Removal of arsenic from polluted water through adsorption onto selected soil

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ABSTRACT

An arsenic-contamination survey was conducted in Lake Datunhai in Southwest China, which is contaminated by arsenic. The arsenic-contaminated soil was selected and arsenic adsorption on the soil solid in the polluted water was studied through field investigation and laboratory experiments. The results showed that the red soil in survey area contained a relatively large amount of arsenic in the range of 36.41–153.52 mg/kg, which is higher than the National Soil Environmental Quality Standard Grade III. The arsenic pollution in the surveyed lake was relatively serious, as the amount of arsenic contained in the water of Lake Datunhai was between 0.23 and 0.663 mg/L. The amount of arsenic in the sediment was between 273 and 755 mg/kg. The results of laboratory adsorption experiments with different soils showed that when the ratio of soil and water was 3.5/1000, the amount of arsenic in the water sample taken from the lake reduced from 0.3 mg/L to 0.03 mg/L, which would satisfy the Water Quality Standard Grade III (below 0.05 mg/L). The selected red soil was relatively effective for arsenic absorption. Based on theoretical calculations, the thickness of sediment would increase by about 0.95 cm by applying fixed arsenic solid on arsenic-polluted water treatment.

Key words: adsorption, arsenic, soil, water treatment

HIGHLIGHT

- An arsenic-contamination survey was conducted in Lake Datunhai in Southwest China, which is contaminated by arsenic. The arsenic-contaminated soil was selected and the arsenic adsorption on the soil solid in the polluted water was studied through field investigation and laboratory experiments.

INTRODUCTION

Arsenic contamination in surface water is a serious environmental problem that has received increasing attention in many areas of the world in the last decades due to arsenic’s high toxicity and mobility. Arsenic is a common pollutant, it is highly toxic and can cause a number of diseases (Li et al. 2012). It can replace nutrient phosphorus to combine with thiol on cells, and thus damage the cells (Ng et al. 2003). In populations with long-term consumption of water containing arsenic of 0.1 mg/L, the prevalence of arsenic poisoning can reach 15.9%; and among patients with chronic arsenic poisoning, the cancer rate can be as high as 15%. The serious contamination of arsenic caused by human activities such as mineral resources mining and smelting and phosphorus chemical production poses not only a threat to water quality and public health and safety, but also brings significant negative impacts on socio-economic development (Wang & Mulligan 2006a). It is known that arsenic often exists in many non-ferrous metal mines, so arsenic contamination can be caused by mining and smelting processes. The surveyed area of this study is a well known mineral resource-rich area, with frequent mining activities and serious environmental pollution (Ye et al. 2004). The mining activities are the main reason for the high arsenic content in the soils around the lake.

Currently, in order to effectively remove arsenic from aqueous solutions, many research areas have been explored such as coagulation, precipitation, ion exchange filtration and adsorption. However, these technologies are usually highly costly, complex, and not efficient (Choong et al. 2007). In general, the adsorption process has been regarded as one of the most...
important and widely used approaches for arsenic removal due to its high removal efficiency, easy operation and low cost. Most treatment technologies for removing arsenic from contaminated water are related to the formation of ferric arsenate or ferric arsenite as well as its adsorption (Zhao 1995; McNeill & Edwards 1997; Xing et al. 2002; Lee et al. 2003; Yuan et al. 2006; Lui et al. 2009; Wang & Tsang 2013). China’s red soil is rich in iron oxides, including goethite, hematite, lepidocrocite and maghemite, etc., of which goethite and hematite are the most common. The content of free iron oxide in red clay is 2%–24% (calculated by Fe₂O₃) (Chen et al. 2014). Red soils are predominant in Southwest China’s Yunnan and Guizhou provinces. These soils have high contents of clay, Fe and Al oxides, and very low P content. Therefore, selecting suitable red soil as adsorbent is important for developing arsenic-removal technology to deal with arsenic-contaminated surface water.

