Effect of Phosphate on the Sorption of Arsenite onto Aluminum– or Iron–Oxide Coated Light Expanded Clay Aggregate (LECA)

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Abstract

Based on human epidemiology, arsenic (As) is classified as a first group carcinogen and lots of efforts have been made to reduce its intake by humans. Nevertheless, more than 120 million people in Bangladesh and West Bengal are still exposed to groundwater where As concentration is above the WHO maximum permissible limit. In groundwater the conditions favor the occurrence of arsenite (As\textsuperscript{III}) that is a more toxic species than arsenate (As\textsuperscript{V}). Moreover, As\textsuperscript{III} has a lower sorption tendency than aluminium (Al) and iron (Fe) oxides. The presence of phosphate in groundwater further reduces the sorption tendency of As\textsuperscript{III}. This study was undertaken to unravel the ability of Light Expanded Clay Aggregate (LECA) without and with Al or Fe oxide coating to remove As\textsuperscript{III} as well as the impact of phosphate on the removal efficiency. The oxide coatings enhanced decisively the sorption. The sorption of As\textsuperscript{III} increased with elevated pH, at pH 7 the apparent maximum sorption ($X_m$) being in LECA 68 µg g\textsuperscript{-1}, in Al-LECA 114 µg g\textsuperscript{-1} and in Fe-LECA 96 µg g\textsuperscript{-1}. At pH 10, on the contrary, $X_m$ for Fe-LECA was greater than for Al-LECA. The competition by phosphate affected less the sorption onto LECA than onto the oxide-coated LECAs. At pH 7 the highest P addition (100 µg L\textsuperscript{-1}) diminished the As\textsuperscript{III} removal by LECA by 4 times, the corresponding decreases in Al-LECA and Fe-LECA being 6– and 5–fold, respectively. At pH 3 and 5, the competition by phosphate was more marked in Fe-LECA than in Al-LECA, while at pH 7 an opposite trend was detected. In general, the uncoated LECA showed to be superior to the oxide-coated LECAs in the As\textsuperscript{III} removal from groundwater.

Keywords: Arsenite, Phosphate, Sorption, Light Expanded Clay Aggregate, Aluminium oxide, Iron oxide.

1. Introduction

In many countries worldwide arsenic (As) concentration in drinking water exceeds the maximum permissible concentration 10µg L\textsuperscript{-1} (World Health Organization, 2004). In Bangladesh and in West Bengal millions of people are exposed to groundwater where this limit value is exceeded (Ratnaike, 2003). In some areas of Bangladesh, As in groundwater approaches even at level 2000 µg L\textsuperscript{-1} (Tondel et al., 1999) and in West Bengal in some tube wells it is as high as 3400 µg L\textsuperscript{-1} (Ratnaike, 2003). Generally, high concentrations are mainly natural and caused by weathering of As containing pyrite sedimentary rocks in contact with the aquifer (Goldberg and Johnston, 2001), by reductive dissolution of As-rich iron oxyhydroxides derived from weathering of sulphide minerals in anoxic groundwater (Nickson et al., 1998) or by agricultural drainage waters discharging from As-contaminated soil. Moreover, in these countries the drinking water does not undergo any
type of purification due to the lack of water treatment facilities (Yan et al., 2012).

Long-term exposure to inorganic As may lead to several types of cancer and to many detrimental non-cancer effects on the human health (Guo and Chen, 2005). Therefore, simple and efficient methods to clean up the groundwater are urgently needed. Common purification methods are reported in the literature, e.g. coagulation-precipitation, reverse osmosis, ion exchange and sorption (Payne and Abdel-Fattah, 2005). Among these methods the sorption is a cheap, efficient and very simple technique that can be applied in small scales in tube wells or after effluent water pumps. This method needs a suitable material as a sorbent and conditions adjusted previously to reach the maximum removal efficiency. Some sorbents of high affinity for As have been tested, but most researchers unanimously agree that materials containing hydrated aluminium (Al) or iron (Fe) oxides are superior and have a high removal capacity (Anderson et al., 1976; Giles et al., 2011; Haque et al., 2008; Raven et al., 1998). Therefore, in many studies cheap materials such as Light Expanded Clay Aggregate (LECA) have been coated with Al or Fe oxides to improve their sorption efficiency e.g. (Amiri et al., 2011; Haque et al., 2008).

