VNU Journal of Science: Earth and Environmental Sciences, Vol. 33, No. 1S (2017) 149-156

# Study on Removal of Arsenic (V) from Groundwater By iron-Rich Adsorbent

Pham Hoang Giang[1,*], Nguyen Quoc Hung[1], Le Danh Quan[1],
Nguyen Manh Khai[1], Pham Thi Thuy[1], Dang Thi Thanh Huyen[2]

[1]*Faculty of Environmental Sciences, VNU University of Science,*
*334 Nguyen Trai, Hanoi, Vietnam*
[2]*National University of Civil Engineering, 55 Giai Phong, Hai Ba Trung, Hanoi, Vietnam*

Received 30 September 2017
Revised 04 November 2017; Accepted 20 November 2017

**Abstract:** Arsenic poisoning has emerged as an environmental problem for the human health in many countries, including Vietnam. This study aims to create the adsorbent from ion-rich materials and evaluate its adsorption capacity to remove arsenic in groundwater by column study. The maximum adsorption capacities of the adsorbents in column study, calculated by Thomas model, were in the range 20.763 – 129.105 mg/g. And the adsorbate breakthrough time of iron-rich adsorbents calculated by Yoon-Nelson model, were in range 312.4 – 2857.4 minutes. Besides, the pilot scale with capacity 5 $m^3$/day was installed at Cu Da Nursery School, Cu Khe commune, Thanh Oai district, Hanoi city where has high arsenic pollution in groundwater (250-400ppb). The pilot system showed a removals of 76 % of arsenic and 85 ÷ 90 % of iron, meeting the QCVN 02: 2009/BYT (National technical regulation on drinking water quality).

*Keywords:* Arsenic, groundwater, adsorbent, column study.

## 1. Introduction

In nature, arsenic exists in hundreds of ores including element type, arsenide, sunfide, oxide, arsenate and arsenite. Arsenic is released into the environment by natural weathering process, geological activity, volcanoes, or by operation of organism. The transformation of arsenic from the solid phase to the liquid phase is determined by pH, redox potential (Eh), DO and ambient temperature [1-4].

Humans may cause major impacts on arsenic contamination in groundwater through mining activities, construction of geothermal power plants, fossil fuel combustion and other industrial activities, especially, bleached wood industry. In agriculture, arsenic might occur in the composition of herbicides, pesticides, additives in livestock feed… [1, 2]. The arsenic-contaminated wastewater discharged directly into the environment without treatment can finally infiltrate groundwater. Therefore, treatment of As in water is an important subject and is of the great interest.

Currently, the common methods of arsenic treatment in the world are: oxidation,

---

[*] Corresponding author. Tel.: 84-904707447.
Email: phamhoanggiang@hus.edu.vn

https://doi.org/10.25073/2588-1094/vnuees.4168

deposition; adsorption on adsorbents, co-precipitation [5-7], sand filtration [6, 8], membrane filtration [9]. Adsorption is by far the most versatile and effective method for removing contaminations of heavy metals like arsenic. Nowaday, the low-cost adsorbents that have been developed from waste products and natural substances for removing heavy metals in water is one of the most considerable research due to the economic efficiency and the advantage in saving energy.

In Vietnam, many studies on the absorption of arsenic in water by natural rich-iron or rich-manganese materials such as red mud [10], laterite [10, 11], combination of zeolite and $MnO_2$ [12]... have shown good results at the laboratory scale. The results showed the highly-efficient adsorbents were modified from iron-rich materials. Therefore, in this study, iron-rich materials were also used as raw materials to produce iron-rich adsorbent for arsenic adsorption. The aim of the study is the adsorbents from iron-rich materials and evaluated its arsenic adsorption capacity by column study. The study carried out in the laboratory for creating adsorbents and testing some kinetic parameters by using column system; after that installing the adsorption column with capacity 5 $m^3$/day at Cu Da Nursery School, Cu Khe commune, Thanh Oai district, Hanoi city where has high arsenic pollution in groundwater (250-400ppb) for validating the kinetic parameters found in the laboratory study.

