Evaluation of the arsenic(V) removal from water by hydrotalcite-like compounds

Chang W¹, Jones H¹, Valsami Jones E² and Garelick H¹
¹ Institute of Social and Health Research, School of Health and Social Sciences, Middlesex University Queensway, Enfield Middlesex
² Department of Mineralogy, The Natural History Museum

ABSTRACT

Arsenic contaminated drinking water is recognized as the greatest threat to public health. WHO has lowered the recommended guideline value to 10ug/L as the maximum contaminant level (MCL), strengthening the need for simple and low cost arsenic removal technology.

Hydrotalcite-like compounds as potential adsorbents have attracted the attention of researchers due to its special properties e.g. anion exchange and memory effect. Three HT-like compounds were synthesized and tested: Mg-Al-NO₃-HT, Mg-Fe-NO₃-HT(1) synthesized under nitrogen atmosphere and Mg-Fe-NO₃-HT(2) synthesized under ambient atmosphere. Batch experiments including time-dependent adsorption, pH-dependent adsorption and adsorbent dose were carried out and adsorption isotherms were elucidated.

Arsenic adsorption onto the three minerals was reached after 18 hours. A two-step arsenic uptake, a faster surface adsorption process and a slower ion exchange process, was observed. In the neutral pH region (6.6-8.8), the arsenic adsorption capacity was found to be quite stable for Mg-Fe-NO₃-HT(1) and Mg-Fe-NO₃-HT(2). The isotherm profiles of Mg-Al-NO₃-HT, Mg-Fe-NO₃-HT (1) and Mg-Fe-NO₃-HT (2) were all S-type (subgroup 3), indicating that the change from external to interlayer adsorption may have occurred to the three minerals.

The experiments indicate that Mg-Fe-NO₃-HT, having high arsenic removal efficiency (97%-98%) and achieving final arsenic concentration of less than the MCL, may be an ideal absorbent for arsenic removal.

KEYWORDS

Iron-based hydrotalcite-like compounds, removal, arsenic(V), water

1. INTRODUCTION

Arsenic contaminated drinking water is recognized as the greatest threat to public health all over the world (www.who.int/inf-fs/en/fact210.html). There are more than 10 countries with the problem of arsenic contamination in drinking water, the top calamitous countries are in Asia: Bangladesh, India (West-Bengal) and China (Sudan et al., 2006). Due to no effective medications for Arsenicosis, reducing arsenic intake becomes the only practical solution.

WHO has lowered the recommended guideline value to 10ug/L as the maximum contaminant level (MCL). Unfortunately, the previous standard value 50ug/L is still to be applied in some developing countries. The reduction of arsenic's maximum contaminant level (MCL) not only reflects the serious concern to the potentially harmful nature of arsenic but also strengthens the need for the
Evaluation of the arsenic(V) removal from water by hydrotalcite-like compounds

simple and low cost arsenic removal technologies.

Conventional arsenic removal technologies include co-precipitation, sorption and membrane techniques (Mondal, et al., 2006). In recent years, hydrotalcite-like compounds, have attracted the attention of researchers due to its special properties e.g. anion exchange and memory effect. The layered structure of HT-like compounds is shown in Figure 1. The general formula is $\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x\text{(OH)}_2\text{A}^{n-}\times\text{yH}_2\text{O}$, where $\text{M}^{\text{II}}$ is a divalent cation ($\text{Mg}^{2+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+}$, $\text{Zn}^{2+}$, $\text{Mn}^{2+}$, $\text{Cd}^{2+}$), $\text{M}^{\text{III}}$ is a trivalent cation ($\text{Al}^{3+}$, $\text{Fe}^{3+}$, $\text{Cr}^{3+}$, $\text{Ga}^{3+}$), $\text{A}^{n-}$ is an anion and $x$ is defined as the $\text{M}^{\text{III}}/($$\text{M}^{\text{II}} + \text{M}^{\text{III}}$) ratio, whose value varying between 0.2 and 0.33 (Ferreira, 2006). The physical–chemical properties of the HT-like compounds depend on the nature of $\text{M}^{\text{II}}$ and $\text{M}^{\text{III}}$, interlayer anion and $x$ values (responsible for the charge in the layers) (Ferreira, 2006).

Previously, calcined and uncalcined HT-CO$_3$$_3$, HT-NO$_3$ and HT-Cl have been studied for arsenic removal; most of them are aluminum-based. Some showed good arsenic removal efficiency, however, few of them can reduce arsenic concentration to less than 10 ppb.

