Research on making material from waste sludge taken from domestic water treatment plant for arsenic removal from water

Nghiên cứu chế tạo vật liệu từ bùn thải nhà máy xử lý nước cấp để xử lý ô nhiễm asen trong nước

Research article

Trinh Thi Hoa*; Nguyen Thi Phuong Thao; Bui Kim Thoa, Dang Thi Uyen; Nguyen Xuan Huan

Faculty of Environmental Sciences, VNU University of Science, Vietnam National University, Hanoi, Vietnam

Iron oxide is a good and inexpensive adsorbent for arsenic (As) compounds and other heavy metals in water (Fe, Cu, Cd, Pb, Ni, Zn). Waste sludge from water treatment plant, which is highly in iron content, can be considered as a great adsorbent. Utilizing this waste as material for water treatment would get benefits on not only environment but also energy, resources and social economy. This study describes experiments to produce arsenic adsorbent material from waste sludge taken from Ha Dinh water treatment plant by using glass water, $Fe(NO_3)_3$ and heat to modify and enrich iron content. This process aims to make a good material for filtration and sorption of As. Other effects of pH, time, adsorbent mass, and adsorbate concentration are also considered. The processes are successful in removing Arsenic ion clearly. Initial As sample of 1000μg/L, contact time 4 hours, material 1 g/L, the efficiency is 99.64%. Treated water is under national technical regulation on domestic water quality (QCVN 02:2009/BYT column I) –, where column I is applicable to water provision units. Research also starts to make material particles, which are more favorable to practical application. These adsorbent productions after modification are beneficial with low-cost and environment-friendly advantages.

Oxít sắt là một chất hấp phụ tốt và rẻ trong việc loại bỏ các hợp chất asen (As) và một số kim loại nặng khác trong nước (Fe, Cu, Cd, Pb, Ni, Zn). Trong khi đó, bùn thải từ các nhà máy xử lí nước giàu thành phần sắt, có thể xem là một vật liệu hấp phụ tốt. Việc tận dụng bùn thải này làm vật liệu xử lý ô nhiễm không chỉ đem lại những lợi ích cho môi trường mà còn về mặt tài nguyên, năng lượng và kinh tế xã hội. Báo cáo này trình bày cách chế tạo vật liệu từ bùn thải của nhà máy xử lý nước cấp Hạ Đình thành vật liệu xử lý ô nhiễm asen bằng cách sử dụng thủy tinh lỏng, $Fe(NO_3)_3$ và nhiệt để biến tính làm tăng hàm lượng sắt trong bùn thải, tạo vật liệu tốt cho quá trình lọc và hấp phụ As. Các nhân tố ảnh hưởng tới hiệu suất hấp phụ như pH, thời gian, khối lượng chất hấp phụ, và nồng độ As cũng được đưa ra đánh giá. Việc loại bỏ As đạt hiệu quả rõ rệt. Với nồng độ As ban đầu là 1000 μg/L, thời gian xử lý 4 giờ, vật liệu sử dụng là 1g/L thì hiệu suất xử lý đạt 99,64%. Nồng độ As sau xử lý đạt tiêu chuẩn QCVN 02:2009/BYT, cột I – Quy chuẩn kỹ thuật quốc gia về chất lượng nước sinh hoạt, cột I áp dụng đối với các cơ sở cung cấp nước. Nghiên cứu cũng bước đầu thử nghiệm chế tạo thành viên vật liệu để thuận lợi hơn trong việc ứng dụng trong thực tiễn. Vật liệu bùn thải sau biến tính có lợi thế về chi phí thấp và thân thiện với môi trường

Keywords: waste sludge, domestic, reatment, arsenic

1. Introduction

In Vietnam, the Red River in Northern Vietnam and the Mekong in Southern Vietnam serve as primary water sources for agriculture and, since the 1980s, groundwater near these rivers are the main source of drinking water for inhabitants. These two river systems have extremely high concentrations of arsenite and arsenate (Ly, Thuy M, 2012). The contamination of arsenic in Red River area is higher and more widespread than that in Mekong Delta.