In groundwater, As mainly exists as arsenate (AsV) or arsenite (AsIII) depending on the redox environment. Arsenous acid (H3AsO3) is a very weak acid (pK1 = 9.2) and, thus, arsenite is weakly dissociated at normal pH predominating in anoxic environment. Arsenate, in turn, is the anion of a stronger arsenic acid H3AsO4 (pK1 = 2.3) that predominates in aerobic environment (Jeong et al., 2007). Mukherjee and Bhattacharya (2001) reported that in Bangladesh the redox conditions in groundwater vary from slightly oxidizing to strong reducing. Therefore, most of As in groundwater is in reduced form AsIII that is more detrimental to human health than is AsV (Raven et al., 1998). Furthermore, in problem areas pH of the groundwater is predominantly near neutral to slightly alkaline (pH 6.5 – 7.6) and the concentration of phosphate is very high (Mukherjee and Bhattacharya, 2001).

At pH less than 9.2, the predominating species can be expected to be the protonated neutral molecule H3AsO3 which can be expected to have an extremely low sorption tendency. However, at the pH range 7 – 8 AsIII is reported to be strongly sorbed onto the activated alumina (Singh and Paut, 2004) and at the pH range 8 – 10 onto iron oxide (Masue et al., 2007). In the Bengal Delta Plain where pH of the groundwater is always around 7, Al oxide can be taken to be a better sorbent than Fe oxide. However, in slightly oxidizing groundwater conditions ferric iron oxide may transform some AsIII to AsV that is able to be retained onto mineral material. Moreover, the contemporary occurrence of phosphate that has the same sorption properties as AsV may further weaken the ability of AsIII to be retained onto Al– and Fe–oxides as shown e.g. by Meng et al. (2002) and Youngran et al. (2007).

This study was undertaken to assess (1) how the coating of LECA by Al– or Fe–oxide affects the sorption of AsIII, and (2) the competitive effect of phosphate on it. Furthermore, sorption isotherms at different pH’s were used to investigate the interactive effect between pH and AsIII speciation on the sorption by various LECA materials.

2. Material and Methods

2.1 Sorbent Materials

The procedure used to prepare the sorbent material is described in detail by Yaghi and Hartikainen (2013). Shortly, LECA (Produced by BioLan Oy) material was crushed by hand and sieved. Then 300 g of material of particle size 1 – 0.63 mm was soaked in 600 ml of 0.01 M HNO3 for 48 hours, rinsed eight times with deionized water and dried in oven for 24 h at 105°C. For iron oxide coatings, 100 g of this material was soaked in Fe(NO3)3·9H2O, or in Al(NO3)3·9H2O to produce Fe– and Al–oxide coating (Fe-LECA and Al-LECA), respectively. Aluminium and Fe (hydr)oxides were formed by means of NaOH treatment. A third 100 g portion left uncoated served as a reference material.

2.2 Experimental Design

2.2.1 Sorption Isotherms

For sorption isotherms, 4.0 L of NaAsO2 solutions of 0, 10, 20, 50, 100, or 200 μg As L⁻¹ were prepared. Each solution was divided into four equal portions and transferred into 500 mL volumetric flasks and their pH’s were adjusted to 3, 5, 7, or 10 by adding 0.1 M HCl or 0.1 M NaOH.
dropwise. Then, a 100 mL of each As\\text{III} solution was introduced into a 250 mL plastic bottle containing around 0.1 g sorbent (weight was recorded). The solution-sorbent mixtures were stirred at 130 rpm at room temperature for 24 hours. Thereafter, the solutions were filtrated through a 0.2 \mu m membrane filter (Nuclepore® polycarbonate) and preserved at 4°C before As analyzes. The sorption tests were carried out with three replicates.

