

ARSENIC REMOVAL FROM GROUNDWATER BY IRON CO PRECIPITATION IN CONTACT FILTER

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ABSTRACT

Natural contamination of groundwater by arsenic has become a threatening problem in many parts in the world, especially in such areas where groundwater is the only or major drinking water resource such as Hanoi City. Recent surveys of our laboratory revealed that Hanoi groundwater has relatively high arsenic concentration in the range of 1 - 3050 µg/L. By conventional treatment, mostly designed for iron removal, arsenic is simultaneously removed at significant extent. But in some cases the quality of treated water can not meet the former Vietnamese standard of 50 µg/L. Meanwhile recently following WHO guideline Vietnamese Ministry of Health just issued a new more strict regulation for arsenic in drinking water of less than 10 µg/L. This is why to find out appropriate arsenic removal technology is an urgent task of Vietnamese water scientists and technologists.

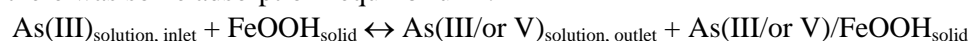
Because of high concentration of Fe(II) in Hanoi groundwater all Hanoi water plants were designed for Fe(II) removal, that includes the four main steps: 1- Aeration by natural or forced aeration tower; 2- Settling by contact horizontal or vertical settler; 3- Filtration by gravity rapid sand filter; and 4- Disinfection by chlorination. The oxygenation of Fe(II) starts soon during aeration and continues in settler to form Fe(III) precipitates. The remained Fe(II) is completely oxidized on the rapid filter along the filtration of Fe(III) particles. In most cases this sequence of processes can remove Fe according to well-known standard of 0.3 mg/L, and nearly 80% of arsenic was removed too. By this technique the former standard of 50 µg As/L can be achieved, but impossible if input As content is higher 250 µg/L, that is common value in many groundwater sources.

Our solution to improve As removal efficiency is to replace conventional settler in existing plants by an upflow-contact filter. Therefore, our arsenic removal technology includes: 1- Aeration; 2- Contact filter; 3- Rapid sand filter; and 4- Disinfection.

The scope of this paper is to find out a model which can describe process of arsenic removal realized in new treatment unit - contact filter.

Experiments were designed as following: natural groundwater with basal concentration of about 20 mg Fe(II)/L was pumped through an injector to saturate water with oxygen. Desired As(III) doses were injected into raw water before aeration. Then aerated groundwater went up-flow through a contact filter with a 1-meter layer of floating spherical polystyrene (PS) particles. Dimension of PS bed was 1mx1mx1m. Flow rate of raw water was kept around 1 m³/h according to one hour empty bed contact time. Samples were collected before aeration device and after contact filter for analyzing Fe(II), total Fe and total As. When raw water was going through the PS bed oxygenation of Fe(II), and may be As(III) occurred. Actually, we still do not know what happens with As(III), either it was absorbed on newly formed FeOOH, then oxidized into As(V) or it was first oxidized then formed As(V) adsorbed on FeOOH.

Supposed there was some adsorption "equilibrium":



If there is such equilibrium we will have: $\frac{[\text{As(III / or V)}_{\text{solution}}]}{\text{As(III)}_{\text{solution}}} = K$. Then K must be constant.

Six independent series with different inlet As(III) concentrations of the range of 1058-3029 µg/L were conducted. At highest arsenic concentration some breakthrough elevation of outlet As is observed. If only outlet As concentrations before elevation are taken into account (with assumption that only before this point adsorption "equilibrium" is more or less realistic) then K will be varied in narrow

range. Actually the K values are varied in the range of 0.11-0.13 and average of 0.12. It was also found that good relationship between ratios of $(As(III)/Fe)_{soluble/inlet}$ and $(mAs/mFe)_{solid}$ with high correlation $R^2 = 0.9866$ was obtained.

