Dynamic desorption of arsenic from polymer-supported hydrated iron(III) oxide in a wastewater treatment plant

Jian-Long Hu, Xiao-Song Yang, Ting Liu, Li-Nan Shao and Wang Zhang

ABSTRACT

Polymer-supported hydrated iron(III) oxide (PHIO) was successfully applied as adsorbent for arsenic removal in a wastewater treatment plant in Nandan, China. The practical PHIO adsorbent samples (PHIO-P) were collected from the adsorption column of the wastewater treatment plant, and desorption experiments of the adsorbent were carried out. Our results showed that the formation of precipitates on the surface of PHIO-P might block the porous channel of the adsorbent and decrease its arsenic adsorption capacity. In the dynamic arsenic desorption experiment, the arsenic desorption equilibrium was achieved more quickly at decreasing desorption velocity, and higher arsenic desorption efficiency was obtained at increasing NaOH concentration in regenerant. It was found that the PHIO-P adsorbent could be well regenerated at 1.0 M NaOH solution and desorption velocity of 5 BV h⁻¹. Comparing with the raw adsorbent, the maximum arsenic adsorption capacity of PHIO-P decreased by 41.1% after practical running for 26 months. Additionally, the frequently used waste PHIO adsorbent could be treated as non-hazardous material in the arsenic-containing wastewater treatment process after long-time use.

Key words | adsorption, arsenic, desorption, hydrated iron oxide, wastewater

INTRODUCTION

The contamination of arsenic draws special attention because of its potential toxic and carcinogenic effects (Choong et al. 2007). Recently, many regulatory authorities have imposed a strict maximum contamination level of arsenic in drinking water, which is 10 μg L⁻¹ in Europe and China. Therefore, it is urgent for arsenic-polluted wastewater treatment facilities to upgrade their traditional process with an economical and higher removal efficiency treatment process.

For wastewater with high concentration of arsenic, the most popular treatment process is precipitation with sulfide or ferrous salt (Fendorf et al. 2010; Onstott et al. 2011). The residual arsenic concentration of effluent from precipitation normally ranges from 0.1 to 0.5 mg L⁻¹. Although it could be gradually decreased by increasing the dosage of precipitant reagent, this would also cause more chemical sludge and treatment cost (Dungkaew et al. 2012). For treatment of wastewater with relatively low concentration of arsenic, the adsorption process has been widely studied. The existing adsorbents for arsenic removal include Fe(III)-bearing materials, such as goethite (Zhang et al. 2007; Mamindy-Pajany et al. 2011), hematite (Zhang et al. 2010; Blanchard et al. 2012), iron-oxide-coated sand (Gupta et al. 2005; Jeon et al. 2009), and Fe(III)-loaded resins (Rau et al. 2000).

The Fe(III)-loaded resins are promising materials for removal of a low level of arsenic, owing to their high arsenic adsorption capacity, stable structure and acceptable running cost (Matsumaga et al. 1996; Rau et al. 2000). The anion exchanger was used as host material for dispersing nanoscale hydrated iron(III) oxide (HFO) particles within the polymer phase by Donnan member effect. The anion-exchanger-supported HFO particles showed extremely high arsenic removal capacity: less than 10% of influent arsenic broke through after 10,000 bed volume (BV) running. Ninety-five per cent arsenic recovery was achieved in 15 BV during desorption using 2% NaOH and 3% NaCl as the regenerant (And & Sengupta 2005). Furthermore, the adsorption kinetics, the effect of competing anions, and the adsorption mechanism of arsenic adsorption on Fe(III)-loaded resins have been investigated (And & Chen 2005; Yu et al. 2013). Among these studies, the desorption characteristics of arsenic from Fe(III)-loaded resins or Fe(III)-bearing materials were mostly determined using static desorption experiments. However, the desorption
characteristics of arsenic from adsorbent in the static experiment, in terms of the effective and economical regenerant concentration, the regeneration velocity, and the regenerant volume, limited the application of arsenic desorption in practical engineering applications. This information for arsenic desorption should be obtained from dynamic desorption experiments, which are more appropriate for real desorption application in arsenic adsorption engineering.

