

# Arsenic Removal Technologies for Drinking Water in Vietnam

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## Abstract

Severe and widespread contamination by arsenic (As) in groundwater and drinking water has been recently revealed in rural and sub-urban areas of the Vietnamese capital of Hanoi with similar magnitudes as observed in Bangladesh and West Bengal, India. This fact has prompted the need to develop simple, rapid and low-cost techniques for lowering As concentrations in supplied water. In the present study, laboratory and field tests were conducted to assess the suitability of using oxidation processes by activated hypochlorite in water treatment plants in Hanoi city and naturally occurring minerals as sorbents in household-based systems to reduce As concentrations in drinking water. Sorption experiments indicated that co-precipitation of arsenate [As(V)] in ferric hydroxide is much more efficient than of arsenite [As(III)]. With Fe concentrations of 5 mg l<sup>-1</sup>, As(V) can be efficiently lowered from concentrations of 0.5 mg l<sup>-1</sup> levels to lower than the Vietnam standard of 0.05 mg l<sup>-1</sup>. Activated hypochlorite was additionally introduced after the aeration tank in the conventional water treatment process that is currently used in the water treatment plants of Hanoi city. This modified process was able to lower arsenic concentrations below the standard level with relatively low Fe concentration (5 mg l<sup>-1</sup>). Investigations on pilot scale equipment indicated that the removal efficiency of As in this system was much higher than that in laboratory experiments. To reduce As concentrations to levels lower than the Vietnamese standard level of 0.05 mg l<sup>-1</sup>, initial Fe/As concentration ratios used in the pilot system and laboratory experiment were 16 and 50, respectively. Laterite and limonite, which are naturally and widely occurring minerals in Vietnam, can be used as potential sorbents for As removal in smaller scale water treatment systems. The sorption capacities of laterite and limonite for As(V) were estimated to be 1100 and 900 mg kg<sup>-1</sup>, respectively. Initial results of field tests indicated that As concentrations decreased to levels <0.05 mg l<sup>-1</sup>. The household system based on an adsorption column packed with these minerals seemed to be a suitable technique for small-scale groundwater remediation in rural and sub-urban areas.

**Keywords:** Arsenic Removal; Co-precipitation; Sorption; Chlorine Oxidation; Naturally occurring minerals; Laterite; Limonite.

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## Introduction

Arsenic (As) contamination in drinking water and groundwater has increasingly been recognized in recent years and now has become a worldwide problem. Severe contamination has been reported for a decade in Bangladesh and West Bengal, India, where millions of people are consuming As-poisoned groundwater (Nickson *et al.*, 1998). Serious arsenicosis has been observed for a large population in these areas (Chowdhury *et al.*, 2000). Arsenic problems have also been observed in developed nations. In the United States, the Environmental Protection Agency has recently decided to lower the maximum contamination level for As in drinking water from  $50 \mu\text{g l}^{-1}$  to  $10 \mu\text{g l}^{-1}$ . The increasing awareness of As toxicity and the regulatory changes have prompted considerable attention towards developing suitable methods for lowering As levels in drinking water.

Natural occurring contamination by As has been also observed in the Red River delta of northern Vietnam. A recent comprehensive survey has revealed elevated As concentrations over a large rural and sub-urban area of the Vietnamese capital (Berg *et al.*, 2001). In four districts of the rural Hanoi area, As concentrations in about 48% of the investigated groundwater exceeded the Vietnam guideline of  $50 \mu\text{g l}^{-1}$ , and hence, point to a high risk of chronic arsenic poisoning. This fact has prompted the need to investigate suitable methods for lowering/removing As concentrations in drinking water with rapid, simple and low-cost techniques.

