Arsenic of Adsorption Characteristics in Taiwan Soils

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Abstract

In soil environment, various forms of solid-phase arsenic of total amount of arsenic and the aqueous form of arsenic in soil solution make a thermodynamic equilibrium system. The uptake of aqueous arsenic by crop roots results in the shift of this equilibrium system. The purpose of this research was thus to investigate the adsorption characteristics of aqueous As (III) and As (V) in Taiwan soils. The results from the adsorption batch experiment showed that the adsorption capability of the soils increased with increasing amounts of Fe, Mn and Al oxides. In addition, the adsorption of As (V) was higher than As (III) by the same soil. Because of the competition between phosphate and arsenite/arsenate anions for the adsorption sites on the soils, the samples with high amount of bound phosphate were less capable to adsorb aqueous arsenic. The desorption of arsenic occurred within 2–3 hr when the soils were submerged in water. This contributed to the increase of concentration of aqueous arsenic in the reaction systems. In the batch experiment, the kinetics analyses of the adsorption of As (III) and As (V) by the soils showed that the main reaction was of zero order in 0 to 24 hr and of the 3rd order in some few reaction periods.

Key Words: Arsenic, Aqueous Form, Adsorption, Desorption, Kinetics

1. Introduction

Naturally arsenic exists in rocks and minerals. Due to weathering, erosion and volcanic emissions, arsenic contacted the groundwater and develops pollutant [1]. Arsenic is one of the most harmful and toxic element found in nature. It was a slowly poisoning element which severely affected the human health and other living organisms [2]. Arsenic is among the inorganic contaminants that have become of evolving environmental concern lately because it is a toxic substance to both animals and plants. Its geochemical dispersion into the environment naturally occurred through weathering processes and this could be enhanced by mining activities which might lead to important local and regional pollution of soil and water. In industry, arsenic was mainly used as the wood preservative, hence it was used in dyes, paints and pigmenting substances. It was also used in glass-making, electronics manufacturing and leather tanning industries. A small amount of arsenic was used in both human and animal medications and care products, and it was present in many food supplement products also [1]. The actual distribution, mobility, bioavailability, toxicity, bioaccumulation, and biodegradability of arsenic depended not only on its total concentration but also on its chemical form in the sample [1]. Arsenic can exist in inorganic form, organic form and gaseous state. Organic arsenic species are less harmful and readily eliminated by the body. However, the inorganic form of arsenic is highly toxic compared to organic arsenic. Inorganic arsenate and arsenite referred to a pentavalent As (V) and trivalent As (III), respectively, were most common in natural waters [3]. As (III) was 60 times more toxic than As (V) because of its greater cellular uptake [3].
Arsenic normally derived from surface water or groundwater, depending on local availability, which are very variable in their arsenic contents, although the highest concentrations were often found in groundwater [4]. The arsenic contamination of soils and water represented a great threat to human health because of its high potential to enter into the food chain [5]. Long-term exposure to inorganic arsenic compounds could lead to various diseases such as conjunctivitis, hyperkeratosis, hyperpigmentation, cardiovascular diseases, disorders of the central nervous system and peripheral vascular system, skin cancer and gangrene of the limbs [5–7]. Additionally, arsenic poisoning also led to death from multisystem organ failure by allosteric inhibition of sulfhydryl containing essential metabolic enzymes. It also interfered with some biochemical processes involving phosphorous owing to the similar chemical properties [5–7].

According to World Health Organization (WHO) and United States Environmental Protection Agency (US EPA), the maximum allowed concentration of arsenic in drinking water is 10 μg L⁻¹ [8]. However, the arsenic concentrations about 100 times more than the permissible limit were found in many areas around the world [1,4]. Blackfoot disease is an endemic peripheral vascular disease found among the inhabitants of a limited area on the southwest coast of Taiwan, where artesian well water with a high concentration of arsenic has been used for more than eighty years [9,10]. The rapid expansion of industry and commerce development in Taiwan had caused the difficulties in land acquisition. As a result, industrial zones built around agricultural areas had caused pollution problems. To increase the agricultural output, farmers used pesticides and fertilizer excessively which were another arsenic pollution source. Adsorption was one of the most commonly reported, and it would occur possibly the initial reaction when arsenic interacted with soils [11]. There were many factors which affected the arsenic adsorption in soil. Arsenic was known to strongly adsorb by inorganic constituents in soils such as clay minerals, iron (Fe) and aluminum (Al) oxides/hydroxides. Both As (V) and As (III) had the strong affinities for Fe and Al oxides [11,12], and even the soil organic matter content exhibited the most important influence on arsenic adsorption [13]. From adsorption research performed on 18 soils with varying soil properties, Burns et al. (2006) reported that arsenic adsorption was highly correlated with the soil pH and iron oxide content [14]. In addition, X-ray spectroscopy studies demonstrated the formation of strong inner-sphere complexes between adsorbed arsenic and the adsorbent surfaces that were mainly composed of Fe/Al oxides [11,12]. The concentration of phosphate (PO₄) was also a main factor which affected the As adsorption negatively, because PO₄ had a competition for adsorption sites with As (V) [15]. Understanding of the As (V) and As (III) adsorption processes in Taiwan soils was poor. Therefore, the objectives of this research were to examine the As (V) and As (III) adsorption behavior with soils samples collected around Taiwan. This fundamental research would be helpful for further application in the treatment of arsenic contaminated Taiwan soils.

