Adsorption and removal of arsenic from water by iron ore mining waste
Tien Vinh Nguyen, Thi Van Trang Nguyen, Tuan Linh Pham, Saravanamuth Vigneswaran, Huu Hao Ngo, J. Kandasamy, Hong Khanh Nguyen and Duc Tho Nguyen

ABSTRACT
There is a global need to develop low-cost technologies to remove arsenic from water for individual household water supply. In this study, a purified and enriched waste material (treated magnetite waste, TMW) from the Trai Cau’s iron ore mine in the Thai Nguyen Province in Vietnam was examined for its capacity to remove arsenic. The treatment system was packed with TMW that consisted of 75% of ferrous-ferric oxide (Fe₃O₄) and had a large surface area of 89.7 m²/g. The experiments were conducted at a filtration rate of 0.05 m/h to treat groundwater with an arsenic concentration of 380 mg/L and iron, manganese and phosphate concentrations of 2.07 mg/L, 0.093 mg/L and 1.6 mg/L respectively. The batch experimental results show that this new material was able to absorb up to 0.74 mg arsenic/g. The results also indicated that the treatment system removed more than 90% arsenic giving an effluent with an arsenic concentration of less than 30 mg/L while achieving a removal efficiency of about 80% for Mn²⁺ and PO₄³⁻. This could be a promising and cost-effective new material for capturing arsenic as well as other metals from groundwater.

Key words | arsenic, drinking water, ferrous-ferric oxide, iron ore

INTRODUCTION
Water is the essence of life. In many regions in the world, however, especially in developing countries, millions of people still suffer from the lack of access to safe drinking water. This endangers peoples health and can cause serious illnesses. One of the problems with drinking water that raises concern all over the world is that millions of people still have to consume arsenic contaminated water. Arsenic occurs in extremely high quantities in groundwater in Bangladesh and a number of other countries (Vietnam, India, Nepal, China, and America). In Bangladesh, 1.2 million tube wells (29%) were found to be contaminated with arsenic. It is estimated that 85 million people are at risk from arsenic (Hossain 2006). In India, 200,000 people suffer from chronic poisoning as a result of arsenic in well water (up to 1,800 µg/L).

An investigation of groundwater samples from private small scale tube-wells in the Red River delta, Vietnam (over an area of 700 km²) showed that arsenic levels varied between 1 to 3,050 µg/L (Berg et al. 2001). The arsenic concentration was more than 50 µg/L in 48% of the samples analysed and above 150 µg/L in 20% of samples. In highly affected rural areas, the average concentration of arsenic was 430 µg/L. The United Nations Children’s Fund estimated that 17% of Vietnam’s population consume...
groundwater from private tubewells for drinking purpose (UNICEF 2002). The high arsenic levels found in the tubewells indicate that the several million people using untreated groundwater are at significant risk of chronic arsenic poisoning. In the United States, about half of drinking water comes from groundwater. Smith et al. (1992) reported that 330,000 people were supplied with water contaminated with more than 50 μg/L of arsenic. Medical research indicates that exposure to arsenic in drinking water causes urinary, bladder, lung and skin cancers, gastrointestinal disorders, muscular weakness, loss of appetite, nerve tissue injuries and blackfoot disease. Due to the high toxicity of arsenic, the regulation of arsenic is stringent. The standard set by different health and quality control authorities varies from 7 to 50 μg/L.

Different treatment technologies such as coagulation, ion exchange, adsorption, and membrane processes are being used to remove arsenic from drinking water to produce water of a safe quality. Appropriate treatment depends on many factors such as concentration of arsenic, water composition, pH and cost effectiveness. In contrast to cyanide, arsenic cannot be destroyed.