XỬ LÝ Ô NHIỄM ASEN TRONG NƯỚC NGẦM BẰNG PHƯƠNG PHÁP ĐỒNG KẾT TỦA SỬ DỤNG KỸ THUẬT LỌC TIẾP XÚC

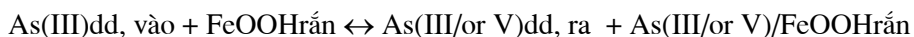
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TÓM TẮT

Mục đích của đề tài nghiên cứu này là nhằm tìm ra một mô hình mô tả quá trình xử lý asen trong bộ phận lọc tiếp xúc phục vụ cho xử lý nước cấp. Thí nghiệm được tiến hành bằng bơm nước ngầm có nồng độ sắt khoảng 20mg/L đi qua cột tiếp xúc khí để bão hoà oxi vào nước sau khi bổ xung một lượng asen nhất định. Nước được bơm với lưu lượng 1m³/h (thời gian tiếp xúc khoảng 1giờ) đã được xúc khí đi qua cột lọc tiếp xúc nhồi 1m các hạt polystyren (PS) hình cầu. Trong quá trình chảy qua cột lọc PS sắt và có thể cả asen sẽ bị oxi hoá. Tuy nhiên trình tự quá trình oxi hoá As(III) thành As (V) cũng như quá trình hấp phụ trên FeOOH vẫn chưa được nghiên cứu kỹ. Cân bằng hấp phụ được giả thiết như sau:



Nếu cân bằng được thiết lập, tỉ lệ: $\frac{[As(III / or V)_{dd}]}{As(III)_{dd}} = K$ sẽ là hằng số.

6 thí nghiệm độc lập đã được tiến hành với nồng độ asen đầu vào khác nhau trong khoảng từ 1058-3029 µg/L. Đã quan sát được một số điểm “đánh thủng” (breakthrough) của trong đồ thị đường hấp phụ asen trên FeOOH trong một số thí nghiệm với nồng độ asen cao nhất. Nếu chỉ tính các giá trị trong khoảng đường hấp phụ trước điểm “đánh thủng” thì giá trị K sẽ biến thiên trong một khoảng hẹp. K thu được từ thực nghiệm trong khoảng 0.11 - 0.13 và trung bình là 0.12. Từ thực nghiệm cho thấy mối quan hệ giữa $(As(III)/Fe)_{dd}/vào$ và $(mAs/mFe)_{rắn}$ là tuyến tính với hệ số tương quan khá tốt $R^2 = 0.9866$.

INTRODUCTION AND HYPOTHESIS

Natural contamination of groundwater by arsenic has become a threatening problem in many parts of the world, especially in such areas where groundwater is the only or major drinking water resource such as Hanoi City. Recent survey of our laboratory revealed that Hanoi groundwater has relatively high arsenic concentration in the broad range of 1-3050 µg/L (Berg et al. 2001). By conventional treatment, which is mostly designed for iron removal, arsenic is simultaneously removed at significant extent. But in some cases the quality of treated water cannot meet the former Vietnamese standard of 50 µg/L. Meanwhile in 2002 following WHO guideline Vietnamese Ministry of Health just issued a new more strict

regulation of arsenic in drinking water less than 10 µg/L. Therefore our task is to find out appropriate arsenic removal technology for Hanoi City to meet new regulation.

Since Bangladesh arsenic crisis, concerning arsenic removal technologies there is abundant literature.

According to (USEPA, 2000, 2003) variety of methods can be applied for arsenic removal, such as precipitative processes including: coagulation/filtration (C/F), iron/manganese oxidation, coagulation assisted microfiltration, enhanced coagulation, lime softening; adsorptive processes including: activated alumina, iron oxide coated sand, ion exchange; membrane processes including electrodialysis reversal; oxidation filtration, sulfur-modified iron, granular ferric hydroxide, iron filings etc. None of these technologies, however, is currently applied on a large scale in developing countries as they are either elaborate technical systems or cost ineffective.