## 2. Materials and methods

### 2.1. Preparation of iron-rich adsorbents

*Materials

Iron–rich materials are iron oxide ore collected from Mirec Factory at Cao Bang and iron (III) hydroxide, which was prepared to mimic the iron content of red hydroxide, prepared in the laboratory based on the reaction of $FeCl_3$ with NaOH. Iron ore and hydroxide iron were prepared to a grain size less than 0.074mm. The above materials were weighed and mixed following two different mixing ratios, in table 2.1. The mixed materials were shaping as a cylinder. After that, materials were dried to 50 °C for 24 hours, then calcined at 500°C for 10h.

Finally, the two adsorbents obtained three different sizes: L size (8,0-9,5mm), M size (3,75-4,75mm) and S size (1,0-2,0mm).

Table 2.1. Mixing ratio (%) by weight

| Material | Iron ore | Ferric Hydroxide | Aluminum hydroxide | Additive 1 | Additive 2 | Kaolin |
|---|---|---|---|---|---|---|
| H1 | N/A | 40 | 10 | 7,5 | 18,5 | 24 |
| O1 | 40 | N/A | 10 | 7,5 | 18,5 | 24 |

### 2.2. Experiments

In this study, microstructure and surface morphology of the adsorbent samples were characterized by a 10 kV HITACHI S-4800 NIHE scanning electron microscope (SEM). Arsenic and iron concentrations were determined by AAS (AAnalyst 400, Perkin Elmer Inc).

*Column study at lab-scale

Fixed bed column experiment was conducted using a glass column with an internal diameter of 20 mm with height 300 mm, 150mm of fixed bed height and flow rate 2ml/min. A layer of glass wool was placed at the bottom of the column to avoid adsorbent loss. The bottle containing As (V) solution with concentration 1000ppb was set at higher elevation so that the solution can be transferred at a constant flow rate to the column by gravitational force. Effluent samples were collected in other bottles, and the concentrations then were analyzed using AAS. Ct/Co was calculated with respect to time for a fixed bed height, initial concentration and flow.

The arsenic adsorption capacity of adsorbents was investigated in three different sizes of adsorbents: size L from 8 ÷ 9.5 mm, size M and S from 3.75 ÷ 4.75mm and 1.0 ÷ 2.0 mmrespectively. The adsorption capacity of adsorbents was calculated by Thomas and Yoone – Nelson kinetic model.

The Thomas model is widely used in column performance modeling. Its derivation assumes Langmuir kinetics of adsorption-desorption and no axial dispersion [8].

The linear form of Thomas model is expressed as follow:

$$\ln\left[\frac{C_o}{C_t} - 1\right] = \frac{k_{Th}\, q_o\, m}{Q} - k_{Th}\, C_o\, t \qquad (15)$$

Where $C_o$ is the effluent concentration (mg/l), $C_t$ (mg/L) are the input concentrations at time t (minutes), $q_o$ is the maximum adsorption capacity (mg/g), m is the total mass of the adsorbent (g), Q is volumetric flow rate (ml/min) and $K_{Th}$ is the Thomas rate constant (ml/min/mg). The value of $k_{Th}$ and $q_o$ can be obtained from the plot of $\ln(C_o/C_t - 1)$versus t (min).

The linear form of Yoon-Nelson model was expressed as following:

$$\ln\left[\frac{C_t}{C_o - C_t}\right] = K_{YN}t - \tau K_{YN}$$

where $K_{YN}$ is the rate constant (l/min), τ is the time required for 50% adsorbate breakthrough (min) and t is the breakthrough time (minutes).

*Column study at pilot scale

The adsorbent columns with capacity 5 $m^3$/day were set up with 760 x 1.500 mm (diameter x height), fixed bed with 300 mm height of sand and 120 mm height of ion-rich adsorbent.

Water samples were taken at V0 – groundwater, V1 –after aeration, V2 –after sedimentation; V3 –after sand filtration; V4 –after iron-rich adsorbents; V5 – treated water pH was measured at the sampling site. Analysis of the iron and arsenic concentrations in water were performed in the laboratory by AAS (AAnalyst 400, Perkin Elmer Inc).

## 3. Result and discussion

### 3.1. Morphology

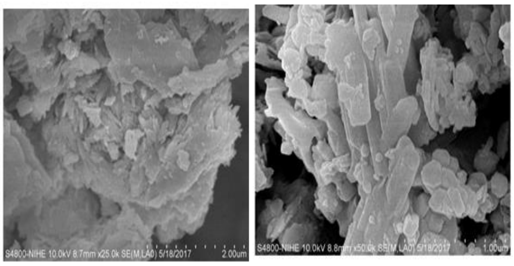
The microstructure and morphology of both the adsorbents from ferric hydroxide (H) and ferric oxide (O) were characterized by SEM and shown in Figure 1.

