



Atomic Absorption Spectrophotometric Determination of Trace Amounts of Arsenic and Some Heavy Metals in Their Treatment Technology by Iron Powder

PHAM THI KIM GIANG^{1,*}, DANG XUAN THU² and HO VIET QUY²

¹Department of Natural Sciences, Hung Vuong University, Campus 1: Nong Trang Ward, Viet Tri City, Phu Tho Province, Vietnam

²Faculty of Chemistry, Hanoi National University of Education, 136 Xuan Thuy Street-Cau Giay District, Hanoi, Vietnam

*Corresponding author: E-mail: tranchunghhvl@gmail.com; kimgiang0378@gmail.com

(Received: 30 October 2012;

Accepted: 29 June 2013)

AJC-13719

Arsenic and heavy metals present in wastewater were determined before and after treatment on the adsorbent column is significant science in Vietnam. In this study, we used the available natural materials, it is powdered and Fe⁽⁰⁾ yellow sand, MnO₂ powder under the granules used as adsorbent in the column. The survey materials were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM). These study showed that the material consists of magnetite Fe₃O₄ 38.18 %, hematite Fe₂O₃ 12.73 %, wuestite FeO 16.36 % of the beneficial minerals for the adsorption of heavy metals. The results showed that the material can remove As and some heavy metals out of the environment, in particular: arsenic adsorption capacity (169.65 mg/kg) and some metals such as Mn, Fe, Cu, Pb, Cd, respectively: 6616.05, 6664.24, 426.07, 143.06 and 120.21 mg/kg and maintained for a period of 4 days. This shows good potential applications of sand and iron powder Fe⁽⁰⁾ in the treatment of heavy metal pollution by column adsorption method.

Key Words: Arsenic, Heavy metals, Iron powder.

INTRODUCTION

Water pollution problems are the global concerns, especially pollution of arsenic and heavy metals^{1,2}. In Vietnam water is seriously contaminated by the amount of heavy metals³⁻⁵. The delivering the measures to reduce pollution is necessary and urgent⁶. In particular, with some low developed economic regions, this pollution is an agony problem⁷. It has been existing for a long time, but the pollution is not properly concerned^{7,8}. Until the consequences left a large number of fatal diseases which claimed many human lives, the people now realizing about environmental issues and the impacts of environmental public health^{4,9-11}. Because the environmental pollution causes some incurable diseases such as cancer, tuberculosis, *etc.*, until now there is no medical treatment effective^{12,13}. Arsenic and heavy metals pollution is also one of the causes of these diseases². Therefore, we conducted the research in analyzing amount of arsenic and some heavy metals by atomic absorption spectrophotometry (AAS) method and initial treatment of metal contaminated in polluted water by iron powder to provide model of wastewater treatment.

EXPERIMENTAL

The As(V), Cd(II), Cu(II), Mn(II), Pb(II), Fe(III) solutions were prepared by the standard solutions (1000 ppm) of Merck

(Germany) production. All research solutions were prepared in volumetric flasks which have been checked volume precision manufacturing by Merck Company of Germany. Studied solutions have been diluted to concentration about 10⁻⁸ to 10⁻⁶ M and used for a short period of time that not exceeding three days. The HCl, HNO₃, H₂SO₄ solutions were all produced by Merck Company in Germany. Using twice distilled water was distilled in Hamilton machine produced in Britain.

The measurements were performed on atomic absorption spectrophotometer Shimadzu 6300 made in Japan. Material (80 g) of constant weight is stuffed into plastic columns with a capacity of 60 mL (disposable plastic syringe). The research solution was prepared from the standard solutions, put in a treatment vessels. This vessels have control valve to have a constant flow rate of 5 mL/min. Conduct experiments continuously and sample flow continuously during the study period. Sample taken is tested by the test kit in the same day, then take measurements on atomic absorption spectrometer to determine the total arsenic content and other metal ions remaining in the water before and after treated through the column. In order to check the accuracy of the Shimadzu 6300 machine, we conducted measurement with one standard sample on a Shimadzu 6800 in a different laboratory and having results matching between two machines (relative error less than 15 %).

Experimental conditions: After research, the optimal conditions are surveyed to identify some heavy metals on Shimadzu 6300 spectrometer, survey the acid background for each metal, plot the standard curve elements Cd(II), Cu(II), Mn(II), Pb(II), Fe(III) by the flame atomic absorption spectrophotometric method. As(V) and As(III) are studied in similar way and surveyed by non-flame atomic absorption spectrophotometry (graphite furnace).