A number of studies have investigated the sorption of arsenic onto amorphous iron oxides and goethite (Bowell 1994; Singh et al. 1996; Wilkie & Hering 1996; Matis et al. 1997; Manning et al. 1998; Jain & Loeppert 2000; Gao & Mucci 2001; Appelo et al. 2002). Previous studies showed that arsenic adsorb well onto iron oxide. However, the arsenic sorption efficiency was strongly dependent on the mineralogy of its oxidation state, iron oxides, pH, and other sorbates such as phosphate and silicic acid. Bowell (1994) showed that sorption efficiency of As(V) was higher than that of As(III). Matis et al. (1997) observed that the sorption of arsenic on goethite decreased when pH increased from neutral to alkaline. The sorption of As(V) on hematite and feldspar was studied by Singh et al. (1996). Their results showed that the sorption of As(V) followed first-order kinetics. As(V) was removed completely by hematite under optimum conditions at concentration of 13.35 μmol/L As(V). Phosphate was found to particularly affect sorption of As(V) on iron oxide minerals (Gao & Mucci 2001; Jain & Loeppert 2000).

There was not much research on arsenic sorption on magnetite (Dixit & Hering 2003; Parga et al. 2005; Giménez et al. 2007). The sorption of arsenic on magnetite was also depended on pH. The sorption of As(III) increased with pH while the pH was lower than 10 whereas in highly alkaline environment (pH > 10), the As(III) sorption on magnetite decreased slightly (Dixit & Hering 2003). Parga et al. (2005) used the electrocoagulation method for removing arsenic from contaminated groundwater in Mexico. Their results from a field pilot study showed that magnetite particles present in the electrocoagulation products could remove more than 99% of arsenic from groundwater contaminated to levels of between 25–50 μg/L, and where the pH of the groundwater was 5.5–7.1. Giménez et al. (2007) showed that arsenic sorption equilibrium was reached in less than 2 days and the data fitted with Langmuir isotherm. The arsenic sorption also decreased at alkaline pH values.

A number of models are used to describe adsorption data in water treatment. In particular, the Langmuir, Freundlich and Sips isotherms are those most commonly used for single solute adsorptions. The Langmuir isotherm is given by:

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$  \hspace{1cm} (1)

where $C_e$ is the equilibrium concentration (mg/L), $b$ is a Langmuir constant related to the binding energy of adsorption (L/mg), and $q_m$ is the saturated maximum monolayer adsorption capacity (mg/g).

The Freundlich isotherm is an empirical equation developed based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites, and each site can be modelled by the following equation:

$$q_e = K_F C_e^n$$  \hspace{1cm} (2)

where $K_F$ is a Freundlich constant indicative of the adsorption capacity of the adsorbent, and $n$ is an experimental constant indicative of the adsorption intensity of the adsorbent.

The Sips model is a different empirical model representing equilibrium adsorption data. This isotherm model has the features of both the Langmuir and Freundlich isotherm models. As a combination of the Langmuir and Freundlich isotherm models, the Sips model contains three parameters,
which can be evaluated by fitting the experimental data. For single solute equilibrium data, the Sips adsorption isotherm model can be written as follows:

\[ q_e = \frac{q_m (bC_e)^n}{1 + (bC_e)^n} \]  

Total reserves of iron ore in the Trai Cau mine in Thai Nguyen province, Vietnam is about 9 million tons. The main iron ores in Trai Cau are magnetite with a Fe content of more than 62% (detrimental impurities are in a permissible range) and abounding limonite with a Fe content of more than 55%, and Mg content of 3–4%. These ores are being exploited and have been supplied to Thai Nguyen Iron and Steel Company since 1963. Up to the present, thousands of tonnes of waste containing magnetite, limonite, kaolin clay, ferruginous clay, silica, etc. has been created.

In this study, detailed experiments were conducted to evaluate a natural material purified and enriched from waste of the Trai Cau iron ore mine (TMW) for its capacity and effectiveness to remove arsenic from natural groundwater in Vietnam and from arsenic contaminated synthetic water under laboratory conditions. The mineral used in this work is naturally abundant and relatively low-cost.

