# Study and Application of Arsenic Adsorptive Materials for Treating Arsenic Contaminated Water

# STUDY AND APPLICATION OF ARSENIC ADSORPTIVE MATERIALS FOR TREATING ARSENIC CONTAMINATED WATER

L. Q. TUAN, H. T. NHUT, N. T. SANG
Faculty of Environment and Natural Resources, Nong Lam University, Vietnam.
K. SHIOMORI
Dept. of Applied Chemistry, University of Miyazaki, Japan

Arsenic is one of the most important global environmental toxicants. Humans can be exposed to arsenic through the intake of air, food, and water. Most arsenic is seen after arsenic exposure from drinking water. Arsenic exposures from drinking water are to the more toxic inorganic forms and occur at relatively high doses (Winski, 1995). Mekong delta has been considered as one of the serious contaminated area in Vietnam. Some surveyed regions have arsenic concentration up to 300μg/L (WHO standard: 10μg/L). That affects to community health and next generation at Mekong delta. Therefore, study to find out suitable materials (cheap, available, and usable) is necessary for communities to treat their potable water. The research results showed that ferrous contaminated sand is the best material for filtering the arsenic in potable water with high efficiency. And X-ray analysis confirmed that arsenic significantly adsorbed on ferrous contaminated sand in filter process.

**Key words**: Arsenic, adsorption, removal, adsorptive materials, X-ray analysis

## INTRODUCTION

Nowadays, people in the world are living in environmental risk, face up with water lack and poor quality water source is a serious problem for countries. Arsenic contaminated water source is a typical example, a trouble for some nations, especially Bangladesh, India, and China...Bangladesh where people found out the arsenic contamination in ground water. 98 percent of ground well water in countryside has been used for drinking and daily life was contaminated. Concentration of arsenic is higher than 0.05 mg/L – a Bangladesh standard, was found in 61/64 districts, 25% samples over 0.05 mg/L and 42% samples over 0.01 mg/L – WHO standard (Rahman, 2004).

In Vietnam, arsenic contamination was found out in ground water in Red river and Mekong deltas. Data collected from a survey of 12,461 drilled wells in 12 provinces showed that wells in Northern were contaminated more than that in Southern. Survey was conducted by Biotechnology, Vietnam Academic of Science and Technology on Thai Nguyen, Quang Ninh, Ha Tay, Ha Noi, Hue, Ho Chi Minh, Long An, Dong Thap and An Giang provinces (Thao, 2005).

In Tien Giang Province, data from a survey show that 392/1132 of drilled wells in 2004, 2005, 2006 were contaminated by ferrous and arsenic (Center for Preventive Medicine). Arsenic concentration ranges from 0.025 – 0.15 mg/L in Chau Thanh Dist. (12 samples), Cho Gao Dist. (12 samples). Especially, a survey by Center for Dept. of Resources and Environment, An Giang province indicated that 12 water supply plants which have arsenic contaminated water with 0.05 – 0.34 mg/L which over than that of Vietnamese and WHO standards.

Obviously, Mekong and Red River deltas have been under risk from the arsenic contamination. The recent analyses indicated that high levels of arsenic contamination in Mekong delta. The groundwater used for drinking water supply in some place reaches to 321 μg/L (Shinkai et al., 2007). Our survey and investigation in 2009 also indicated that the arsenic contamination in not only in groundwater but also surface water. It is a severe risk for communities in Mekong delta. To help people in contaminated areas, we design the simple and cheap unit, which can remove the arsenic from the contaminated water by available materials in Mekong delta. As a result, our filter unit can remove nearly 95 percent of arsenic in potable water and reduced the level of arsenic to WHO provisional guidelines (10 μg/L). The filter unit will be applicable for many areas in Vietnam and the other in the world.

$As^{+3}$ is difficult to be removed than $As^{+5}$. According to EPA (2005), there are seven methods to remove arsenic from ground water: (1) oxidation-filter, ion exchange, activated aluminum absorption, flocculation-filter, upflow filter, growth flocculation, and electrolysis. In Vietnam, arsenic contamination in ground water was warned for long but there are no water supply plants that are responsible to treat arsenic. These plants have been in charge to treat ferrous but not efficient and difficult to be controlled (Con, 2008).