For arsenic, we have the conditions surveyed in this equipment by furnace graphite with parameters of wavelength: 193.7 nm, HCL intensity 12 mA, slit width 7 nm. Parameters of Furnace graphite for measurement: drying temperature in steps 1, 2, 3 are at 150 °C during 20s, 250 °C during 10 s, 600 °C during 10 s, respectively and ashing temperature in step 1 is 600 °C for 10 s, step 2 is 600 °C for 3 s. Temperature of atomization is in 2200 °C for 2 s and cuvette is cleaned for 2 s at 2500 °C. Determination arsenic in linear range: 2-80 ppb.

Wastewater treatmental technology by iron powder:

We present the results of application materials available in nature for the treatment by the column adsorption experiments of arsenic and heavy metal pollution polluted water such as: Cd(II), Cu(II), Mn(II), Pb(II), Fe(III). Using a scanning electron microscope (SEM) on a GEOL 6490 made in Japan (Institute of Materials Science) and X-ray fluorescence analysis (XRD) on a Siemens D5005 in Faculty of Physics, HUS-VNU to investigate the original material before conducting the experiment shown in Figs. 1 and 2, respectively. Fig. 1 showed that the surface area is different with particle size from 14.45-31.80 μm .

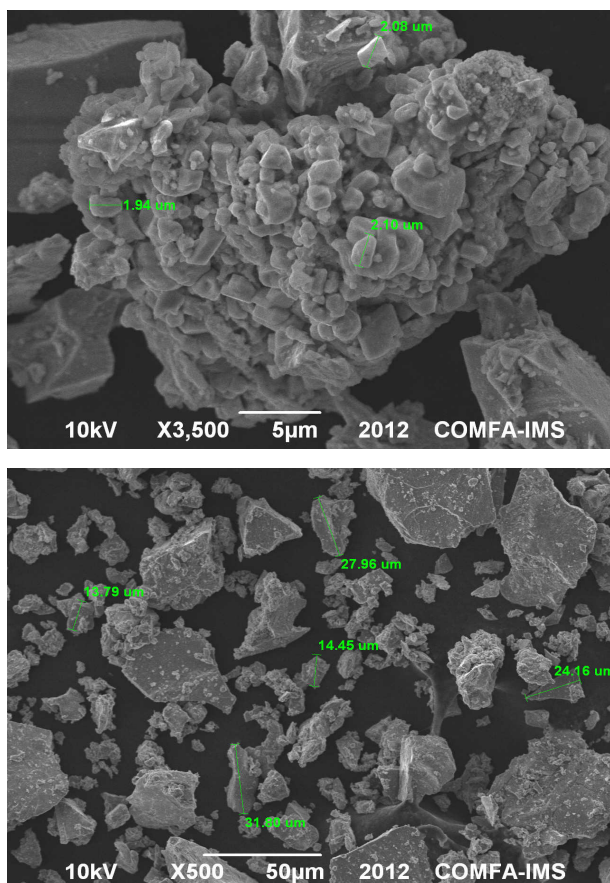


Fig. 1. SEM graph of iron powder material samples

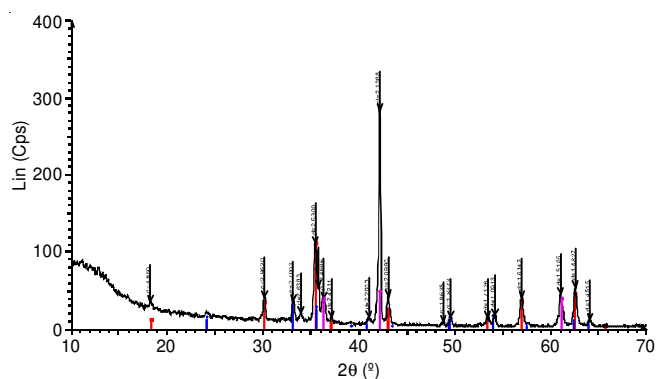


Fig. 2. Spectrum schematic analysis results of Fe powder materials by XRD method

The results show that adsorptive material Fe(0) including magnetite Fe_3O_4 38.18 %, hematite Fe_2O_3 12.73 %, wustite FeO 16.36 % is a suitable mineral for the adsorption of heavy metals.

Preparation of the column of material: Components of material are iron powder sold on the market and natural sand and soaked and washed carefully twice with distilled water. Using the original standard solution of As(V), As(III) and metal ions: Cd(II), Cu(II), Mn(II), Pb(II), Fe(III) prepared from the stock solutions with concentration of 1000 ppm Merck Company in Germany to dilute into the concentrations closed to the actual wastewater samples to conduct experiments adsorption in column. pH is the same with the pH of wastewater samples of the environment. In this experiments, ion forces at $I = 0.01 \text{ M}$ were adjusted by NaNO_3 salt solution to keep the ion forces similar to the natural environment samples. The industrial wastewaters were collected from Lam Thao Chemical factory, discharged into the environment through the sewage system containing elements in excess of permission standard. Treatment procedure: In this study, the adsorption column made of (disposable) plastic syringe with a volume of 60 mL is inserted by 80 g of the material particles including yellow sand and black sand washed several times with twice distilled water and mixed with iron powder with the proportion with 2, 5 and 10 % Fe in weight, respectively, at a constant height and flow from the top to down through the clean plastic container system with controlling valve to have the flow constant rate *ca.* of 5 mL/min.