The morphology of the H adsorbent had a crystalline form, large cavities, plates, high porosity, and large surface area. The morphology of O adsorbent had fissures folded, crystals in stacked plates and pores. H adsorbent showed larger multiple cavities and higher porosity than O adsorbent. Base on the highly indicated intricacy surface structure from those SEM images, it is clearly predicted that iron-rich adsorbent might express the best ability of arsenic removal.

*The X-ray diffraction pattern of adsorbent materials*

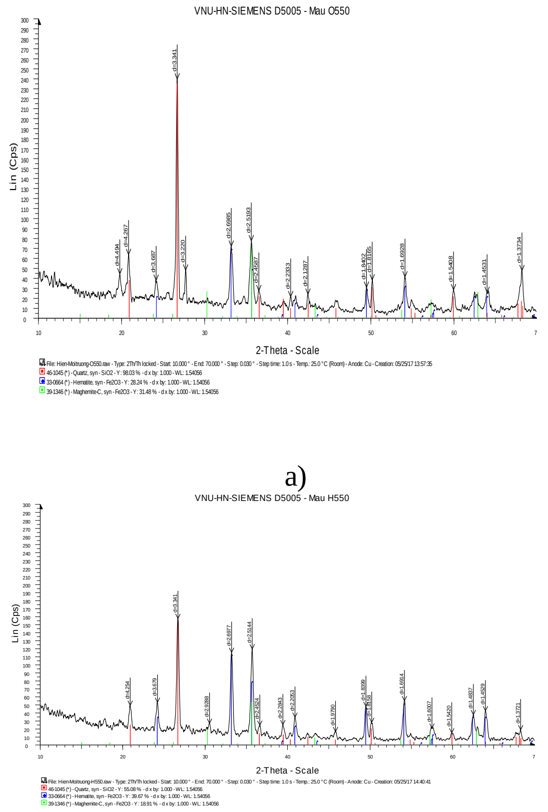
The results of the X-ray diffraction of two adsorbents showed that the peaks of the Quartz ($SiO_2$), Hematite ($Fe_2O_3$), Maghemite (γ - $Fe_2O_3$) here is obvious, but remains impure.

Hence, two adsorbents had the conversion from iron oxide to Maghemite, and Hematite.



a) b)

Fig. 3.1. SEM micrograph of two iron-rich adsorbents.
(a) H- adsorbent from ferric hydroxide.
b)O- adsorbent from ferric oxide



a)

b)

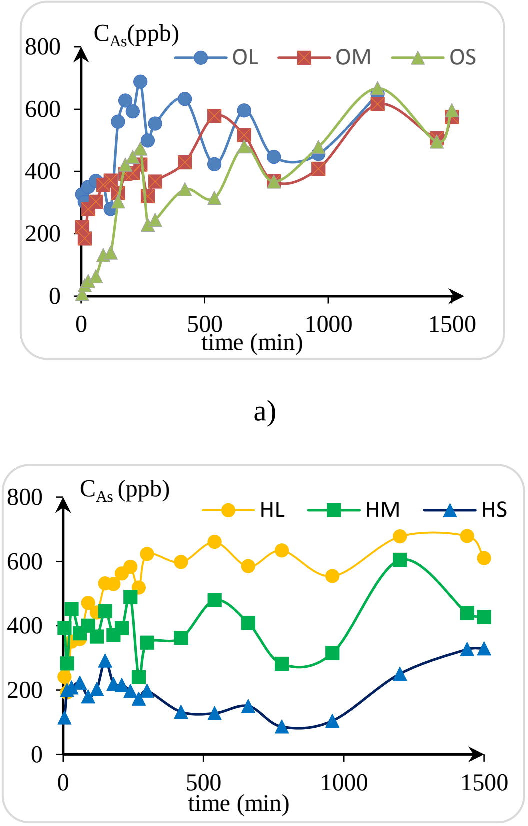
Fig. 3.2. XRD patterns of two iron-rich adsorbents. O – adsorbent from ferric oxide, H – adsorbent from ferric hydroxide.

