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Laterite as a low-cost adsorbent in a sustainable decentralized filtration system

to remove arsenic from groundwater in Vietnam

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Abstract

In the Red River Delta, Vietnam, arsenic (As) contamination of groundwater is a serious problem where more than seventeen million people are affected. Millions of people in this area are unable to access clean water from the existing centralized water treatment systems. They also cannot afford to buy expensive household water filters. Similar dangerous situations exist in many other countries and for this reason there is an urgent need to develop a cost-effective decentralized filtration system using new low-cost adsorbents for removing arsenic. In this study, seven locally available low-cost materials were tested for arsenic removal by conducting batch adsorption experiments. Of these materials, a natural laterite (48.7% Fe₂O₃ and 18.2% Al₂O₃) from Thach That (NLTT) was deemed the most suitable adsorbent based on arsenic removal performance, local availability, stability/low risk and cost (US\$ 0.10 /kg). Results demonstrated that the adsorption process was less dependent on the solution pH from 2.0 to 10. The coexisting anions competed with As(III) and As(V) in the order, phosphate > silicate > bicarbonate > sulphate > chloride. The adsorption process reached a fast equilibrium at approximately 120–360 min, depending on the initial arsenic concentrations. The Langmuir maximum adsorption capacities of NLTT at 30 °C were 512 µg/g for As(III) and 580 µg/g for As(V), respectively. Thermodynamic study conducted at 10 °C, 30 °C, and 50 °C suggested that the adsorption process of As(III) and As(V) was spontaneous and endothermic in nature. A water filtration system packed with NLTT was tested in a childcare centre in the most disadvantaged community in Ha Nam province, Vietnam, to determine arsenic removal performance in an operation lasting six months. Findings showed that the system reduced total arsenic concentration in groundwater from 122-237 µg/L to below the Vietnam drinking water standard of 10 µg/L.

Keywords: arsenic removal; adsorption; decentralised filter; groundwater; laterite; low-cost adsorbent

1. Introduction

Arsenic (As) is a highly toxic element and is ranked number 1 in the 2001 priority list of hazardous substances by the United States' Agency for Toxic Substances and Disease Registry. Arsenic contamination in drinking water and groundwater has become a serious issue in many countries such as Bangladesh, Vietnam, India, China, etc. (Khan and Ho, 2011). In natural water bodies, arsenic is mostly found in two states: trivalent As (As(III), arsenite) and pentavalent As (As(V), arsenate). Both forms are highly toxic inorganic species (Smedley and Kinniburgh, 2002). The toxicity of arsenite is much higher than that of arsenate. Consumption of arsenic contaminated water over a long period of time can lead to damage being done to lung, liver, skin and other systems of the body (Jain and Chandramani, 2018).

In Vietnam, total arsenic concentrations of 1–845 μ g/L (average 39 μ g/L) and 1–3050 μ g/L (average 159 µg/L) are found in groundwater in the Mekong River Delta and Red River Delta, respectively (Berg et al., 2007). Researchers from the Swiss Federal Institute of Aquatic Science and Technology and Vietnam National University estimated that around one million people in the Red River Delta had to use drinking water with a total arsenic concentration greater than 50 µg/L. This is 5 times higher than the WHO's guidelines and Vietnam drinking water quality standards (Winkel et al., 2011). In the Red River Delta, Hanam province is reported as the area most seriously affected by arsenic contamination in its groundwater. It is a province where approximately 52% groundwater samples were found to be higher in total arsenic concentration than what the Vietnam drinking water quality standards specify (Nga, 2008). The Hoang Tay commune (Kim Bang rural district, Hanam province) is one of the poorest communes in Hanam province, with per capita annual income of 28 million VND/year (around 1270 USD/year). Around 5,370 people (51.6% female) live in Hoang Tay commune which consists of 10 villages. Most households and community places are using rainwater and contaminated groundwater as their main water sources for daily activities. Similar to other communes in Vietnam, sand filters are widely used in this commune to treat contaminated water. However, this treatment method generally cannot produce

safe drinking water, so there has been a failure to keep the total arsenic concentration below the Vietnam drinking water quality standard for the local villagers.

Given this problem, a number of techniques have been developed for removing arsenic from water. The major techniques include ion exchange, chemical precipitation - coagulation, adsorption, membrane, and phytoremediation (Glocheux et al., 2013; Luong et al., 2018). Of these techniques, adsorption is considered the most cost-effective method for removing arsenic in household and small community levels because of its high removal efficiency, low energy consumption, simplicity in design and operation and minimal waste generation. Iron- and aluminium-containing materials are considered to be suitable adsorbents because they possess a high affinity to arsenic (Giles et al., 2011; Pena et al., 2005). Nanomaterials (i.e., nano iron oxides/hydroxides, nano TiO₂, nano zerovalent iron, nano CuO, nano ZnO, and layered double hydroxides) have also been identified as highly-effective adsorbents for removing As(III) and As(V) from water media (Goh et al., 2008; Lata and Samadder, 2016; Pena et al., 2005; Siddiqui and Chaudhry, 2017). However, such nanomaterials exist in a fine powder form and it is difficult to separate them from water after adsorption. In column-based filters they cause hydraulic problems by clogging the filters. Other popular commercial adsorbents (i.e., activated carbon and activated alumina) can also effectively remove arsenic from water (Kalaruban et al., 2019). However, relatively high cost might prevent them from practical applications in villages. In addition, these materials need to be regenerated for reuse options (Mohan and Pittman Jr, 2007). Low cost natural adsorbents (clay, goethite, zeolites, laterite, red mud, fly ash, etc.) have been investigated as a replacement for the current expensive adsorbents in treating arsenic from contaminated water and wastewater due to their local availability, low cost and efficiency (Mohan and Pittman Jr, 2007). However, the applications of those low-cost adsorbents in pilot scale and full scale scenarios are still limited.