Specifically, according to the study, 65% of all studied wells exceed the WHO guideline values for heavy metals or a combination of them with 27% of the wells exceeded the As WHO guideline value of 10 μg/L (Berg Michael, etc, 2007).

2. Materials and Method

2.1 Materials

Iron (III) for coating: $Fe(NO_3)_3$ 0.5M; adhesive glass water Na_2SiO_3 0.5M; pH regulators: NaOH 0.1M, and HCl 0.01M. Modify waste sludge: Raw waste sludge firstly is dried upon sunlight, then is physically comminuted to about diameter size of 0.1 mm. Weigh 10 g of this sludge and mix with 100mL Na_2SiO_3 0.5M. Slowly pour 100mL $Fe(NO_3)_3$ 0.5M into this mixture and stir well. After that, move the mixture into the hot-water boiler at 70^oC for 35 hours to achieve a mixture with layers. The mixture then is cleaned gently with tap water (pH=7), discard surface water and dry at 70^oC. Finally heat the comminuted solid obtained after drying at 650^oC within 3 hours. Examination the solubility of the heated solid with water is negative, the solid is not soluble.

2.2 Methods

2.2.1 Research on impact of time and pH on the adsorption efficiency

Take 5 samples of 20mL arsenic solution 1M. Titrate with NaOH 0.1M to adjust pH of 7. Take 5 samples of 0.02g modified waste sludge, pour into each arsenic solution. Shake at 150 prm for a series of 0.5, 1, 2, 3, and 4 hours. Filtrate the received solution with filter paper. Finally, take AAS of them. Repeat the steps with pH of 5, 6, 7, 8, 9.

2.2.2 Research on impact of modified material mass on adsorption efficiency

Take 6 samples of 100mL arsenic solution 1mg/L and 6 samples of modified waste sludge of 0.01; 0.02; 0.05; 0.1; 0.2; 0.5g, and pour into each arsenic solution. Shake at 150 prm for 30 minutes. Filtrate the received solution with filter paper. Finally, take AAS of them.

2.2.3 Research on impact of arsenic concentration on adsorption efficiency

Take 3 samples of 20mL arsenic of 1mg/L, 2.5mg/L and 5mg/L with pH 6-7 and 3 samples of 0.02 g modified waste sludge and pour into each arsenic solution. Shake at 150 c/min for 4h 30 minutes. Filtrate the received solution with filter paper. Finally, take AAS of them.

3. Results and discussion

3.1 SEM images

SEM image gives a closer look at the surface of the material. At 500nm scale, particles are magnified 50,000 times, and we saw group of particles covering with iron oxide.

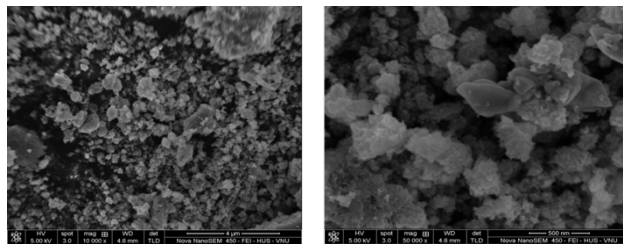The surface is not smooth but rough, it looks spongy and fluffy that is a good adsorption media.

Figure 1. SEM image of modified waste sludge

3.2 X-ray

The surface charges of modified waste sludge are represented on the figure 2. It varies with pH condition.
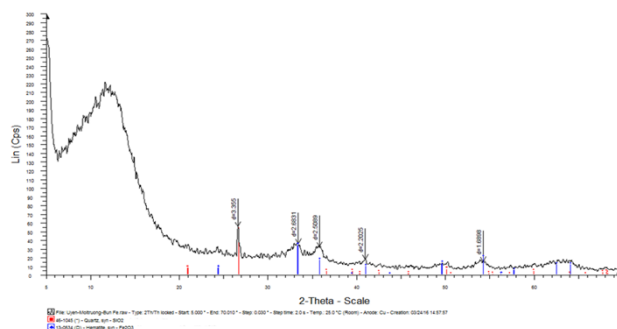