### *3.2. Effect of particle size on the removal of arsenic in column study at lab-scale*

The effect of particle size on the adsorption of As (V) onto two iron-rich adsorbents using fixed bed column, studied by varying the particle size of L size (8,0-9,5mm), M size (3,75-4,75mm) and S size (1,0-2,0mm) while keeping the inlet As (V) concentration of 1000ppb and fixed bed height of 150mm, was given in Figure 3.3.

The optimal particle size of both O and H adsorbents for removing As (V) was 1 ÷ 2 mm. The results in Figure 3.3 showed that the smaller adsorbent particle size got, the greater the adsorption capacity was.

After 5 minutes running the continuous flow through column analysis, the concentration of As (V) in the treated water of O adsorbent column with three particle sizes OL, OM, OS columns was 326, 222 and 8 ppb, respectively. In the first 100 minutes of reaction time, the difference in concentration of As (V) was significantly removed. At the 800 minutes time of the experiment, the difference in concentration of As (V) was not clear with the As (V) concentration of treated water in three particle sizes: OL, OM, OS were 447, 367 and 367 ppb, respectively.



a)

b)

Fig. 3.3. Effect of the particle size of iron-rich adsorbents on removal As (V) capacity.

O – adsorbent from ferric oxide, H – adsorbent from ferric hydroxide, (HL & OL – (8,0-9,5 mm); HM & OM – (3,75-4,75 mm); HS & OS – (1,0-2,0 mm))

With the H adsorbents, at 90 minutes, the As (V) concentrations in treated water with three different sizes of HL, HM, HS were 470, 400 and 180 ppb, respectively. After 660 minutes of reaction time, the concentration of As (V) of treated water with three different sizes of HL, HM, HS were 584, 408 and 150 ppb. Hence, at the reaction time of 660 minutes, the As (V) removal efficiency of two adsorbents reached 50%.

### *3.4. The Thomas and Yoone – Nelson kinetic model in column study at lab-scale*

The Thomas and Yoone-Nelson model parameters in column study at lab-scale were given in Table 3.2. The Thomas model was fitted to investigate the breakthrough curve of As(V) adsorption onto O and H adsorbent. Application of the Thomas model in the concentration (Ct) ranged from 1 to 1,000 ppb with the fixed bed of 150mm in height, 2ml/min flow rate was calculated the Thomas' kinetic coefficients. These coefficients were determined from the slope and intercepts obtained from the linear regression. The regression coefficients ($R^2$) was from 0.706 - 0.76 with almost particle sizes. The maximum adsorption capacity $q_0$ was in the range 20.763 – 129.105 mg/g; and the highest maximum adsorption capacity of two adsorbents were in the small size.

The Yoon–Nelson model was applied to investigate the adsorbate breakthrough time of As(V) onto fixed bed layer. The experimental data exhibited good fits to the model with linear regression coefficients ranging from 0.7089 to 0.7453 (Table 3.2). The τ-values were from 312.417 – 2857.4 minutes.

The results also indicated that the decrease size of adsorbents would bring an increase in maximum adsorption capacity as well as a longer time to absorb 50% As (V). From the above results, it seemed that two adsorbents had the ability to adsorb arsenic, so it can be applied for larger scale.

Table 3.2. Thomas and Yoone - Nelson model parameters in column study at lab-scale

| | Thomas | | | Yoone - Nelson | | |
|---|---|---|---|---|---|---|
| | $R^2$ | $K_{Th}$ (ml/min/mg) | $q_o$ (mg/g) | $R^2$ | $K_{YN}$ (l/min) | τ (min) |
| OL | 0.718 | 0.000967 | 39.7183 | 0.718 | 0.0009 | 616.000 |
| OM | 0.742 | 0.001294 | 20.7630 | 0.742 | 0.0011 | 454.273 |
| OS | 0.760 | 0.001985 | 50.8752 | 0.760 | 0.0019 | 1056.316 |
| HL | 0.710 | 0.001315 | 21.9686 | 0.710 | 0.0012 | 312.417 |
| HM | 0.638 | 0.000353 | 73.2814 | | 0.0003 | 1344.000 |
| HS | 0.745 | 0.000573 | 129.105 | 0.527 | 0.0005 | 2857.400 |