Laterite is formed commonly in hot and wet tropical areas and is distributed widely in many areas throughout Vietnam (Thach That and Tam Duong areas). This material can be used as a potential adsorbent for arsenic removal due to the natural presence of Fe and Al oxides/hydroxides

in its composition (Glocheux et al., 2013). In this study, the natural laterite from Thach That (NLTT) together with six other local low-cost mineral and waste materials were first tested in the laboratory with synthetic water spiked with arsenic for their ability to remove arsenic. Based on the initial laboratory results, the NLTT material was selected and evaluated in a detailed batch study for its performance in arsenic removal. NLTT was then packed in the newly developed community water treatment system for a long-term trial with real contaminated groundwater. The new system has been implemented in the childcare centre in Hoang Tay commune since June 2018. This paper presents the results concerning the performance of the locally available low-cost NLTT in removing arsenic over a period of 6 months: firstly, from synthetic water through detailed batch adsorption studies; and secondly and subsequently, testing its use in the community water filtration system with natural groundwater. The community filtration system also incorporated the simultaneous removal of iron and pathogens.

2. Materials and methods

2.1. Preparation of adsorbent materials

Natural laterite (NLTT) used in this study was collected at Thach That district, Hanoi City, Vietnam. The collected NLTT was firstly washed with water three times to eliminate any adhering dirt and soluble compound on its surface and then placed in an oven at 105 °C for 48 h to remove excess water and moisture. The dried NLTT was ground and sieved into relatively homogeneous particle sizes ranging from 0.5 to 1 mm. These NLTT particles were washed with distilled water, dried at 85 °C for 24 h, and stored in tightly closed bags.

In this project, we also selected six other low-cost and waste materials (abundant in Vietnam) to explore their adsorption capacity of arsenic in aqueous solution. They include laterite (collected from Tam Duong, Vinh Phuc province), bentonite (Tay Ninh, Thanh Hoa province), feralite soil (Thai Nguyen province), red mud (the Bao Loc's mine, Lam Dong province), iron ore mining waste

(the Trai Cau's iron ore mine, Thai Nguyen province), and iron ore mining waste (the Ban Cuon's iron ore mine, Bac Kan province). Such collected materials were ground to a particle-size range similar to NLTT (0.5–1.0 mm), washed, dried, and then stored in sealed bags.

A commercial granular activated carbon (GAC) used as a second adsorbent in the community filtration system was purchased from Phuong Nam Company Limited in Vietnam.

2.2. Characterization of adsorbent materials

The morphology and element compositions of pristine and arsenic-loaded laterite were examined using scanning electron microscopy (SEM; Quanta-650) and energy dispersive X-ray spectroscopy (EDS) techniques. The mineral and chemical compositions of laterite were determined using X-ray Diffraction (XRD; Empyrean-PANalytical) and X-ray Fluorescence (XRF; Pioneer-S4), respectively. The surface area of adsorbent was determined using N₂ adsorption isotherm with a Micromeritics sorptometer (Accu Pyr II 1340. V1.02) at 77 K. The presence of main function groups on the NLTT' surface was measured by Fourier transform infrared spectroscopy (FTIR; Nicolet iS5). Finally, using the common drift method (Maiti et al., 2013; Partey et al., 2009; Tran et al., 2017a) the pH value of NLTT at the point of zero charge (pH_{PZC}) was determined. According to this method, solutions of 0.01 mol/L NaCl in 100 mL test tubes were adjusted to pH values ranging from 2 to 9 (pH initial) using 0.1 mol/L NaOH and 0.1 mol/L HCl. Then, 2.5 g of NLTT were added to test tubes and shaken at 150 rpm at 25 °C. After 24 h the final pH (pH final) of samples were measured. (pH final – pH initial) values were plotted on the Y-axis against initial pH in the X-axis. The intersection point of the resulting curve with the X-axis ((pH final – pH initial) = 0) was taken as the pH_{PZC}.

The NLLTT's element composition was also determined by chemical analysis using strong acid digestion. In this method, 0.1 g NLTT sample was digested in a solution of 5 mL concentrated

HNO₃ and 5 mL concentrated HCl in a microwave digester for 3 h. The digested solution was diluted and analysed for metal concentrations using ICP-OES (Perkin Elmer 7300).

2.3. Batch adsorption experiment

Stock solutions of As(III) and As(V) (1000 mg/L) were prepared by dissolving NaAsO₂ (ACE chemicals company) and Na₂AsO₄•7H₂O (BDH chemical Ltd.) in distilled water, respectively. Both NaAsO₂ and Na₂AsO₄•7H₂O had been dried at 105 °C for 4 h and kept in a desiccator before they were used to prepare the stock solutions. All working As(III) or As(V) solutions were prepared by diluting the relevant stock solutions. All chemicals and reagents used in this work were of analytical grade.

Initially, an adsorption experiment was conducted to identify the potential of NLTT and the other six materials for removing arsenic from water. Briefly, 0.25 g of each material was added into Erlenmeyer flasks containing 100 mL As(V) solution of 200 μ g/L. The flasks were sealed, placed on a mechanical shaker, and shaken at 160 rpm for 24 h at 30 °C. Subsequently, the liquid samples were strained through a 0.45 μ m filter before the As(V) residual concentration was examined. The results (presented in more detail in **Section 3.1**) demonstrated that the natural laterite material from Thach That (NLTT) was the most suitable adsorbent. For this reason, it was selected for subsequent studies, i.e., characterization, adsorption, and application.

Detailed batch adsorption experiments were conducted to study the effect of several operating parameters (i.e., solution pH values, contact times, initial arsenic concentrations, coexisting anions, temperatures, and desorbing agents) on using NLTT to remove arsenic. Briefly, the effect of solution pH on the adsorption capacity of NLTT was determined by mixing 0.75 g material with 100 mL of 500 µg arsenic/L solution in Erlenmeyer flasks at different pH values. The pH of the arsenic solutions was adjusted from 2.0 to 10 ± 0.2 by adding either 1M NaOH or 1M HNO₃. To evaluate the effect of coexisting anions on arsenic adsorption capacity of NLTT, similar experiments were carried out with the addition of different anions (such as Cl⁻, CO₃²⁻, HPO₄²⁻,