### MATERIALS AND METHODS

#### Materials

**Water**

In this study, synthetic water and groundwater were used. In order to evaluate the effectiveness of material in practice, actual groundwater samples from Hanoi, Vietnam were also used in tests. The characteristics of the synthetic water and groundwater used are presented in Table 1.

**TMW material**

Waste (iron tailing) from the Trai Cau’s mine was purified and enriched by screening, floating and gravitational-centrifugal processes.

#### Standards and reagents

All chemicals used in the studies were reagent grade, and were used without any purification.

#### Experimental study

**Batch kinetic studies**

In kinetic studies, 200 mL arsenite solutions of 2,000 µg/L were transferred to 250 mL Erlenmeyer flasks containing 0.2 g TMW adsorbent. The flasks were sealed with parafilm. The samples were placed on a mechanical shaker and shaken at 130 rpm. Samples were collected at regular time intervals and analysed for residual arsenic.

**Batch equilibrium studies**

Equilibrium studies were conducted at normal pH using TMW and tap water spiked with the predetermined concentrations of As(III). Equilibrium studies were conducted at a temperature of 25°C. In these experiments, different amounts of TMW adsorbent (0.1–2 g) were placed into 250 mL Erlenmeyer flasks containing 0.2 g TMW adsorbent. The flasks were sealed with parafilm. The samples were placed on a mechanical shaker and shaken at 130 rpm for 96 hours. After 96 hours of contact time, samples from each flask were decanted and analyzed for the residual arsenic in the solution.

**Column experiment**

Glass columns of 40 mm diameter and 600 mm height were used in this study. The synthetic water was run through the

### Table 1 | Water quality parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Synthetic water</th>
<th>Hanoi groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.25–10</td>
<td>0.380</td>
</tr>
<tr>
<td>Iron</td>
<td>ND</td>
<td>2.07</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.097</td>
<td>0.093</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.135</td>
<td>0.104</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.05</td>
<td>13.8</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.33</td>
<td>1.6</td>
</tr>
<tr>
<td>Silicate</td>
<td>12.1</td>
<td>8.1</td>
</tr>
<tr>
<td>Calcium</td>
<td>31</td>
<td>24</td>
</tr>
</tbody>
</table>

Note: All parameters are in mg/L, ND: not detectable.
packed column in the down-flow mode at flow rates of 0.1 m/h and 0.15 m/h. In experiments, the column was packed with either 430 g or 1,400 g of TMW.

Bucket experiment

A bucket packed with 13 kg of TMW was tested with contaminated groundwater with an arsenic concentration of 380 mg/L. Groundwater was pumped regularly into the bucket through a plastic influent pipe. The bucket contained a collection pipe at the bottom. Small holes were drilled in both the influent and collection pipes for sampling. The experiment was run at a filtration rate of 0.05 m/h.

RESULTS AND DISCUSSION

Characterization of TMW adsorbent

Morphological analysis of the samples was performed by field emission scanning electron microscopy (FE-SEM) using a Hitachi 4,800 microscope (at 15 kV) with energy-dispersive X-ray (EDX) analyses. Powder samples were prepared by mounting it on carbon tape followed by platinum coating. The components of TMW determined by FE-SEM are shown in Table 2.

![Figure 1](https://iwaponline.com/wst/article-pdf/60/9/2301/447752/2301.pdf)  
**Figure 1** Removal efficiency of As (III) as a function of adsorption time (Initial As (III) concentration = 2,000 µg/L; TMW’s weight = 0.2 g; temperature = 25°C; volume of As (III) solution = 200 mL).

![Figure 2](https://iwaponline.com/wst/article-pdf/60/9/2301/447752/2301.pdf)  
**Figure 2** Prediction of equilibrium adsorption of As(III) by different adsorption models (contact time = 96 hours, mixing rate = 130 rpm, temperature = 25°C).