Many kinds of material were used to remove arsenic from contaminated water such as activated alumina, some polimer... and some high technologies such as nano membrane, reserve osmosis have been also used but they are so expensive for countryside people. Therefore, it is urgent to have some techniques and materials to remove arsenic from arsenic contaminated water sources. Each technology fixes the different condition and has to use chemicals. The present study was conducted to satisfy the requirement of arsenic removal with high efficiency, low cost materials, and easily operation. No chemical or little chemical used, available materials in nature, easily operation that are the advantages of this study and able to be applied in reality.

## MATERIALS AND METHODS

### *Materials*

Sodium arsenate was supplied by Merck (Germany). Sand, laterite, brick and the other materials was collected in nature and bought in the market, activated carbon from India.

### *Methods*

Relying on the arsenic concentration in analyzed water, experiments were run in Environmental Technology Laboratory, Faculty of Environment and Natural Resources, HCMC, Vietnam.

Water was contaminated by arsenic with concentration 19.27 ppb, pH at 6.8 - 7.0. Columns were packed with different materials as Ferrous contaminated sand ($A_1$); Activated carbon, Activated carbon and ferrous contaminated sand; Laterite; Brick; Laterite, brick and ferrous contaminated sand.

Arsenic contaminated water of inflow and outflow was analyzed at Analysis Center for Chemistry, Nong Lam University, Vietnam. Arsenic was measured by Atomic Adsorption Spectrometry method (AAS). X ray analysis was conducted by D8 - Advance Bruker (Germany), at room temperature 25°C, voltage 40 kV at 40 mA, measuring configuration theta/2theta, X ray from electrode copper, at $\lambda$ 0.154 nm.

Model was run stably with arsenic and a flow rate 2.2 L/min in 2 days. Model was let for a rest in 1 day, and then run out the water. The arsenic contaminated water with arsenic 19.27 ppb was applied in model in 30 days at a flow rate 2.2 L/min, samples were analyzed. Samples were daily collected and analyzed.

## RESULTS AND DISCUSSION

### *The results of arsenic removal by different materials*

Arsenic contaminated water with concentration **19.27 ppb** as arsenic was run through the experiment columns packed with different material as shown in table 1.

**Table 1**. The results of arsenic adsorption by materials

| No. | Material | Arsenic concentration in outlet (ppb) | Adsorption efficiency (%) |
|---|---|---|---|
| 1 | **Control ($A_0$)** | **19.27** | 0 |
| 2 | Ferrous contaminated sand ($A_1$) | 0.28 | 98.55 |
| 3 | Activated carbon | 12.63 | 34.46 |
| 4 | Activated carbon and ferrous contaminated sand | 1.86 | 90.35 |
| 5 | Laterite | 9.31 | 51.69 |
| 6 | Brick | 7.5 | 61.08 |
| 7 | Laterite, brick and ferrous contaminated sand | 0 | 100 |

After running arsenic contaminated water through the material columns, there were five samples having arsenic concentration meet WHO standard (< 10 ppb). The material composed from sand, brick and laterite getting highest efficiency by 100 %, next the ferrous contaminated sand by 98.55 %, and lowest is activated carbon by 34.46 %, with outlet concentration at 12.63 ppb. The rest sample had efficiencies from 52 to 90 %, and meet WHO standard.