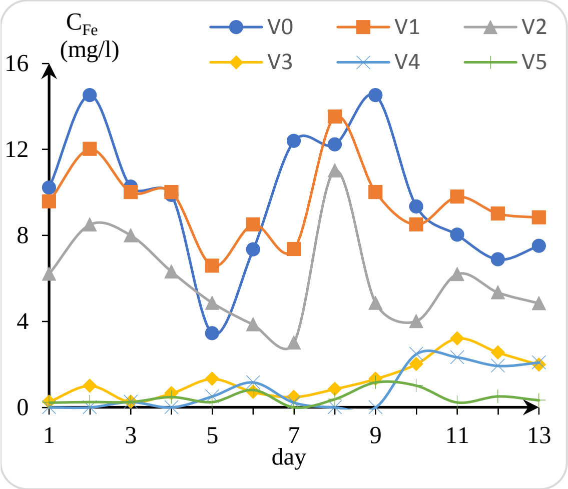
### *3.5. Evaluation of adsorption column in pilot-scale with capacity of 5m3/day*

The pilot scale was installed in Cu Da Nursery School, Cu Khe commune, Thanh Oai district, Hanoi city. The adsorption columns with capacity of 5 $m^3$/day were set up after pre-treatment stage such as: aeration, sedimentation and sand filtration. The groundwater had the iron concentration of 40 mg/L and As (V) concentration of 250 to 400 ppb. Water sample were taken in 5 points: V0 – groundwater, V1 – water after aeration, V2 – water after sedimentation; V3 – water after sand filtration; V4 – water after iron-rich adsorbent; V5 – treated water; to test the removal of As(V) and iron in each treatment stage.

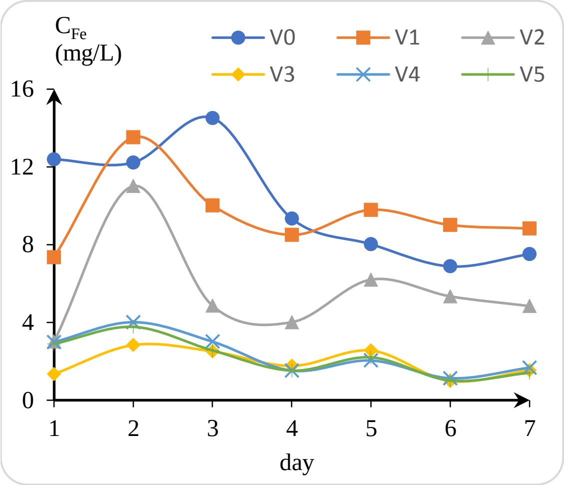
Iron removal during treatment stage using ion-rich adsorbents was given in Figure 3.4. The results from Figure 3.4 shows that after aeration and sedimentation, iron concentration reduced from 40 mg/L to 8 to 12 mg / L, and after sand filtration to 2 ÷ 3 mg / L; reached 85-90% iron treatment efficiency. After sand filtration (V3), the iron concentration was not changed much, hence, it indicated that adsorbents were no longer corroded.

After iron-rich adsorbents (V4), the iron concentration in O adsorbent column was almost unchanged in comparison with water sample in sand filtration (V3), indicating that the O adsorbent was persistent, non-corrosive and iron from iron-rich adsorbent was not to be released into water. Meanwhile, the iron concentration in H adsorbent column increased slightly, which may be explained by the corrosion of the H adsorbent's surface for a short initially operated. Therefore, The O adsorbent was more durable and wear – resistant in operation than H adsorbent.

Arsenic removal during treatment stage using ion-rich adsorbents was given in Figure 3.5. After sedimentation (V3), the concentration of As (V) decreased considerably to about 150 ppb, reached approximately 50% removal efficiency due to As (V) absorbed into $FeAsO_4$ surface in this layer. When flow went through the sand filtration layer, As (V) continued to be absorbed into $Fe(OH)_3$ precipitates in sand layer that reduced As (V) to 55 ppb. After this stage, the water was adjusted to flow into the main iron-rich adsorbent layer by up flow direction.



