process it is helpful to have a mathematical model of the process that will predict the performance of the process under different conditions. Marc Edwards (1994) presented modeling results based on the equilibrium chemistry approach of Dzombak and Morel (1990). Edwards (1994) concluded that arsenic removal is primarily dependent on pH and independent of initial arsenic concentration and coagulant dose for As (V), whereas As (III) removals are primarily controlled by coagulant dose and relatively unaffected by solution pH. Edward’s model looks at two initial levels of arsenic: 5 and 50 µg/L over a wide range of pH’s (6-9.5) and different iron doses starting from 5 mg/L. His results, however, do not take into account the use of a lower iron dose, which may be of interest to suppliers with source water arsenic concentrations only modestly above the drinking water standard. In subsequent research, McNeill and Edwards (1997) developed a simple, empirical model with data obtained from water utility surveys for predicting arsenate removal at full-scale alum coagulation, ferric coagulation, and iron-manganese removal plants. This model takes into account coagulant dose, but does not account for pH, which can have a significant impact in arsenic removal. In addition, the arsenic removal fraction is modeled as independent of initial arsenic concentration. This assumption is acceptable when arsenic concentrations
are low relative to the concentration of sorption sites, but would not be accurate at higher arsenic concentrations when competition for available sorption sites becomes a factor (Hering et al. 1997).

**SCOPE OF THE MODEL**

In this study the sorption of arsenic to ferric hydroxide is modeled using the equilibrium chemistry approach of Dzombak and Morel (1990). A spreadsheet is used to simultaneously solve a set of equilibrium and mass-balance equations describing the chemical species present. The spreadsheet models the sorption of arsenic(V) present as $\text{H}_2\text{AsO}_4^-$, $\text{AsO}_4^{3-}$, $\text{HAsO}_4^{2-}$ in the water onto the iron hydroxide surface sites. Arsenic(III) species are not considered. Arsenic(V) is usually the predominant form of arsenic. Water treatment plants with large amounts of arsenic(III) may wish to consider pre-oxidation to convert the arsenic(III) to arsenic(V), since arsenic(V) is removed more readily than arsenic(III). This model incorporates the pH at which the water is to be treated, the iron dose and the initial arsenic concentration. In addition, the calculations include a coulombic correlation factor, denoted by CCF, a type of activity coefficient for sorbed species which reflects the effects of net surface charge on the sorption reaction. The coulombic correction factor depends on ionic strength and pH. Activity coefficients for soluble species, denoted by $\gamma$, are also included in the model and are dependent on ionic strength and charge of the ion. After adding the ferric salts into the contaminated water a combination of different iron and arsenic species are formed as a result of coagulation. Three different species are taken into account in this model: $≡\text{FeH}_2\text{AsO}_4^-$, $≡\text{FeHAsO}_4^-$, and $≡\text{FeOHAsO}_4^{3-}$, where $≡$ is used to denote solid phase constituents. In addition to those compounds, the model takes into account the presence of iron as $≡\text{FeOH}^+$, $≡\text{FeOH}^-$, and as $≡\text{FeO}^−$.

**CHEMICAL EQUILIBRIA CONSIDERED**

Having established the forms in which arsenic and iron will be present after coagulation, two mass balance equations were derived to determine total arsenic and total iron present.

Equation #1:

$$[≡\text{FeOH}_2^+] + [≡\text{FeO}^−] + [≡\text{FeOH}] + [≡\text{FeH}_2\text{AsO}_4] + [≡\text{FeHAsO}_4^−] + [≡\text{FeOHAsO}_4^{3−}] = [≡\text{Fe}]_{\text{Total}}$$

Equation #2:

$$[\text{AsO}_4^{3−}] + [\text{HAsO}_4^{2−}] + [\text{H}_2\text{AsO}_4^−] + [≡\text{FeHAsO}] + [≡\text{FeH}_2\text{AsO}_4] + [≡\text{FeOHAsO}^{3−}] = [\text{As}]_{\text{Total}}$$

The different species in equation (1) are all formed from equilibrium reactions involving $≡\text{FeOH}$. The equilibrium equations for these reactions (given in Dzombak and Morel
1990) can be written in terms of \([\equiv \text{FeOH}]\) and the equilibrium constant. The resulting expressions can then be substituted into equation (1) to yield equation (3).

