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ARSENIC REMOVAL FROM WATER BY CHEMICAL OXIDATION AND ADSORPTION ON IN-SITU FORMED FERRIC HYDROXIDE

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Abstract

The efficiency of arsenic removal from groundwater by using chemical oxidation and adsorption on in-situ formed ferrihydroxide (FeOOH) was investigated in this study. Three popular oxidants (chlorine, permanganate, hydrogen peroxide) with different doses were used in the presence of Fe(II) to remove As(III) with concentration of about 200 µg/L. The results showed that As(III) was adsorbed well on in-situ formed FeOOH. However, arsenic concentration in treated water did not meet Vietnamese standard of 10 µg/L in oxygenation proccess of 8 mg/L Fe(II). Using chlorine and permanganate with content just enough for oxidation of Fe(II) can decrease arsenic content down to below 10 µg/L in ten minutes. However, H_2O_2 showed less effectiveness as compared to chlorine and permanganate. In addition, this study also indicated that the newer FeOOH, the more effective As removal by adsorption proccess.

1. Introduction

In Vietnam, 30% of supplied water was exploited from groundwater, which is better than surface waters in aspects of mocroorganisms, suspension and anthropogenic pollution. However, the content of dissolved minerals in groundwater is normally higher than that in surface water. Some groundwaters are contaminated by heavy metals such as Pb, Hg..., especially As. Recently, arsenic pollution in groundwater was found to be serious in Red River Delta [1]. In aqueous solution, arsenic occurs in valence states of +3 and +5 in inorganic or organic form. Under reductive condition of groundwater, arsenic mainly exists in inorganic form of the valence state of +3.

Arsenic is a highly toxic element. Its toxicity depends on valance state and existing form. Inorganic arsenic was found to be more toxic than organic – arsenic. As(III) is about 60 times more toxic than As(V). Long-term comsumsion of water containing arsenic content of 50 µg/L can raise cancer probability up to 13/1000 [2]. Arsenic can cause poisoning at very low doses and affect on many body organs. Due to human health effects, WHO had revised the maximum concentration limit (MCL) for arsenic in drinking water from 50 down to 10 µg/L in 1993. In 2001 USEPA adopted this value [3], and Vietnam accepted the same value in 2002. To adapt this strict regulation, numerous studies have been carried out and reviewed [4-6]. Arsenic treatment methods can be categorized into three main groups: (1) adsorption, (2) coagulation/precipitation, (3) membrane filtration.

In the first group, various adsorbents were examined such as oxides of Fe, Al, Mn, Zr or mixture of these oxides, activated carbon, ionic exchange resins. These adsorbents have different adsorption abilities and optimum pHs. Some materials for arsenic adsorption are now commercially available such as GFH^{TM} produced by Siemens, GTO^{TM} by Dow [7]. In Vietnam, a new material for As adsorption named MF97 was produced by Institute of Chemistry, Vietnam Academy of Sci. & Tech.. This product has adsorption capacity of 1 g As/kg at filtration rate of 6-8 BV/h. Our research group are developing another material with similar adsorption capacity based on a Vietnamese natural mineral pyrolusite.

In the second group, arsenic was removed by co-precipitation/adsorption phenonmenon in coagulation proccess using Fe(III) or Al(III) salts, or in softenning proccess using lime. Various reports on these methods showed that removal of As(V) is more effective than that of As(III) [8, 9].

Membrane filtrations include reverse osmosis (RO), nanofiltration (NF), ultrfiltration (UF) and electrodialysis (ED) proccesses having different arsenic removal efficiencies. RO and NF can remove nearly 100 % of arsenic. UF and ED are less efficient as compared to RO and NF. One of main disadvantage of membrane technique for Vietnam's situation is the high cost of investment.

In Vietnam there are 2 scales in supply water: (1) household tubewells and small facilities, (2) large plants. The biggest difference between 2 scales is system operating ability. The conventional adsorption-filtration is suitable for the first scale because of lacking of operating skills. Nevertheless, this proccess requires high investment for the second one, large scale, especially when As treatment as a retrofitting measure is needed. Hence, to solve arsenic problem for water supply in Vietnam, this study focused on coagulation/precipitation proccesses, the conventional, popular techniques in the history of water treatment. As mentioned above, using Al(III) or Fe(III) salts gives better results for As(V) as compared to As(III) [8, 9], meanwhile groundwater in Vietnam is commonly contaminated by iron(II) with concentration range of 5 – 10 mg/L, this values are quite common in drinking water coagulation technique. However, in cases with elevated arsenic content (above 60 ppb), water treated by conventional Fe(II) removal process (aeration/oxidation-settling-filtration) does not meet new Vietnamese standard for arsenic. Our survey showed that in Hanoi groundwater arsenic mostly exists in As(III) form. A feasible option to improve arsenic problem is oxidizing As(III) to As(V) that enables to use As(V) adsorption capacity on FeOOH *in-situ* formed during conventional Fe(II) treatment process. Chlorine, permanganate and hydrogen peroxide are strong oxidants and widely used in Vietnam. They can be promising agents for practice. This study evaluated their effect in model groundwater for further application.