Figure 2. X-Ray image of modified waste sludge

3.3 The composition of material before and after modification

Table 1. The composition of material before and after modification

Element containing	Waste sludge Concentration (ppm)	Modified waste sludge Concentration (ppm)
Na	834	1232
Mg	636.4	3417
Al	3573	11466
P	8134	22550
S	644.6	2798
K	688.5	2052
Ca	275.4	21360
Mn	249.5	1344
Fe	**416470**	**547273**
Cu	6.797	6.133
Zn	65.79	13.79
As	2681	1332
Ba	3661	675.3

Table 1 indicates the chemical compositions of the studied material. The content of iron before and after modification increases remarkably. According to previous research, iron oxides were the good adsorbents for un-complex metals, some metal-ligand complexes (Mark M. Benjamin , Ronald S. Sletten, Robert P. Bailey, Thomas Bennett, 1996). So, increasing iron content in material makes adsorption capacity increase.

3.4 The impact of time and pH on the adsorption efficiency

The initial arsenic solution: 1mg/l (1000ppb).

In general, with the initial arsenic solution having concentration of 1000ppb, the adsorption efficiency of modified material is highest at the pH= 9 and decrease as pH decreases. Furthermore, after 4 hours of contact between this material with the arsenic, the adsorption efficiency is highest in comparison with at the other times. At the pH= 9, the adsorption efficiency is 98.70% after 30 minute and it increases to 99.64 % after 4 hours. At the pH= 7, the efficiency is 98.16% after 30minutes and increases to 99.43% after 4 hours. Moreover, although the efficiency at pH=5 is lowest in comparison with the one at other pH but it was also adsorbed about 98.99% after 4 hours and 97.39 % after 0.5 hour.
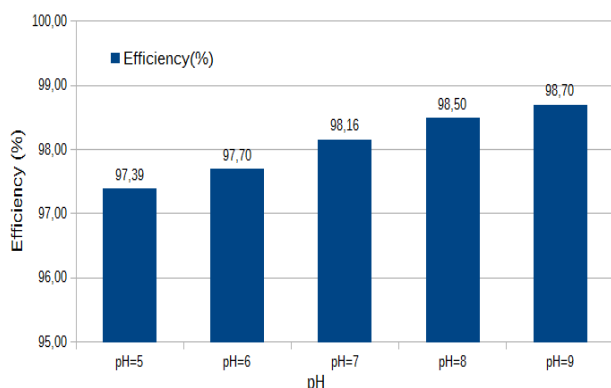

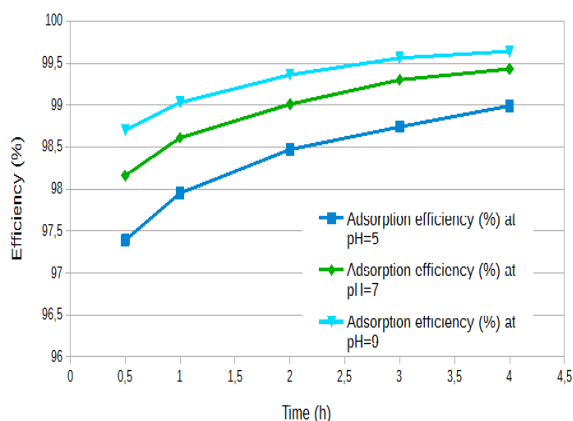**Figure 3. The adsorption efficiency of modified material vs. pH after 0.5h**

Figure 4. The adsorption efficiency of modified material vs. time, pH

According to QCVN 02:2009/BYT, the concentration of arsenic in the drinking water should not exceed 0.05 mg / L (50 ppb) for the exploitation household water. The arsenic concentrations which are adsorbed are lower than this condition at all the interval times and pH.