![Table 3](https://iwaponline.com/wst/article-pdf/60/9/2301/447752/2301.pdf)  
**Table 3** Isotherm equations for arsenic removal using TMW

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Arsenite</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>q_m (mg/g)</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>b (L/mg)</td>
<td>0.20</td>
</tr>
<tr>
<td>Freudlich</td>
<td>k_F</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>1/n</td>
<td>0.412</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>2.43</td>
</tr>
<tr>
<td>Sips</td>
<td>q_m (mg/g)</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>b (L/mg)</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>1/n</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.59</td>
</tr>
</tbody>
</table>

The specific surface area of the TMW adsorbent was measured using the Micromeritics ASAP 2010 Analyser. The value of TMW adsorbents surface area was 89.7 m²/g, and was much higher than the 14/4 m²/g of natural hematite (Singh et al. 1996) and goethite (Dixit & Hering 2003).

Table 2 | Component of TMW

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>32.16</td>
</tr>
<tr>
<td>Al</td>
<td>1.08</td>
</tr>
<tr>
<td>Si</td>
<td>1.01</td>
</tr>
<tr>
<td>Mn</td>
<td>1.92</td>
</tr>
<tr>
<td>Fe</td>
<td>54.64</td>
</tr>
<tr>
<td>Co</td>
<td>7.41</td>
</tr>
</tbody>
</table>

The dimension size of the TMW observed by SEM was from 15 to 70 µm.
Adsorption kinetics

Figure 1 shows the removal of arsenite as a function of adsorption time of TMW. The results show that TMW could remove only 5% of As (III) after a 1 hour contact with TMW. An eight-hour adsorption led to 29% arsenite adsorption and after 32 hours, the removal efficiencies remained virtually unchanged (about 34%). In these experiments, only 0.2 g of TMW was placed in a flask containing up to 200 mL of arsenite solution at a concentration of 2,000 \( \text{mg/L} \).

Equilibrium adsorption experiments

The equilibrium adsorption data were than fitted with the Langmuir, Freundlich, Sips isotherm equations. The adsorption isotherms of all of these models fitted well with the observed values. Figure 2 shows the comparison between the predicted and the experimental concentrations of the remaining arsenic. The model equations and the isotherm parameters are given in Table 3.

Table 4 | Comparison of arsenic adsorption capacity of TMW with other adsorbents

<table>
<thead>
<tr>
<th>Name of adsorbent</th>
<th>Adsorption capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated alumina</td>
<td>0.18</td>
<td>Singh &amp; Pant (2004)</td>
</tr>
<tr>
<td>Red mud</td>
<td>0.66</td>
<td>Altundogan et al. (2000)</td>
</tr>
<tr>
<td>Ferruginous manganese ore</td>
<td>0.68</td>
<td>Chakravarty et al. (2002)</td>
</tr>
<tr>
<td>Iron oxide impregnated activated alumina</td>
<td>0.73</td>
<td>Kuriakose et al. (2004)</td>
</tr>
<tr>
<td>TMW</td>
<td>0.74</td>
<td>This study</td>
</tr>
</tbody>
</table>

The low value of \( 1/n (< 0.7) \) in the Freundlich isotherm suggests that any large change in the equilibrium concentration of soluble arsenic would not result in a change in the amount of arsenic sorbed by the TMW.

It can be seen that the Langmuir and Sips models had nearly the same values for the arsenic adsorption capacity (\( q_m \)). The values were 0.74–0.78 mg As(III)/g TMW. Value of the adsorption capacity of TMW (\( q_m \)) is higher than that of other adsorbents (Table 4). This indicates that TMW has a good arsenic adsorption capacity.

TMW column experiments

Synthetic water

Column experiments were conducted to study the removal of arsenite in synthetic water. A glass column of 40 mm diameter and 600 mm height was used in this study. The column was packed with two different weights of TMW (430 g and 1,400 g). The column tests were conducted in the down-flow mode and at normal pH of the water. In this study...
study, the column was run at 2 flow rates of 0.1 m/h and
0.15 m/h for the adsorption of arsenic on the TMW media.
The initial arsenite concentration was 250 and 500
m$^2$g/L respectively.