 SO_4^{2-} , SiO_3^{2-}), with the concentration of each anion being 10 mM. Studies on adsorption kinetics were conducted at time intervals of 1, 5, 10, 20, 30, 60, 120, 180, 240, 300, 360, 420, 480, and 960 min at initial concentration of As(III) or As(V) of 500 µg/L and 250 µg/L, respectively. Equilibrium adsorption experiments were conducted using As(III)/As(V) concentrations ranging from 100 to 25000 µg/L at temperatures of 10 °C, 30 °C, and 50 °C. In these experiments the suspensions were shaken for 24 h to ensure equilibrium has reached. In all the above experiments the flasks containing the respective suspensions were placed in a shaker and shaken at 160 rpm. After predetermined shaking time, the solid was separated from solution by glass fiber filters. The liquid was then filtered through a 0.45 µm syringe filter before analysing it for arsenic. Meanwhile, the above solid samples were dehydrated at 80 °C for 12 h and then stored in tightly closed bags for further analysis (i.e., FTIR, the textural, morphological properties and desorption). The total arsenic concentration in the filtered samples was determined by an Inductively coupled plasma mass spectrometry (ICPMS-NexION 2000, US). The amounts of, firstly, arsenic adsorbed onto NLTT at equilibrium, q_e (µg/g) and secondly, arsenic uptake at time *t*, q_t (mg/g) were calculated using **Equations 1** and **2**, respectively.

$$q_{e} = \frac{C_{o} - C_{e}}{m_{1}} V_{1}$$

$$q_{t} = \frac{C_{o} - C_{t}}{m_{1}} V_{1}$$
(1)
(2)

where C_0 , C_e , and C_t are the total arsenic concentrations (mg/L) at beginning, equilibrium, and time t, respectively; m_1 (g) is the mass of NLTT used; and V_1 (L) is the volume of the arsenic solution. All experiments were conducted in duplicate and the average value was reported. Whole batch experiments were carried out at the constant ratio of NLTT amount/solution of 7.5-g NLTT/1.0 L of arsenic solution.

Desorption experiments were carried out to determine the reversibility of the adsorption. In this study, the flasks containing 0.1 L of different desorbing agents (V_2) and predetermined amount (approximately 0.75 g) of arsenic loaded NLTT (m_2) were placed in a shaker and shaken at 160 rpm for 24 h. The tested desorbing agents include deionized (DI) water at pH 12, 0.5M HCl, 0.5M NaOH, 0.5M NaCl and ethylenediaminetetraacetic acid (EDTA; 5%). The amount of arsenic remaining on NLTT and the percentage of desorption were determined using **Equations 3** and **4**, respectively.

$$q_{r} = q_{e} - q_{d} = q_{e} - (\frac{C_{d}}{m_{2}}V_{2})$$
(3)

$$\% Description = \left(\frac{q_e - q_r}{q_e - q_d}\right) \tag{4}$$

where C_d (mg/L) is the concentration of arsenic in solution after desorption; q_r (mg/g) is the mass of arsenic that remained adsorbed after desorption; and q_d (mg/g) is the mass of arsenic desorbed if the adsorption process is reversible.

2.4. Field trial in Hanam province

According to the Ministry of Natural Resources and Environment (MONRE, 2015), the Hoang Tay commune (located in Kim Bang rural district, Hanam province, Vietnam) is identified as a commune severely affected by arsenic contaminated groundwater. It is one of the villages that have the most polluted sources of water in Vietnam.

The primary finding of our water quality survey from June to September 2017 indicated that the total arsenic concentration in some surrounding local wells (ranging from 28 to 447 μ g/L) was overwhelmingly higher (approximately 3 to 45 times, respectively) than the arsenic safety limit recommended by the World Health Organisation (WHO) and the Vietnam drinking water quality standard (QCVN01:2009/BYT). Consequently, Hoang Tay Childcare Centre is selected as a target

area for conducting a field trial. The characteristics of the groundwater before and after sand filter in the Hoang Tay childcare are presented in **Table S1**. The results showed that the total arsenic concentrations of groundwater in the childcare centre varied from 122 to 237 μ g/L. Notably, the existing treatment using the sand filter did not provide safe drinking water for the childcare centre. This is because the total arsenic concentrations (42–110 μ g/L; **Table S1**) after passing the traditional sand filter-based treatment system were dramatically higher than the WHO regulation (10 μ g/L). It is therefore critical to develop a simple, economical, and efficient removal technology eradicating arsenic from water. In order to supply safe water for the childcare centre, a new water supply system (**Figure S1**) was designed and installed through the cooperation between University of Technology Sydney and the Institute of Environmental Technology, Vietnam Academy of Science and Technology. The designed system can supply 500 L/h to meet the water demand of around 440 children and 32 staff members in the investigated childcare centre.

The designed water treatment system principally includes: a combined aeration and clarifier tank (main purpose being the simulation of the co-precipitation process between iron and arsenic as well as the removal of the Fe-As precipitates, respectively); an adsorption column (for the removal of arsenic and other pollutants); an ultrafilter (for removing microorganisms); and a storage tank. **Figure 1a** and **Figure S1** illustrate the schematic diagram and digital picture of the designed system, respectively. Notably, in this system, the up-flow adsorption column comprises three ordering layers: sand, NLTT, and commercial GAC, with their bed height being 0.5 m, 0.4 m, and 0.3 m, respectively. The adsorption column with its diameter of 0.76 m contained approximately 288 kg of sand (particle size: 2–4 mm), 220 kg of NLTT (0.5–1.0 mm), and 140 kg of GAC (0.5–2.5 mm) in each layer. To evaluate how well the childcare centre functioned, the water samples were collected weekly from six different positions (from C1 to C6 in **Figure 1a**) for around six months.

Figure 1. (a) Schematic diagram of the water treatment system and (b) performance of the system over a period of six months

3. Results and discussion

3.1. Comparison of the adsorption capacity of Vietnam low-cost adsorbents

The removal of As(V) by the seven low-cost adsorbents used are presented in Figure S2.

Results show that the removal efficiency of As(V) declined in the following order: BTN (78,6%) > NLTT (76.0%) > IMWBC (72.4%) > IMWTC (71.0%) > NLTD (70.0%) > FTN (67.2%) > RMBL (62.4%). Although BTN had the highest removal percentage of As(V), after the adsorption process, the medium swelled inside the flask due to the presence of bentonite in this material. This phenomenon can be explained by the fact that bentonite is a phyllosilicate clay with 2:1-layer silicate structure and contains mainly smectite which has high swell index (Bhattacharyya and Gupta 2008). The iron mining wastes (IMWBC and IMWTC) also exhibited good adsorptive removal due to their high iron content, which facilitates arsenic removal (Altundoğan et al., 2000; Nguyen et al., 2009). However, using industrial waste as an adsorbent does pose the high risk of generating toxic heavy metals in the treated water. Considering the following aspects - removal efficiency, availability, stability/potential risk and cost (including exploration, transportation from the source to workshops, processing/grinding), of the adsorbents tested - NLTT from Thach That, Hanoi was found to be the most suitable media for arsenic removal. The total cost including transport and processing is only US\$ 0.20/kg. Transporting from the mine site and processing costs can be cut drastically when many communities around the childcare centre start using the filtration technique and a large quantity of NLTT is transported in a single trip. In this case, the cost of the material can be reduced to US\$ 0.10/kg. Thus, NLTT from Thach That, Hanoi was chosen for subsequent tests and pilot trial.