For *ferrous contaminated sand*, the arsenic adsorption efficiency is really high at 98.55%, arsenic concentration at outlet only 0.28 ppb which reaches WHO standard as well as Vietnamese standard (< 10 ppb). That material play a role as supporting substrate where arsenic attaches and the material surface contain pores which increase stacking ability of arsenic. Besides, material collected from Mekong delta and its surface contaminated ferrous actually. While arsenic contaminated water passed through, Fe (II) hydroxide will be oxidized by oxygen in water or in air to become Fe (III) hydroxide. Fe (III) hydroxide continuously precipitates on material and constitutes thin layer. Arsenic (V) and arsenic (III) in water will be absorbed by Fe (III) hydroxide and this compound will be kept on material. The reaction in material column is shown as equations below:

$$Fe\ (II) + O_2 \rightarrow Fe\ (III)$$
$$Fe\ (III) + As\ (III) \rightarrow Fe\ (II) + As\ (V)$$

$$Fe\ (II) + O_2 \rightarrow Fe\ (III)$$
$$Fe\ (III) + As\ (V) \rightarrow FeAsO_4$$

$FeAsO_4$ precipitates with Fe $(OH)_3$ and will be kept on the material surface. As the result, arsenic in contaminated water was removed or adsorbed by ferrous contaminate sand material.

For *activated carbon*, the adsorptive efficiency was really low, 34.46%. Arsenic concentration remained after filtration by column was 12.63 ppb higher than that of standard for potable water. That was because of activate carbon is neutral although it contains many pores in its structure. In filtration process activated carbon can absorb some soluble substances in water resulting in the pores having no more space for arsenic adsorption.

Activated carbon is porous material containing many kinds of pores with different diameters. Under electron microscope, activate carbon has a structure like ant's nest. Therefore it has large contacting surface to adsorb contaminants. However, activated carbon was used in those experiments has a diameter from 3 to 5 mm, and arsenic contaminated water passing through spaces among particles instead of going into pores. Moreover, the main reason is that activated carbon only adsorbs the high electrolytes instead of low electrolytes as arsenic. As the result, arsenic was absorbed by activated carbon at low efficiency.

For *carbon and ferrous contaminated sand material*, the result indicated that arsenic was adsorbed with nearly high efficiency at 90.35%. Arsenic in outlet was 1.86 ppb.

Material was packed by 2 layers with thickness of activated carbon and ferrous contaminated sand was 20 cm and 25 cm, respectively. Activated carbon adsorbs high electrolyte substances. Therefore, arsenic was only kept a little on activated carbon layer. In that case, activated carbon played a role as supporting filter which adsorbs contaminant in water. Arsenic contaminated water continues to run down to ferrous contaminated sand and arsenic was kept on second layer with high efficiency in 4 days running.

With *laterite*, filtering efficiency was 51.69%, and arsenic concentration at outlet was 9.31 ppb, which satisfies WHO standard. That is also a material can be used for arsenic adsorption. For material structure, laterite is porous, containing many spaces and its chemical composition is ferrous abundant. When arsenic contaminates water runs into material, reaction can be occurred as:

$$H_3AsO_3 + O_2 \rightarrow 2H_2AsO_4^- + 2H^+$$
$$Fe(OH)_3 + H_3AsO_4 \rightarrow FeAsO_4.2H_20 + H_2O$$

Arsenic co-precipitate with $Fe^{3+}$ and create a complex which attach to laterite layer with high concentration. However, for long time filtration, laterite could be broken down into smaller partical and runs down with attached arsenic, resulting in reducing the filtering efficiency of laterite material.

*For brick,* with filtration efficiency 61.08%, arsenic concentration 7.5 ppb at outlet, brick has average filtering efficiency but meet WHO standard for drinking water. Brick after milling into smaller particles has 2 – 4 mm in diameter. Material is high permeable for water, sporous and containing iron, manganese...Iron in brick includes Fe (III) and Fe (II), while be oxidizing Fe (II) become Fe(III) in precipitation state. Fe (III) contacts arsenic to form $FeAsO_4$ which attach to brick particles. Therefore, arsenic contaminated water significantly reduces. Brick has a lifetime longer than laterite, filteration efficiency higher than that of laterite for long time.