A number of recent studies have proposed the use of zerovalent iron filings as filter medium for removing arsenite [As(III)] and arsenate [As(V)] from groundwater (Su and Plus, 2001a, 2001b; Farrell *et al.*, 2001). The process is based on the adsorption and co-precipitation of As(III) and As(V) onto Fe(III) oxides (Melitas *et al.*, 2002). Adsorption capacity of As in the form of arsenite and arsenate onto various ferric clay minerals has been well investigated (Farpuhar *et al.*, 2002). In Bangladesh, several efforts have been made to develop household filtration systems with effective low-cost technologies. Co-precipitation with ferric chloride is an effective and economic technique for removing As from water, because iron hydroxides formed from ferric salt have a high sorption capacity for arsenate (Meng *et al.*, 2001). However, the applicability of such methods depends largely on the geological characteristics of the groundwater. For example, in Bangladesh, elevated concentrations of phosphate and silicate may enhance the mobility of As(V) in soils contaminated with arsenate (Peryea and Kammereck, 1997, Hug *et al.*, 2001). In addition, recent studies have suggested that silicate may disturb the removal of As(III) and As(V) by co-precipitation with ferric chloride (Meng *et al.*, 2000).

In Vietnam, recent investigations showed that the current As contamination in the Red River delta area has been as serious as observed in Bangladesh and West Bengal (Berg *et al.*, 2001). Furthermore, the chemical composition of groundwater in Vietnam is similar to that in Bangladesh. The present study investigated the applicability of a simple and economic technique for removing As in groundwater during the treatment process in water treatment plants of urban Hanoi. Furthermore, this paper evaluates laterite and limonite, which occur very widely in Vietnam, as potential sorbents for As. The sorption kinetics of these minerals for As(III) and As(V) were investigated and their applicability in household adsorption and filtration system for As removal was assessed.

## Materials and Methods

### *Experiments for As removal by adsorption onto Fe hydroxide and oxidation by hypochlorite.*

Raw groundwater samples were collected from water supplies of Hanoi city. Appropriate Fe(II) chloride amounts were added and the pH was maintained at  $7.0 \pm 0.2$ . Fe(II) was oxidized to Fe(III) by air purging until Fe(II) could not be detected by the orthophenantroline method. As(III) and As(V) in the form of  $\text{AsO}_3^{3-}$  and  $\text{AsO}_4^{3-}$  at concentrations of  $0.5 \text{ mg l}^{-1}$  were added. Solutions were stirred gently for 10 min. and allowed to settle for 15 min for precipitation.

The precipitate was discarded and the solution was analyzed for As and Fe concentrations. Chlorine in the form of hypochlorite was added to a series of Fe(II) solutions with concentrations of 1, 5, 10, 15, 20, 25 and  $30 \text{ mg l}^{-1}$  and As constant concentration of  $0.5 \text{ mg l}^{-1}$ . For As analysis, an on-line hydride generation device coupled with Atomic Absorption Spectroscopy (HVG-AAS) (Shimadzu, Kyoto, Japan) was used. Further details for chemical analysis of As can be found in Berg *et al.*, 2001.

### *Sorption capacity of laterite and limonite for As(III) and As(V)*

Laterite and limonite were first treated (see below) and then subjected to determination of their chemical composition as well as naturally occurring As contents (Table 3). Arsenic possibly present in these minerals was removed by washing in an alkali solution (10M NaOH) and by heating to  $900^\circ\text{C}$  for 2 hours. Isothermal sorption experiments were carried out using treated laterite and limonite as sorbents, with initial As(III) and As(V) concentrations of 2, 5, 10, 20, 30, 40, 50 and  $100 \text{ mg l}^{-1}$  and under atmospheric pressure and  $28^\circ\text{C}$ . The suspensions were centrifuged and the supernatant solutions were filtered through  $0.45 \mu\text{m}$  membrane filters prior to As determination.

The treated laterite and limonite were packed into an adsorption column and applied as filtration device in a household water treatment system. Raw groundwater was pumped through the column. Raw groundwater and filtered water samples were collected periodically (3 - 4 times a week) and were analyzed for total As concentrations.

## Results and Discussion

### *Removal of arsenic in the form of arsenite*

In anoxic groundwater, arsenic is present in the form of arsenite (products of  $\text{H}_3\text{AsO}_3$ ) due to the reducing conditions. After aeration in the Hanoi water treatment plants, most Fe(II) is oxidized to Fe(III). After Fe is completely oxidized, the dissolved oxygen increases and then facilitates the oxidation of As(III). In treated water of the water treatment plants, As(V) concentration after aeration varied substantially with a