3.2. Basic characteristics of the NLTT

The physisorption isotherm of the NLTT's nitrogen gas is illustrated in **Figure 2a**. According to the IUPAC technical report (Thommes et al., 2015), the physisorption isotherm can be classified as the reversible Type II. In addition, the hysteresis loop (Type H3) appeared in the isotherm at the relative pressure (p/p°) higher than 4.0. These results suggested that the collected NLTT was a typical nonporous adsorbent. This conclusion was further confirmed by its textural parameters that were calculated from the nitrogen adsorption/desorption isotherm in **Figure 2a**. The calculation performance showed that the NLTT was a non-porous material, with its low BET specific surface area (S_{BET} ; 155 m²/g) and total pore volume (V_{Total} ; 0.5489 cm³/g). Similarly, the relatively low S_{BET} (m²/g) and V_{Total} (cm³/g) values of other kinds of laterite derived from different geographical regions were reported in the literature, such as 17.5–18.5 m²/g and 0.02–0.05 cm³/g (Maiti et al., 2012) and 71–182 m²/g and 0.07–0.35 cm³/g (Maiti et al., 2013). Because the natural adsorbent is a non-porous material, the adsorption mechanism of arsenic ions in solution involved in pore filling might be less important than some surface interactions, i.e., complexation (Cheng et al., 2019).

Figure 2b provides the FTIR spectrum of the NLTT. The presence of main function groups on the NLTT's surface was observed at several corresponding bands at approximately 1100 cm⁻¹ (Si–O–Fe), 1030 cm⁻¹ (Si–O), 910 cm⁻¹ (Al–OH), 798 cm⁻¹ (Fe–OH), and 530 and 460 cm⁻¹ (Fe–O). In addition, the bands in the region between 3730 cm⁻¹ and 3100 cm⁻¹ can be assigned to the OH stretching vibration in Si–OH, Al–OH, and even water. Lastly, the bands located at around 1630 cm⁻¹ ¹ might belong to the mica group or water. These results were very consistent with studies done on other natural laterites (Maiti et al., 2013; Mitra et al., 2016). With arsenic being intensively reported in the literature, the abundant presence of hydroxyl groups on the adsorbent's surface was expected to form the complexation reaction with arsenic ions in aqueous solution (Cheng et al., 2019; Siddiqui and Chaudhry, 2017; Zhao et al., 2018).

Figure 2. (a) Nitrogen adsorption/desorption isotherm of NLTT before and after arsenic adsorption; and their pore size distribution (inset); and (b) FTIR spectrum of NLTT before and after arsenic adsorption

According to the literature, manganese and titanium oxides function as oxidants that convert As(III) to As(V) (Cheng et al., 2019; Partey et al., 2008). In their study, Zhao et al. (2018) found that iron (hydro)oxides (i.e., ferrihydrite, hematite, and magnetite) can act as a promising catalyst in simulating the oxidation of As(III) onto As(V). Moreover, some clay minerals (nacrite, kaolinite, and illite) were expected to effectively adsorb arsenic ions [As(III) and As(V)] and possibly oxidise As(III) to As(V) (Manning and Goldberg, 1997). The results of XRD analysis (**Figure 3a**) demonstrated that NLTT was composed of goethite, hematite, nacrite, quartz, and anatase. Furthermore, the XRF analysis (**Figure 3b**) indicated that the principal components of NLTT were Fe_2O_3 (48.7%), Al₂O₃ (18.2%), and SiO₂ (14.0%), while the minor ones were TiO₂ (2.89%), P₂O₅ (0.49%), and MnO (0.37%). Such available compounds make the NLTT a unique material that can act as a potential catalyst and promising adsorbent able to remove arsenic contaminant from solution.

Figure 3. (a) XRD spectrum and (b) XRF analysis result of the NLTT

The surface morphology of NLTT (determined by SEM) is provided in **Figure S3a.** The image indicated that the NLTT possessed a relatively irregular and heterogeneous surface morphology. In addition, the surface element analysis (obtained by EDS; **Figure S3b**) indicated the presence of dominant elements (i.e., O, Fe, Al, Si, Ti, and Mn) that possibly play an important role

in the removal of arsenic ions from water media. However, some heavy metals were observed in the EDS data, such as Zn (0.16% atomic), Cu (0.06%), Cr (0.02%), and Pb (0.01%). Therefore, further study was conducted employing the acid digestion method to analyse the concentration of such elements in the NLTT. Results (**Figure S3c**) showed that the NLTT exhibited a high concentration of Fe (199 mg/g), Al (74.9 mg/g), Ti (3.90 mg/g), Mn (3.05 mg/g), and Si (2.06 mg/g). Notably, some heavy metals (i.e., Cr and Cu) were still detected in the structure of NLTT (**Figure S3c**). Therefore, when this material was applied in the real water treatment system (**Section 3.9**), it was necessary to evaluate the concentrations of potential heavy metals after passing the system.

In general, adsorbent often exhibits an amphoteric nature in solution. In this study, the electrical state of the NLTT's surface in solution was determined by the point of zero charge (PZC). The pH_{PZC} of NLTT is 7.1 as determined by the drift method (**Figure S4**). Similarly, researchers found that the pH_{PZC} of other natural laterites collected from different geographical locations ranged from 7.4 to 8.3 (Maiti et al., 2013; Partey et al., 2009). Therefore, electrostatic attraction between the positively charged surface of laterite and target anionic pollutants in the solution was expected to simultaneously occur when the pH value of solution (pH_{solution}) was lower than the pH_{PZC} value.

3.3. Effect of initial solution pH values

In essence, the pH value exerts a strong effect on the surface charge of NLTT (**Figure S4**) and the stability of arsenic species in solutions (**Figure S5**). **Figure 4a** shows that the process of As(III) and As(V) adsorption onto NLTT was less dependent on the solution pH values from 2.0 to 10. A similar finding was reported elsewhere for the study of As(III) and As(V) adsorption onto: synthesized goethite (Lenoble et al., 2002), amorphous Fe oxide (Goldberg, 2002), laterite iron concretions (Partey et al., 2009), Fe(III)-impregnated activated carbon (Mondal et al., 2007), and acid- activated laterite (Maiti et al., 2010a).