The C/F process has traditionally been used to remove solids from drinking water supplies. However, the process is not restricted to the removal of particles. Coagulants render some dissolved species (e.g., natural organic matter (NOM), inorganics and hydrophobic synthetic organic compounds (SOCs)) insoluble and the metal hydroxide particles produced by the addition of metal salt coagulants (typically aluminum sulfate, ferric chloride or ferric sulfate) can adsorb other dissolved species.

In the case of Fe(II) bearing groundwater of Hanoi City we have the case of Fe/Mn- oxidation mentioned in (USEPA, 2000). This process is dominant in facilities treating groundwater in Vietnam. Oxidation to remove iron and manganese leads to the formation of hydroxides that remove soluble arsenic by co-precipitation or adsorption reactions.

As showed by Edwards arsenic removal during iron precipitation is expected to be fairly efficient (Edwards, 1994). Removal of 2 mg/L of iron achieved a 92.5 percent removal of As(V) from a 10 µg/L As(V) initial concentration by adsorption alone. Even removal of 1 mg/L of iron is capable of adsorbing 83 percent of a 22 µg/L As(V) influent concentration. However, removal of arsenic during manganese precipitation is relatively ineffective when compared to iron even when removal by both adsorption and co-precipitation are considered. For instance, precipitation of 3 mg/L manganese removed only 69 percent of As(V) of a 12.5 µg/L As(V) influent concentration. Unfortunately, most of total arsenic in Hanoi groundwater is in the form of As(III), which has much less adsorption capacity than As(V) does. This is the reason why we have to check the possibility of application of Fe(II) oxidation in combination of C/F process for As(III) removal.

As(III) removal during coagulation with alum, ferric chloride, and ferric sulfate has been shown to be less efficient than As(V) under comparable conditions (Hering, et al., 1996; Edwards, 1994; Shen, 1973; Gullledge and O'Conner, 1973; Sorg and Logsdon, 1978). If only As(III) is present, consideration should be given to oxidation prior to coagulation to convert As(III) to As(V) species.

Because of high concentration of Fe(II) in Hanoi groundwater all Hanoi water plants were designed for Fe(II) removal, that includes the four main steps: 1- Aeration by natural or forced aeration tower; 2- Settling by contact horizontal or vertical settler; 3- Filtration by gravity rapid sand filter; and 4- Disinfection by chlorination. The oxygenation of Fe(II) starts

soon during aeration and continues in settler to form Fe(III) precipitates. The remained Fe(II) is completely oxidized on the rapid filter along with filtration of Fe(III) particles. In most cases this sequence of processes can remove Fe according to well-known standard of 0.3 mg/L, and nearly 80% of arsenic was removed too. By this technique the former standard of 50 µg As/L can be achieved, but impossible if input As content is higher 250 µg/L, that is usual As value in many Hanoi groundwater sources. To reduce As content application of oxidation (eg. by chlorine) prior to filtration is one of options, but in the case of Hanoi groundwater which has high content of reducing Fe(II), and in some places also ammonia, then a large amount of chlorine will be consumed before As(III) oxidation.

To facilitate improvement of existing Hanoi drinking water plants to meet new arsenic regulation a new treatment unit was tried. This is an up-flow contact filter (CF). In this case improvement of As removal efficiency is expected owing to combination of Fe/Mn/As oxidation and C/F process. If it will be succeeded, it can be applied as a replacement for conventional settler in existing plants. Therefore, our arsenic removal technology will include: 1- Aeration; 2- Contact filter; 3- Rapid sand filter; and 4- Disinfection. This sequence has enough flexibility because after CF, most of Fe(II) is removed, then if additional oxidation is required for better As removal in rapid filter (eg. by addition of chlorine or permanganate) it will be easy done by addition of small amount of oxidizing chemical before final rapid sand filter. The scope of this paper is to find out possible models which could describe the As removal process being realized in this new treatment unit.

EXPERIMENTS

Scheme of arsenic removal by co-precipitation experiments are designed as following (Fig 1).