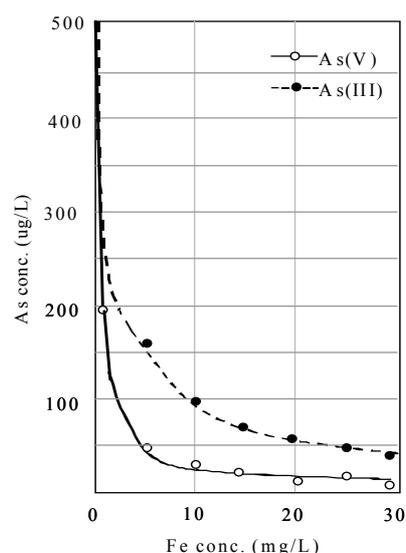


Figure 1. Removal ability of precipitated iron (oxy) hydroxides for As (III) and As (V)

maximum level of about 20 % of total As concentration. However, the co-precipitation and the mechanism of sorption is much more efficient for As(V) as compared to As(III). To clarify this the sorption capacity of As(III) and As(V) onto iron (III) hydroxide under the conditions of the water treatment plants in Hanoi was investigated.

Figure 1 shows the As sorption capacity of Fe(III) hydroxide in the sorption experiment. Fe(II) concentrations of 1, 5, 10, 15, 20, 25 and 30 mg l<sup>-1</sup> were used and the As(III) concentration was kept constant at 0.5 mg l<sup>-1</sup>. The sorption of As(III) increased with increasing Fe(II) concentration. As shown in Figure 1, to reduce the As concentration to below the Vietnamese Standard (0.05 mg l<sup>-1</sup>), a minimum Fe(II) concentration of 25 mg l<sup>-1</sup> was required. If this technique is applied for water treatment plants in Hanoi, it is difficult to reduce As concentrations to the WHO standard (0.01 mg l<sup>-1</sup>). Therefore, the possibility of lowering As concentrations in supplied water in the form of As(V) have been further investigated.

#### *Removal of arsenic in the form of arsenate*

In this experiment, As(III) was oxidized to As(V) using hypochlorite. In the water treatment plant, the active chlorine solution was added in excess (0.5 mg l<sup>-1</sup>) for complete oxidation of As(III) to As(V). The sorption isotherm for As(V) onto iron (III) hydroxide showed that the adsorption capacity for As(V) is much more efficient than that of As(III) (Figure 1). For example, with a relatively low Fe concentration of 5 mg l<sup>-1</sup>, the As concentration can be substantially reduced to a level below 0.05 mg l<sup>-1</sup>. If treated water contains As concentrations <0.5 mg l<sup>-1</sup>, the required Fe concentration for lowering such As levels should be > 5 mg l<sup>-1</sup>.

#### *Influence of chlorine concentrations in lowering As concentrations*

In this experiment, chlorine concentrations ranging from 0.25 to 1.25 mg l<sup>-1</sup> were used and the initial As(III) concentration was kept constant at 0.5 mg l<sup>-1</sup>. The capacity for total inorganic As removal (%) was examined with Fe concentrations of 1, 5, 15 and 25 mg l<sup>-1</sup> (Figure 2). Interestingly, the removal efficiency remained constant at more than 80 % for relatively high concentrations of Fe. However, for lower Fe concentrations, the removal efficiency curve had a maximum and the efficiency decreased thereafter with increasing chlorine concentrations (Figure 2). This phenomenon may be due to the oxidation of other compounds or/and the formation of other Fe species (Meng *et al.*, 2000). Fortunately, the Fe(II) concentration in groundwater of the Red River Delta is quite high (average 15 - 20 mg l<sup>-1</sup>). The effect of other compounds such as silicate and phosphate was not investigated in this study.