The results on the removal of As(III) from synthetic
water using TMW column system are presented in (Figures 3
and 4). In case of the lower flow rate (0.1 m/h), arsenite
removal efficiency was more than 90% during the first 2
weeks of operation. The column packed with 430 g of TMW
produced an effluent with an arsenite concentration of less
than 10$^6$g/L (World Health Organisation guideline value
for arsenic in drinking water). The bed volume achieved
was more than 113 (throughput volume of more than 19
litres).

The results show that with an increase in the amount
of TMW in the column, the arsenite removal effectiveness
also increased. More than 98% of arsenite was removed
during the first 2 weeks of the experiment. Although the
arsenite in the influent increased to 500 $^6$g/L, arsenite
concentration in the effluent was still below 10$^6$g/L and
the throughput volume was 68 L (the bed volume was
up to 122).

**Hanoi groundwater, Vietnam**

To evaluate the effectiveness of TMW under real conditions,
a simple system (Figures 5 and 6) was tested with arsenic
contaminated groundwater. Groundwater was pumped
regularly into a bucket through a plastic influent pipe.
The bucket contained a collection pipe at the bottom. Small
holes were drilled in both the influent and collection pipes
for sampling.

**Figure 4** | Removal arsenite in synthetic water by TMW column (Initial As(III) concentration: 500 $^6$g/L; weight of TMW: 1,400 g, flow rate: 0.15 m/h).

**Figure 5** | Arsenic removal pilot in Hanoi.
Bucket experiments were carried out using groundwater with an arsenic concentration of 380 mg/L from a well in Nhi Khe Village, Hanoi, Vietnam. The system was run at a filtration rate of 0.05 m/h. A 10 litre bucket was packed with 2 kg of sand at the bottom of the bucket, topped with 13 kg of TMW.

The results of the experiment show that the TMW adsorbent could remove more than 92.1% of arsenic. Arsenic concentrations in effluent were found to be in the range of 9–30 mg/L. After a bed volume of 74, the bucket could still remove more than 95% of arsenic.

The filtration process not only removed arsenic concentration in treated water but also reduced other contaminants. The results showed that more than 80% of PO₄³⁻, Fe⁴⁺ and Mn²⁺ in the groundwater were removed. The Fe⁴⁺, Mn²⁺ and PO₄³⁻ concentrations in groundwater were 2.07 mg/L, 0.093 mg/L and 1.6 mg/L respectively (Table 5). In the experiment, Fe³⁺, Mn³⁺ reacted with oxygen to form hydroxide and was then removed by the TMF’s filter.

PO₄³⁻ in the groundwater was removed by precipitation with iron and alum. However, the TMW system was not a biological filter and could not remove ammonium.

There were no increases in the concentration of components (Fe²⁺, Si²⁺, Al³⁺, Mn²⁺) in the influent water. This means that the elements in TMW did not contaminate the treated water.

**CONCLUSIONS**

TMW from Traicau’s iron mine exhibited a high arsenic removal capacity in both batch and column experiments. The high removal capacity of TMW was due to its high specific surface as well as its high iron oxide content (about 75%). The TMW adsorption equilibrium results with synthetic water were successfully simulated by Langmuir, Freundlich and Sips models. The adsorption capacity of TMW (up to 0.74 mg of As(III) per gram of TMW) was higher than that of a number of adsorbents such as ferruginous manganese ore (0.680 mg/g), activated alumina (0.180 mg/g), red mud (0.66 mg/g). The filter packed with TMW yielded consistent arsenic removal efficiency for a long period. A 10 litre bucket packed with 13 kg of TMW reduced arsenic concentrations from 380 μg/L to less than 30 μg/L with the throughput volume of nearly 600 litres. Since this material produced from unused waste is very cheap (0.07–0.08 USD/kg), it has high applicability as a packing material in filters for households in developing countries.
ACKNOWLEDGEMENTS

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REFERENCES