The objective of this study was to decipher the arsenic release characteristic from Fe(III)-loaded resins using a dynamic column desorption experiment to provide significant information for desorption in real engineering. The surface characterization of adsorbent, effect of desorption velocity and regenerant concentration on desorption efficiency, and the sorption isotherm of adsorbent were studied in detail. Moreover, disposability of the wasted adsorbent was investigated by the toxicity characteristic leaching procedure (TCLP) experiments.

**MATERIALS AND METHODS**

**Adsorbent preparation and arsenic adsorption**

The preparation of the polymer-supported hydrated iron(III) oxide (PHIO) mainly followed the procedure of a previous report (And & Sengupta 2005) with a few modifications. Briefly, commercially available anion exchanger D201 (Jiangsu Suqing Water Treatment Engineering Group) was immersed in a mixed solution containing 8% (w/v) FeCl₃ and 5% (w/v) HCl. The iron(III) ions within the framework of D201 were precipitated with mixed a solution containing 8% (w/v) NaOH and 5% (w/v) NaCl. Then, the D201 loaded with iron(III) was washed to neutral pH with deionized water and dried at 60–70°C for 4 h.

The practical PHIO samples (PHIO-P) were collected from the adsorption column of a wastewater treatment plant in Nandan country, Guangxi province, China. The main metal elements of PHIO-P are listed in Table 1. The PHIO adsorbent was used in this project in order to remove the arsenic from the beneficiated wastewater. The capacity of the wastewater treatment plant is 1,200 cubic meters per day. Before sampling, the plant had been running for about 26 months and the adsorbent had been regenerated about eight times with 0.8 M NaOH solution.

**Column desorption experiment**

Glass columns (internal diameter: 11 mm) were packed with PHIO-P samples (particle size: 0.35–0.90 mm) up to a height of 325 mm. The dried weight of PHIO loaded with arsenic was 3.219 g. At room temperature, the regenerants were continuously passed from the bottom of the column at a constant rate using a peristaltic pump (BT100-1F, Longer pump). The empty bed contact time (EBCT) was approximately 45 min. The deionized water was pumped into the columns packed with PHIO-P as control.

The elutriants were collected at regular intervals for every 2 BV (10 mL), then filtered through a filter of 0.45 μm, acidified with nitrate acid and stored at 4°C for analysis. The efficiency of arsenic desorption could be derived from Equation (1).

\[
A = \frac{C_t V}{q Q}
\]

where \(A\) is the arsenic desorption efficiency (%); \(C_t\) (mg L \(^{-1}\)) is the arsenic concentration of elutriant with regenerant at desorption dynamic run time \(t\); \(V\) (L) is the volume of elutriant; \(q\) (mg g \(^{-1}\)) is the arsenic content of adsorbent; \(Q\) (g) is the dry weight of adsorbent.

To investigate the effects of desorption velocity, the NaOH (1.0 mol L \(^{-1}\)) solutions were injected continuously into the column at various flow rates (5–20 BV h \(^{-1}\)). To study the effects of regenerant concentration, the NaOH solution at various concentrations (0.1–1.0 mol L \(^{-1}\)) was pumped into the column at a constant velocity of 20 BV h \(^{-1}\).

**Sorption isotherm study**

Batch experiments were carried out to examine the adsorption capacity for As(III) of raw PHIO adsorbent and PHIO-P samples after desorption with 1.0 M NaOH solution.