Experimental procedure

Natural groundwater with basal concentration of about 20 mg Fe(II)/L is pumped through an injector to saturate water with oxygen. Desired As(III) doses are spiked by dosing pump into raw water before aeration. Then aerated groundwater goes up-flow through a contact filter with a 1-meter layer of floating spherical polystyrene (PS) particles. Dimension of PS bed is 1x1x1 m. Flow rate of raw water is kept around 1 m³/h according to one hour empty bed contact time. Samples are collected before aeration device and after contact filter for Fe(II), total Fe and total As analysis (points M1 and M2). In some experiments after CF water goes down-flow through conventional rapid sand filter (figure 1).

Six independent series with different inlet As(III) concentrations of the range of 1058-3029 µg/L were conducted.

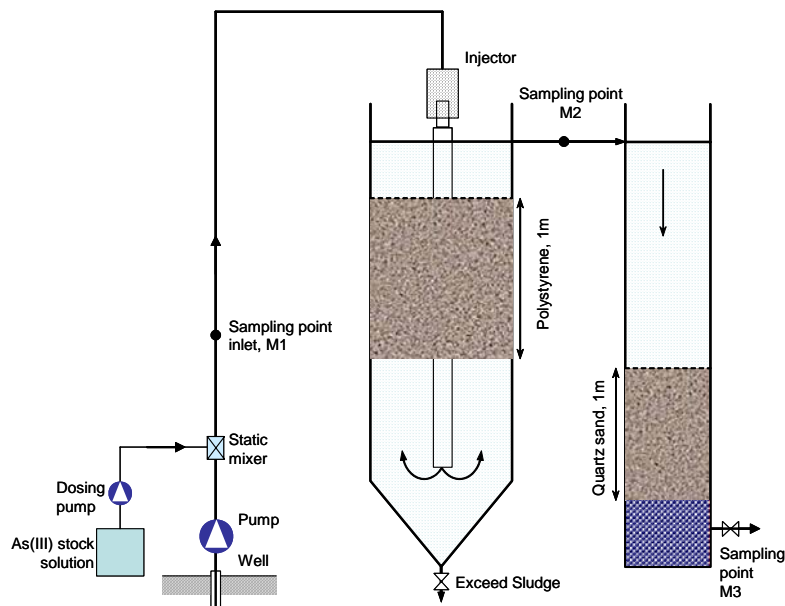


Figure 1. Experimental scheme for Fe(II) and As(III) removal

Analytical methods

Fe(II) and Fe(total) are analyzed according to 3500-Fe phenanthroline method (APHA, 1995). Arsenic as total value was analyzed by atomic absorption spectroscopy equipped with an on-line hydride generation device (HVG-AAS, Shimadzu AA-6800, Japan). Other groundwater parameters were determined according to APHA methods too.

Arsenic(III) stock solution

As(III) solution was prepared by weighting predetermined amount of commercial As_2O_3 , dissolved in water, add stoichiometric amount of NaOH for dissolution, then neutralized by addition of HCl. After quantitative analysis of As_{total} as mentioned above this solution was used as a stock solution, and appropriate dilution must be done as experiments required.

RESULTS AND DISCUSSION

Raw groundwater characteristics and Fe, As removal efficiency are shown in table 1 below.

Table 1. Raw groundwater characteristics and removal efficiency without As addition

Items	M_1	M_2	M_3
pH	6.7-6.8	-	-
PO_4^{3-}	0.12	-	-
Fe(II)	19-24	0.07	0.02
Fe _{total}	20-25	0.39	0.09
As	20-28.5	8.2	2.25

Groundwater quality data showed that it is heavily contaminated by iron, and in less extent arsenic, phosphate. Preliminary runs showed that our facility treats well iron, arsenic to required level of 0.3 mg/L and 10 $\mu\text{g/L}$ respectively.