Through screening soils with arsenic-contaminated water and to allow arsenic adsorption as the treatment for arsenic-contaminated water, this study is intended to provide a technical basis to the eventual development of an arsenic-removal soil adsorption technology. Findings from this research will provide strong technical support to the establishment and improvement of the national ‘Water Environment Quality Safety Guarantee and Key Supporting Technology’ system and ‘Emergency Water Environment Pollution Control Technology’ to strengthen environmental protection and water management.

MATERIALS AND METHODS

Water and sediment sampling

Twenty-four sampling sites were selected in Lake Datunhai as shown in Figure 1. A 2 L surface water sample (0–1 m) was collected at each site using a Plexiglas water sampler and transported to the laboratory in a brown glass bottle for analysis. Sediment was collected at the same site and time. Sediment samples from the lake bottom were collected by means of a column sampler (in a 20 cm layer). The collected sediment samples were first cleaned by removing grass roots, gravel, etc., and then dried in the laboratory. After drying, sediment samples were ground to pass through a 100 mesh sieve. The sieved samples were then prepared with sulfuric acid and nitric acid digestion for later measurement uses.

Test soil

Lake Datunhai is located in Yunnan province in China, a hilly region with widely distributed red soil. To investigate the possibility of practical application of soil for arsenic adsorption in the treatment of arsenic-contaminated lake water, this study selected 10 soil samples from the lake surrounding areas (3–8 km away from the lake). The soil samples were dried and ground for standby application after collection.

Reagents

The reagent purity used in this method was analytical pure or guarantee reagent, and the water for determination was deionized water.
(1) Na₂HAsO₄·7H₂O; (2) 1% potassium borohydride (KBH₄) solution: 0.2 g of potassium hydroxide was weighed and dissolved in 100 mL deionized water, and then 1 g of potassium borohydride solution was added to the mix; (3) Carrier: 2% hydrochloric acid solution was made by taking 10 mL of concentrated hydrochloric acid and diluted with deionized water to 500 mL; (4) Sample pre-reduction: 1 mL of water sample was taken to a 10 mL colorimetric tube, then 1 mL of concentrated hydrochloric acid and 0.1 g of thiourea and ascorbic acid were added, to dissolve in deionized water to 10 mL. Measurements began after 30 min.

**Instruments and working conditions**

Instrument: Beijing Purkinje General, PF6 non-dispersive atomic fluorescence spectrometer; working conditions: photomultiplier tube (PMT) negative high voltage 265 V, atomization temperature 180 °C, lamp current 40 mA, carrier gas flow rate 300 mL/min, shielding gas flow rate 600 mL/min.

**Measurement of arsenic content in water (SEPA 2002)**

Water sample processing: 1 mL water sample was taken into a 10 mL colorimetric tube, 1 mL concentrated hydrochloric acid, 0.1 g thiourea and ascorbic acid were added into the tube, and then all materials were dissolved with deionized water, finally deionized water was added to 10 mL mixed, and measured after 30 min.

**Measurement of arsenic content in sediment (GB/T 22105.2-2008 2008)**

Sediment sample processing: 0.2–1.0 g of air drying soil was taken, dissolved in 6 mL hydrochloric acid and 2 mL nitric acid, and then digested in boiling water for 2 h. After cooling, a specified amount of digestion solution was added into a 50 mL colorimetric tube, plus 3 mL hydrochloric acid, 5 mL thiourea and 5 mL ascorbic acid solution, and a constant volume of water was added to scale before testing.

**Different arsenic concentrations**

Test conditions: different soil–water ratios were set according to different initial concentrations. When the initial concentration was 0.3 mg/L As (V), the soil-water ratio was 2/1000; and when the initial concentration was 0.9 mg/L As (V), the soil-water ratio was 6/1000; according to the aforementioned soil-water ratio, 200 mesh sieve red soil was weighed and added into 100 mL arsenic solution with the concentrations of 0.3 mg/L and 0.9 mg/L respectively, and the sample was then shaken for 10 min at a rotation speed of 225 rpm.