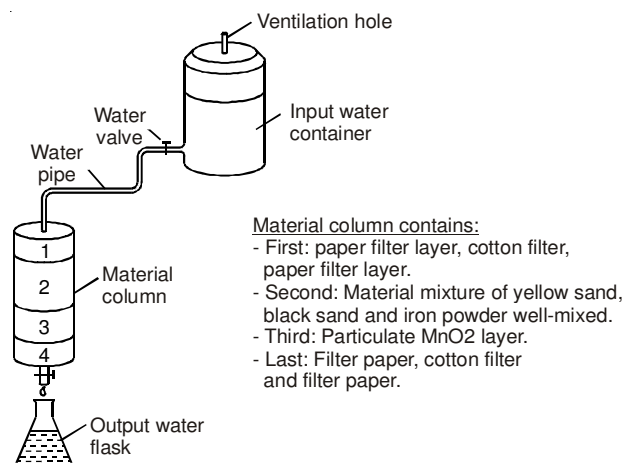


Fig. 3. Model diagram of water treatment types a pilot in the laboratory

Samples were daily analyzed simultaneously with the initial concentration of arsenic and other metals. The column adsorption experiments were carried out at room temperature. In the survey, the flowing rate is checked and adjusted so that the flow rate does not change based on the data of the volume of output solution changed in range of the rate 2, 5 and 10 mL/min. The conduct experiments were kept continuously during from 1 day to 30 days, from 7 am to 5 pm for a day. The samples were taken and analyzed pre- and post-treatment on the test kit before analyzing by AAS analysis Shimadzu machines 6300 and 6800.

RESULTS AND DISCUSSION

Results of As and heavy metals absorption in authentic water sample: We conducted the preparation of authentic samples having concentration of elements like real sample (wastewater sample of Chemical factory), pH of sample is also similar to that of real sample (pH is 5-6). To have better performance of adsorption column, we increase the pH of the sample to 7.0-7.5 with bicarbonate salts. Then let the flow pass through the adsorption column; at the first time, the performance is 90-99 % (C_{in}/C_{out}); after 3 days the performance decreased from 90 to 70 %. After 3 days, the performance is 30 % and at that time the column should be replaced. Thus, based on experiment, the amount of the elements after 3 days may exceed the permission. Therefore, after 3 days, the column material was replaced. The results are shown in Fig. 4.

Fig. 4 showed that the material adsorbed As and heavy metal very effectively, especially in the first 3 days, but the adsorption was decreasing after that. The measured output pH (6.5-7.0) was not significantly reduced in compare with the input (pH was raised to 7.0-7.5). Some metals give the high performance As, Mn, Fe, Pb, Cd: even at the 7th day, the performance was still 70-80 %. The column adsorption capacity of As and heavy metals at the durations of 1-8 days (3, 6, 9, 12, 15, 18 and 24 L) were shown in the Table-1.

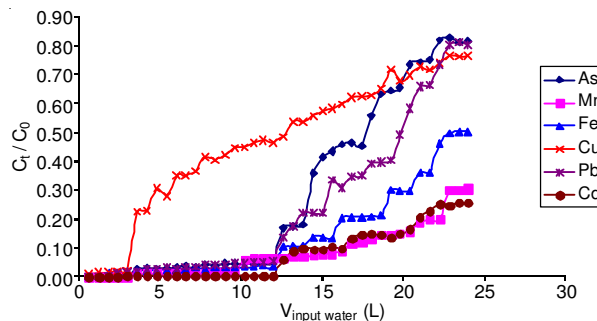


Fig. 4. Graph shows the dependence of C_i/C_o on the input water volume

Adsorption results of arsenic and heavy metals in factory wastewater: The waste sewage water of Lam Thao Superphosphate Factory was taken as the Vietnam National Standard No. 6663-6:2008 of water quality and sample taking in river and streams. Measured the concentration in the wastewater pre- and post- treatment by AAS to determine the input and output concentration through the material column as described above. The results are shown below in the Table-2.

The results (Table-2) showed that the adsorption capacity of arsenic and heavy metals slightly reduced from the 1st to 4th day. The material can adsorb arsenic and heavy metal very well. Only with the case of Cu, the capacity dropped rapidly. After 4 days, the column should be replaced. The low cost material of sand and iron powder can adsorb arsenic and heavy metals simultaneously is very prospective to apply onto the reality. In this article, only the adsorption of arsenic and heavy metals is mentioned.