With the composition of *sand, brick and laterite* in column, result indicated that experimental material got highest efficiency (100%), and did not remain arsenic at outlet. That can be explained as: formation of three kinds of material from upper laterite, center brick, and lower sand, while arsenic contaminated water running form up to down, at laterite layer containing Fe, Mn..., Fe, Mn will be oxidize, then contacte arsenic to form $FeAsO_4$ precipitation and be kept partly there and on the following lower layer. While continously running brick which containing much Fe (II) be oxidized into $Fe(OH)_3$ and arsenic react with Fe(III) to form $FeAsO_4$ precipitation. A mount of arsenic will be kept on this layer. Finally, while running through sand layer, sand has many small spores playing a role of supporting layer where $FeAsO_4$ coagulants attach. Mowever, sand collected from Mekong delta where ferrous contaminated water appears casually. Sand surface can be contaminated by ferrous and reaction for keeping arsenic on material easily occurs, then $FeAsO_4$ coagulants fix to materials. As the result, three layers all can react with arsenic to keep it on their surface with high efficiency.

***Comparison of filtration ability by different materials***

When compare the efficiency of *ferrous contaminated sand – activated carbon and ferrous contaminated sand – laterite, brick and ferrous contaminated sand*, three materials getting high filtering efficiencies. The results showing in figure 1 indicated that ferrous contaminated sand was a material that is able to absorb arsenic with high efficiency (98.55%). However, when ferrous contaminated sand combines with activated carbon, filtering efficiency reduces a little because activated carbon slowly adsorbs arsenic and filtering efficiency reduces to 90.35 %. For complex of laterite, brick and ferrous contaminated sand, filtering efficiency increases to maximum and no more arsenic at outlet. However, when increasing the filtration time, ferrous contaminated sand material keep high efficiency and nearly constant in comparison to two rest materials. Therefore, the benefit from filtration process and needed time for cleaning filtering material, ferrous contaminated sand is considered as a kind of highest benefit material for design an arsenic filtration model for treating arsenic contaminated water.

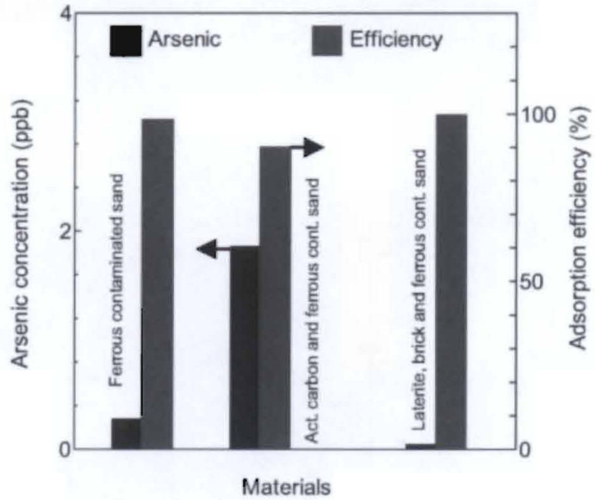


**Figure 1.** Comparison of three materials having high filtering efficiency

For composition of *laterite – brick – laterite, brick and ferrous contaminated sand*, the results showing in figure 2 indicated that laterite adsorbs arsenic relatively. The filtering efficiency decreases for long time operation because of easily broken down in filtering process. As the result, after 4 days of operation, filtering efficiency declines to 51.69 % (9.31 ppb at outlet), and continuously decreases to lower. Brick can overcome the disadvantage of laterite, so filtering efficiency after 4 days was 61.08 % (7.5 ppb at outlet). A composition of laterite, brick and ferrous contaminated sand increases filtering efficiency significantly because laterite mattress can be kept on brick and outlet water not containing arsenic for long time operation.