The sorption parameters for each sorbent were calculated from Langmuir equation, rearranged to a linear form (Barrow, 1978):

\[
\frac{C}{Q} = \frac{1}{k_LX_m} + \frac{1}{X_m}c
\]

where C stands for the concentration of As in the equilibrium solution (\mu g L\textsuperscript{-1}), Q is the amount of As sorbed onto sorbent (\mu g g\textsuperscript{-1}), X\text{m} is the sorption maximum (\mu g As g\textsuperscript{-1} sorbent), and K\text{L} is the coefficient related to bonding energy (L g\textsuperscript{-1}). A plot of \frac{C}{Q} versus C has a slope \frac{1}{X_m} and intercept \frac{1}{k_LX_m}.

2.2.2 Effect of Phosphate on the Sorption of Arsenite

To unravel the effect of P on the sorption of As\\text{III}, five 1.0 L portions of KH\textsubscript{2}PO\textsubscript{4} solution (0, 10, 20, 50, and 100 \mu g P L\textsuperscript{-1}) were prepared. A volume of 50 mL of each solution was transferred into a 250 mL plastic bottle containing about 0.1 g sorbent (weight was recorded) and 50 mL of 50 \mu g As\\text{III} L\textsuperscript{-1} and the pH of the mixture was adjusted to 3, 5, 7, or 10 by adding 0.1 M HCl or 0.1 M NaOH. The solution-sorbent mixtures were stirred at 130 rpm at room temperature for 24 hours, whereafter the solutions were filtrated through a 0.2 \mu m membrane filter (Nuclepore® polycarbonate) and preserved at 4°C before As analyzes.

3. Arsenic Analysis

Arsenic was determined by Hydride Generation–Inductively Coupled Plasma Optical Emission spectroscopy (HG-ICP-OES) (Perkin Elmer 5100, sampler Perkin Elmer AS 90 Controller). The principle of this method is based on the conversion of soluble As to the volatile arsine (AsH\textsubscript{3}) by acidifying the sample with 5% HCl. Thereafter the acidified sample reacts with 0.5% sodium borohydride (NaBH\textsubscript{4}) prepared in 0.05% sodium hydroxide solution (NaOH). This reaction occurred in the four channel sample pump (iCAP 6500 instruments). After that, the vapor introduced to ICP-OES was analyzed for As\\text{III} at the wavelength 189 nm.

4. Results and Discussion

4.1 Arsenite Sorption Isotherms

The sorption isotherms in Figure 1 shows that the oxide coatings decisively enhanced retention of As\\text{III}. This can also be seen in Table 1 where the apparent maximum sorptions (X\text{a}) of As\\text{III} calculated from Langmuir equation (equation 1) were higher in the coated LECAs than in the uncoated one. It also increased with elevated pH. As expected, the most drastic increase in the sorption occurred when pH was elevated from 7 to 10. However, the oxide-coated LECAs’s differed in their responsiveness to pH. When pH was elevated from 5 to 7 the sorption of As\\text{III} onto Fe-LECA seemed not to increase whereas that onto Al-LECA increased (Figure 1). In all cases the sorption was highest at pH 10 where As\\text{III} exists mainly as monovalent anion (H\textsubscript{2}AsO\textsubscript{3}\textsuperscript{-}). Thus, a high pH is a prerequisite for efficient As\\text{III} sorption. At pHs lower than 9.2 (pK\text{a} value of H\textsubscript{2}AsO\textsubscript{3}) arsenite exists to large extent as an undissociated molecule not able to be retained.

Ligand exchange, firstly described by Hingston et al. (1967), is the basic mechanism in the sorption the oxyanion As species. They replace either a hydroxyl group (OH\textsuperscript{-}) or an aqua group (OH\textsuperscript{2}-) on the oxide surface. Commonly, the aqua group is easier to be replaced by As\\text{III} anion than is the OH\textsuperscript{-} group. At pH 3, the apparent retention maximum X\text{m} for LECA was about 30% lower than for Al-LECA and Fe-LECA (Table 1). The superiority of the oxide-coated materials became more apparent with increasing pH. Interestingly, at pH 7 the X\text{m} of Al-LECA was higher than that of Fe-LECA, but an opposite pattern was seen at pH 10. As expected, the bonding strength values (K\text{L}) were higher for oxide-coated LECAs than for the uncoated one, and tended to increase with increasing pH.