**Different adsorption times**

Test conditions: for the initial concentration 0.3 mg/L As (V), the soil-water ratio was 2/1000. A 200 mesh sieve red soil sample was weighed in to a 100 mL arsenic solution with the concentration of 0.3 mg/L, the sample was then shaken for 10 min at a rotation speed of 225 rpm. Soil arsenic adsorption was measured at different shaking times of 5 min, 10 min, 15, 20 and 30 min.

Test conditions: the soil-water ratios of 2.5/1000 and 3.5/1000 were used for the outer lake; and the soil-water ratio of 1/1000 for the inner lake; 200 mesh sieve red soil 6# was added into the 100 mL actual water sample, and then shaken 10 min at the rotation speed of 225 rpm. The water arsenic content was measured after precipitation to calculate the soil arsenic adsorption effect and removal rate.

**Statistical analysis**

SPSS 19.0 was used for data processing and correlation analysis.

**RESULTS**

**Arsenic contamination in waterbody and sediment of Lake Datunhai**

The Lake Datunhai catchment area in this survey is 284.5 km² with water surface area of 12.4 km². The average water depth is 2.3 m and the maximum water depth is 2.7 m, and the average annual lake water inlet amount is 27 million m³.

Figures 2 and 3 show the arsenic concentration distribution in the Datunhai water and sediment samples. Arsenic could be detected in water and sediment at all sampling sites. Arsenic concentration in Lake Datunhai water body seriously exceeded the national standard, and mainly was As(V). Arsenic concentrations at water sampling points S13 and S22 were relatively high (0.663 mg/L and 0.583 mg/L), and those at other points ranged from 0.23 to 0.39 mg/L. The average arsenic...
concentration in the whole lake was 0.32 mg/L. Arsenic concentrations in the sediments at the 24 sites ranged from 273 to 755 mg/kg, with an average of 460.4 mg/kg.

Screening of soils for arsenic adsorption

The average arsenic content in the Earth’s crust is about 3 mg/kg, and China’s average soil arsenic background content is 9.2 mg/kg generally not exceeding 15 mg/kg (Weng et al. 2000). Because of China’s large territory of large regional differences, some areas have high arsenic background values and the red soil arsenic content in Yunnan reaches 16.40–19.20 mg/kg (Tian et al. 2007). However, in the vicinity of non-ferrous metal mining areas, due to the impact of man-made factors like mining washing, the soil and water arsenic content has partial abnormality and results in contamination (He & Zeng 2008).

Ten soil samples were collected from sites that were 3–8 km away from the lake, and some basic physicochemical properties of these soils are shown in Table 1. The pH values of all soil samples varied between 4.91 and 6.65, indicating that all soils are acidic soil. The content of organic matter in these soil samples was in the range from 6.35 g/kg to 22.48 g/kg, and the
arsenic content in these soils ranged from 36.41 mg/kg to 153.52 mg/kg, which all exceed the standards of National Soil Environmental Quality Standard Grade III.

As shown in Table 2, the 10 soils exhibited different adsorption capacities for arsenic. When the initial concentration of arsenic in water was 0.3 mg/L, the removal rate of arsenic achieved by soil 1#, soil 7# and soil 9# was 50.0%, 66.8% and 67.5%, respectively, whereas the removal rates achieved by other soils were much higher, ranging from 87.6% to 93.0%. When the initial concentration changed to 0.9 mg/L, the arsenic-removal rate of soil 1#, soil 7# and soil 9# was 56.9%, 68.6% and 72.6% respectively, while that achieved by other soils was in the range from 93.8% to 97.5%. After the adsorption treatment by the soils, the residual arsenic concentration in most waters was lower than 50 μg/L, which is the limit of China national standards for surface water, except that treated by soil 1#, soil 7# and soil 9#. Therefore, soil 1#, soil 7# and soil 9# were not suitable for arsenic removal from water in the present study due to their relatively low adsorption capacities for arsenic, and the other seven soils can be used for the removal of arsenic from the waterbody of the lake through the adsorption process. Furthermore, considering the future earthwork for soil collection, soil 3#, soil 5# and soil 6# were selected for further investigation.