2. Experimental part

2.1. Materials and chemicals

Distilled water was used to prepare chemical solutions, for experiments with chlorine, deionized water was used. Stock solutions of As(III) was prepared from As_2O_3 produced by Russia. Other chemicals (oxidants, $FeCl_2$, NaOH, HCl, $NaNO_3$,...) were obtained from Chinese chemical companies and used without further purification. 1-mL polyethylene tip packed with 0.8 g of As(V) selective aluminosilicate adsorbent was used for removing As(V) from samples. Equipments used in this study are: pH, DO meters, magnetic stirring plate, spectrophotometer.

2.2. Experimental procedures

Arsenic removal efficiency of chemical oxidation and adsorption process was examined as follow:

a. As(III) removal in Fe(II) oxidation by air oxygen, the case of in-situ *formed FeOOH*

This experiment was conducted in 500 mL of 0.01 M $NaNO_3$ solution under genlte mixing condition. After adding stock solution of As(III) to gain required concentration (about 200 µg/L), a given amount of Fe(II) solution was added to solution, then pH of reaction solution was adjusted to 7. Three different Fe(II) concentrations (2, 5, 8 mg/L) represent for typical iron contents in groundwater were used in this study. Others condition of this experiment was given in table 1.

Table 1. Conditions for As(III) removal in Fe(II) oxidation by air-oxygen

Item	**$[Fe(II)]_0$** mg/L	**$[As(III)]_0$** µg/L	**pH**	**Temp.** °C	**DO** mg/L	*$NaNO_3$* ***M***
Value	2, 5, 8	~ 200	7.0 – 7.2	23 – 25	7.3 – 8.7	0.01

During experiments, samples were collected in time interval of 10 minutes for analyzing concentration of aqueous Fe(II) and As. Fe(II) was analyzed by 1, 10 – orthophenaltroline method.

As samples were filtered through 0.45 μm membrane and preserved in HCl solution (pH<1) then analyzed by ICP method. According to M.J. Kim [10], As(III) was very slowly oxidized by air-oxygen, therefore it assumes that remaining arsenic in fitrate is As(III).

b. As(III) removal by adsorption on newly formed ferric hydroxide (FeOOH)

Arsenic adsorption efficiency may be different, depending on As(III) was added before or after completion of Fe(II) oxidation. To varify this fact, As(III) adsorption on newly formed FeOOH was carried out. Conditions for this experiment were the same as given in table 1. But one change in procedure was that stock solution of As(III) was added after Fe(II) oxidation completion. In this experiment, samples were also collected in time intervals, filtered through 0.45 μm membrane and preserved in HCl solution (pH<1) for arsenic analysis.

c. As(III) removal by using chemical oxidation and adsorption on in-situ formed FeOOH

Three oxidants (clorine, permanganate, hydrogen peroxide) were used to improve arsenic adsorption on FeOOH. Due to negligible oxidant demand for small amount of As(III), oxidant doses used were calculated just enough for Fe(II) oxidation. Initial Fe(II) concentrations were 2, 5, 8 mg/L. Conditions for experiments of each oxidant are given in tables 2, 3, 4.

Table 2. Conditions for As(III) removal using $KMnO_4$

Items	**[Fe(II)]$_0$** mg/L	**[As(III)]$_0$** μg/L	**pH**	**Temp.** °C	**DO** mg/L	**$NaNO_3$** M	*$KMnO_4$* ***mg Mn(VII)/L***
No. 1	2	213	6.8	25	7.1	0.01	0.65
No. 2	5	200	6.8	28	6.6	0.01	1.64
No. 3	8	213	7.2	27	6.8	0.01	2.62

Table 3. Conditions for As(III) removal using Cl_2

Items	**[Fe(II)]$_0$** mg/L	**[As(III)]$_0$** μg/L	**pH**	**Temp.** °C	**DO** mg/L	**$NaNO_3$** M	*Cl_2* ***mg/L***
No. 1	2	208	7.3	25	6.7	0.01	2.6
No. 2	5	200	7.2	26	6.9	0.01	6.34
No. 3	8	179	7.1	25	7.3	0.01	10.4