Figure 4. Effect of (**a**) initial solution pH values and (**b**) coexisting anions on the adsorption capacity of the NLTT towards As(III) and As(V)

According to the arsenic species stability diagram as a function of pH (**Figure S5**), pentavalent arsenic is a triprotic acid (H₃AsO₄), and its p K_a values were determined to be approximately 2.3 (p K_{a1}), 6.8 (p K_{a2}), and 11.5 (p K_{a3}) (Kartinen and Martin, 1995; Lenoble et al., 2002; Sharma and Sohn, 2009; Smedley and Kinniburgh, 2002). In other words, arsenate species often exist as anionic forms when pH_{solution} was higher than 2.3 (the p K_{a1} of pentavalent arsenic). They included monovalent H₂AsO₄⁻ (within the pH range from approximately 3.0 to 6.0), divalent HAsO₄²⁻ (pH = 7.0–11), and trivalent AsO₄³⁻ (pH = 12–14) (Mondal et al., 2007). Therefore, electrostatic attraction might play a dominant role in adsorbing As(V) anions in the solution when NLTT has net positive surface charge (pH below the pH_{PZC} of 7.1), and other contributors (i.e., pore filling and complexation) may dominate when pH solution >7.1.

In contrast, arsenous acid (H₃AsO₃) is a weak acid, and the pK_a values of As(III) are approximately 9.2 (pK_{a1}), 12.1 (pK_{a2}), and 12.7 (pK_{a3}) (Kartinen and Martin, 1995; Lenoble et al., 2002; Sharma and Sohn, 2009; Smedley and Kinniburgh, 2002). Because of a high value pK_{a1} , trivalent arsenic exists mainly in the form of no charge (H₃AsO₃⁰) within the solution's pH which ranges from 1.0 to 9.0 (Mondal et al., 2007; Partey et al., 2008). Thus, the adsorption of uncharged H₃AsO₃⁰ through electrostatic attraction was not favorable. In this case, NLTT can remove As(III) from the solution through other potential mechanisms, such as pore filling (Mondal et al., 2007), oxidation-coupled adsorption (Muthu Prabhu et al., 2019), and surface complexation (Siddiqui and Chaudhry, 2017).

3.4. Effect of coexisting single and mixed anions on As(III)/As(V) adsorption

The effect of coexisting anions (denoted as guest anions) on the arsenic adsorption capacity of NLTT is illustrated in **Figure 4b**. Results indicated that the presence of other ions in solution caused a significant reduction in the removal efficiency of arsenic, with the increasing order being: anion absence < chloride < sulphate < bicarbonate < silicate< phosphate < mixed anions (Cl⁻, SO₄²⁻, $CO_3^{2^-}$, SiO₃²⁻, and HPO₄²⁻). An identical order of adsorption has been reported in the literature (Maiti et al., 2010b; Maji et al., 2007; Sun et al., 2017; Wen et al., 2018). The decline in adsorption capacity might result from the competition between the guest anions (acting as competitors) and As(V) anions for the adsorption sites on the surface of NLTT. Notably, although As(III) exists as the uncharged H₃AsO₃⁰ form (**Figure S5**), the adsorption capacity of NLTT was still affected by the guest anions' presence. This outcome suggests the existence of competition. In fact, As(III) was possibly partly oxidized into As(V) ions in solution through particular oxidants, i.e., FeOOH, Fe₂O₃, MnO₂, and TiO₂ (Cheng et al., 2019; Guan et al., 2018) that are available in the structure of the NLTT (see Section 3.2).

3.5. Adsorption kinetics

Figure 5a–b depicts the influence of contact time on removing arsenic with NLTT. The rate of As(V) and As(III) adsorption by NLTT increased quickly during the first 1 h of contact. Subsequently, the adsorption rate gradually decreased until the plateau was reached at around 120–360 min. In this study, three adsorption kinetic models—pseudo-first-order (PFO), pseudo-second-order (PSO), and Elovich models—were used to model the experimental data. The non-linearized form and detail information of such models were provided in **Section S1**.

Figure 5. (a)–(b) Effect of contact time on the arsenic adsorption process onto the NLTT at different initial arsenic concentrations; and (c)–(d) isotherm of arsenic adsorption onto the NLTT at different temperatures

To minimize the error functions, the parameters of such models were calculated from the non-line technique. The best fitting model was obtained with high R^2 and low χ^2 values. **Table 1** lists the relevant kinetic parameters for the arsenic adsorption onto the NLTT. In general, the adsorption process was better described by the PSO ($R^2 = 0.934-0.993$ and $\chi^2 < 18.4$) and Elovich (0.951–0.991 and $\chi^2 < 22.5$) models than the PFO model (0.829–0.988 and $\chi^2 58.5-82.1$). According to the PSO adsorption rate constant k_2 , it can be concluded that the adsorption process of As(V) onto the NLTT reached a faster equilibrium than that of As(III). Similarly, a higher value of the initial rate constant α for the As(V) adsorption suggested the adsorption process of As(V) onto the NLTT occurred much more quickly than that of As(III). These results suggested that As(V) had a higher affinity to the NLTT than As(III) in solution. Notably, the k_2 value decreased remarkably when the initial concentrations of As(III) and As(V) increased, thus confirming the negligible contribution of the driving force during the arsenic adsorption process.

Table 1. Relative adsorption kinetic parameters for the As(III) and As(V) adsorption by NLTT at different initial arsenic concentrations (250 and 500 μ g/L)

3.6. Equilibrium adsorption isotherm

In essence, adsorption isotherm plays an important role in identify the region of arsenic adsorption (i.e., Henry, Langmuir, or Freundlich) and maximum contaminant limit (MCL) of arsenic for drinking water (Simeonidis et al., 2016). Additionally, three common adsorption isotherm models (i.e., Langmuir, Freundlich, and Redlich-Peterson) were applied to model the

experimental data of the adsorption equilibrium study. They also helped to describe the adsorption behaviour of arsenic ions onto the NLTT. Detailed information was provided in **Section S2**.