Equation #3:

\[
\left[\equiv \text{FeOH}\right]^* \left( H^+ \right)^* CCF^* 10^{7.29} + 10^{-8.93} \left( H^+ \right)^{1} CCF^{-1} + 1 + 10^{29.31} \gamma_{\text{As}}^* \left[ \text{AsO}_4^{3-} \right]^* \left( H^+ \right)^{3} + 10^{23.51} \left( H^+ \right)^{3} \left[ \text{AsO}_4^{3-} \right]^* \gamma_{\text{As}}^* CCF^{-1} + 10^{10.58} \left[ \text{AsO}_4^{3-} \right]^* \gamma_{\text{As}}^* CCF^{-3} \right) = \left[\equiv \text{Fe}\right]_{\text{Total}}
\]

An analogous process can be carried out to put equation (2) in terms of \([\text{AsO}_4^{3-}]\).

Equation #4:

\[
\left[\equiv \text{FeOH}\right]^* \left( H^+ \right)^* 10^{11.6} \left[ \text{H}_2 \text{AsO}_4^{-1} \right]^{-1} + \gamma_{\text{As}}^* \left( H^+ \right)^{2} 10^{18.4} \left[ \text{H}_2 \text{AsO}_4^{-1} \right]^{-1} + \gamma_{\text{As}}^* \left( H^+ \right)^{3} \gamma_{\text{As}}^* CCF^{-1} + 10^{29.31} \gamma_{\text{As}}^* \left( H^+ \right)^{3} \gamma_{\text{As}}^* \left[\equiv \text{FeOH}\right]^* + 10^{10.58} \left[\equiv \text{FeOH}\right]^* \gamma_{\text{As}}^* CCF^{-3} \right) = \left[\text{As}\right]_{\text{Total}}
\]

Combining equations (3) and (4) will finally yield a complex nonlinear equation.

Equation #5:

\[
\left( \left[\equiv \text{Fe}_{\text{Total}}\right] - \left[\equiv \text{FeOH}\right]^* \left( H^+ \right)^* CCF 10^{7.29} + 10^{-8.93} \left( H^+ \right)^{1} CCF^{-1} + 1 \right) \left( 1 + \gamma_{\text{As}}^* \left( H^+ \right)^* 10^{11.6} \left[ \text{H}_2 \text{AsO}_4^{-1} \right]^{-1} + \gamma_{\text{As}}^* \left( H^+ \right)^{2} 10^{18.4} \left[ \text{H}_2 \text{AsO}_4^{-1} \right]^{-1} + \gamma_{\text{As}}^* \left( H^+ \right)^{3} \gamma_{\text{As}}^* CCF^{-1} + 10^{23.51} \left[\equiv \text{FeOH}\right]^* \left( H^+ \right)^{3} \gamma_{\text{As}}^* CCF^{-3} \right) \right) - \left[\text{As}\right]_{\text{Total}} = 0
\]

Equation (5) has only one unknown, \([\equiv \text{FeOH}]\). The arsenic concentration, \([\text{As}]_{\text{total}}\) before treatment is a model input, \([H^+]\) is also considered a model input as pH is commonly measured at water treatment plants, and \([H^+]=10^{-pH}\). \([\equiv \text{Fe}_{\text{total}}]\) was determined by multiplying the dose of total iron added times 0.2 to obtain the total available sorption sites (Dzombak and Morel 1990). All terms preceded by \(\gamma\) are activity coefficients and are constants calculated from:
Equation #6:

$$\log \gamma = -0.5 z^2 \frac{\mu^{1/2}}{1+\mu^{1/2}}$$

$z$ represents the charge of the ion and $\mu$ represents ionic strength (Sawyer, McCarty, Parkin 1994). The coulombic correction factor used depended on pH and ionic strength and was obtained from Dzombak and Morel (1990). Where necessary, values were calculated by interpolation.