2. Materials and Methods

2.1 Soil Sample Collection

Two alluvial soil samples with low arsenic concentration were collected from cultivated land at Xihu Township in Changhua and Gueiren District in Tainan, one red soil was collected from Pingzhen District in Taoyuan. All samples were used for the batch of adsorbability test for inorganic arsenic.

Each sample consisted of ten random sub-samples, and each sampling point included surface soil (0–15 cm) and bottom soil (15–30 cm). The soil samples for the batch of adsorbability test were collected from surface soil (0–15 cm). Individual sub-samples were mixed, air dried, grinded, and stored in plastic bottles after 2 mm sieving.

2.2 Analysis of Soil Characteristics

Soil pH was measured in soil suspension at 1:1 (w/v) soil solution ratio using glass electrode [16]. Electrical conductivity (EC) was measured with electric conductor using the soil suspension prepared as described above [17]. Organic carbon was determined by dry heating method [18]. Soil texture was tested with the hydrometer method [19]. Cation exchange capacity of the soil was evaluated with the ammonium saturation method [20]. Valid phosphorous was determined with Bray NO. 1 method [21]. Crystallized manganese, iron and aluminum oxides were determined using the methods of Mehra and
Jackson (1960) [22]. Citrate-bicarbonate-dithionite (CBD) reagent solution was used to dissolve oxidized manganese, oxidized iron and oxidized aluminum in the soil and then the concentration of manganese, iron and aluminum in soil. Irregular iron, manganese and aluminum oxides extracted by ammonium oxalate were analyzed by Schwertmann (1964) method [23], using 0.2 M of ammonium oxalate at pH 3.0 for extraction.

2.3 Batch Experiments on the Adsorbability of Arsenic Based on Soil Compositions

Each 10 g surface soil sample collected from Pingzhen District (red soil), Xihu township (alluvial soil), and Gueiren District (alluvial soil) was added with 100 mL of HAsO₄²⁻ or AsO₄³⁻ solution whose As concentration was 6 mg L⁻¹ to mix into suspension with soil and solution ratio at 1:10 (w/v). Then the samples were oscillated for 1 h, 2 h, 4 h, 8 h, 12 h, 16 h and 24 h, and centrifuged (33,000 g), the supernatant was filtered (No. 42) and measured the residue concentration of arsenic by inductively coupled plasma atomic emission spectrometry (ICP-OES, IRIS Intrepid II XSP, Thermo Scientific).

3. Results and Discussion

The adsorption tendency of soil samples in this research were shown in Figures 1–3. The adsorption follows in the order: Pingzhen > Gueiren > Xihu soil. It was interesting to note that Pingzhen soil contain the higher content of oxides as well as lower content of phosphorous (P) as compared with Xihu and Gueiren soil series (Table 1). In this research, the contents of P in soil samples collected from Pingzhen, Gueiren and Xihu were 7.62 mg kg⁻¹ and 42.1 mg kg⁻¹ and 212 mg kg⁻¹, respectively, thus Pingzhen and Gueiren soil provided less valid adsorptive positions for P than Xihu soil. These results indicated that the tested soils could provide valid adsorptive positions to P and As (Figures 1–3, Table 1). Violante and Pigna (2002) studied the competitive sorption of PO₄³⁻ and As(V) on selected clay minerals [15]. They found that PO₄³⁻ could inhibit As (V) sorption on clay minerals such as gibbsite and kaolinite. Smith et al. (2002) observed that the presence of PO₄³⁻ greatly decreased As (V) sorption by soils containing low amounts of Fe sorption but had little effect on the amount of As (V) adsorbed by soils with high Fe content [24]. Chen et al. (2010) found that there was no competitive effect of the presence of equimolar As (III) or As (V) adsorption [25].
were in agreement with these previous reports that the P content negatively correlated with arsenic adsorption.