<table>
<thead>
<tr>
<th>Element</th>
<th>Content (mg kg (^{-1}) dw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.634 × 10⁵</td>
</tr>
<tr>
<td>Ca</td>
<td>6,716</td>
</tr>
<tr>
<td>Mg</td>
<td>2,401</td>
</tr>
<tr>
<td>Zn</td>
<td>167</td>
</tr>
<tr>
<td>Cd</td>
<td>0.08</td>
</tr>
<tr>
<td>Cu</td>
<td>76</td>
</tr>
<tr>
<td>Pb</td>
<td>3.3</td>
</tr>
<tr>
<td>As</td>
<td>620</td>
</tr>
<tr>
<td>Hg</td>
<td>0.046</td>
</tr>
<tr>
<td>Cr</td>
<td>373</td>
</tr>
</tbody>
</table>

**Table 1** | Main metal element content of PHIO-P
Stock solutions of As(III) (1,000 mg L\(^{-1}\)) were prepared by dissolving sodium arsenite (NaAsO\(_2\)) (Beijing Chemicals, China) in deionized water. Working solutions for experiments were freshly diluted from the stock solution. All experiments were conducted in triplicate. The relative standard deviation of triplicate analyses was normally lower than 5%.

Adsorption isotherm studies were performed under the conditions of initial As(III) concentration of 5–150 mg L\(^{-1}\), initial pH 7, reaction time 24 h (equilibrium was achieved at 2 h), and 120 rpm shaking at 25 ± 1 °C. All the batch experiments were conducted in a 250 mL conical flask with a cover by taking 200 mg (dry weight) of adsorbent with 100 mL of As(III) working solution. All samples were collected, filtrated with 0.45 μm filter and stored for analysis.

Toxicity characteristic leaching procedure

The TCLP tests of waste PHIO-P were carried out according to the procedure described by US EPA method 1311 (Lakshmipathiraj et al. 2006). The extraction fluid consisting of a buffered acetic acid solution (pH 4.93 ± 0.05) was prepared by adding NaOH and glacial acetic acid to water, and then diluting to a final volume.

The dried solid samples were mixed with extraction fluid (solid/liquid ratio of 1:20), and then agitated (speed of 280 ± 5 rpm) for 18 h at 30 °C using a mechanical shaker. The supernatant was separated by centrifugation at 4,000 rpm for 15 min, filtered through 0.45 μm filter, acidified with concentrated nitric acid, and stored in amber vials at 4 °C. The Cd, Cr, Pb and As concentrations in the supernatant were then measured by inductively coupled plasma–atomic emission spectrometry (ICP-AES). Mercury (Hg) concentration was determined by an atomic fluorescence spectrometer (XGY-1011A, Haiguang Corp., Beijing).

Analytical methods

The pH in batch suspensions and column elutriants was determined by a portable pH meter (Sens ion2, Hach). The arsenic concentration of solution was measured with ICP-AES (725, Agilent). The amount of adsorbed arsenic was obtained by calculating the difference between initial and residual concentrations. Imaging was obtained using a scanning electron microscope (S-360, Cambridge Instruments, UK). All experiments were run in triplicate.

RESULTS AND DISCUSSION

Characterization of PHIO

The surface images and chemical composition of PHIO and PHIO-P determined by the scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) analysis are shown in Figure 1. In comparison with raw PHIO adsorbent (Figure 1(a)), block-shaped precipitates were deposited on the surface of PHIO-P (Figure 1(b)). The diameter of the precipitate was found to range from 20 nm to 150 nm. The EDS data shown in Figure 1(c) and 1(d) confirmed that the major constituents of block precipitate were calcium and magnesium hydroxide. Other heavy metals such as arsenic, zinc and copper were not detected on the surface of PHIO-P by the EDS due to their relatively low weight content percentage. In the practical wastewater treatment plant, the PHIO was regenerated with NaOH solution, and calcium and magnesium hydroxide might be formed in the alkaline regeneration process. To obtain more specific component data, the contents of main metal elements in PHIO-P were analyzed by strong acid dissolution and measurement of metal concentration in digestion solution. Except for Fe, Ca and Mg, many sorts of other heavy metals such as As, Zn, Cu and Cr were detected in PHIO-P due to the comprehensive adsorption ability of loaded hydrated iron oxide. The formation of precipitates might impede the diffusion process of arsenic to the hydrated iron oxide loaded in the resin framework. Gradually, the porous channel in the PHIO would be blocked, which leads to the significant decrease of arsenic adsorption capacity (Caporale et al. 2013; Jiang et al. 2015).