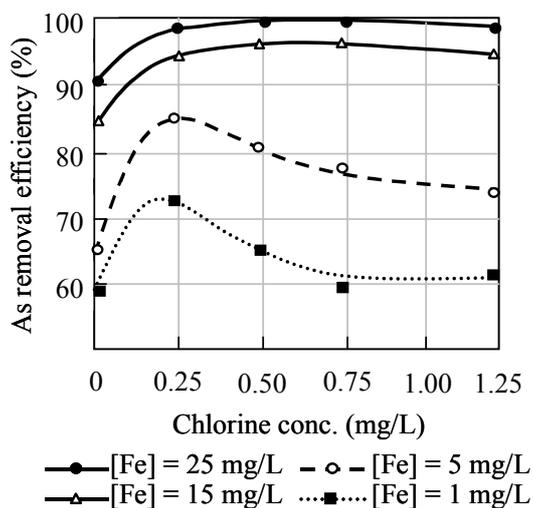
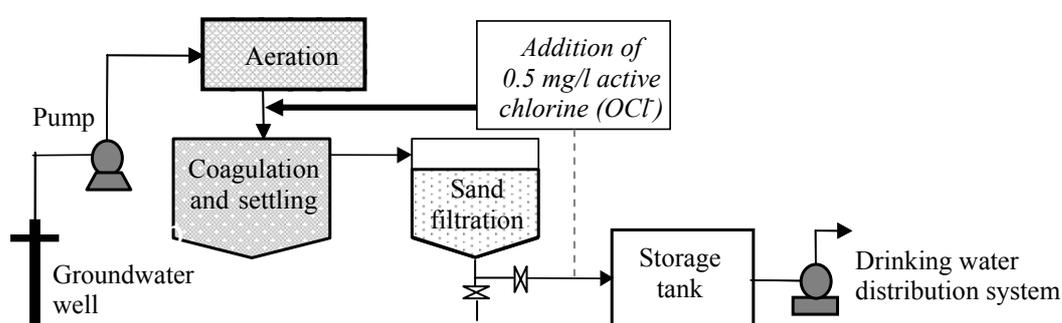


Figure 2. Influence of active chlorine concentrations on As removal efficiency.

*Treatment of As in urban Hanoi water treatment plants using hypochlorite.*

Based on the efficiency of As removal in the form of As(V), it was proposed to add hypochlorite right after the aeration step in the conventional process for water treatment in the urban Hanoi water treatment plants (Figure 3). After aeration, Fe(II) was fully oxidized to Fe(III), and As(III) was oxidized to As(V). The removal of As(V) was efficient and the hypochlorite can also act for water sanitation purposes. It is therefore suggested that this process can be applied for lowering As concentrations in the city water treatment plants. In this process, the added amount of  $\text{ClO}^-$  depends on the chemical composition of the groundwater and the fact that the residue must be of  $0.5 \text{ mg l}^{-1}$  chlorine.

Figure 3. Proposed schematic diagram for additional oxidation by active chlorine in the water treatment process of the urban Hanoi water treatment plants

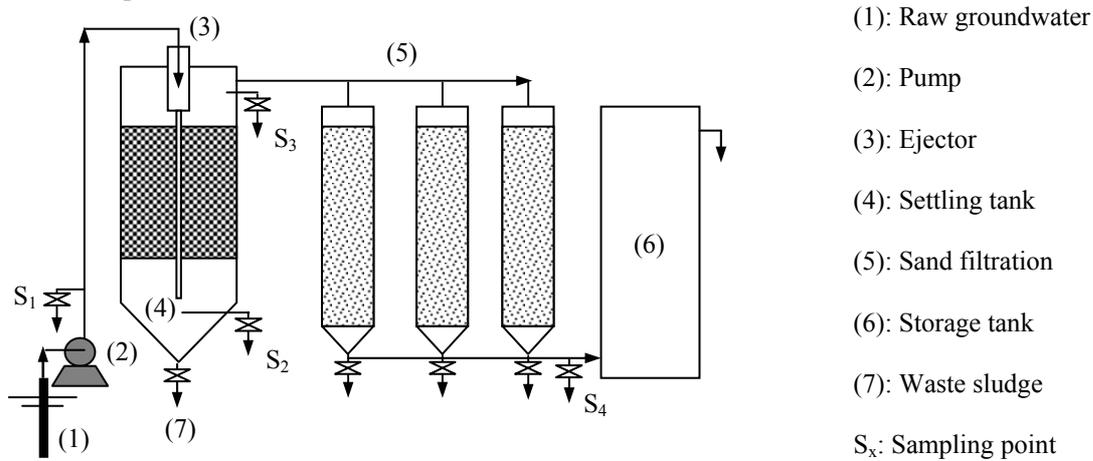


To further investigate the suitability of this method for As removal in water, the removal efficiency on the pilot equipment for groundwater treatment that is currently installed in one city water treatment plant was also tested (Figure 4). Groundwater is pumped from a 40m deep well (1) to an ejector (3) placed in a pre-filtration tank (4). The oxidation of Fe(II) to Fe(III), precipitation of iron(oxy)hydroxides and co-precipitation of As(V) takes place in this tank. After coagulation and pre-filtration, the water is transferred through the sand filtration system (5) and finally to the reservoir (6) (Figure 4). In order to evaluate the quality of the raw groundwater, samples were taken and were analyzed for total Fe, As, phosphate, soluble silicate concentrations, dissolved oxygen and pH continuously for 2 weeks. The composition of the groundwater before treatment in the pilot plant is presented in Table 1.