Mg-Fe-NO$_3$$_3$-HT was selected for arsenate removal in this study. The selection of iron-based HT-like compound (Mg-Fe-HT) based on the affinity of iron oxides for arsenic adsorption and reduced potential toxicity of aluminum in drinking water (Ferreira, 2004). NO$_3$ is the selected anions due to its lower affinity for HT-like compounds, while the molar ratios of Mg/Fe and Mg/Al are 2, because the higher metal molar ration should have higher anion content.

2. MATERIALS AND METHODS

2.1 Preparation and characterization of HT-like compounds

Three minerals were synthesized and tested. These were: Mg-Al-NO$_3$$_3$-HT, Mg-Fe-NO$_3$$_3$-HT(1) synthesized under nitrogen atmosphere and Mg-Fe-NO$_3$$_3$-HT(2) synthesized under ambient atmosphere. The synthesis procedure is shown in Figure 2.

Metal contents of the HT-like compounds (The molar ratio of the metals of HT-like compounds) were determined by a Perkin-Elmer Plasma 40 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Fourier transform infrared spectroscopy (FTIR) spectra was employed for Characterization of inter layer anions, carbonate or nitrate (Ferreira, 2006). CHN Analyzer was employed for Carbon and nitrogen contents of the HT-like compounds.

2.2 Arsenic removal experiments

Batch experiments including time-dependent adsorption, pH-dependent adsorption and adsorbent dose were carried out and adsorption isotherm were elucidated.
Evaluation of the arsenic(V) removal from water by hydrotalcite-like compounds

Batch equilibration experiment is to assess arsenic removal by HT-like compounds under different conditions, time-dependent, pH-dependent, adsorbent dose and adsorption isotherms experiments were carried out. The general procedure is as follows:

(i) The pH of the arsenic solution was adjusted by using 0.1 M HNO₃ or 0.1 M NaOH solutions;
(ii) 20 ml arsenic solution was measured and put into conical flask;
(iii) HT-like compounds was weighed and added to the arsenic solutions;
(iv) The mixture in the conical flasks were put into the shaking water bath at 25°C;
(v) The samples were collected at certain time interval, then put into centrifuge tube, centrifuge at 3000 rpm for 15mins;
(vi) The arsenic concentrations in the supernatant were determined by HG-AAS.

The time-dependent sorption were carried out by adding 0.02 g adsorbent into 20 ml of 0.5mg/l arsenate solution at pH=8.8±0.1. The time intervals were 10min, 30min, 1h, 4.5h, 18h and 5d, respectively.

The effect of the adsorbent dose was examined by addition different adsorbent quantities: 0.01, 0.02, 0.05, 0.10 and 0.15g respectively, into 20 ml of 0.5 mg/ l arsenate solutions at pH=8.8±0.1.

pH-dependent experiments was conducted to add 0.02 g adsorbent into 20 ml of 0.5 mg/ L arsenate solutions with the pH range from 4.4 to 9.9 (4.4, 5.5, 6.6, 7.7, 8.8, 9.9 respectively).

Adsorption isotherms were elucidated by addition of 0.02 g adsorbent into 20 ml of arsenate solutions at pH =8.8±0.1, with arsenic concentrations ranging from 0 to 1.5 mg/l.(0.05, 0.1, 0.25, 0.5, 1.0 and 1.5mg/l).

3. DISCUSSION

3.1 Effect of contact time

Table 1 shows the arsenic concentrations at different time intervals. The result suggests that 18h is sufficient to reach the equilibrium for Arsenic adsorption onto the three minerals. In the first 60
Evaluation of the arsenic(V) removal from water by hydrotalcite-like compounds

minutes, the arsenic concentration dropped extremely rapidly from 588.88µg/L to around 20µg/L. Then the arsenic uptake slowed down significantly from 60 minutes to 1080 min (18h) with only about 10µg/L drop, arsenic concentration bottomed out at 1080 min.