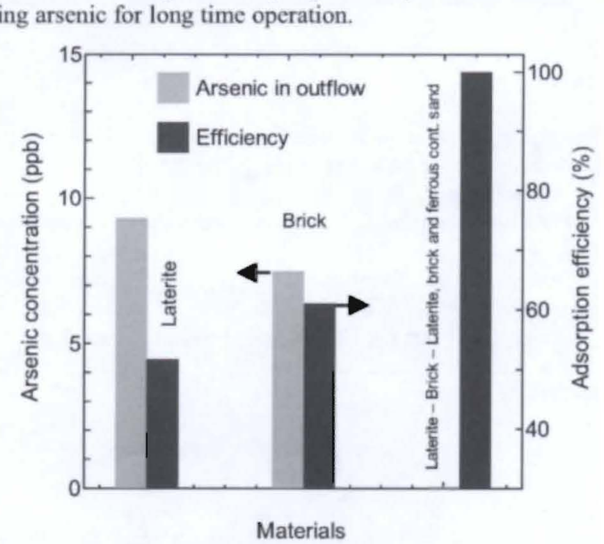


**Figure 2.** Comparison of three materials having relative and high filtering efficiency

***X ray analysis for ferrous contaminated sand in filtering process***

Sample *ferrous contaminated sand* ($A_0$) was collected from Tien River belonging to Mekong delta. The result of X-ray analysis showed that sand structure contains Iron Arsenate ($Fe_2As_4O_{12}$), at d = 3.7087.

Sample $A_1$ (sand after filtering process), X ray analysis showed that sand also had crystal iron arsenate ($Fe_2As_4O_{12}$) at d = 3.7087, with an intensity (Lin) 21.

**Figure 3** shows a comparison of sample $A_0$ and $A_1$. The intensity of crystal iron arsenate of sample $A_1$ is higher than that of $A_0$. Intensity of sample $A_1$ is 21 in comparison to $A_0$, 15. The result justifies that amount of arsenic attaches on sand after filtering process. Therefore, the X ray analysis result is suitable to AAS analysis, ferrous contaminated sand adsorbed arsenic with high efficiency.

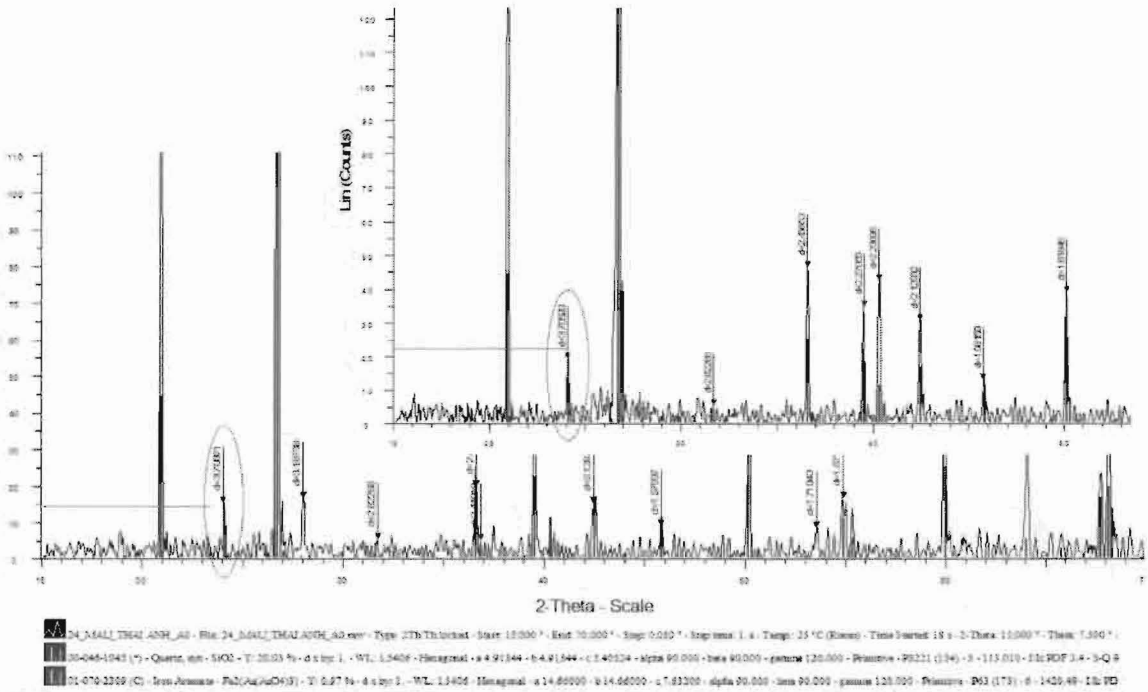


**Figure 3.** Result for X ray analysis of ferrous contaminated sand before (lower) and after filtering process (upper)

## CONCLUSION

The adsorption efficiency of arsenic will significantly increase by using laterite, brick and ferrous contaminated sand (100%) and ferrous contaminated sand (98.55%), but the second materials was more stable than the first and time for operation is also longer. Therefore, ferrous contaminated sand was chose for designing filter model which used for households in Mekong delta. The X ray analysis once confirmed that arsenic was strongly adsorbed on sand surface.