Table 4. Conditions for As(III) removal using H_2O_2

Items	**[Fe(II)]$_0$** mg/L	**[As(III)]$_0$** μg/L	**pH**	**Temp.** °C	**DO** mg/L	**$NaNO_3$** M	***H_2O_2*** ***mg/L***
No. 1	0	185	6.9	25	-	0.01	0.63
No. 2	2	188	6.9	26	-	0.01	0.63
No. 3	5	180	6.9	25	-	0.01	1.53
No. 4	8	177	7.0	26	-	0.01	2.43

In the experimental procedure, after adding As(III), Fe(II) to gain required concentration and adjusting pH to 7, oxidant was added last. During experiment, samples were taken after every 10 minutes, filtered in to quenching agent (ascorbic acid) then quenched samples were divided in to two portions. The first portion was preserved in HCl solution (pH<1) for total arsenic analysis. The second one was filtered through cartridge containing aluminosilicate to remove As(V), and the filtrate was preserved in HCl for As(III) analysis.

3. Results and discussion

3.1. As(III) removal in Fe(II) oxidation by air oxygen, the case of in-situ *formed FeOOH*

The results of Fe determination indicated that Fe(II) was completely oxidized during first 5 minutes. Hence, in following experiments with the time interval of 10 minutes, oxidized iron was assumed to be in the form of FeOOH. The depletion of aqueous As(III) due to adsorption on solid FeOOH accompaning with Fe(II) oxygenation was depicted in figure 1.

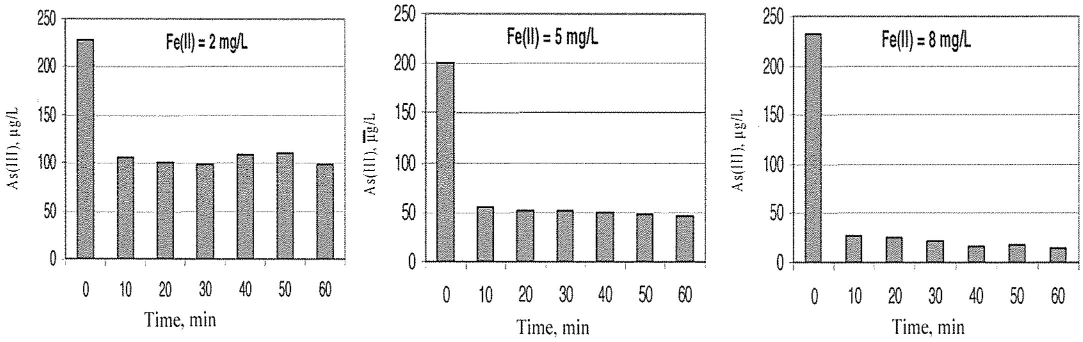

Figure 1. Variation of aqueous [As(III)] with time in Fe(II) oxygenation experiments

As discussed, As(III) was hardly oxidized by air oxygen. So the obtained results enable us to make some conclussions:

- Considerable amount of As(III) was removed by adsorption on *in-situ* formed FeOOH in Fe(II) oxygenation proccess.
- Increasing Fe(II) concentration resulted in higher treatment efficiency – with initial As(III) of about 200 µg/l, the removal yields for initial Fe(II) concentrations of 2, 5, 8 mg/L were 56, 77, 93 % after 1 hour. However, As content in treated water did not meet new standard (10 µg/l) even with Fe(II) concentration up to 8 mg/L.
- Results on figure 1 showed that in first 10 minutes when Fe(II) oxidation and fast Fe(III) hydrolysis happened, adsorption was really fast and most effective. After this stage, adsorption was much less slow. To verify the last conclussion, the rate of As(III) adsorption on newly formed FeOOH was evaluated and the results was shown in the next part.

3.2. As(III) removal by adsorption on newly formed ferric hydroxide (FeOOH)

Conditions of this experiment was the same as that of the Fe(II) oxygenation experiment. A difference in procedure was that As(III) was added after completion of Fe(II) oxidation. The variation of aqueous [As(III)] was analysed and represented in figure 2.