Table 1. Composition of groundwater before the pilot water treatment system

Composition	Total Fe ( $\text{mg l}^{-1}$ )	Total As ( $\mu\text{g l}^{-1}$ )	DO ( $\text{mg l}^{-1}$ )	pH	$\text{PO}_4^{3-}$ ( $\text{mg l}^{-1}$ )	Soluble Si ( $\text{mg l}^{-1}$ )
Level	25.5	20.1	1.2	6.8	0.12	4.36

Figure 4. Schematic diagram of the water treatment pilot system installed in a city water treatment plant



Because the initial Fe(II) concentration is quite high, Fe(II) was not added into the pilot system. To assess the ability of As removal, As(III) was introduced in the form of  $\text{AsO}_3^{3-}$  with a series of concentrations from 0.15 to 1.7  $\text{mg l}^{-1}$ . The results are presented in Table 2 and Figure 5.

Figure 5. As concentrations in the inlet and outlet of the pilot equipment as an indication of As removal

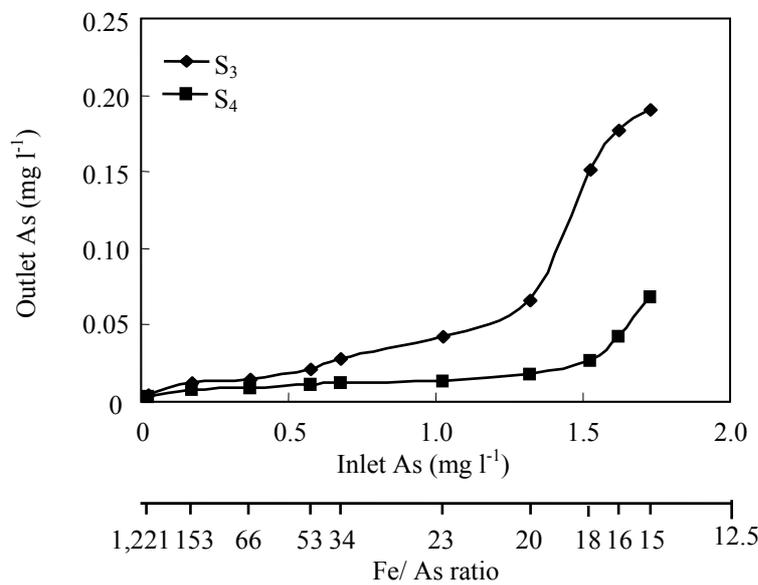


Table 2. Arsenic removal efficiency at different sampling points in the pilot water treatment system (Ref. Figure 4)

Spiked As (mg l <sup>-1</sup> )	Fe/ As ratio	As (mg l <sup>-1</sup> ) and Fe (mg l <sup>-1</sup> ) at sampling points							
		S <sub>1</sub>		S <sub>2</sub>		S <sub>3</sub>		S <sub>4</sub>	
		Fe	As	Fe	As	Fe	As	Fe	As
0.00	1,221	25.64	0.021	22.36	0.020	1.42	0.004	0.53	0.003
0.15	153	26.54	0.173	-	-	2.86	0.012	0.32	0.008
0.35	66	24.56	0.372	-	-	2.61	0.015	0.11	0.009
0.55	53	30.41	0.574	-	-	1.34	0.021	0.43	0.011
0.65	34	23.32	0.677	-	-	1.86	0.028	0.08	0.012
1.00	23	23.43	1.024	-	-	1.67	0.043	0.12	0.014
1.30	20	26.52	1.319	-	-	2.06	0.066	0.01	0.018
1.50	18	27.04	1.522	-	-	4.32	0.151	0.01	0.027
1.60	16	26.02	1.621	-	-	4.22	0.177	0.08	0.043
1.70	15	26.05	1.725	-	-	3.75	0.191	0.21	0.068