As seen in Figures 1–3 and Table 2, the concentration of As (III) and As (V) in water soluble form of surface soil collected from Pingzhen and Gueiren decreased rapidly in 0–1 h. In particular, the concentration of As (V) decreased from 6.01 mg kg⁻¹ to 0.10 mg kg⁻¹ and 0.57 mg kg⁻¹, respectively. During the same period, the content of As (III) decreased in Pingzhen and Gueiren soils from 5.65 mg kg⁻¹ to 2.01 mg kg⁻¹ and 4.02 mg kg⁻¹, respectively. These results indicated that as soon as arsenic entered into the soil, it was adsorbed by iron, aluminum and manganese oxides in soil, and this led to a rapid drop in concentration of As (III) and As (V) in solution (Table 2). In addition, the data also indicated that the concentration of As (V) in Pingzhen and Gueiren soils remained nearly stable from 1 h to 24 h, while the same for As (III) from 1 h to 16 h because of the occupation of valid adsorption positions by As (III) and As (V) within 0–1 h, and the slowdown of adsorption. Previously, it was reported that the adsorption of As (V) from aqueous solution was rapid in the initial stages of contact and reached a maximum in the range of 35–60 min for soil [26]. In this research, within 0–1 h the residual concentration of

**Figure 3.** The adsorption tendency of aqueous As (III) and As (V) on Gueiren soil at room temperature.

**Table 1.** Physical and chemical properties of the soils for the adsorption of batch experiments

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Texture</th>
<th>pH</th>
<th>EC</th>
<th>CEC</th>
<th>Org-C</th>
<th>Total As</th>
<th>Bray-I P</th>
<th>Citrate-bicarbonate-dithionite extractable</th>
<th>Oxalate extractable</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe</td>
<td>Al</td>
<td>Mn</td>
<td>Fe</td>
</tr>
<tr>
<td>Pingzhen</td>
<td>C</td>
<td>4.52</td>
<td>0.210</td>
<td>7.16</td>
<td>0.62</td>
<td>10.51</td>
<td>7.62</td>
<td>3.83 % 0.61</td>
<td>187</td>
</tr>
<tr>
<td>Xihu</td>
<td>LS</td>
<td>6.79</td>
<td>0.209</td>
<td>4.87</td>
<td>0.42</td>
<td>8.0</td>
<td>212</td>
<td>0.60 % 0.05</td>
<td>192</td>
</tr>
<tr>
<td>Gueiren</td>
<td>L</td>
<td>5.09</td>
<td>0.651</td>
<td>7.89</td>
<td>0.72</td>
<td>8.3</td>
<td>42.1</td>
<td>0.71 % 0.09</td>
<td>120</td>
</tr>
</tbody>
</table>

**Table 2.** The remaining concentrations of As (III) and As (V) after the absorption of aqueous arsenic in surface soils at various reaction periods

| Reaction period | Pingzhen | | | | Xihu | | | | Gueiren | |
|-----------------|---------|---|---|---|---|---|---|---|---|
| As (III) mg kg⁻¹ | As (V) mg kg⁻¹ | As (III) mg kg⁻¹ | As (V) mg kg⁻¹ | As (III) mg kg⁻¹ | As (V) mg kg⁻¹ |
| 0               | 5.65 ± 0.01 | 6.01 ± 0.02 | 5.65 ± 0.01 | 6.21 ± 0.03 | 5.65 ± 0.01 | 6.01 ± 0.03 |
| 1               | 2.01 ± 0.02 | 0.10 ± 0.01 | 5.74 ± 0.02 | 6.18 ± 0.10 | 4.02 ± 0.03 | 0.57 ± 0.02 |
| 2               | 2.15 ± 0.01 | 0.08 ± 0.00 | 5.57 ± 0.02 | 5.28 ± 0.14 | 4.56 ± 0.02 | 0.76 ± 0.03 |
| 4               | 1.61 ± 0.05 | 0.05 ± 0.01 | 4.78 ± 0.06 | 4.65 ± 0.01 | 3.75 ± 0.05 | 0.30 ± 0.02 |
| 8               | 1.61 ± 0.06 | 0.03 ± 0.00 | 4.81 ± 0.14 | 4.28 ± 0.07 | 3.40 ± 0.08 | 0.35 ± 0.00 |
| 12              | 0.93 ± 0.00 | 0.03 ± 0.00 | 3.75 ± 0.03 | 4.02 ± 0.03 | 3.29 ± 0.10 | 0.31 ± 0.00 |
| 16              | 1.42 ± 0.01 | 0.03 ± 0.00 | 4.02 ± 0.08 | 3.82 ± 0.01 | 3.23 ± 0.06 | 0.30 ± 0.00 |
| 24              | 0.05 ± 0.01 | ND | 0.28 ± 0.01 | 3.31 ± 0.03 | 0.16 ± 0.015 | 0.21 ± 0.02 |