Generally, As\\text{III} is assumed to be sorbed onto LECA as on outer sphere complexes. Nevertheless, several spectroscopic studies have provided
evidence that As$^{\text{III}}$ is sorbed on the Fe-oxide surface as a bidentate binuclear complex (Guo and Chen, 2005; Jain et al., 1999; Manning et al., 1998).

According to Arai et al. (2001) at pH equal or less than 5.5, As$^{\text{III}}$ is sorbed onto Al oxide surface forming predominantly inner-sphere bidentate binuclear complexes, whereas at pH higher than 5.5 Al oxide forms a mixture of inner–and outer–sphere complexes.

**Table 1**

Apparent maximum sorption ($X_m$) of arsenite onto LECA, AL-LECA and Fe-LECA, bonding strength $K_L$ and their standard deviation ($\pm$SD) at different pH values.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>pH</th>
<th>$X_m$ $\mu g$ $g^{-1}$</th>
<th>$K_L$ $L \mu g^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LECA</td>
<td>3</td>
<td>16.9±1.4</td>
<td>3.9±0.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>30.8±2.3</td>
<td>4.5±0.4</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>67.8±1.2</td>
<td>4.9±0.2</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>183.8±8.8</td>
<td>6.2±0.5</td>
</tr>
<tr>
<td>AL-LECA</td>
<td>3</td>
<td>25.2±7.4</td>
<td>5.5±0.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>64.4±1.4</td>
<td>6.5±0.2</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>113.8±2.7</td>
<td>6.7±0.2</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>238.5±6.6</td>
<td>7.0±0.5</td>
</tr>
<tr>
<td>Fe-LECA</td>
<td>3</td>
<td>26.1±2.8</td>
<td>6.1±0.2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>70.0±2.8</td>
<td>6.6±0.4</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>95.8±0.7</td>
<td>6.6±0.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>278.2±7.5</td>
<td>10.9±0.2</td>
</tr>
</tbody>
</table>

In terms of chemistry, Al$^{3+}$ ($pK_1 = 5.0$) is a weaker acid than Fe$^{3+}$ ($pK_1 = 2.2$). Thus, at pH range 5 – 7, Al$^{3+}$ will have more aqua groups in its coordination sphere than does Fe$^{3+}$. Upon increase the pH to 10, the predominating Al species is $[\text{Al(H}_2\text{O)}_3\text{(OH)}_4]^{-1}$, while in case of Fe the number of aqua group in the coordination sphere is higher, the predominating species being $[\text{Fe(H}_2\text{O)}_3\text{(OH)}_3]^{0}$ and $[\text{Fe(H}_2\text{O)}_2\text{(OH)}_4]^{1-}$.

**4.2 Effect of Phosphate on Arsenite Sorption**

Batch experiment revealed that phosphate in solution diminished the As$^{\text{III}}$ sorption by all LECA sorbents (Figure 2). This response in harmony with earlier findings of Guan et al. (2009) and Qiao et al. (2012). However, the competition by phosphate for the sorbent surface was highly pH-dependent, being most pronounced at low pH’s 3 and 5. This outcome agrees with the results reported by Su and Puls (2001). In the oxide-coated LECAs, the added phosphate lowered the As$^{\text{III}}$ sorption more than in LECA. Figure 2 also demonstrates that the competitive effect of phosphate on the As$^{\text{III}}$ sorption was less distinct in LECA than in AL-LECA and Fe-LECA. On the other hand, in the latter cases the impact of phosphate on As$^{\text{III}}$ sorption drastically diminished with elevated pH.
At pH 3, the phosphate additions of 20 µg L⁻¹ decreased the removal of AsIII by Fe-LECA 18.9 times, while in Al-LECA and LECA only 6.8 times and 2.4 times, respectively.