In utilization, people recognize the filtering model is able to remove ferrous efficiently. In arsenic contaminated regions, there are usually an amount of ferrous in water. Relying on the co-precipitaion of arsenic and ferrous and natural oxidation of arsenic and ferrous, the proposed model is useful for arsenic removal with low cost design and operation. That is the need of countryside people. Model never use any chemical to improve the efficiency, thus it is friendly for environment.

**Referrence**

1. The World Bank - Towards a More Effectective Operational Response
2. EPA - Arsenic Treatment Technology Eduation Handbook for small System, www.spa.gov
3. Abernathy, C. O.; Thomas, D. J.; Calderon, R. L. (2003). Health Effects and Risk Assessment of Arsenic. Journal of Nutrition 133, 1536 – 1538.
4. Baolin Deng (2005). Arsenic adsorption onto iron-chitosan composite from drinking water.

5. Danh Dinh Bach, 2006. Environmental Chemistry Curriculum, Science and Technique Press.
6. Ferguson, J.F.; Gavis, J.A. (1972). A review of the arsenic cycle in natural waters. Water Research 6, 1259 1274.
7. Habibur Rahman et al., 2004. Arsenic Contamination of Groundwater in Bangladesh and Its Remedial Measures.
8. Le Quoc Tuan, Nguyen Hoang Lam, Nguyen Thi Binh An, Le Tan Thanh Lam (2011). Study on arsenic removal from ground water by upflow-filter model connect to aeration system. J. Agri. Sci. and Tech., 01/2011, 70 – 73.
9. Le Quoc Tuan, Tran Thi Thanh Huong, Pham Thi Anh Hong, Tomonori Kawakami, Toshinori Shimanouchi, Hiroshi Umakoshi, and Ryoichi Kuboi (2008). Arsenic (V) Induces a Fluidization of Algal Cell and Liposome Membranes. Toxicology in Vitro, 22, 1632-1638.
10. Le Quoc Tuan, Tran Thi Thanh Huong, Pham Thi Anh Hong, Tomonori Kawakami, Toshinori Shimanouchi, Hiroshi Umakoshi, and Ryoichi Kuboi (2007). Partitioning of arsenic (V) on Biomembrane. The Symposium on Solvent Extration. Kyushu, JAPAN.
11. Le Quoc Tuan, Hiroshi Umakoshi, Ryoichi Kuboi (2006). Effect of light on removal ability of arsenic by cell membrane. The 6th International Symposium on Advanced Environmental Monitoring. Heidelberg, GERMANY.
12. Lili W., and Abrahma S.C., 2004. Technology selection and system design U.S EPA arsenic removal technology demonstration program round 1. Water Supply and Water Resources Division 31: 24-26
13. Nguyen Thi Phuong Thao, 2005. Arsenic contamination in domestic water. Information Journal, vol. 3.
14. Shinkai, Y.; Truc, D. V.; Sumi, D.; Canh D.; Kumagai, Y. (2007). Arsenic and other metal contamination of groundwater in the Mekong River Delta, Vietnam. Journal of Health Science 53, 344 – 346.
15. Tran Hong Con, 2008. 30% of ground wells in Hanoi are contaminated by arsenic. Electronic journal of VTC.
16. Vagliasindi, J. G., 1996. Comparison of arsenic (V) and arsenic (III) adsorption onto iron oxide minerals: implications for arsenic mobility. Environ. Sci. Techn 37 (15): 418-425
17. Vahter, M. (2002). Mechanisms of arsenic biotransformation. Toxicology 181–182, 211–217.