* Standard deviation of the mean. b Not detectable.
As (V) in solution was lower than As (III) (Table 2). Therefore, the adsorption of As (V) was higher than that of As (III) and the results were in agreement with the results reported earlier [27,28]. The high adsorption of Arsenic had been a global problem, challenges for Safe Water Production reported that adsorption of As (V) was higher than that of As (III) when the molar ratio of As (III)/As (V) equaled 5:1 and 10:1 [28]. Jain and Loeppert (2000) found that in the dual-anion system at equimolar As concentrations of ≤ 156 mg L⁻¹ each, As (V) influenced the retention of As (III) in the pH range of 4 to 10 more pronouncedly than As (III) influenced the retention of As (V) [29]. The oxidation state of As depended primarily on pH and redox conditions, with As (V) being the most stable form under aerobic conditions as the pH-dependent deprotonated oxyanions of arsenic acid (H₂AsO₄⁻ and HAsO₄²⁻) and As (III) the chemically dominant forms in reducing environment as a neutral species (i.e., pKₐ1 = 9.2) at natural pH. Therefore, the As (III) was more difficult to remove from water at neutral pH by means of adsorption and coprecipitation because of the lack of electrostatic attraction [30]. However, most As-enriched groundwater was generally dominated by As (III), up to 96% of total As [31]. McGeehan and Naylor (1994) reported that the Fe and Mn oxides were restored and dissolved by the release of adsorbed arsenic to the solution [32]. Barrachina et al. (1996) observed that 80% of the total amount of As (III) adsorbed was sorbed by Spanish soil in the first 30 min [31]. O’Reilly et al. (2001) discovered that As (V) sorption on goethite was initially rapid, with over 93% As (V) adsorption within 24 h [32]. In this research, the concentration of As (III) in Pingzhen and Gueiren soils decreased rapidly from 16 h to 24 h. The reason was considered that the saturated soil in anaerobic state reduced Fe and Mn, hence the reduction of Mn increased the As (III) adsorption and As (III) was oxidized into As (V). In addition, the concentration of As (III) in Pingzhen soil, As (III) and As (V) in Gueiren soil might increase after two hours immersed because of the arsenic desorption (Figures 1 and 3). Further studies were required to examine the kinetics of both As (III) and As (V) adsorption in the same soil system. This information was essential because both As (III) (predominantly in the reduced condition) and As (V) (predominantly in the oxidized condition) were often discovered in either redox environments because of the relatively slow redox transformation of As [33].

The adsorption of As (III) and As (V) by Xihu soil during the period of 0–16 h was lower (Figure 2) than Gueiren soil (Figures 1 and 3). These results might possibly be derived from the relationship between the factors of valid adsorption position and oxide content. Another explanation was the relationship between pH and pE. The pH of Xihu soil was 7.21 and increased when the soil immersed in water, while the pE drops noticeably. During this time, As (V) might undergo reduction and transformed into As (III) in the reaction system. For another, the researchers studied the adsorption of As on the soil minerals (oxides, hydroxides, or clays) and found that adsorption decreased with increasing pH [28]. Desorption of As (III) and As (V) occurred after oscillation for 1 h (Figure 2). In 16–24 h of reaction time, the concentration of As (III) in Xihu soil dropped to near zero (Figure 2), perhaps the Xihu alluvial soil contained relatively large amounts of carbonate. Sadiq (1997) pointed out that arsenic in alkaline soil was adsorbed by carbonate, and the sediment of calcium arsenate formed by calcium ions might lead to decrease the As (III) [34]. Previous reports about pH influence on As adsorption suggested that As (III) sorption was maximum at around pH 7 [35,36], whereas As (V) sorption reached to maximum sorption around pH 4–7 and then decreased with increasing pH [36,37]. However, further studies required to know the reason for the concentration of As (V) was not decreased within 16–24 h.

The evaluation on the As (III) and As (V) adsorbatibilities of surface soil collected from Pingzhen, Gueiren and Xihu were calculated with the following dynamics equation according to different reaction level simulated at different time blocks.

\[
\frac{dC}{dt} = kC^n
\]

where \( C \), \( t \), \( k \), and \( n \) were represents the concentration, reaction time, rate constant and reaction order, respectively. The equations of zero and third degree were as follows:

\[
C = C_0 - kt
\]
where $C_0$ was the initial concentration.