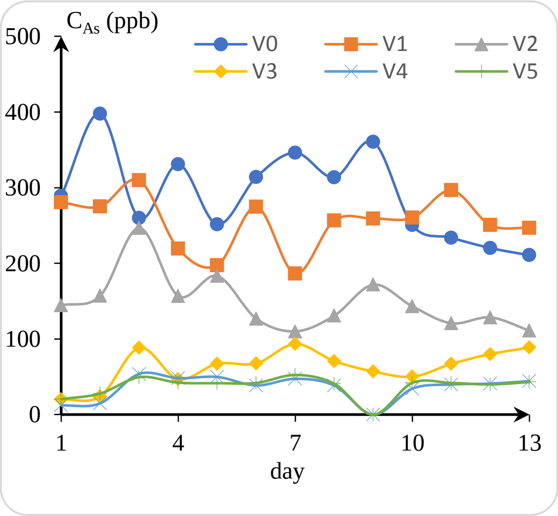
a)



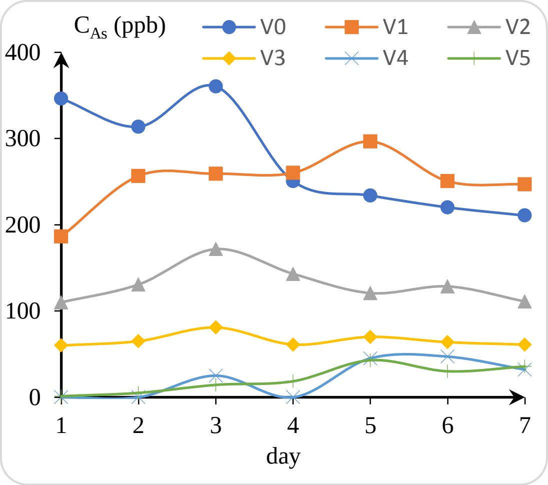
b)

Fig. 3.4. Iron removal during treatment stage:
a) O - adsorbent from ferric oxide
b) H - adsorbent from ferric hydroxide
V0 – groundwater, V1 –water after aeration, V2 – water after sedimentation; V3 – water after sand filtration; V4 – water after iron-rich adsorbent; V5 – treated water).

After iron-rich layer, the As (V) concentration in O and H adsorbent was ranged from 12 to 50 ppb, meeting the QCVN 02: 2009/BYT standards; so the O and H adsorbent showed the effectiveness of arsenic removal in groundwater.



a)



b)

Fig. 3.5. As (V) removal during treatment stage: a) O - adsorbent from ferric oxide b) H - adsorbent from ferric hydroxide.
V0 – groundwater, V1 –water after aeration, V2 – water after sedimentation; V3 – water after sand filtration; V4 – water after iron-rich adsorbent; V5 – treated water).

During the first two days operation, the As (V) concentration after H adsorbent layer was less than 10 ppb, meeting the QCVN 01: 2009 / BYT standards.

## 4. Conclusion

The As (V) adsorption capacity of iron–rich adsorbents show the great removal effiency in small particle size. Two adsorbents fitted with Thomas model and Yoon-Nelson kinetic model. The maximum adsorption capacity to remove As (V) using iron-rich adsorbents were in the range 20.763 – 129.105 mg/g. The adsorption column in pilot scale achieved 76 % of removal of arsenic and about 85 ÷ 90% removal of iron in groundwater, meeting the QCVN 02: 2009/BYT. These confirmed that using modified iron-rich adsorbent materials for removal of arsenic in groundwater is an effective method in terms of economic as well as amelioration of water quality.

## Acknowledgment

The authors send many thanks to Hanoi Department of Science and Technology for providing financial assistance, belong to the project 01C-09-TC/05-15-03. The authors also thank Laboratory of Environmental Analysis, Hanoi University of Science, Vietnam National University for the use of their facilities.

## References

[1] Hanoi University of Mining and Geology (2008), Final scientific and technological report in 2007-2008: Sources and distribution of ammonia and arsenic in Red River Delta aquifers, Hanoi

[2] Institute for Technology of Radioactive and Rare Elements (2008), Final report: Arsenic and Flo contamination’s treatment using rare soil material

[3] Smedley P.L., Kinniburgh D.G., (2002), A review of the source, behaviour and distribution of arsenic in natural waters, *Applied Geochemistry* 17, pp. 517–568.

[4] Tournassat. C and Charlet. L Appelo.C.A.J (2006), Surface complexation of ferrous ion and carbonate on ferrihydrite and the mobilization of arsenic, Environmental Science Technology, 36, tr. 3096-3103.