<table>
<thead>
<tr>
<th>Time interval(min)</th>
<th>Minerals</th>
<th>Mg-Al-NO₃-HT (µg/L)</th>
<th>Mg-Fe-NO₃-HT(1) (µg/L)</th>
<th>Mg-Fe NO₃-HT(2) (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>588.88</td>
<td>588.88</td>
<td>588.88</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>103.20</td>
<td>90.35</td>
<td>116.13</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>80.85</td>
<td>59.05</td>
<td>75.68</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>20.25</td>
<td>19.69</td>
<td>20.38</td>
</tr>
<tr>
<td>270</td>
<td></td>
<td>20.20</td>
<td>14.69</td>
<td>20.06</td>
</tr>
<tr>
<td>1080</td>
<td></td>
<td>10.16</td>
<td><strong>6.94</strong></td>
<td>11.33</td>
</tr>
<tr>
<td>7200</td>
<td></td>
<td>21.17</td>
<td>14.37</td>
<td>11.64</td>
</tr>
</tbody>
</table>

The observed the two-step arsenic uptake may indicate two different removal processes have occurred--anion exchange and external adsorption due to the anions between the lamellae and positively charged surface. Generally, the adsorption process is faster than ion exchange. Therefore, a faster adsorption process was the dominant in the first 60 min, and a slower anion exchange was the dominant from 60min to 1080min.

It is worth noting that after 18h’s contact with Mg-Fe-NO₃-HT(1) the arsenic concentration was less than 10µg/L.

### 3.2 Effect of solution pH

Table 2 shows the final arsenic concentrations at different pH after 18h’s contacting with HT-like compounds. The final arsenic concentrations for Fe-based-HT reached much lower final arsenic concentration than Al-based-HT (Mg-Al-NO₃-HT), except that at pH 8.8 Mg-Al-NO₃-HT reached a comparable value of 8.88. In the range of pH from 4.4 to 8.8 Mg-Fe-NO₃-HT (1) was able to reach the arsenic concentration of less than 10µg/L.

<table>
<thead>
<tr>
<th>Initial concentration 468.18µg/L</th>
<th>Mg-Al-NO₃-HT (µg/L)</th>
<th>Mg-Fe NO₃-HT(1) (µg/L)</th>
<th>Mg-Fe NO₃-HT(2) (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4</td>
<td>62.26</td>
<td><strong>8.28</strong></td>
<td>10.20</td>
</tr>
<tr>
<td>5.5</td>
<td>61.70</td>
<td><strong>8.21</strong></td>
<td>10.23</td>
</tr>
<tr>
<td>6.6</td>
<td>71.57</td>
<td><strong>9.82</strong></td>
<td>10.80</td>
</tr>
<tr>
<td>7.7</td>
<td>48.69</td>
<td><strong>9.01</strong></td>
<td>9.95</td>
</tr>
<tr>
<td>8.8</td>
<td>8.88</td>
<td><strong>8.99</strong></td>
<td>13.14</td>
</tr>
<tr>
<td>9.9</td>
<td>47.27</td>
<td>16.69</td>
<td>18.62</td>
</tr>
</tbody>
</table>

The pH of solutions affects the surface charge of HT-like compounds and the dissociation of arsenic, thereby influencing the arsenic removal efficiency.

### 3.2.1 The surface charge of HT-like compounds

It has been reported that the point of zero charge (pHpzc) for the uncalcined HT-like compounds is in the range of 6.8-8.9 (Yang, et al, 2005). When pH of the solution is less than pHpzc the surface of
Evaluation of the arsenic(V) removal from water by hydrotalcite-like compounds

the HT-like compounds is positively charged, which benefits the adsorption of the anionic species. While when pH of the solution is higher than pHpezc, the surface of the HT-like compounds is negatively charged, repelling the anion uptake. This may explain that Fe-basted-HT maintain quite stable high arsenic removal efficiency (around 98%) through the pH range of 4.4 to 8.8 and drop slightly at pH 9.9.

3.2.2 The dissociation of arsenic

Figure 3 and Figure 4 show that arsenate dominant species vary with pH. Therefore the solutions with the same arsenic concentration may have arsenate with different charge density. In the pH range of 6.7-11.2, the dominant arsenate (HAsO$_4^{2-}$) has higher charge density than that (H$_2$AsO$_4^-$) in the pH range of 2.1-6.7. HT-like compounds generally have greater affinities for anions with higher charge density, therefore, Al based-HT has higher arsenic removal efficiency at pH 7.7, 8.8 and 9.9.

![Figure 3 Dissociation of As (Mohan. et al, 2007)](image)

![Figure 4 Dominant arsenic species across a range of pH (from Sadiq et al, 1983)](image)

It is obvious that Fe based-HT have higher arsenic removal efficiency. Moreover in the pH region (6.6-8.8), the arsenic removal efficiency is quite stable therefore no requirement for the pH adjustment.