Interestingly, at pH 7 the differences between the coated sorbents became less distinct and even opposite. The added phosphate seemed to lower the AsIII sorption by Fe-LECA not more than 2.1 times, by Al-LECA 2.3 times and by LECA 1.7 times. These responses indicate that at pH 5 or lower the sorption onto Fe-LECA was most sensitive to competition by phosphate. When pH was elevated, the impact of phosphate on the AsIII sorption onto Fe-LECA was decisively lowered and that onto Al-LECA was even less distinct. This outcome is in harmony with previous finding of Yaghi and Hartikainen (2013) that at pH equal or greater than 6, Al-LECA retains phosphate to a higher degree than does Fe-LECA, while in solution with pH less than 6 the feature is opposite.

Moreover, in LECA, Al is the main octahedral cation and, thus, LECA is much higher in total Al than in total Fe. However, according to Yaghi and Hartikainen (2013) in Al-LECA used in this study more than 56% of total Al is amorphous, while the amorphous Fe fraction in Fe-LECA did not exceed 28%. On the basis of the solubility diagrams given by Lindsay (1979), at elevated pH the oxidic Fe³⁺ in LECA materials were more easily dissolved than oxidic Al³⁺. Thus, it can be expected that increase in pH is able to convert some structural Al in LECA and oxide coated LECA into a more amorphous form rather than into soluble form.

It is noteworthy that when phosphate addition at pH range 3 – 5 was higher than 50 µg P L⁻¹, it inhibited AsIII sorption onto Al-LECA and Fe-LECA. Phosphate is an anion of relatively strong phosphoric acid (pK₁=2.1), and at this pH range its dominating species is monovalent anion H₂PO₄⁻ (pK₂=7.2). It has a decisively stronger sorption tendency than AsIII. However, at pH 10 phosphate addition reduced the sorption of AsIII only slightly. At this pH, the surface of oxide will be saturated with OH⁻ groups, which render the oxide surface more negative and hamper the retention of phosphate. Arseneous acid (H₃AsO₃, pKₑ = 9.2), in turn, is a weak acid and, thus, it is able to protonate the OH groups on oxide surface and to form arsenite anion H₂AsO₃⁻. This is able to replace the aqua groups formed in protonation. At low pH, an opposite feature will be seen; the AsIII will exist as a neutral molecule while phosphate will exist as a monovalent anion H₂PO₄⁻ able to be retained by ligand exchange.

Although LECA had a lower sorption capacity than the oxide-coated LECAs (Table 1) at the pH range 3 – 7, it was less affected with phosphate than the other sorbents. This is can be attributed to the fact that LECA is lower in amorphous Al– and
Fe–oxides due to their crystallization reactions during the manufacturing process (Yaghi and Hartikainen, 2013). In other words, LECA seemed to be the best option to remove As^{III} from groundwaters high in phosphate. This result is supported with the previous finding of Meng et al. (2001) in Bangladesh that As from the well groundwater is difficult to remove by Fe-hydroxides because of high phosphate concentrations.

5. Conclusion
This study indicated that the sorption of As^{III} onto uncoated and oxide-coated LECA sorbents is highly pH-dependent. The apparent maximum sorption ($X_m$) of As^{III} increases upon elevated pH. Presence of phosphate in solution reduces the sorption of As^{III} by all LECA materials, more efficiently with higher phosphate dosage. However, the competitive role of phosphate in the As^{III} sorption decreased with increasing pH. At low pH, the retention of phosphate was greater than that of arsenite, whereas an opposite trend was seen at high pH. The most significant effect of phosphate on arsenite removal by Fe-LECA occurred at pH 3 and pH 5 whereas in case of Al-LECA at pH 7. LECA was less affected with phosphate at the pH range 3 – 7. Therefore, LECA seemed to be the best option among our materials for removing arsenite from groundwaters high in phosphate.

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