To clarify arsenic removal capacity of this system a predetermined doses of arsenic (III) is spiked just after groundwater pump. Samples are taken every 0.5-1.0 hour interval through out all time courses. Due to head loss caused by Fe sludge accumulated under filtering bed each run was carried out in 12-14 hours until raw water overflows from central tube.

Because most of iron and consequently arsenic are removed in the contact filter, in experimental procedures most of samples are taken at M1 and M2 sampling ports. These data are basic for calculations of models expressing performance of central treatment unit-CF of the whole treatment sequence.

Performance of contact filter

Iron removal in time course

Iron removal efficiency was demonstrated in figure 2. One can find increasing removal efficiency along with the time course.

At the first hours Fe outlet concentration was varied in the range of 3-7 mg/L, and it was gradually reduced to as low as less than 1 mg/L. By the meantime concentrations of Fe(II) were very low, therefore Fe concentrations expressed herein were total Fe ones.

Iron concentration after CF can be express by a power function $[\text{Fe}]_{\text{out}} = 18.846x^{-1.232}$ where t is time of filtration in hours, and correlation was good enough $R^2 = 0.983$.

Results showed that iron removal in CF was quite effective, and after final filter product water always meet demands of National standard as well as international ones (table 1).

Arsenic removal in time course

Data on outlet of CF arsenic concentration versus time during six runs with increasing spiked or inlet arsenic concentration are presented in figure 3.

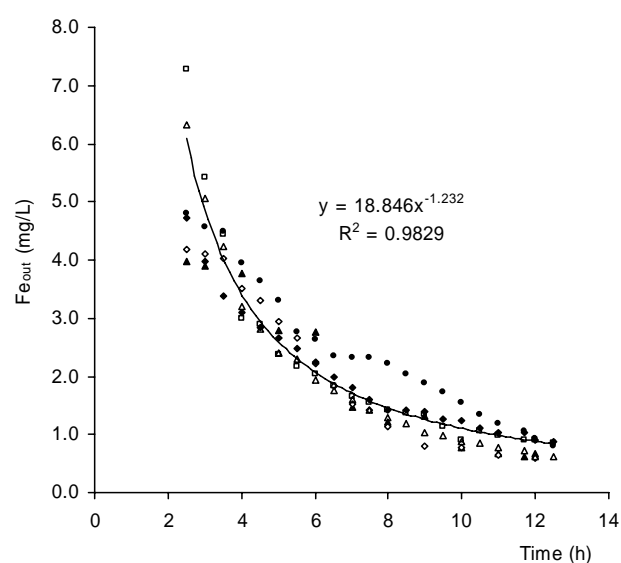
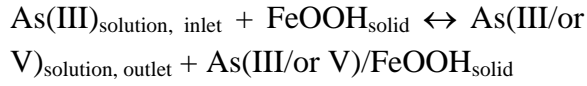


Figure 2. Relationship between iron removal by CF and filtering time

Consequently, owing to co-precipitation or adsorption phenomenon of arsenic on ferrihydroxides it is expected that some arsenic removal must occur.

One can reveal that at the inlet concentrations lower than 2200 µg/L arsenic outlet content of each run seems to vary around some average value. But when inlet concentration exceeds the value of 2200 ppb some break point was observed (fig.3, curves of $[As]_{inlet} = 2497.9$ and 3029.0 ppb). In this case one can put forward that there is some adsorption "equilibrium":



If there is such equilibrium we will have:

$$\frac{[As(III / or V)_{solution}]}{As(III)_{solution}} = K \text{ (Eq. 1).}$$

Then K must be constant. Discussion on this equilibrium will be below.

(As/Fe(III))_{solid} ratios in time course

If we take a differences between inlet and outlet average concentrations of iron and arsenic, and multiply them by flow then we got $(mAs/mFe)_{solid}$ ratios at predetermined filtering time. mAs and mFe represent mass of arsenic and iron in sludge detained in filtering bed. The dependence of $(mAs/mFe)_{solid}$ on filtering time was presented in figure 4.