Conclusion

Arsenic and heavy metals column adsorption of natural material of sand and iron powder shows its high adsorptivity of As (169.65 mg/kg) and some other metals Mn, Fe, Cu, Pb, Cd (6616.05, 6664.24, 426.07, 143.06 and 120.21 mg/kg, respectively in 4 days of 0.08 kg material. It has shown the high applicability of sand and iron material in heavy metals treatment by column adsorption.

TABLE-1
ADSORPTION CAPACITY OF As AND HEAVY METALS OF AUTHENTIC SAMPLE

Day	Output water volume (L)	L_{As} (mg/kg)	L_{Mn} (mg/kg)	L_{Fe} (mg/kg)	L_{Cu} (mg/kg)	L_{Pb} (mg/kg)	L_{Cd} (mg/kg)
1	3	186.6650	6875.6182	6694.5089	853.3984	146.8357	111.7299
2	6	180.3000	6797.9773	6642.2768	567.6563	144.6920	111.6183
3	9	178.6000	6773.9773	6594.5089	502.5000	142.5725	111.4621
4	12	177.8667	6441.0909	6563.7054	466.0938	141.2319	111.3917
5	15	109.6333	6336.3864	5860.8929	371.1523	115.7367	101.2277
6	18	83.1667	5976.1364	5370.0000	323.0859	90.2114	95.1339
7	21	48.2833	5583.8864	4325.1116	236.4648	50.5072	89.0625
8	24	34.5667	4788.4091	3371.9643	204.6094	28.9251	83.5045

TABLE-2
ADSORPTION CAPACITY OF As AND HEAVY METALS ON THE TREATMENT COLUMN

Day	Output water volume (L)	L_{As} (mg/kg)	L_{Mn} (mg/kg)	L_{Fe} (mg/kg)	L_{Cu} (mg/kg)	L_{Pb} (mg/kg)	L_{Cd} (mg/kg)
1	3	186.3833	6995.3636	6928.9732	821.2695	149.0399	120.5580
2	6	185.8500	6884.0227	6765.1339	549.9609	146.7935	120.5022
3	9	185.0000	6847.3636	6721.8304	451.3086	144.4384	120.3125
4	12	169.6500	6616.0455	6664.2411	426.0742	143.0616	120.2121
5	15	161.0667	6468.2273	6066.3393	329.7266	116.8780	109.8884
6	18	86.8500	5436.7955	5600.0000	294.8828	91.0628	103.3594
7	21	45.7333	4777.7727	4463.7723	217.3047	52.1800	89.8326
8	24	33.9667	4306.5000	3507.8571	175.8594	30.9300	87.1987

REFERENCES

1. M. Kumaresan and P. Riyazuddin, *Curr. Sci.*, **80**, 837 (2001).
2. P.L. Smedley and D.G. Kinniburgh, *Appl. Geochem.*, **17**, 517 (2002).
3. M. Berg, H.C. Tran, T.C. Nguyen, H.V. Pham, R. Schertenleib and W. Giger, *Environ. Sci. Technol.*, **35**, 2621 (2001).
4. P.H. Viet, T.H. Con, C.T. Ha, H.V. Ha, M. Berg, W. Giger and R. Schertenleib, Investigation of Arsenic Removal Technologies for Drinking Water in Vietnam, In Arsenic Exposure and Health Effects V, Published by Elsevier Science, Ch. 35, pp. 459-469 (2003).
5. W. Giger and M. Berg, *Neue Zürcher Zeitung*, **22**, 56 (2001).
6. T. Takamatsu, M. Kawashima and M. Koyama, *Water Res.*, **19**, 1029 (1985).
7. H.A. Aziz, M.N. Adlan and K.S. Ariffin, *Bioresour. Technol.*, **99**, 1578 (2008).
8. M. Berg, H.C. Tran, K.T. Pham, R. Schertenleib and W. Giger, Arsenic Pollution of Water Resources in Vietnam-A Plea for Early Mitigation Actions, Arsenic in Soil and Groundwater Environment Biogeochemical Interactions, Uppsala, Sweden, pp. 8-9 (2003).
9. M.J. Demarco, A.K. Sengupta and J.E. Greenleaf, *Water Res.*, **37**, 164 (2003).
10. D.Q. Hung, O. Nekrassova and R.G. Compton, *Talanta*, **64**, 269 (2004).
11. A. Gomez-Caminero, P. Howe, M. Hughes, E. Kenyon, D.R. Lewis, M. Moore and J. Ng, in eds.: A. Aitio and G. Becking, Arsenic and Arsenic Compounds, Environmental Health Criteria 224, World Health Organization, Geneva (2001).
12. A. Seidel, J.J. Waypa and M. Elimelech, *Environ. Eng. Sci.*, **18**, 105 (2001).
13. N. Balasubramanian and K. Madhavan, *Chem. Eng. Technol.*, **24**, 519 (2001).