Generally, within two adjacent test times, sample with rapid change in concentration was treated as 0 order reactions to calculate its rate constant. In consecutive times, the trend of concentration change was simulated from order 0 to 3, and the highest reaction order was selected to simulate the optimal order. The results were shown in Table 3.

In 0–24 h, Pingzhen soil was of 0 order reaction to As (III) and As (V). The rate constant of As (V) adsorption was higher than that of As (III) during 0–1 h, but the constant of As (III) was higher than As (V) (Figure 1 and Table 3) because of the oxidization of As (V) from As (III). In Xihu soil system, the rate constant of As (V) in 0–4 h was five times larger than that in 4–24 h; the reason might be As (V) not yet transformed into As (III) during the response time. In 4–24 h, As (V) gradually transformed into As (III) caused the reaction rate decrease. As (III), in 16–24 h, increased four times because As (III) and calcium arsenate produced by calcium ion was settled (Figure 2 and Table 3). As (III) adsorption into Gueiren soil showed the 3rd order reaction in 0–16 h, and 0 order reaction in 16–24 h. As (V) adsorption showed level 0 reaction in 0–1 h, and the 3rd order reaction in 1–24 h (Figure 3 and Table 3). The reason for direct proportional reaction between reaction speed and concentration in 0–16 h and 1–24 h was yet to be studied. As seen in Table 3, most soil samples showed 0 order reaction to As (III) or As (V). Thus, the adsorption reaction rate had no correlation with arsenic concentration. Any reaction over order 0 should be caused by different compositions of soil.

### 4. Conclusions

1. The main link for arsenic in soil was based on iron, aluminum and manganese oxides and hydrated oxides. Thus, in the batch adsorbability test, soil with high content of oxides had high arsenic adsorbability. However, results of Pingzhen soil showed that adsorptive positions, such as phosphate of high adsorbability could compete for adsorptive position with arsenic and result in reduction in arsenic adsorbability. The arsenic adsorbability of three soil series showed that As (V) adsorbability was higher than As (III), and desorption at the initial stage of soil immersed in water could cause increase of arsenic concentration in solution.

2. For the adsorptive dynamics of As (III) and As (V) in 0–24 hr in batch adsorbability test, only As (III) adsorbability in 0–16 hr and As (V) adsorbability in 1–24 hr of Gueiren soil were of the 3rd order and the arsenic adsorbability of reaction system was of the 0 order.

### References


4. Brammer, H. and Ravenscroft, P., “Arsenic in Groundwater: a Threat to Sustainable Agriculture in South and

### Table 3. The kinetic analyses of aqueous As (III) and As (V) absorbed by various soils

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Reaction period (h)</th>
<th>Reaction order</th>
<th>Correlation coefficient (R)</th>
<th>Rate constant (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>00–01 0</td>
<td>1.000</td>
<td>3.628 &lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>01–24 0</td>
<td>0.921</td>
<td>0.073 &lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>Pingzhen</td>
<td>00–16 0</td>
<td>0.880</td>
<td>0.122 &lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16–24 0</td>
<td>1.000</td>
<td>0.480 &lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Xihu</td>
<td>00–16 3</td>
<td>0.901</td>
<td>0.002 &lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16–24 0</td>
<td>1.000</td>
<td>0.379 &lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>Gueiren</td>
<td>00–01 0</td>
<td>1.000</td>
<td>5.890 &lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>01–24 0</td>
<td>0.994</td>
<td>0.002 &lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>As(V)</td>
<td>00–04 0</td>
<td>0.933</td>
<td>0.382 &lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Pingzhen</td>
<td>00–04 0</td>
<td>0.933</td>
<td>0.382 &lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
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<tr>
<td></td>
<td>04–24 0</td>
<td>0.990</td>
<td>0.063 &lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>Xihu</td>
<td>00–01 0</td>
<td>1.000</td>
<td>5.443 &lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
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<tr>
<td></td>
<td>01–24 3</td>
<td>0.895</td>
<td>0.414 &lt;sup&gt;b&lt;/sup&gt;</td>
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</tr>
<tr>
<td>Gueiren</td>
<td>00–01 0</td>
<td>1.000</td>
<td>5.443 &lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>01–24 3</td>
<td>0.895</td>
<td>0.414 &lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a,b</sup> The units for the rate constants indicated are mg L<sup>-1</sup> h<sup>-1</sup> and [(mg L<sup>-1</sup>)<sup>2</sup>] h<sup>-1</sup>, respectively.


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