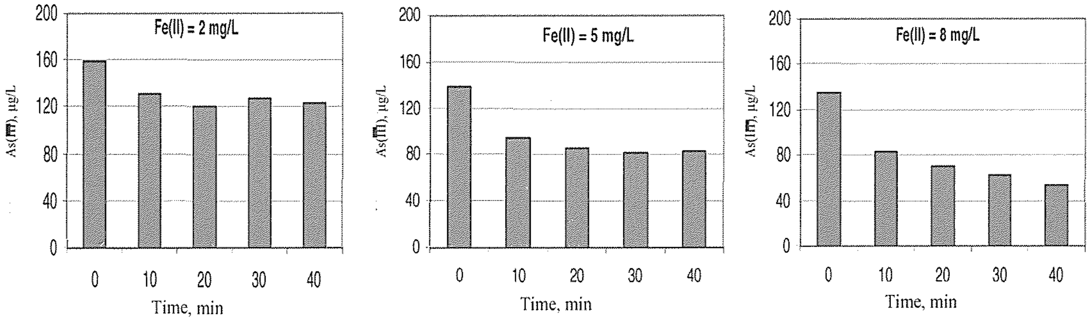

Figure 2. As(III) adsorption on newly formed FeOOH

Figure 2 confirmed that the rate of As(III) adsorption on readily formed FeOOH after Fe(II) oxidation was less effective than that during *in-situ* Fe(II) oxidation as described in previous paragraph. After 1 hour, the yields of this proccess were only 23, 40, 60 % for initial Fe(II) concentrations of 2, 5, 8, respectively. The lower efficiency was due to changes of FeOOH morphology leading to decreases in active surface area of solid FeOOH. This phenomenon was also evidenced by our earlier study in which 1-month aged FeOOH was used. The results showed that As(III) content decreased 13 % (from 150 down to 130 µg/L) after 1 hour when using 500 mg/L FeOOH (corresponding to 323 mg Fe/L). It means that the older FeOOH, the lower adsorption efficiency.

From achived data, it can conclude that some groundwaters contaminated by arsenic of about 200 µg/L, conventional Fe(II) oxygenation of Fe content below 8 mg/L could not remove arsenic to meet required value of 10 µg/L. To solve this problem, oxidants were tested to oxidize As(III) to As(V) that should lead to better As adsorption capacity. Early research on kinetics of As(III) oxidation showed that chlorine can extremely fast oxidize As(III) to As(V), reaction rate constan k = $2.6\ 10^5\ M^{-1}s^{-1}$ [11]. This study tested three oxidants (chlorine, permanganate, hydrogen peroxide) in the presence of Fe(II).

3.3. As(III) removal by using chemical oxidation and adsorption on FeOOH

Using $KMnO_4$

$KMnO_4$ doses were taken just enough for oxidation of Fe(II). During experiment, samples were taken in 10-min. time interval, filtered and handled as described above for As(III), total As analysis. Concentrations of As(III), As(V) at different time were presented in figure 3.

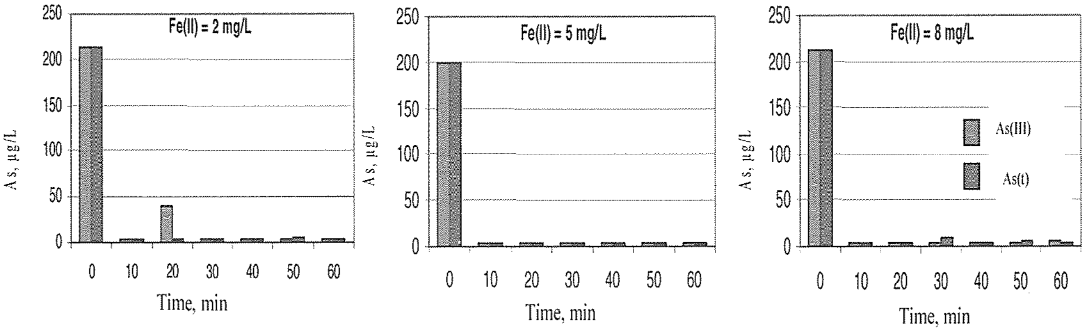

Figure 3. Variation of arsenic species in aqueous solution when using $KMnO_4$

The results indicated that $KMnO_4$ considerably enhanced As treatment, As concentration in treated water was below 10 μg/L. The yield of As removal reached 98 % with the lowest Fe(II) content of 2 mg/L within 10 minutes.