Figure 5c–d and **Table 2** present the adsorption isotherms and isotherm parameters for the adsorption of arsenic by NLTT at three temperatures, respectively. The isotherm shapes of As(III) and As(V) can be classified into a L-type, suggesting that the NLTT has a strong affinity to As(III) and As(V) ions. The high R^2 indicates that the adsorption equilibrium data is adequately described by all three models (**Table 2**). Furthermore, the experimental data reveal that the adsorption capacity of NLTT, in general, increased with temperature for both As(III) and As(V).

Table 2. Relative isotherm parameters for the As(III) and As(V) adsorption by NLTT

As shown in **Table 2**, the Langmuir maximum adsorption capacity (Q°_{max}) of NLTT towards arsenic ions significantly increased from 409 to 602 µg/g for As(III) and from 514 to 638 µg/g for As(V) when the temperature rose from 10 °C to 50 °C. An identical adsorption tendency was reported by Maiti et al. (2007) for the As(III) adsorption onto nature laterite at the following temperatures: $Q^{\circ}_{max} = 150 \ \mu g/g$ at 15 °C < 170 µg/g at 30 °C < 210 µg/g at 45 °C. These results suggested that the adsorption process might be endothermic in nature and weak electrostatic attraction (also known as out-sphere complexation) might play a less important role than the others (inner-sphere complexation, i.e., complexation) in the adsorption of As(III) and As(V) are generally similar to or higher than those reported in the literature for many other iron-containing low-cost adsorbents where adsorption experiments were conducted at the realistic As(III) or As(V) concentration (**Table S2**).

Notably, because the residual concentration of arsenic ions plays an important role in designing and applying the adsorbent material for real water treatment, it may be necessary to

estimate the index of regulation limit (Q_{RL}) of arsenic pollutant as suggested in one study (Simeonidis et al., 2016). This index was obtained based on the maximum contaminant limit (MCL) of arsenic for drinking water (10 µg/L WHO) and the equilibrium arsenic concentration (C_e ; µg/L). According to the experimental data of adsorption equilibrium and adsorption isotherm (**Figure 5c– d**), the Q_{RL} value was estimated to be approximately 33 µg/g for As(III) and 39 µg/g for As(V) at the operation conditions (i.e., 30 °C, pH = 7.0, and solid/liquid ratio of 7.5 g/L). The value for As(V) adsorption in our study is similar to the Q_{RL} values of 20-50 µg/g for As(V) adsorption on iron hydroxide modified activated carbon (Vitela-Rodriguez and Rangel-Mendez, 2013), 25 µg/g for As(V) adsorption on iron oxide coated sand (Thirunavukkarasu et al., 2003), and 5-20 µg/g for As(V) adsorption on red mud (Genç et al., 2003).

3.7. Adsorption thermodynamics

In this study, the thermodynamic parameters—the standard Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°)—were calculated from the van't Hoff equation (**Equations 5-7**). The thermodynamic equilibrium constant ($K_{\rm C}$; dimensionless) was calculated based on the Langmuir constant ($K_{\rm L}$). To tackle the unit problem, we changed all concentrations to molar form and took into account the standard state $C^{\circ} = 1$ mol/L as suggested by many scholars (Mouni et al., 2018; Salvestrini et al., 2014; Tran et al., 2017c; Zhou and Zhou, 2014). As a result, the $K_{\rm C}$ value (unit-less) was obtained from **Equation 8**.

$$\Delta G^o = -RT \ln K_C \tag{5}$$

$$\Delta G^{o} = \Delta H^{0} - T \Delta S^{0} \tag{6}$$

$$\ln K_c = \frac{-\Delta H^o}{R} x \frac{1}{T} + \frac{\Delta S^o}{R}$$
(7)

$$K_C \approx K_L \times M_{As} \times C^o \times (10^6)$$

where K_L (L/µg) is the Langmuir constant provided in **Table 2**; M_{As} (g/mol) is the arsenic molar mass; and C° is the standard state ($C^\circ = 1 \text{ mol/L}$); the factor 10^6 makes it possible to convert the unit from gram to microgram; R is the universal gas constant (0.00831 kJ/mol×K); and T is the absolute temperature in degrees Kelvin (K).

The results showed that the ΔG° values for both arsenic species at three studied temperatures are negative, implying that the adsorption process occurred spontaneously. In addition, the positive ΔH° values indicate that the adsorption process of As(III) and As(V) are endothermic in nature. According to magnitude of ΔH° , it might be concluded that the NLTT has a higher affinity to As(V) adsorption than As(III) in solution because its higher ΔH° magnitude. Moreover, the positive ΔS° values demonstrate an increase in randomness at the solid/solution interface during the adsorption process of As(III) and As(V). A similar conclusion was reported by Maiti et al. (2007) for As(III) adsorption by natural laterite (ΔG° = from -5.22 to -6.65 kJ/mol, ΔH° = 35.6 kJ/mol, and ΔS° = 0.142 kJ/mol×K).

Table 3. Thermodynamic parameters for the adsorption of As on NLTT

3.8. Desorption study

To explore the desorption efficiency of arsenic from the laden NLTT samples, different solvents—deionized water (pH = 12), HCl, NaOH, NaCl, and EDTA—served as target desorbing agents. The experiment results demonstrated the desorption efficiency of As(III) was considerably higher than that of As(V) for all desorbing agents used (**Table S3**). This was presumably because As(III) was weakly adsorbed by NLTT when compared to As(V). Of the agents, the desorption

(8)

efficiency of both As(III) and As(V) was highest for 0.5M NaOH (approximately 48% and 29%, respectively). This is probably due to the electrostatic repulsion of the negatively charged arsenic anions and increased surface negative charges on the adsorbent at high pHs caused by NaOH. It could also be due to the increased competition of arsenic adsorption with the greater number of OH⁻ ions produced at high pHs. Arsenic adsorption is expected to be irreversible in salt solution (0.5M of NaCl) because Cl⁻ is a weakly adsorbing anion and cannot compete with the strongly adsorbing arsenic (as reported in **Section 3.4**). This explained the inability of 0.5M NaCl to desorb arsenic.