Equation (5) was introduced into a Microsoft Excel spreadsheet and the value of $[\equiv \text{FeOH}]$ was found by an iterative search using the Solver function. The value of $[\text{AsO}_4^{3-}]$ can then be obtained by substituting $[\equiv \text{FeOH}]$ into equation (4). The concentrations of all remaining species can be obtained from the equilibrium expressions relating their concentrations to $[\text{AsO}_4^{3-}]$ and $[\equiv \text{FeOH}]$ that were used to derive equations (3) and (4) from equations (1) and (2).

RESULTS

The spreadsheet tool developed in this research was tested and compared with experimental results reported by Hering, et al. (1997). In this research, several experiments were run comparing the percentage of arsenic removed against pH at a certain dose of iron or aluminum. Considered here are the experiments with ferric chloride. The water to be treated was spiked with 20 $\mu$g/L and ferric chloride was added to a Fe concentration of 4.9 mg/L. Identical values were substituted into the equation obtained in this model. Both sets of results (Figure 1) demonstrated the same trend, the percentage of arsenic removed is reduced significantly when pH is above 9. When pH is below 8 Hering’s results show that at least 80 percent or more of the arsenic is removed, while our results show that 90 percent or more of the arsenic is removed. The lower removals observed in the experimental results may be due to competition for sorption sites by other anions which sorb to iron hydroxide, such as carbonate, silicate, and phosphate (Holms 2002). These competitive effects were not included in the model developed here.
As a second test, the results of this model were compared with the results obtained by Edwards (1994). The results of the two models agree closely (Table 1) which is to be expected as both are based on the equilibrium chemistry approach of Dzombak and Morel (1990). The small differences are most likely due to the propagation of rounding errors.

**Table 1 – Comparison of results with Edwards (1994)**

<table>
<thead>
<tr>
<th>AsTotal (µg/L)</th>
<th>FeTotal (mg/L)</th>
<th>pH</th>
<th>Edward's Results</th>
<th>Model’s results</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>5</td>
<td>7</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>50</td>
<td>5</td>
<td>8.2</td>
<td>90</td>
<td>93</td>
</tr>
<tr>
<td>50</td>
<td>5</td>
<td>9.6</td>
<td>21</td>
<td>15</td>
</tr>
</tbody>
</table>

The model developed in this research was also compared with the empirical approach of McNeill and Edwards (1997). In this research, McNeill and Edwards develop a simple model with data obtained from surveys of actual arsenic removals obtained at water treatment plants.

Equation #7:

\[
\text{As sorbed (percent)} = \frac{K*[Fe]}{1+K*[Fe]}
\]

K is a model constant estimated from their survey data. McNeill and Edwards report that K values between 80 and 120 mM\(^{-1}\) provided a satisfactory fit to the data. Nevertheless, they recommend that for site-specific predictions, each water treatment plant should find its own K value. Comparing their results with the model developed in this study showed...
that our model modestly over-predicted arsenic removals (Figure 2). This is most likely due to the presence of competing anions in most source waters which somewhat lower arsenic removals. As higher pH values are used in the spreadsheet model, the results begin to resemble the predictions of the empirical model more closely. This is because hydroxide is itself a type of competing anion. Including higher pH in the model allows hydroxide to serve as a type of surrogate for other competitive anions that are not modeled explicitly.