Using Cl_2

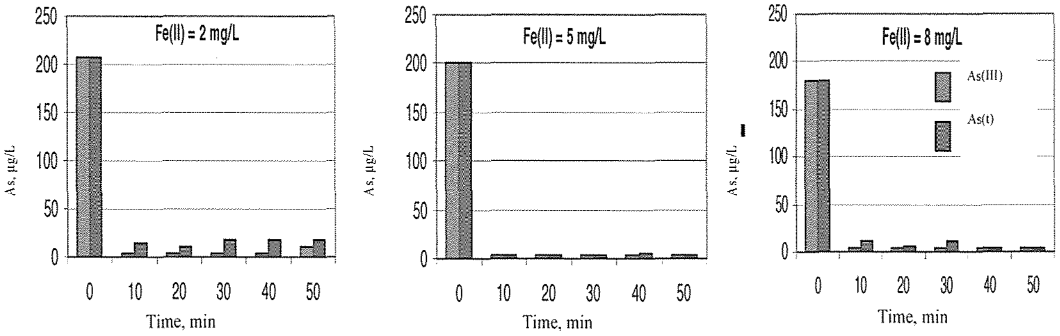

Figure 4. Variation of arsenic species in aqueous solution when using Cl_2

This experiment was conducted with the same procedure as for $KMnO_4$. Chlorine used were equivalent to $KMnO_4$. Variation of concentration of arsenic species was depicted in figure 4.

As stated above, chlorine reacts with As(III) very fast. It can see in figure 4 that As(III) concentration decreases quickly in first ten minutes. However, to meet standard for arsenic, in this case Fe(II) content was required to be 5 mg/L – corresponding to 98 % As removal. Compared to results for $KMnO_4$, efficiency of using Cl_2 was a little lower. This phenonmenon can be explained by the formation of MnO_2 when using $KMnO_4$. Formed MnO_2 can catalyticaly oxidize As(III), and adsorb both As(III) and As(V) on its surface.

Using H_2O_2

Concurrent presence of Fe(II) and H_2O_2 can lead to Fenton proccess. However, Fenton proccess is most powerfull at pH of 3 – 4. At pH of the experiment of about 7, effect of Fenton reaction may not be significant. Results in figure 5 and 6 proved this fact.

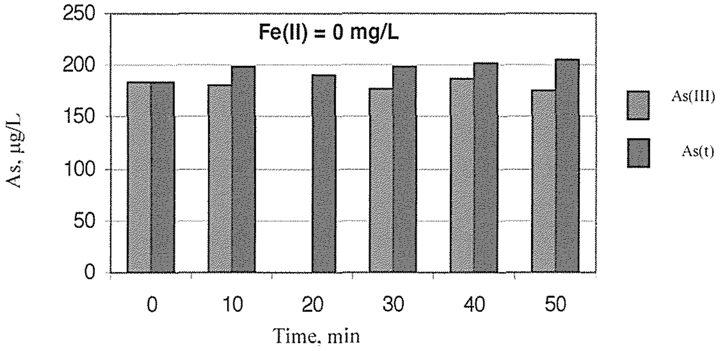

Figure 5. Arsenic species in solution at different time ($[H_2O_2]_o = 0.63$ mg/L, $[Fe(II)]_o = 0$ mg/L)

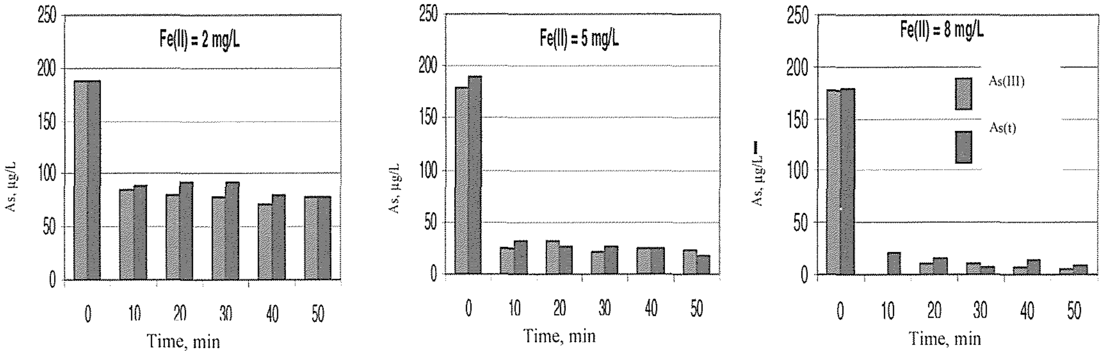

Figure 6. Variation of arsenic species in aqueous solution when using H_2O_2

The run without Fe(II) (Fig.5) revealed that in aqueous solition H_2O_2 did not oxidize As(III). In the presence of Fe(II), using H_2O_2 (Fig.6) could raise As adsorption as compared to Fe(II) oxygenation preccess as showed in table 5. But the use of H_2O_2 was less effective than that of Cl_2 or $KMnO_4$. To lower As content from about 200 µg/L down to below 10 µg/L (95 % removal), it required Fe(II) concentration of as high as 8 mg/L. This result seemed that Fenton reaction played insignificant role in the proccess.