3.9. Results of removing arsenic in the field trial

Based on the batch adsorption experiments, a field trial was conducted to remove groundwater arsenic contamination at Hoang Tay Childcare Centre for a period of 6 months. **Figure 1b** shows how well the water filtration system performed. In general, the arsenic concentration in groundwater strongly depends on the groundwater levels (or water aquifer) that often vary greatly between the dry and rainy seasons (Berg et al., 2007). In this study, total arsenic concentration in the feedwater (the **C1** position in **Figure 1**) ranged from 122 μ g/L to 237 μ g/L (average 165±38.9 μ g/L). In addition, the groundwater contained a high concentration of total iron (3.78–7.24 mg/L). In essence, a Fe/As atomic ratio (ranging from 40.4 to 41.1) higher than 40 is expected to efficiently remove arsenic from groundwater through a common co-precipitation mechanism.

The above assumption was very consistent with the total arsenic concentration in the C2 position. As previously mentioned, after the groundwater had been extracted from the well, it was oxygenated through the aeration tank. The essential role of this tank (used as a typical pre-treatment process) in a groundwater treatment system has been discussed in other studies (Farrell and Chaudhary, 2013; Luong et al., 2018; Rott et al., 2002). This tank is mainly responsible for successfully removing some pollutants (i.e., arsenic, iron, manganese, etc.) and enhances the effectiveness of the whole system (especially, the adsorption column). In essence, when the iron-

groundwater was exposed to natural air through the aeration tank, the oxidation process of Fe²⁺ into Fe³⁺ can spontaneously occur (**Equation 9**). As well, As(III) was oxidized to As(V) in this scenario (Berg et al., 2007; Luong et al., 2018) (**Equation 10**). The co-precipitation process neither between Fe³⁺ (oxidized) and As(V) nor Fe²⁺ (un-oxidized) and As(V) was primarily regarded as the mechanism for removing arsenic from water in the **C2** position. This mean that the aeration tank can effectively simulate the co-precipitation process between arsenic and iron to form the precipitates of FeAsO₄•2H₂O and Fe₃(AsO₄)₂•8H₂O through **Equations 11–12** (Lenoble et al., 2005). However, such a co-precipitation process is strongly dependent on the Fe/As ratio and oxidation conditions (i.e., contact time and oxygen concentration). For example, the Fe/As atomic ratio in water fell dramatically from 40 in the **C1** position to 2,4 (a Fe/As range from 2.3 to 2.5) in the **C2** one. Although the total arsenic concentration passing through the aeration tank significantly decreased by approximately 70%±13%, its concentration (23.2–89.2 µg/L; average 53.7±22.9 µg/L) still exceeded the Vietnamese drinking water standard and WHO guideline (10 µg/L). Therefore, it is necessary to apply the adsorption column with certain appropriate adsorbents to remove arsenic from water.

$$\operatorname{Fe}^{2+} \rightleftharpoons \operatorname{Fe}^{3+} + 1e^{-}$$
 (9)

$$H_3AsO_3^{\circ} + H_2O \rightleftharpoons HAsO_4^{2^-} + 4H^+ + 2e^-$$
(10)

$$\operatorname{Fe}^{3+} + \operatorname{HAsO}_{4}^{2-} \rightleftharpoons \operatorname{FeAsO}_{4} + \operatorname{H}^{+}$$
 (11)

$$3Fe^{2+}$$
 (un-oxidized) + $2HAsO_4^{2-} \rightleftharpoons Fe_3(AsO_4)_2 + 2H^+$ (12)

After the aeration and clarifier tank, the supplied water was passed through the adsorption filter containing three material layers (i.e., sand, NLTT, and activated carbon). Firstly, the total arsenic concentration after passing the sand layer (the **C3** position) varied from 8.05 to 84.9 μ g/L (average 32.5±19.4 μ g/L), which was lower than the arsenic concentration in **C2** position (23.2–89.2 μ g/L). In addition, the data collected at different operation times indicated the total arsenic

concentration decreased gradually (data not shown). Such a reduction might result from a common reaction between incomplete reaction between iron and arsenic in the **C2** position. Another reason might be that the iron (III) formed by the oxidation of dissolved iron (II) was slowly deposited on the sand layer, which might act as an arsenic adsorbent (Gibbons and Gagnon, 2010; Nur et al., 2019). Secondly, the total arsenic concentration in the **C4** position (0.97–9.87 μ g/L; average 4.86±3.38 μ g/L) was always lower than 10 μ g/L during the first 6 months operational period with a continuous input of water of more than 206 m³. This outcome suggested that the NLTT can efficiently remove the arsenic contaminant from real groundwater. Thirdly, the total arsenic concentration in the **C4** one, suggesting that the used GAC exhibited poor adsorption capacity to arsenic ions in solution. Similarly, the efficient removal of arsenic by the ultra-membrane was negligible, with the total arsenic concentration ranging from 1.69 to 9.50 μ g/L (average 4.44±3.49 μ g/L).

The NLTT in the filter was replaced after 7 months' operation due to receiving the new batch of NLTT and availability of technical staff. At the time of replacement, the filtration system continued to function and provided a total of 240 m³ of water with less than 10 μ g/L of arsenic. The cost of locally available NLTT adsorbent for providing water for 7 months with this low arsenic concentration is US\$ 0.09/m³ (220 kg x 0.10 US\$/kg/240 m³). This cost is less than that of commercial 'imported' adsorbents such as Bayoxide. For example, <u>Katsoyiannis et al. (2015</u>) reported that the cost of Bayoxide in treating water containing 41 μ g/L to the permissible level of 10 μ g/L was 0.09 Euro/m³ (0.10 US\$/m³). The exhausted spent adsorbent is carefully stored and can be recycled to produce concrete for road construction.

To sum up, the experimental results after approximately 6 months demonstrated that the total arsenic (1.69–9.50 μ g/L) and Fe (0.02–0.13 mg/L) concentrations remained below the upper permitted limits (10 μ g/L and 0.3 mg/L, respectively). In addition, the concentrations of other cations (total Fe, Mn, Cu, total Cr, Pb, Hg, Ni, Se and Cd) in the treated water were below the

Vietnamese drinking water quality standard (**Table S4**). It is important to note here that Coliform and E. Coli were not found in the treated water after the ultrafilter unit had done its job.