Effect of desorption velocity

Sodium hydroxide solution is the most practicable reagent for arsenic desorption due to its high desorption efficiency, low cost and easy availability. It was applied as the reagent for the PHIO-P in industry. Figure 2 shows the desorption efficiency of As from PHIO-P as a function of desorption velocity (5, 10, 15 and 20 BV h\(^{-1}\)) using 1.0 M NaOH solution. It is obvious that the As desorption equilibrium was reached quickly with decreasing desorption velocity. It took 64 min for 5 BV h\(^{-1}\), 76 min for 10 BV h\(^{-1}\), 102 min for 15 BV h\(^{-1}\) and 178 min for 20 BV h\(^{-1}\) respectively to reach the desorption efficiency of greater than 90%. Furthermore, less regenerant volume was necessary to get a relatively high desorption efficiency at lower desorption velocity.
When the desorption efficiency was greater than 90%, only 9.3 BV of regenerant was consumed for the desorption velocity of 5 BV $h^{-1}$, where this value increased to 13.5 BV for the desorption velocity of 20 BV $h^{-1}$. It is noted that desorption velocity of 5 BV $h^{-1}$ equals an EBCT of 6.05 min, which is sufficient for the desorption reaction in the dynamic column experiment.

In general, physical or non-specific (outer-sphere) adsorption describes rapid, reversible reactions and relatively weak bonds. However, specific adsorption (inner-sphere complexation) involves a stronger, less reversible adsorption process due to the relatively high bonding energies (Pena et al. 2006; Mohapatra et al. 2007). According to a previous study, the process of arsenic adsorption on goethite following the pseudo-second-order model suggested the presence of a chemisorption reaction in the process of arsenic adsorption (Sigrist et al. 2014). Although the arsenic adsorption process involves inner-sphere complexation, the adsorption of arsenic on the goethite (FeOOH) particle surface may be attributed to electrostatic attraction (Shi et al. 2009). The highest desorption efficiency of arsenic was 93.6% at desorption velocity of 15 BV $h^{-1}$ for 136 min, which indicated that the adsorbed arsenic could be desorbed well with NaOH solution. Similar results for elution efficiency with NaOH solution have been observed for arsenic desorption from granular hydrous ferric oxide (Streat et al. 2008).

**Effect of regenerant concentration**

To investigate the effect of NaOH concentration on arsenic desorption efficiency, the dynamic desorption study was carried out using NaOH solution with various concentrations (0.2 M–1.0 M) at desorption velocity of 5 BV $h^{-1}$. Arsenic desorption efficiencies decreased substantially with the NaOH concentration decreasing from 1.0 M to 0.2 M (Figure 3(a)). The arsenic desorption efficiencies corresponding to NaOH concentration of 1.0 M and 0.2 M were 93.2% and 73.5% within the first effluent volume of 22 BV, respectively. However, the amount of arsenic desorbed

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**Figure 1** | SEM images and SEM-EDS. (a) Raw PHIO, (b) PHIO-P, (c) EDX of PHIO, (d) EDS of PHIO-P.
with lower NaOH concentration increased faster at the effluent volume of more than 8 BV. It implied that more volume of regenerant was required in order to get a relatively high desorption efficiency. The adsorption sites occupied by arsenic could easily be replaced by OH− during the desorption process (Manceau 1995; Jessen et al. 2005). After the desorption experiments, the loaded goethite could be rapidly recovered from the solutions.

**Sorption isotherm study**

Adsorption isotherms provide insight on the adsorption performance difference between the raw PHIO adsorbent and PHIO-P adsorbent after regeneration with 1.0 M NaOH solution (Figure 4). PHIO adsorbent had significantly greater As(III) adsorption capacity than PHIO-P adsorbent after regeneration. To provide more quantitative information,
these data were fitted to the models of Langmuir and Freundlich (Equations (2) and (3), respectively), and the fitting values are presented in Table 2.

\[
q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (2)
\]

\[
q_e = K_F C_e^{1/n} \quad (3)
\]

where \(C_e\) (mg L\(^{-1}\)) is the arsenic concentration at equilibrium, \(q_e\) (mg g\(^{-1}\)) is the amount of adsorbed arsenic per unit weight of adsorbent, and \(q_m\) (mg g\(^{-1}\)) is the maximum adsorption capacity of adsorbent. \(K_L, K_F\) and \(n\) are the isotherm constants.