The sample of Arsenic used is high in species of As V+. According to the book *Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil* pulished in 1991 by Patrick H. Masscheleyn, it is known that this As V+ ion exists at high pH, thus when pH increases, more As V+ appears in the sample, as the result,

more arsenic is absorbed. With increase contact time, it is obvious that more arsenic is absorbed.

Although at pH 8, 9, the adsorption efficiency is higher than at pH 7, the pH 7 is suitable for water in the environment. Thus pH 7 is chosen in the two following experiments.
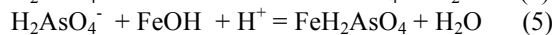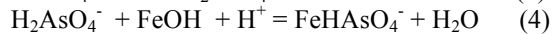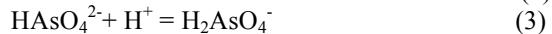
3.5 The impact of modified material mass on adsorption efficiency

Material mass increases from 0.1mg/L to 1mg/L, the arsenic concentration decreases from 52.864 ppb (94.71%) to 18.542 ppb (95.22%). Material mass is up from 1mg/L to 5mg/L, the arsenic concentration decrease slightly (from 18.54 ppb to 6.906 ppb). At 5mg/L point of material mass, the sample reaches the water quality standard (Arsenic concentration < 10 ppb).

According to the book *Chemistry of the surface-water interface* pulished in 1992 by Werner Stumm, Laura Sigg and Barbara Sulzberger, the absorption mechanism of arsenic on iron material surface is based on the OH group formed on the iron surface which is in contact with water.

$$AFe + H_2O = AFeOH^- + H^+$$
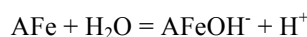
Arsenic then combined tightly to the OH-group (Nguyen Manh Khai, 2010) as following:

$$FeOH + H^+ = FeOH_2^+ \qquad (1)$$
$$FeOH = FeO^- + H^+ \qquad (2)$$
$$HAsO_4^{2-} + H^+ = H_2AsO_4^- \qquad (3)$$
$$H_2AsO_4^- + FeOH + H^+ = FeHAsO_4^- + H_2O \qquad (4)$$
$$H_2AsO_4^- + FeOH + H^+ = FeH_2AsO_4 + H_2O \qquad (5)$$

The result shows that when more materials are added, the efficiency increase, since more As will precipitate with iron content, and be adsorbed on the materials' surface.
At weight of 0.1 gram, the efficiency starts growing drastically to the point of 1mg/L which mean almost arsenic ion in the sample has been absorbed. Thus, when the material quantity is considerable, the adsorption is better.
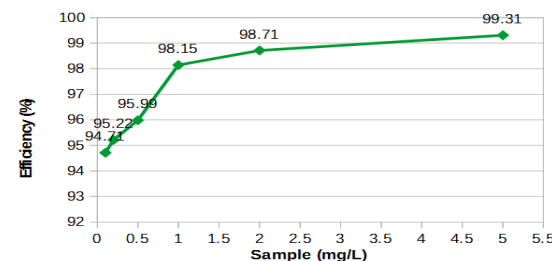

Figure 5. The adsorption efficiency of modified material affected by dose

3.6 The impact of arsenic concentration

The Langmuir's adsorptive isotherm equation:

$$Qe = Q_{max} \frac{b.C_e}{1 + b.C_e} (*)$$

Where:

Ce - equilibrium concentration of adsorbed substance (mg/L);

Q_e - adsorptive capacity (mg/g);

Q_{max} - maximum adsorptive capacity calculated by theory (mg/g);

b - Langmuir equations coefficients (determined from experiments).