[5] Quy T.V., Huan N.X., Son TV (2012), “Study on the status and effectiveness of arsenic contamination’s treatment in groundwater using available natural materials in Hoai Duc district, Hanoi”. VNU Journal of Science, Natural Sciences and Technology. 28, p.174-180

[6] Emily R. (2006), Development of an iron-oxide coated ceramic filter for removal of As (III) and As (V) in developing nations, Master of Science in Environmental Engineering, Department of Civil, Environmental and Architectural Engineering, University of Kansas.

[7] Kiem B. Vu, Michael D. Kaminski & Luis N. (2003), Review Of Arsenic Removal Technologies For Contaminated Groundwaters, Argonne National Laboratory, Chemical Engineering Division.

[8] Ashraf Ali M., Badruzzaman A.B.M., Jalil M.A., Delwar Hossain M., Hussainuzzaman M. M., Badruzzaman M., Mohammad O.I., Akter N. (2001), "Development of Low-cost Technologies for Removal of Arsenic from Groundwater",

Technologies for Arsenic Removal from Drinking Water, tr. 99 - 119.

[9] Said B., Alessandra C., Alberto F., Agnieszka L., Silvia S., Mohammed B. & Enrico D. (2010), "Removal of As (V) by PVDF hollow fibers membrane contactors using Aliquat-336 as extractant", Desalination. 264(3), tr. 193-200.

[10] Minh N.T. (2016), "Material particles made from Red mud in Bao Loc Bauxite and oriented applications in the treatment of wastewater pollution", Earth Sciences, p. 231-237

[11] Nga N.T.H. (2014), "Study on the ability to treat arsenic in contaminated water by tropical weathering soil", Annual Scientific Conference, Faculty of Water Resources Engineering, Thuy Loi University.

[12] Thang V.M. (2012), "Study on Arsenic removal from groundwater by $MnO_2$-modiffed zeolite material", Master thesis in Environmental Science, Hanoi University of Science, VNU.

# Xử lý Asen (V) trong nước ngầm bằng vật liệu giàu sắt

Phạm Hoàng Giang[1], Nguyễn Quốc Hưng[1], Lê Danh Quân[1],
Nguyễn Mạnh Khải[1], Phạm Thị Thúy[1], Đặng Thị Thanh Huyền[2]

[1]*Đại học Khoa học Tự nhiên, ĐHQGHN, 334 Nguyễn Trãi, Hà Nội, Việt Nam*
[2]*Đại học Xây dựng, 55 Giải Phóng, Hai Bà Trưng, Hà Nội, Việt Nam*

**Tóm tắt:** Những năm gần đây, ảnh hưởng của asen đến sức khỏe con người đang được coi như là một vấn đề môi trường nóng và cấp bách ở rất nhiều nước trên thế giới, trong đó có Việt Nam. Nghiên cứu này hướng đến các quá trình hiệu quả để loại bỏ asen trong nước ngầm từ các vật liệu giàu sắt trong mô hình hấp phụ cột. Khả năng hấp thụ tối đa để loại bỏ thạch tín của chất hấp thụ trong nghiên cứu cột, được tính toán bởi mô hình Thomas, nằm trong khoảng 20.763 - 129.105 mg / g. Và thời gian bão hòa 50% vật liệu được tính toán theo mô hình Yoon-Nelson, nằm trong khoảng 312.417 - 2857.4 phút. Sử dụng các kết quả có được trong phòng thí nghiệm, nghiên cứu được áp dụng với quy mô pilot với công suất $5m^3$/ngày.đêm tại địa điểm thực tế là trường mầm non Cự Đà, xã Cự Khê, Thanh Oai, Hà Nội (nơi có nồng độ Asen trong nước ngầm dao động trong khoảng 250-400ppb). Nước sau xử lý đạt kết quả tốt khi loại bỏ được 76% asen, đồng thời loại bỏ được 85-90% sắt trong nước, các thông số như pH, As, Fe đều đảm bảo QCVN 02: 2009/BYT (Quy chuẩn kĩ thuật Quốc Gia về chất lượng nước sinh hoạt).

*Từ khóa: A*sen, nước ngầm, vật liệu hấp phụ, thí nghiệm cột.