What can we say about figure 4? Mostly they are straight lines, except the curve of $[As]_{inlet} = 1754.5$ ppb. It seems that except this curve all remained 5 curves were parallel.

Declining of $(mAs/mFe)_{solid}$ along the filtering time means adsorption capacity of ferrihydroxides cake detained under filtering layer is not exhausted, but due to limited contact time only a part of arsenic can be adsorbed. The other reason may be a morphological change of ferrihydroxide precipitate with the time that leads to lowering adsorption capacity of ferrihydroxide regarding to As. Meanwhile due to limited analytical facility we could not find exact As speciation, As(III) or As(V). Therefore question on the nature of the process is still open.

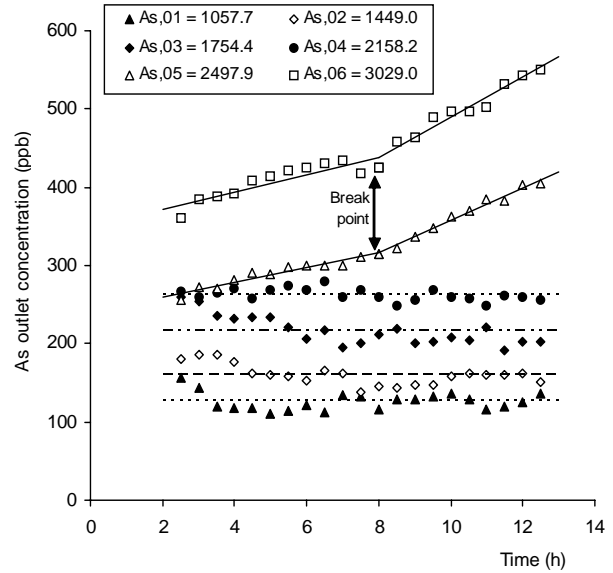


Figure 3. Arsenic removal by CF versus filtering time

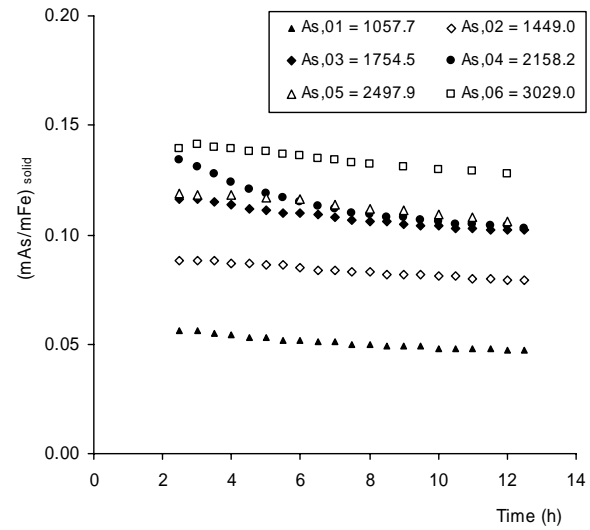


Figure 4. Dependence of (mAs/mFe)_{solid} on filtering time

Correlation between $s(\text{III})/\text{Fe}$ _{soluble} and $(\text{As}/\text{Fe}(\text{III}))$ _{solid}

Interestingly, if we calculate $(\text{As}(\text{III})/\text{Fe})$ _{soluble} ratios that means ratio between inlet concentrations of As and total Fe in six runs and put them in relation with above mentioned $(\text{As}/\text{Fe}(\text{III}))$ _{solid} ratios a relatively good linear independence was observed (figure 5).

This good independency serves as a potential measure for predicting arsenic removal capacity of proposed CF technique. On the other hand it is an evidence of accuracy of our experimental data.