Table 2. The efficient adsorb arsenic of modified material impacted by the initial concentration of arsenic

Initial concentration of arsenic (ppm)	Final concentration of arsenic (ppm)	Absorbed arsenic (ppm)	The efficiency (%)
0.5	0.000622	0.499378	99.88
1	0.005721	0.994279	99.43
2.5	0.189	2.311	92.44
5	1.471	3.529	70.58
7.5	3.06	4.44	59.20

To determine the constants in the Langmuir's isotherm equation, the graph method converting equation (*) into linear equation, in which C_e/q_e depends on first order of C_e as the following:

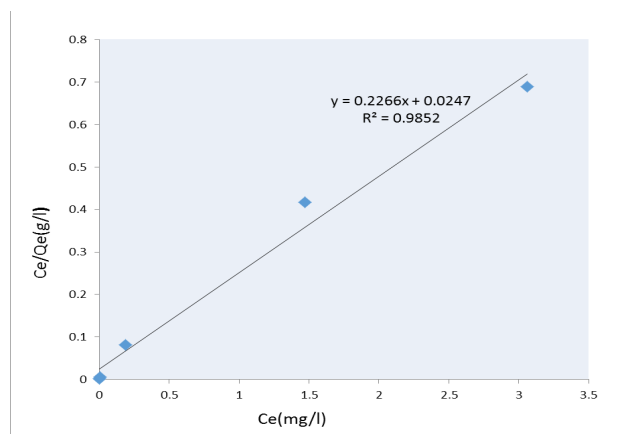$$\frac{Ce}{Qe} = \frac{1}{Q\max}.Ce + \frac{1}{b.Q\max} \quad (**)$$
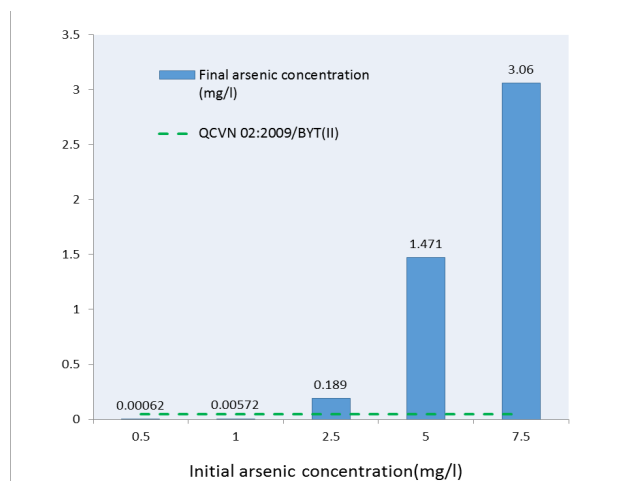

Figure 6. Langmuir isotherm

Figure 7. Arsenic conc. after treatment compare with initial conc. of arsenic

Apply the langmuir equation (**) to determine the maximum adsorption capacity of materials, Q_{max} = 4413 mg/kg and, Langmuir equations coefficient that shows the interaction between absorbent and absorbate, b= 9.17 l/g.

The figure 6 indicates that modified waste sludge works very well on removal of arsenic ion. The efficiency decreases as the arsenic concentration increase. With the initial concentration of arsenic less than 1 mg/l, modified waste sludge dose is 0.02g, time is 4h30min at pH=7, the final concentration of arsenic is suitable for domestic water treatment according to national technical regulation on domestic water quality (QCVN 02:2009/BYT, 2009). With the initial concentration of arsenic more than 2.5 mg/l, the final concentration of arsenic is not suitable for national standard.

4. Conclusion and recommendation

The waste sludge modified after being taken from water treatment plant has high efficient treatment to remove arsenic from water. The ability of As removal of modified waste sludge is better than raw waste sludge. The maximum adsorbent capacity is 4413 mg/kg. With the initial arsenic concentration is 500-1000 μg/L, the efficient adsorption reaches 99.88% which is suitable for household treatment system in Vietnam. The more pH is, the more efficient arsenic adsorption is. Optimum pH and contact time level for arsenic removal was found to be at pH = 9 within 4 hours (efficient adsorption is 99.64%). When more materials are added, the efficiency increases. In range 0.01-0.1 grams of material, the efficiency increases drastically (94.71%- 98.15%). In range 0.1 – 0.5 grams of material, the efficiency increases slightly (98.15% - 99.31%).