It can be seen from Figure 4 that the selected three kinds of red soil can adsorb arsenic from water very rapidly. The removal of arsenic from water by the three soils reached more than 90% in only 5 minutes, after that the removal rates became stable.

<table>
<thead>
<tr>
<th>No.</th>
<th>pH</th>
<th>OM/(g/kg)</th>
<th>Fe_2O_3/%</th>
<th>MnO/(g/kg)</th>
<th>CaO/%</th>
<th>Al_2O_3/%</th>
<th>As/(g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>6.65</td>
<td>22.48</td>
<td>12.78</td>
<td>1,263.08</td>
<td>1.74</td>
<td>22.24</td>
<td>153.52</td>
</tr>
<tr>
<td>2#</td>
<td>6.05</td>
<td>9.57</td>
<td>8.01</td>
<td>1,518.87</td>
<td>0.48</td>
<td>25.14</td>
<td>63.13</td>
</tr>
<tr>
<td>3#</td>
<td>6.55</td>
<td>6.35</td>
<td>12.86</td>
<td>627.43</td>
<td>0.39</td>
<td>26.51</td>
<td>86.54</td>
</tr>
<tr>
<td>4#</td>
<td>6.15</td>
<td>9.02</td>
<td>12.05</td>
<td>760.71</td>
<td>0.38</td>
<td>31.48</td>
<td>107.25</td>
</tr>
<tr>
<td>5#</td>
<td>6.36</td>
<td>9.68</td>
<td>11.29</td>
<td>612.38</td>
<td>0.52</td>
<td>25.96</td>
<td>91.13</td>
</tr>
<tr>
<td>6#</td>
<td>4.91</td>
<td>6.92</td>
<td>14.04</td>
<td>441.91</td>
<td>0.21</td>
<td>25.86</td>
<td>36.41</td>
</tr>
<tr>
<td>7#</td>
<td>5.73</td>
<td>13.99</td>
<td>10.91</td>
<td>1,200.36</td>
<td>0.65</td>
<td>18.28</td>
<td>43.33</td>
</tr>
<tr>
<td>8#</td>
<td>5.61</td>
<td>6.62</td>
<td>12.59</td>
<td>501.38</td>
<td>0.25</td>
<td>26.70</td>
<td>63.88</td>
</tr>
<tr>
<td>9#</td>
<td>5.56</td>
<td>17.06</td>
<td>9.59</td>
<td>398.57</td>
<td>0.36</td>
<td>18.49</td>
<td>59.31</td>
</tr>
<tr>
<td>10#</td>
<td>5.15</td>
<td>13.12</td>
<td>13.59</td>
<td>146.34</td>
<td>0.23</td>
<td>19.09</td>
<td>45.66</td>
</tr>
</tbody>
</table>