Table 5. Comparation of As treatment by using H_2O_2 and O_2 in the presence of Fe(II)

$[Fe(II)]_o$, mg/L	2	5	*8*
O_2	57 %	77 %	94 %
H_2O_2	58 %	90 %	95 %

4. Conclusion

Arsenic(III) well adsorbed on *in-situ* formed FeOOH during Fe(II) oxygenation proccess, older FeOOH had lower adsorption yield.

However, the presence of 8 mg Fe(II) could not lower As(III) content of about 200 µg/L to meet new Vietnamese As standard of 10 µg/L.

Chlorine and permanganate owning to extremely fast As(III) oxidation considerably enhanced arsenic removal by oxidation and adsorption on *in-situ* formed FeOOH. In artificial groundwater, initial As(III) concentration of about 200 µg/L can be reduced below 10 µg/L with 2 and 5 mg Fe(II)/L when using permanganate and chlorine, respectively. Hydrogen peroxide could also improve As(III) treatment efficiency, but much less effective than chlorine and permanganate did.

The results of this study suggest an alternative method to improve arsenic removal of conventional water treatment plants, which were designed only for iron removal. The suggestion is that using common oxidants, such as chlorine and permanganate to oxidized As(III) to As(V) before filtration step in treatment sequence. But before application at full scale, pilot scale should be tested to evaluate effects of contaminants such as amonia (for chlorine), photphate, sillicate... in real groundwater.

Acknowledgment

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References

1. Pham Hung Viet, Pham Thi kim Trang, Michael Berg, Nguyen Thi Minh Hue, Bui Hong Nhat, Vi Thi Mai Lan, Tran Thi Hao, Pham Thi Dau, Vu Thi Mai, Nguyen Van Mui (2004) *Risk of arsenic contamination at tubewell in red river delta*. The 3rd HUS Scientific Conference – Division of env. tech. & sust. Dev., Hanoi University of Science, pp 1- 7.
2. F.W. Pontius, K.G. Brown, J.C. Chen (1994) *Health implications of arsenic in drinking water*. J. Am. Water Works Assoc. , V. 86, 52–63.
3. USEPA (2001) National primary drinking water regulations; *Arsenic and clarifications to compliance and new source contaminants monitoring;* Final rule. Federal Register, Part VIII, 40 CFR Parts 9, 141, and 142. US Government Printing Office, Washington, DC.
4. USEPA 816-R-03-014 (2003) *Arsenic Treatment Technology Evaluation Handbook for Small Systems,* EPA, July 2003.
5. M. Bissen, F.H. Frimmel (2003) *Arsenic – a Review. Part II: Oxidation of Arsenic and its Removal in Water Treatment.* Acta hydrochim. hydrobiol. V. 31, No. 2, pp. 97–107.
6. Kuan-Seong Ng, Zaini Ujang & Pierre Le-Clech (2004). *Arsenic removal technologies for drinking water treatment* Reviews in Environmental Science and Bio/Technology 3, pp.43–53.

   http://www.industry.siemens.com/water/en.
7. P.K. Dutta, A.K. Raya, V.K. Sharma, F.J. Millero (2004) *Adsorption of arsenate and arsenite on titanium dioxide suspensions*, J. of Coll. and Interface Sci., 278, pp. 270 – 275.
8. B.K. Mandal, K.T. Suzuki (2002) *Arsenic round the world: a review*, Talanta, 58, pp.201- 235.
9. M.J. Kim, J. Nriagu (2000) *Oxidation of arsenite in groundwater using ozone and oxygen.* The Science of the Total Environment 247, pp. 71-79.
10. M.C. Dodd, V.N. Duy, A. Ammann, L.V. Chieu, R. Kissner, P.V. Viet, C.T. Ha, M. Berg, and U. von Gunten (2006) *Kinetics and Mechanistic Aspects of As(III) Oxidation by Aqueous Chlorine, Chloramines, and Ozone: Relevance to Drinking Water Treatment,* J. of Eviron. Sci. & Technol., V. 40, No 10, pp. 3285-3292.