In rural areas, the locals still use filtration tanks with sand and gravel to filter ground water. After a period of time of filtration, a thin layer of waste sludge appears causing water-pipes to be blocked, and the households do not know how to utilize this layer and reject it. However, this layer can be used to remove arsenic by the way: dry and crash this waste sludge in order to increase arsenic efficient adsorption, then sprinkle it on the sand layer. Arsenic will co-precipitate with iron on the surface and remain through the tank. To increase the efficiency of treatment, using the modified material in this report is recommended.

5. References

[1] Abhijit Maiti, Sunando Dasgupta, Jayant Kumar Basu, Sirshendu De. s1 Adsorption of arsenite using natural laterite as adsorbent, Department of Chemical

Engineering, Indian Institute of Technology, Kharagpur. - 2007.

[2] Berg Michael, etc Magnitude of arsenic pollution in the Mekong and Red River. Science of the Total Environment 372 (2007) 413–425, 2007.

[3] CIEM Trung tâm Thông tin. 2012. Tư liệu Environmental protection in socio-economic development [Báo cáo]. - Hà Nội : Viện NC quản lý kinh tế TW, trung tâm thông tin- tư liệu, 2012.

[4] ĐH Khoa Học Tự Nhiên. 2001. ĐHQGHN, Viện Địa Chất và Môi Trường - Hội Địa Chất Việt Nam. s1 Hiện trạng ô nhễm Asen ở Việt Nam. Thông tin khoa học địa chất. - 2001.

[5] Geetha Varma. V, Dr Ram Karan Singh, Vaishali Sahu. 2013. A Comparative Study on the Removal of Heavy Metals by Adsorpion Using Fly Ash and Sludge: A review. International Journal of Application or Innovation in Engineering & Management, 2(7), 45-56.

[6] James Farrell, Dhananjay Mishra. 2015. Mechanisms for Arsenic Removal by Ferric Hydroxide Adsorbents. Department of Chemical and Environmental Engineering, University of Arizona.

[7] Ly, Thuy M. 2012. Arsenic Contamination in Groundwater in Vietnam: An Overview and Analysis of the Historical, Cultural, Economic, and Political Parameters in the Success of Various Mitigation Options. Pomona Senior Theses. Paper 41.

[8] Mark M. Benjamin, Ronald S. Sletten, Robert P. Bailey, Thomas Benett. 1996. Sorption and Filtration of Metals Using Iron-oxide-coated Sand. Water Research, 30(11), 2609-2620.

[9] Mohammad A. Hoque, Adrian P. Butler. 2015. Medical Hydrogeology of Asian Deltas: Status of Groundwater Toxicants and Nutrients, and Implications for Human Health. Int J Environ Res Public Health, 13(1), 81.

[10] Nguyễn Mạnh Khải Nguyễn Xuân Huân, Lê Thị Ngọc Anh. 2010. Nghiên cứu xử lí Asen trong nước ngà ở một số vùng nông thôn bằng hydroxit sắt (III). Tạp Chí Khoa Học ĐHQGHN

[11] Patrick H. Masscheleyn, Ronald D. Delaune, William H. PAtrick, Jr. 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environ. Sci. Technol., 25, 1414-1419.

[12] QCVN 01:2009/BYT National Technical Regulation on Drinking Water Quality, BYT, 2009.

[13] QCVN 02:2009/BYT National Technical Regulation on Domestic Water Quality. BYT, 2009.

[14] Ratnaike, RN. 2003. Acute and chronic arsenic toxicity. Postgrad Med J., 79, 391-396

[15] Werner Stumm, Laura Sigg, Barbara Sulzberger. 1992. Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems. Wiley, ISBN: 978-0-471-57672-3

[16] Zeng, Le. 2004. Arsenic Adsorption from Aqueous Solutions on an Fe(III)-Si Binary Oxide Adsorbent. Water Quality Research Journal of Canada, 39(3), 267.