According to the determination coefficient \(R^2\) (Table 2), the Langmuir model shows good agreement with adsorption data for both raw PHIO and PHIO-P adsorbents. It implies that the arsenic adsorbed formed a monolayer coverage on
the adsorbent surface (Antelo et al. 2005). The \( q_m \) values of PHIO and PHIO-P adsorbents were calculated to be 36.12 and 21.27 mg g\(^{-1}\), respectively. In comparison with the raw PHIO adsorbent, the maximum arsenic adsorption capacity of PHIO-P decreased by 41.1% after 26 months of practical running. Although the adsorbed arsenic on PHIO-P was displaced with NaOH solution, the FeOOH on the surface of PHIO would not be recovered completely. At NaOH solution with high concentration, leaching of the bound arsenic was accompanied by FeOOH disintegration, leading to a major reduction of its mechanical strength that is required for reuse (Tresintsi et al. 2014).

**Waste adsorbent disposal**

In this study, the TCLP was also carried out to assess the disposal safety of PHIO-P, which represented the adsorbent replaced from the practical adsorption column after a long time running. Table 3 lists the leached pollutants (Hg, Cd, Cr, Pb, As) concentration for PHIO-P after NaOH solution regeneration. For all the samples, the leached Hg, Cd, Cr, Pb, and As concentrations in TCLP fluid were significantly lower than the US Environmental Protection Agency (EPA) specified limit. These results suggest that the binding forces between PHIO-P surface and residual heavy metals such as As, Hg, and Cr were relatively strong. Thus, the waste PHIO adsorbent could be regarded as non-hazardous material in the arsenic-containing wastewater treatment process.

**CONCLUSIONS**

The desorption parameters of PHIO-P were investigated in column desorption experiments. Arsenic desorption efficiency was extremely dependent on the desorption velocity and NaOH concentration of regenerant. Decreasing

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**Table 2** | Fitting results of arsenic adsorption isotherms

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_m ) (mg g(^{-1}))</td>
<td>( K_L ) (L mg(^{-1}))</td>
</tr>
<tr>
<td>PHIO</td>
<td>36.12</td>
<td>0.59</td>
</tr>
<tr>
<td>PHIO-P</td>
<td>21.27</td>
<td>0.14</td>
</tr>
</tbody>
</table>

**Table 3** | TCLP results of PHIO-P

<table>
<thead>
<tr>
<th>Leached pollutants</th>
<th>PHIO-P</th>
<th>EPA regulated level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg (mg L(^{-1}))</td>
<td>( 8 \times 10^{-5} )</td>
<td>0.2</td>
</tr>
<tr>
<td>Cd (mg L(^{-1}))</td>
<td>&lt;0.03(^a)</td>
<td>1.0</td>
</tr>
<tr>
<td>Cr (mg L(^{-1}))</td>
<td>&lt;0.08(^a)</td>
<td>5.0</td>
</tr>
<tr>
<td>Pb (mg L(^{-1}))</td>
<td>&lt;0.30(^a)</td>
<td>5.0</td>
</tr>
<tr>
<td>As (mg L(^{-1}))</td>
<td>&lt;0.007(^a)</td>
<td>5.0</td>
</tr>
</tbody>
</table>

\(^a\)Below detection limits.
desorption velocity reduced the regenerant volume which is necessary to obtain high desorption efficiency. The arsenic desorption efficiency could be improved by increasing the NaOH concentration. The optimal dynamic desorption condition could be obtained at the desorption velocity of 15 BV h⁻¹, regeneration time of 136 min and NaOH concentration of 1.0 M in regenerant. Comparing with the raw adsorbent, the maximum arsenic adsorption capacity of PHIO-P decreased by 41.1% after 26 months’ practical running. Additionally, the waste PHIO-P can be treated as non-hazardous waste according to the TCLP tests.

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