3.10. Possible mechanism of arsenic adsorption onto NLTT

In this study, a possible adsorption mechanism of arsenic ions onto the collected NLTT was conducted with a pH level of 7.0. As discussed in **Section 3.2**, the NLTT exhibited a smaller specific surface area (155 m²/g) than activated carbon (566–1302 m²/g) (Tran et al., 2017b) and biochar (188–543 m²/g) (Boakye et al., 2019); therefore, although the pore-filling mechanism might play an important role in the adsorption process, it is not significant. In this case, the surface interactions played a vital role rather than pore filling. The existence of arsenic element on the surface of NLTT (**Figure S6**) after adsorption confirmed that the adsorption of As(III) and As(V) onto NLTT was successful and occurred mainly on the surface of NLTT. Notably, referring to the adsorption of As(V), the surface interaction possibly involved weak electrostatic attraction (outer-sphere complexation) and surface complexation (inner-sphere complexation) (Kalaruban et al. 2019). Meanwhile, the oxidation of arsenite As(III) to arsenate As(V) and the complexation between arsenic ions in solution and the –OH groups on the surface of NLTT might be dominant reactions for the adsorption of As(III) (Cheng et al., 2019; Partey et al., 2009; Pozdnyakov et al., 2016; Zhao et al., 2018).

4. Conclusions

Among seven locally available low-cost materials in Vietnam, a natural laterite from Thach That district, Hanoi (NLTT) is found to be the most promising material for removing arsenic from groundwater. The NLTT with PZC of pH 7.1 and composed of high weight percentages of iron and aluminium contained mainly goethite and hematite, and some minor minerals (titanium dioxide, manganese oxide), all of which play an important role in adsorbing As(V) and As(III). Adsorption

of As(V) was higher than As(III). Adsorption equilibrium was achieved within 120-360 min and the Langmuir adsorption capacities of NLTT at pH 7 for As(III) and As(V) were 512 and 580 μ g/g, respectively, which are mostly higher than the values reported for many other low-cost adsorbents at realistic total arsenic concentrations in water. A new filtration system packed with low cost NLTT was designed and successfully implemented in a childcare centre in Hanam province, Vietnam to remove groundwater arsenic. The system consists of a combined aeration and clarifier tank, adsorption column, an ultrafilter and a storage tank. The adsorption column had a sand layer at the bottom followed by NLTT and GAC layers. Monitoring results from different sampling points in the filtration system during the first 6 months of operation confirmed this system produced safe drinking water with arsenic levels below the WHO and Vietnam drinking water limits. The filtration system successfully removed many other contaminants from the water.

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Table 1. Relative adsorption kinetic parameters for the As(III) and As(V) adsorption by NLTT at different initial arsenic concentrations (250 and 500 μ g/L)

			As(III)			As(V)			
		Unit	250	500	250	500			
			μg/L	μg/L	μg/L	μg/L			
	1. Pse	udo- first- order							
model									
	q _e	µg/g	19.9	37.6	21.1	56.9			
	1	1/	0.02	0.01	0.16	0.06			
	К ₁	1/min	1	3	89	36			
	R		0.94	0.98	0.82	0.97			
2			4	8	9	6			
	2		2.71	2.46	82.1				
	χ^2		1	1		58.5			
	2. Pseud	o- second- order							
model									
			22.1	43 5	25.3	61.5			
	q _e	µg/g	3	6	23.3	01.5			
			0.00	0.00	0.00	0.00			
	k_2	$g/\mu g \times min$	0.00	0.00	0.00	0.00			
			128	035	125	120			
	R	_	0.97	0.99	0.93	0.99			
2			8	2	4	3			
	χ^2	_	1.03	1.79	10.2	18.4			
	λ		4	8					
	3. Elovich	model							
		, ·	1.59	1.15	18.5	10.0			
	α $\mu g/g \times \min$		2	1					

		Journal	Pre-proof		
0	ug/g	0.24	0.10	0.25	0.09
ρ	μg/g	9	5	1	1
R		0.97	0.96	0.95	0.99
2	—	6	2	1	1
χ^2		1.13	8.24	22.5	22.2
	—	9	7		

Some

		As(III)					As(V) adsorption			
	Uni		adsorpti	ion						•
	t		1	•		4		-	3	5
		0 °C	0 °C		0 °C		0 °C	0 °C		0 °C
1. Langmuir 1	nodel									
08	µg/		2	1		(5	6
Q ⁺ max	g	09	12		02		14	80		38
$V_{(10^{-3})}$	L/µ		((((0	1
$\mathbf{K}_{\mathrm{L}}(\times 10^{\circ})$	g	.227	.670		.867		.193	.604		.170
\mathbf{P}^2			((((0	0
K	_	.997	.990		.993		.984	.967		.930
v^2	_		<u>,</u>	<		4		2	2	1
X		5.2	1.0		6.2		7.5	6.9		30
2. Freundlich	model									
Κ_	(µg/		2			4		2	2	4
ιτ _F	$g)(L/\mu g)^n$.76	6.00		8.67		.33	3.32		3.48
n	2		((((0	0
11		.43	.35		.31		.46	.33		.28
\mathbf{R}^2	_		((((0	0
K	_	.980	.951		.942		.970	.984		.989
\sim^2	_			ļ		1			5	2
χ		3.9	9.1		61		35	0.1		76

Table 2. Relative isotherm parameters for the As(III) and As(V) adsorption by NLTT

3. Redlich–Peterson model

Journal Pre-proof								
K _{RP}	L/g	.1035	(.3809	.5218	((2 3.5403	1 3.1488
а	(µg/ L) ^{-g}	.0005	.0012	(.0009	(()007	0 .4051	0 .4770
g		.94	(.96	(.00	1	(.90	0 .75	0 .69
R^2	_	.996	(.988	.992	((982	0 .983	0 .993
χ^2	_	0.2	² 7.5	: 06		² 2.5	4 3.6	1 82

Sontal

		K)	(Van't Hoff equation	∆G° (kJ/mol)	∆H° (kJ/mol)	∆S° (kJ/mol)
)	As(III	83	<u>,</u>	y = -3096x + 20.8	-22.9	25.7	0.173
		03	-	$R^2 = 0.911$	-27.3		
		23			-29.8		
)	As(V	83		y = -4142x + 24.3	-22.5	34.4	0.202
		03	•	R ² = 0.987	-27.0		
		23	-	<u>S</u>	-30.6		

Table 3. Thermodynamic parameters for the adsorption of As on NLTT

Research highlights

A natural laterite from Vietnam effectively removed arsenic from groundwater.

Thermodynamic constant ΔG° negative but ΔH° and ΔS° positive for As(III) and As(V).

A community water filter system was successfully designed using the laterite.

The filter reduced high arsenic levels in groundwater to below WHO drinking water level.







Figure 2