3.3 Effect of adsorbent dose

Figure 5 shows the curve of the final arsenic concentration at different adsorbent dose. The three minerals exhibit generally the same pattern; the arsenic concentration dropped extremely rapidly from the beginning to 1g/l or 2g/l, and then generally leveled off. Mg-Al-NO$_3$-HT and Mg-Fe-NO$_3$-HT (1) bottomed out at 1g/l and 2g/l respectively, however, Mg-Fe-NO$_3$-HT (2) showed a continuous tendency of decreasing concentration.

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Al-based-HT always reaches higher equilibrium arsenic concentration and lower adsorption ratio at different doses than Fe-based-HT. The peak adsorption ratio in Figure 5 may indicate certain limit of adsorption capability of the three minerals, therefore the adsorption capacity at dose level lower than 1g/l or 2g/l, should be further investigated

3.3 Adsorption isotherms

Table 3 shows the final arsenic concentration after arsenic removal under different initial concentrations. All three minerals were able to reduce arsenic concentration to less than 10µg/L at initial concentration of 41.64µg/L. Mg-Fe-NO₃-HT (1) has the highest arsenic removal efficiency; it was able to reach a final arsenic concentration of 8.84µg/L even at a very high initial arsenic concentration of 432.80µg/L.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Initial arsenic concentration (µg/L)</th>
<th>Final Arsenic concentration</th>
<th>Mg-Al-NO₃-HT (µg/L)</th>
<th>Mg-Fe-NO₃-HT (1) (µg/L)</th>
<th>Mg-Fe-NO₃-HT (2) (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Al-NO₃-HT</td>
<td>41.64</td>
<td></td>
<td>4.70</td>
<td>4.76</td>
<td>4.66</td>
</tr>
<tr>
<td>Mg-Fe-NO₃-HT (1)</td>
<td>88.91</td>
<td></td>
<td>13.38</td>
<td>5.06</td>
<td>6.30</td>
</tr>
<tr>
<td>Mg-Fe-NO₃-HT (2)</td>
<td>203.41</td>
<td></td>
<td>19.15</td>
<td>7.20</td>
<td>8.02</td>
</tr>
<tr>
<td>Mg-Fe-NO₃-HT</td>
<td>432.80</td>
<td></td>
<td>51.16</td>
<td>8.84</td>
<td>11.02</td>
</tr>
<tr>
<td>Mg-Fe-NO₃-HT</td>
<td>1049.84</td>
<td></td>
<td>135.27</td>
<td>13.67</td>
<td>18.21</td>
</tr>
<tr>
<td>Mg-Fe-NO₃-HT</td>
<td>1475.88</td>
<td></td>
<td>240.84</td>
<td>62.41</td>
<td>62.18</td>
</tr>
</tbody>
</table>

Adsorption isotherms can be classified into four types: S, L, H and C (Giles, 1960), which is shown in Figure 9. The adsorption isotherms are shown in Figure 6, Figure 7 and Figure 8. Comparing with the system of isotherm classification, the isotherm profiles of three minerals are S-type (subgroup 3). S type isotherm of the HT-like compounds has been reported in previous studies-- the adsorption of anionic MCPA.

“Strong competition for substrate sites from another adsorbed species” is one of the three conditions for the occurrence of S type isotherm. The experiments were carried at the pH around 8.8, the concentration of OH⁻ is around 1185ppb, much higher than some of the initial concentration of arsenate, such as 50ppb, 100ppb, 250ppb and 500ppb. At low initial concentration the arsenate meets the strong competition from OH⁻ for HT-like compounds. With the increase of the arsenic concentration, the adsorption ratio decreases significantly.
Evaluation of the arsenic(V) removal from water by hydrotalcite-like compounds

concentration, the competition form OH⁻ decreases, the adsorption of arsenate begins to increase.

Figure 6 Isotherm for As(V) uptake by Mg-Al-NO₃-HT

Figure 7 Isotherm for As(V) uptake by Mg-Fe-NO₃-HT(1)

Figure 8 Isotherm for As(V) uptake by Mg-Fe-NO₃-HT(2)

Figure 9 System of isotherm classification (Giles, 1960)

4. CONCLUSION

In conclusion, Mg-Fe-NO₃-HT (1) may be an ideal absorbent for arsenic removal. The anion exchange property of HT-like compounds, the less affinity of NO₃⁻ for HT-like compounds, higher affinity of arsenic for Iron oxides and larger surface area all contribute to the high arsenic removal efficiency (around 98%). Moreover, the stable arsenic removal and the less than MCL final arsenic concentration at pH 6.6-8.8 provide a simple arsenic removal technology with no requirements for pH adjustment.

Acknowledgement

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Evaluation of the arsenic(V) removal from water by hydrotalcite-like compounds