**Figure 2 – Comparing McNeill and Edwards (1997) results with the model’s results. Model results are based on an arsenic concentration of 50 µg/L, an ionic strength of 0.1, and a pH of 8.3.**

The results of the two models match fairly well, despite the fact that the McNeill and Edwards empirical approach does not take into account pH or initial arsenic concentration. The equilibrium model can be used to verify that the omission of these factors is reasonable based on the underlying water chemistry and to define appropriate bounds for the use of the empirical model. The equilibrium modeling approach indicates that removals are not very sensitive to pH changes from 7 to 8, but decline rapidly at pH values above 8 (Tables 1-4). The net surface charge of ferric hydroxide becomes negative at pH values greater than 8. This creates an electrostatic repulsion between the surface and the negatively charged arsenate anion which greatly reduces the favorability of the sorption reaction. Accordingly, the equilibrium modeling approach supports the omission of an explicit consideration of pH from the empirical model, provided that the pH is below 8. As McNeill and Edwards report that pH values for the water treatment plants surveyed ranged from 7.1 to 8.5, the model may still be reasonably accurate in the range of 8.0 to 8.5, but care should be taken that the empirical model may over-predict removals at pH values above 8.
A second factor omitted from the empirical model is the initial arsenic concentration. Figure 3 shows the results of the equilibrium model for various initial arsenic concentrations. It can be seen that at an iron dose of 1.4 mg/l, removal fractions decrease at higher initial arsenic concentrations. This effect becomes pronounced at initial arsenic concentrations exceeding 200 µg/l.

**Figure 3 – Percent of arsenic removed as a function of initial arsenic concentration**

Model results are based on an Fe concentration of 1.4 mg/L, an ionic strength of 0.1 and a pH of 8.

Our spreadsheet model was used to develop general tables comparing the effects of pH, ferric dosage, and ionic strength. Similar results are reported by Edwards (1994) research, but only for dose of 5 mg/L or larger and only for a single ionic strength. In our own runs three different iron doses were considered: 0.5, 1.4, and 5 mg/L. The arsenic concentration was kept constant at 100 µg/L. Since the effect of a very low pH and a very high pH has already been shown (Table 1), three different pHs typical of water treatment plant operations are shown here: 7.5, 8, and 8.5. The ionic strengths of 0.01 and 0.1 were considered. A total of nine different calculations were made with the results presented in Tables 2-4.
Table 2 – Percentage of As removed keeping a pH of 7.5 and varying the dose of Fe

<table>
<thead>
<tr>
<th>AsTotal (µg/L)</th>
<th>FeTotal (mg/L)</th>
<th>pH</th>
<th>Ionic Strength 0.1</th>
<th>%As removed</th>
<th>Ionic Strength 0.01</th>
<th>%As removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.5</td>
<td>7.5</td>
<td>43.1</td>
<td>44.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.4</td>
<td>7.5</td>
<td>91.2</td>
<td>96.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>7.5</td>
<td>99.0</td>
<td>99.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3 – Percentage of As removed keeping a pH of 8 and varying the dose of Fe

<table>
<thead>
<tr>
<th>AsTotal (µg/L)</th>
<th>FeTotal (mg/L)</th>
<th>pH</th>
<th>Ionic Strength 0.1</th>
<th>%As removed</th>
<th>Ionic Strength 0.01</th>
<th>%As removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.5</td>
<td>8</td>
<td>36.2</td>
<td>40.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.4</td>
<td>8</td>
<td>75.6</td>
<td>84.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>8</td>
<td>95.5</td>
<td>97.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4 – Percentage of As removed keeping a pH of 8.5 and varying the dose of Fe

<table>
<thead>
<tr>
<th>AsTotal (µg/L)</th>
<th>FeTotal (mg/L)</th>
<th>pH</th>
<th>Ionic Strength 0.1</th>
<th>%As removed</th>
<th>Ionic Strength 0.01</th>
<th>%As removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.5</td>
<td>8.5</td>
<td>21.4</td>
<td>24.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.4</td>
<td>8.5</td>
<td>47.4</td>
<td>53.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>8.5</td>
<td>80.8</td>
<td>85.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results demonstrate that when the iron dose is below 5 mg/L, the percentage of arsenic removal becomes affected by both pH and the low iron dose, when before, arsenic removal was only affected by the pH value. From Table 2, it can be seen that at a pH of 7.5, the percentage of removed arsenic at an iron dose of 5 mg/L was 99%. When we lowered the iron dose to 1.4 mg/L that percentage went down to 91%. Moreover, when the iron dose was decreased to 0.5 mg/L the percentage of arsenic removed drops to 43%. The same trend can be observed in Tables 3 and 4 with the other two pH values.