It is clear that for As concentrations in the pre-filtration tank (sampling site S<sub>2</sub>) that is based on the co-precipitation of As(V) onto ferric hydroxide with initial Fe concentration of around 25 mg l<sup>-1</sup>, only about 1.3 mg l<sup>-1</sup> As in groundwater could be removed, with an initial concentration ratio of Fe/As = 20. After the sand filtration, As was continuously removed and the efficiency of As removal in the whole pilot system was increased (with initial Fe/As concentration ratio of 16).

#### *Household sorption and filtration system*

In Vietnam, private wells have been used for a long period of time in rural and sub-urban areas. In 1990s, UNICEF's pumped tube well systems have been widely developed and used throughout the country. The UNICEF wells have played a very important role and are the main source of water supply for many people in Vietnam, when surface water was contaminated. However, as mentioned above, recent findings of the unexpected severe As pollution in groundwater raised a serious concern that millions of people living in rural and sub-urban areas are consuming As-enriched groundwater and are at risk for As poisoning (Berg *et al.*, 2001). Due to the lack of knowledge and education, the risk of As exposure for people in rural areas may be more serious. In this study therefore the applicability of naturally occurring iron minerals having a high sorption capacity for some inorganic ions, including As(III) and As(V) was also investigated. Such minerals, namely laterite and limonite, are abundant in Vietnam (Ha Tay, Vinh Phu Province in Northern Vietnam) and are often relatively clean. It was anticipated that these minerals could be used as potential sorbents for a household sorption and filtration system to lower arsenic concentrations in tube wells.

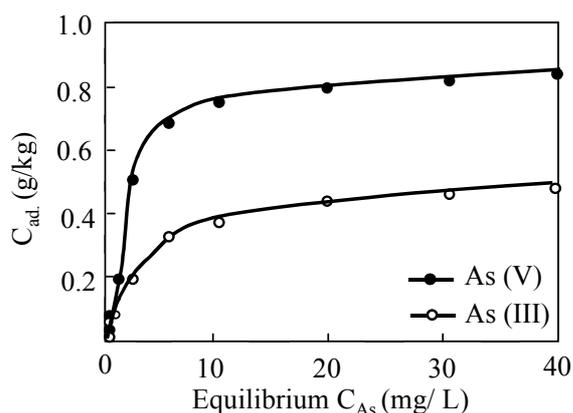


Figure 6. Sorption isotherm of As(III) and As(V) onto limonite (initial As conc. = 500  $\mu\text{g l}^{-1}$ )

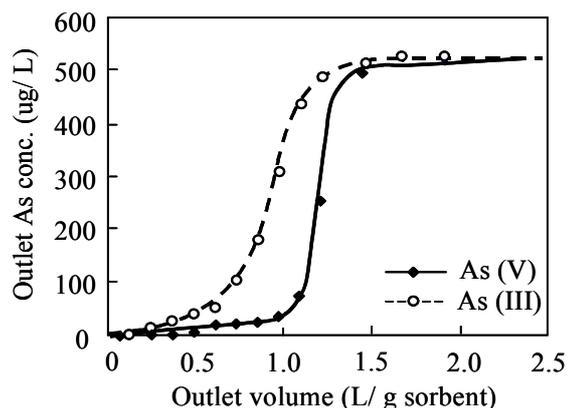


Figure 7. Breakthrough curves of sorption of As(III) and As(V) for limonite (initial con. = 500  $\mu\text{g l}^{-1}$ )

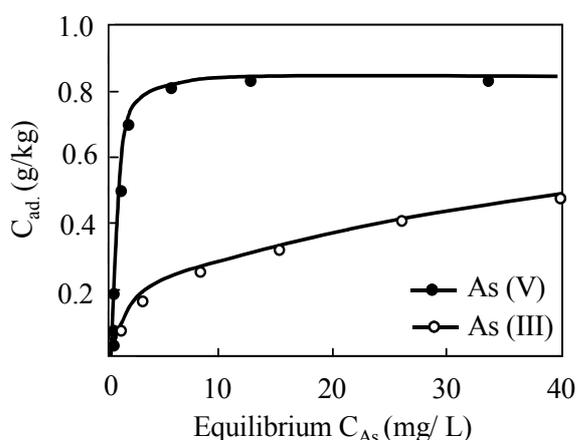


Figure 8. Sorption isotherm of As(III) and As(V) onto laterite (initial conc. = 500  $\mu\text{g l}^{-1}$ )