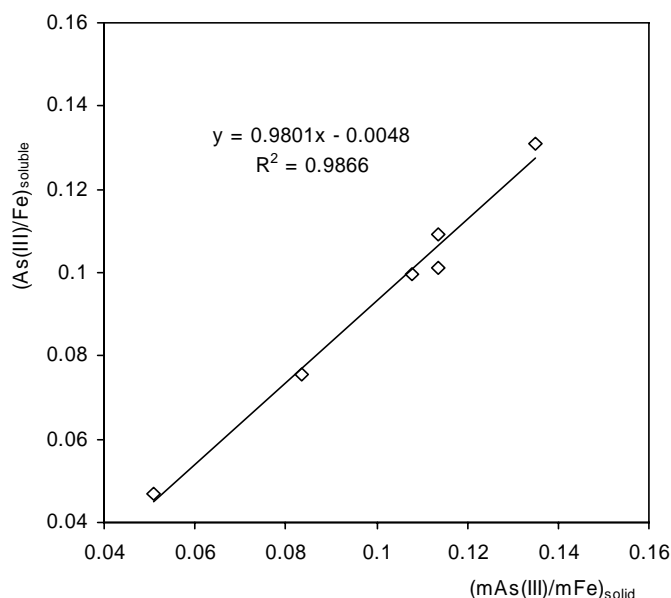


Figure 5. Relation between $(\text{As}(\text{III})/\text{Fe})$ _{solid} and $(m\text{As}/m\text{Fe})$ _{solid} in six runs

Evidence of a "dynamic adsorption equilibrium" and a K adsorption constant

In points 1 and 3 we just concerned possible adsorption equilibrium, but it must be not real thermodynamic one, because data of figure 4 show potential for further As adsorption on ferrihydroxides. If we calculate values of K in eq. (1) from our experimental data for six independent runs, we get results given in table 2.

Table 2. Values of K from data of six runs

<i>No of Run</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>
<i>K value</i>	0.119	0.111	0.123	0.122	0.114	0.134

Then $K_{\text{average}} = 0.1205$. Calculation of experimental error using confidence coefficient = 0.95 with $n = 6$, herein, Student statistic $t_s = 2.57$ gave fair result: $K = 0.1205 \pm 0.0085$. Then relative deviation was about 7%.

These results lead to thinking that there must be not a real thermodynamic adsorption equilibrium, but a dynamic one, therefore we can use either this K or dependence in figure 5 for predicting arsenic removal performance of our CF. Using these simple models one can easily extrapolate to broader range of iron contents. The application of CF instead of conventional settler can easily enhance arsenic removal by iron oxidation-filtering process. On the other hand, if additional oxidation is needed for better arsenic removal one can do it easily by adding oxidizing agent at the port M2 (figure 1) without significant change of whole construction.

Due to limited resource data were obtained just at the sole flow of $1 \text{ m}^3/\text{h}$ with one groundwater resource with very high Fe content. Therefore these models should be verified with groundwater resources with different Fe contents, and at different flows.

CONCLUSIONS

A simple and effective technological sequence for arsenic removal in combination with conventional iron removal from groundwater was proposed.

The performance of the main treatment unit-CF regarding to iron and arsenic removal efficiency was determined. As removal was around 88%.

Two simple models with good correlations were proposed, and a dynamic adsorption equilibrium model and corresponding K for arsenic adsorption on ferrihydroxides was proved.

These two models can be used for designing arsenic-iron removal facility, just know Fe and As concentrations in raw water.

ACKNOWLEDGEMENT

The authors thank a lot SDC's ESTNV project in financial support for experimental set-up, and also our friends-teachers Drs. Urs von Gunten, Michael Berg, Prof. Walter Giger from EAWAG for frequent and useful discussions and consultations. We are in deep acknowledgement our partners from Vietnam National University and Shimadzu Cooperation Joint Analytical Lab for providing a vast work in arsenic analysis.

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HỘI NGHỊ KHOA HỌC LẦN THỨ III
TRƯỜNG ĐẠI HỌC KHOA HỌC TỰ NHIÊN

**Khoa học - Công nghệ Môi trường
và Phát triển Bền vững**



**Tiểu ban Liên ngành:
Khoa học và Công nghệ Môi trường**

Hà Nội, 11 - 2004