Table 2 | Removal rate and adsorption capacity of As in different soils

<table>
<thead>
<tr>
<th>0.30 mg/L</th>
<th>0.90 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal rate/Adsorption concentration/Adsorption capacity/</td>
<td>Removal rate/Adsorption concentration/Adsorption capacity/</td>
</tr>
<tr>
<td>% (μg/L) (mg/kg)</td>
<td>% (μg/L) (mg/kg)</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>1# 50.0 180.2 90.0</td>
<td>56.9 380.9 251.7</td>
</tr>
<tr>
<td>2# 87.6 44.8 157.8</td>
<td>93.8 55.2 414.5</td>
</tr>
<tr>
<td>3# 92.2 28.1 166.1</td>
<td>97.4 22.8 430.7</td>
</tr>
<tr>
<td>4# 87.6 44.6 157.9</td>
<td>96.6 30.1 427.1</td>
</tr>
<tr>
<td>5# 88.3 42.2 159.1</td>
<td>97.5 22.2 431.0</td>
</tr>
<tr>
<td>6# 93.0 25.4 167.5</td>
<td>97.5 22.3 430.9</td>
</tr>
<tr>
<td>7# 66.8 119.5 120.4</td>
<td>68.6 277.2 303.5</td>
</tr>
<tr>
<td>8# 88.2 42.5 158.9</td>
<td>96.5 30.9 426.7</td>
</tr>
<tr>
<td>9# 67.5 117.0 121.7</td>
<td>72.6 242.6 320.8</td>
</tr>
<tr>
<td>10# 91.1 32.2 164.1</td>
<td>97.2 24.6 429.8</td>
</tr>
</tbody>
</table>
Treatment of lake water by soil 6#

According to arsenic-adsorption capacities of the tested soils, soil 6# was selected for the treatment of water samples collected from both inner lake and outer lake. It can be seen from Table 3 that, after the adsorption treatment, arsenic content of water sample collected from inner lake was 43.13 μg/L which can fulfill the requirement of China’s National Standards for Surface Water. The residual arsenic content of water samples collected from the outer lake was 54.14 μg/L, slightly higher than the national standard for surface water of 50 μg/L, when the soil-water ratio was 2.5/1000, but its value decreased to as low as 32.02 μg/L when the soil-water ratio was 3.5/1000, thus fulfilling the national standard. Although the water quality of the lake was very poor due to the high content of N and P, it seems that the arsenic adsorption by soil had not been influenced by the N and P present in the water, probably due to no adsorption competition between N or P and arsenic. This may deserve further investigation to confirm no adsorption competition.

Earthwork estimation for lake water treatment

According to the results obtained above, if the target concentration of arsenic in lake water after treatment is 50 μg/L, the soil-water ratio should be between 3/3000 and 3.5/3000 when using soil 6# for the treatment. The surface area of the lake is 12.4 km², and the water depth is 4–5 m. Thus, there is in total 50 million m³ water in the lake to be treated. An amount of 175,000 tons of soil is required to reduce the arsenic content in the lake water to below 50 μg/L when the soil-water ratio of 3.5/1000 is applied. Under normal circumstances, the density of naturally deposited sediment is 1.5 g/cm³. Thus, after pouring 175,000 tons’ soil into the lake, the level of lake sediment would increase about 0.95 cm.

DISCUSSION

It is known that arsenic often exists in many non-ferrous metal mines, so the arsenic contamination can be caused by the mining and smelting process. The surveyed area of this study is a well-known mineral resource-rich area, with frequent

<table>
<thead>
<tr>
<th>Table 3</th>
<th>As adsorption on soil solid phases for environmental water samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner lake</td>
<td>Outer lake</td>
</tr>
<tr>
<td>The ratio of soil and water (1/1000)</td>
<td>The ratio of soil and water (2.5/1000)</td>
</tr>
<tr>
<td>Removal rate/%</td>
<td>76.94</td>
</tr>
<tr>
<td>Adsorption concentration/μg/L</td>
<td>43.13</td>
</tr>
<tr>
<td>Adsorption capacity/mg/kg</td>
<td>143.89</td>
</tr>
</tbody>
</table>
mining activities and serious environmental pollution (Ye et al. 2004). The mining activities are the main reason for the high arsenic content in the soils around the lake.