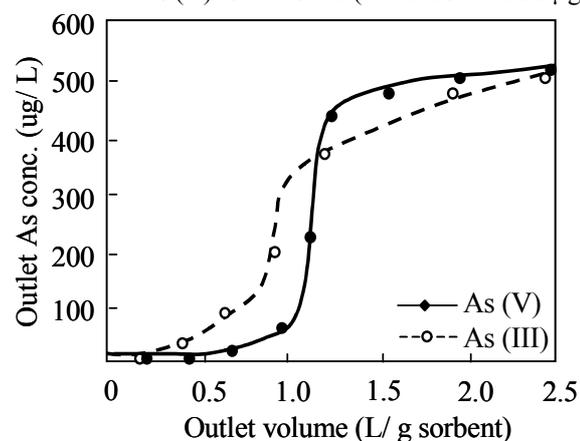


Figure 9. Breakthrough curves of sorption of As(III) and As(V) for laterite (initial conc. = 500  $\mu\text{g l}^{-1}$ )

Table 3. Laterite and limonite composition and As content

Material	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	MgO (%)	As <sub>2</sub> O <sub>3</sub> (mg kg <sup>-1</sup> )		
						Initial	After washing by alkali solution	After heating at 900°
Laterite	40.96	14.38	32.14	0.14	0.18	41.83	33.77	5.36
Limonite	11.25	4.12	84.24	0.25	0.16	16.25	14.27	1.29

Laterite and limonite minerals were collected, treated, sieved and subjected to determination of composition as well as naturally occurring As contents. The results of the analysis of laterite and limonite compositions and As contents in these minerals is shown in Table 3. Sorption isotherms and breakthrough curves of limonite and laterite are shown in Figures 6 and 7 and Figures 8 and 9, respectively. A Langmuir sorption isotherm was able to describe the sorption kinetics of As(III) and As(V) onto laterite and limonite. It is clear that the sorption capacity of As(V) is apparently higher than that of As(III), suggesting the suitability of using these materials to remove As in the form of As(V) from groundwater.

Based on the sorption isotherm, the sorption capacity of limonite for As(III) and As(V) was calculated as 500 and 900 mg kg<sup>-1</sup>, respectively. For laterite, the sorption capacity was slightly higher [600 mg kg<sup>-1</sup> for As(III) and 1100 mg kg<sup>-1</sup> for As(V)], suggesting a more effective sorption ability of this mineral for lowering As concentrations in groundwater using household-based filtration and adsorption system. Further, the arsenic concentrations before and after the sorption column were also tested. The initial results show that this system was able to reduce As concentrations below the Vietnam Standard of 0.05 mg l<sup>-1</sup>. In addition, manganese was also efficiently removed and there was no contamination by sorbent-originated elements. Further investigations are necessary to provide detailed information on the efficiency and capacity of arsenic removal of this household water treatment system.

## Conclusions

The preliminary investigations into suitable techniques for lowering As concentrations in water treatment plants of Hanoi city and household adsorption and filtration systems for rural and sub-urban areas indicates that As can be efficiently removed from drinking water in the form of arsenate. In the water treatment plants, hypochlorite (NaClO) for oxidizing As(III) to As(V) was added to the conventional process applied in the plants. With a Fe concentration of 5 mg l<sup>-1</sup>, As concentrations can be lowered to a level below the Vietnam Standard from an initial concentration of 0.5 mg l<sup>-1</sup>. The investigation of the pilot scale equipment indicates that removal of As in this system is more effective than that in the laboratory experiments. For smaller scale water treatment systems in rural and sub-urban areas, naturally occurring minerals such as laterite and limonite, can be used as potential sorbents for As in adsorption and filtration columns. The relatively high sorption capacity for arsenite and arsenate of these minerals suggests the suitability of using them in household-based water treatment systems.

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