The results displayed on the last column of Tables 2-4 show that lowering the ionic strength value slightly increases the percentage of arsenic removal. This effect is more pronounced with high pH values. For example, from Table 2 with a pH of 7.5 and an iron dose of 5 mg/L, the percentage of arsenic removed was 99.7%. From Table 3, same conditions of pH and iron dose, but a higher ionic strength, the percentage of arsenic removed went just slightly down, to 99.0%. On the other hand, taking a pH of 8.5, ionic strength of 0.01 and iron dose of 5 mg/L, the percentage of arsenic removed is 85.4%, while if we use an ionic strength value of 0.1, the percentage varies more, to a value of 80.8%. This indicates that the higher the pH, the more the ionic strength value will affect the percentage of arsenic removed. The two trends observed in our previous results are
encountered again, the lower the pH value the greater the percentage of arsenic that is removed and if an iron dose below 5 mg/L is used, the iron dose will also become a factor in determining the percentage of arsenic removed.

CONCLUSIONS

The results of this study indicate that when the iron dosage is above 5 mg/L, arsenic removal will depend primarily on pH. At a higher pH arsenic removal decreases considerably; at pH 7, arsenic removal is almost 100 percent when the iron dosage is 5 mg/L or greater. Nevertheless, when we lower the iron dosage below 5 mg/L, arsenic removal is affected not only by pH, but also by the iron concentration. Hence, decreasing the iron dosage below 5 mg/L will also decrease considerably the percentage of arsenic that will be removed. In addition, the ionic strength value was seen to have a small effect on the percentage of arsenic removed. Using a lower value of ionic strength slightly increased the percentage of arsenic being removed, at all pH values and at all iron doses. However, the effect of ionic strength was more pronounced at higher pH. Lastly, varying the initial arsenic concentration in the water to be treated did not strongly affect the percentage of arsenic removed, as long as the initial arsenic concentration was less than 200 µg/L. Given that most water treatment plants operate in a fairly narrow range of pH values and initial arsenic concentrations, the empirical approach of Edwards and McNeill, which considers only the effects of iron dosage appears to be justified. However, high pH water treatment plants (pH >8) should apply this model with care as it may over-predict removals for such plants.

Further research needs to be done in order to incorporate the effects of competing ions for the ferric hydroxide sites. Inorganic carbon, silica, and phosphate are found in many natural waters, and they can act as competing ions with the arsenic for ferric hydroxide sites. While the effects of these have been modeled and validated with laboratory data (Holm 2002), there is currently not a practical tool available for water treatment suppliers to estimate arsenic removals in the presence of competing anions. The development of such a tool is of interest since the speciation of competing anions may change with pH, leading to an overall increase in the sensitivity of arsenic removals to pH.

While both the spreadsheet tool developed in this study and the empirical model of McNeill and Edwards have limitations, both are capable of producing rough estimates of arsenic removal during coagulation with ferric salts. The spreadsheet developed here is most appropriate when the source water has low levels of competing anions. The McNeill and Edwards empirical model is most appropriate when initial arsenic concentrations are below 200 µg/l and the pH of coagulation is below 8, although reasonably accurate values have been obtained for a plant with a pH as high as 8.5. Neither approach is sufficiently accurate for design purposes, but they can be used to determine the conditions to investigate in more detail during pilot studies.
REFERENCES