Yunnan is a plateau region, with main water supply brought by southwest monsoon rainfall, featured by semi-closed streams with low flow and long water changing cycles, so heavy metals easily accumulate in the lake. As China’s major mineral resources province, Yunnan boasts 17.5% of the world’s zinc reserves, 11.7% of the national manganese reserves, and 48.2% of the identified national cadmium mineral reserve; it has the nation’s third largest copper and nickel reserves and is also a main production area for China’s lead and zinc (Yu & Ma 2005). However, for a longtime, Yunnan’s non-ferrous industry has been in extensive operation, with few product varieties, large proportion of primary products, which mostly are smelting products. Due to the lack of awareness of resource planning and environmental protection, some townships and private enterprises have carried out excessive exploitation of these resources and generated a large amount of acidic waste water and hazardous waste. Consequently, the toxic and harmful heavy metals entering the water due to acid mine drainage, tailing and heap leaching and weathering as well as torrential rain and flood, has resulted in serious heavy metal pollution and damage to the water environment (Huang 2002; Wang et al. 2002). With the arsenic industrial waste-water produced in processing non-ferrous metals such as tin, lead, mining, dressing, smelting and yellow phosphorus and acid production in the lake basin, the sewage of nearby towns discharged into the lake and the years of reservoir sludge accumulation, the pollutants eventually exceed the environment carrying capacity, leading to the excessive reservoir water arsenic concentration.

Adsorption methods have been widely used in arsenic removal of drinking water and wastewater treatment due to their advantages of economic efficiency and convenient operation (Maji et al. 2008). However, it is more urgent to study and develop new adsorption materials with low cost and high performance for the treatment of arsenic-polluted water with large amounts of volume. A comprehensive analysis of the principles of different chemical treatment technologies for arsenic-contaminated water is mainly related to the formation of iron arsenate and its adsorption by the combination of Fe³⁺ and As(V) (Hu et al. 2017). Red soil contains a large number of iron oxides (such as goethite, hematite, etc.) and aluminum oxides (aluminosilicate, etc.). This study has confirmed that iron and aluminum oxides have adsorption and fixation effects on arsenic. The soil with higher iron and aluminum content and lower arsenic content had a better adsorption effect. It has a good application prospect in Yunnan, Guizhou and Sichuan provinces in southwestern China, which are rich in red soil and mineral resources and have a high risk for arsenic pollution in water.

Many studies have shown that the iron and aluminum in the soil played an important role in arsenic adsorption. Arsenate can form insoluble arsenide with iron and aluminum cations and produce co-precipitation with amorphous iron and aluminum hydroxide. The more amorphous the Fe and Al oxides contained in the soil, the stronger is the arsenic adsorption capacity (Arai et al. 2005). Arsenic can be fixed on the surface of metal oxide through specific adsorption and non-specific adsorption. Specific adsorption refers to the entrance of anions into the metal atom coordination shell on the oxide surface to re-coordinate with the ligand hydroxyl or hydrated to combine on the solid surface directly through covalent bonds or coordinate bonds (Huang 2000). Spectroscopic studies have confirmed that As(III) and As(V) can conduct ligand exchange through OH⁻ or OH⁵⁺ on the ion surface to generate the inner ligand (Wang & Mulligan 2006b). By Raman spectroscopy and Fourier transform infrared technology, and combined with electrophoretic mobility testing as well as surface complexation model, etc., Goldberg and colleagues reported that As(V) formed inner ligands on amorphous aluminum oxide, whereas As(III) was adsorbed in the form of an outer ligand.

**CONCLUSIONS**

The lake investigated in the present study is seriously contaminated by arsenic, with arsenic content in lake water between 0.496 and 0.535 mg/L. Its content in lake water from the inner lake was in the range 0.199 mg/L to 0.23 mg/L. The sediment arsenic content was between 224.26 and 377.72 mg/kg.

When the soil-water ratio was 3.5/1000, the arsenic content in water samples reduced from 0.3 mg/L to 0.03 mg/L, reaching the level of surface water quality Grade III (0.05 mg/L).

After arsenic adsorption by soil and settlement to the bottom of the lake, the soil arsenic concentration increased to 112 mg/kg, lower than the initial arsenic content of the lake sediment. By theoretical calculation, to treat the lake water by soil adsorption, 175,000 tons’ soil will be required and the level of the lake sediment layer would increase by about 0.95 cm after treatment.
ACKNOWLEDGEMENTS

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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