

Studies on Removal of As(III) by Several Types of Ferrated Salt in Aqueous Medium

Guiqiu Liu, Qingsong Liu, Xingchun Zhu, *Member, IAENG*

Abstract—The element arsenic usually exists mainly as As(III) and As(V) in aqueous medium, and the migration and toxicity of arsenite are higher than those of arsenate. In order to improve the removal efficiency of arsenic, As(III) is generally oxidized to As(V). There are many kinds of methods to remove arsenic in an aqueous medium. When compared with others, coagulation and precipitation in ferrated sulfate salt is relatively simple and economical, which is suitable for use in remote rural locations. Because the As(III) is the main form of arsenic in groundwater, its transformation and removal are of widespread concern. In this paper, the behaviour of As(III) being removed in aqueous medium by FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$ and polymeric ferric sulfate (PFS) were investigated. It was found that when increasing amounts of sulfate ferrated salts are added the corresponding As(III) removal rates increased gradually until a limiting state was reached. The treatment effect of chemical agents can be shown as $\text{PFS} > \text{Fe}_2(\text{SO}_4)_3 > \text{FeSO}_4$. The data for arsenite removal rates fitted the Langmuir equation well. The As(III) removal rates were influenced by pH, and the optimal removal rate of arsenic occurred at pH 7~9. Adsorption and co-precipitation could be the removal mechanism of As(III).

Index Terms—Arsenite, Coagulation, Co-precipitation, Ferrated salt, pH

I. INTRODUCTION

Elevated levels of arsenic concentration are often present in the environment due to both natural and anthropogenic sources, including weathering of rocks, industrial products and wastes, agricultural use of herbicides containing arsenic and pesticides, wood preservatives, and mine drainage [1]. Hyperpigmentation or hypopigmentation, skin, internal cancers, cardiovascular and neurological disorders have been found to be attributed to chronic arsenic exposure via drinking water. These adverse health effects have been observed in endemic arsenic poisoning areas [2-4]. Various treatment technologies have been used to remove arsenic from water. The routine methods include coagulation (precipitation), adsorption, ion exchange, membrane

Manuscript received October 28, 2008. This work that has been presented in this paper was supported by the Chinese foundation committee of nature and science, under the projects, No.50576078.

Guiqiu Liu: full-time PhD student. Institute of Environmental Engineering, School of Dynamics and Energy, Northwestern Polytechnical University, Xi'an, ShaanXi, 710072, China (phone: +86-029-88492440; fax: +86-029-87293429; e-mail: liu-guiqiu@tom.com).

Qingsong Liu, Corresponding author of the paper, lecturer, Department of Clinical Laboratory, Affiliated Hospital Northern Sichuan Medical college, Sichuan Nanchong 637000, China (phone: +86-0817-2247431; e-mail: liuqingsong00@yahoo.com.cn).

Zhu Xingchun: lecturer, Department of Clinical Laboratory, Affiliated Hospital Northern Sichuan Medical college, Sichuan Nanchong 637000, China.

filtration, electrocoagulation and biological process, etc [4-10]. Among these treatment processes, coagulation is most promising for arsenic removal from water containing high levels of arsenic. This method has been widely used in developing countries owing to the low cost and high efficiency for the removal of arsenic, turbidity and color [11].

The coagulation process is traditionally performed by adding ferric or aluminum ions. Coagulation with ferric ions for arsenic removal can be traced back to the late 1960s in Taiwan to treat deep-well water with naturally elevated arsenic concentrations [4]. Since then, there had a lot of reports on coagulation process for arsenic removal. It has been reported that the removal of As(V) was more effective than that of As(III) by coagulation. In this case, As(III) should be preoxidized before the process of oxidation to As(V), and then be coagulated. The complicated disposal process and high-cost for input of chemical agents may result in unacceptable levels of disinfection by-products. Thus studies of removal efficiencies for As(III) can provide insights into the general mechanisms for removal of trace inorganic contaminants by coagulants, and are helpful for water treatment. In this work, several types of ferrated sulfate, such as polymeric ferric sulfate (PFS), ferric sulfate (FS(III)) and ferrous sulfate (FS(II)), were chosen as coagulants, and the removal effect was studied for simulate sewage containing As(III). The influencing factors for removal effect, such as pH, the molar ratio of ferric and As(III), and PAM, were also investigated.

II. MATERIALS AND METHODS

A. Standards and reagents

All chemicals were reagent-grade and were used without purification. All solutions were prepared with deionized water and all glassware was acid-washed. NaAsO_2 was used to prepare arsenite standard solution. Secondary arsenic stock solution was always freshly prepared from the arsenic stock solution by dilution with deionized water. Ferric stock solutions (1000 mg/L Fe^{3+}) were prepared with PFS, $\text{Fe}_2(\text{SO}_4)_3$ and FeSO_4 respectively, and stored in a dark polyethylene bottle. Their secondary stock solutions were prepared immediately before use.

Background electrolyte solutions were prepared with NaNO_3 and NaHCO_3 . Stock solutions were sonicated for 30 min in a sonicating bath prior to each experiment.

B. Coagulation experiments

Coagulation experiments were conducted with a background electrolyte of 0.01 M NaNO_3 and 0.001M NaHCO_3 . Test solutions were contained in 1.0 L cylindrical beakers and mixed using a variable-speed, flat-paddle stirrer. Before coagulant adding, the pH of 1.0 L of the background

electrolyte was pre-adjusted to the desired value (± 0.1 pH unit) with addition of 0.1 M HCl or NaOH. Solutions were amended for the specific experiment and spiked with As(III) to the desired concentration. Predetermined concentrations of NaOH were added simultaneously with the coagulant under rapid-mix conditions: 5 min rapid-mix at 100 rpm, 5 min slow mix at 45 rpm, and 30 min quiescent settling. After the settling period, about 100 mL solution was collected using a 20 mL disposable syringe from 2 cm below the liquid surface and filtered using a vacuum filter flask assembly.

C. Sorption isotherms

Adsorption studies of As(III) were carried out at pH 7.0 by adding aliquots of As(III) to ferric suspensions in centrifugation tubes (40 g/L). The suspensions with As(III)-containing solution and blank solutions were placed in a reciprocal shaker at 25 °C for 24 h. The pH of the suspensions and blank solutions was measured with a PHS-3 meter (Shanghai Rex Instrument Factory). The suspensions were then centrifuged and filtered through 0.20- μ m cellulose membranes afterwards.

D. Analysis

Arsenic levels were determined by the molybdenum blue spectrophotometric method [12]. Ferric concentration was determined by 1,10-phenanthroline spectrophotometric method [13].

III. RESULTS AND DISCUSSION

A. Effects of Fe dosage on arsenite removal

Figure 1 shows the relationship between the molar ratio of Fe / As(III) and As(III) removal at pH 7.0 with 10 mg/L As(III) initial concentration. As(III) removal rates increase till equilibrium at six of Fe^{3+}/As and eight of Fe^{2+}/As , respectively. As(III) removal rate by PFS was over 90%, which was higher than that by $\text{Fe}_2(\text{SO}_4)_3$. The residual As(III) concentration was below 0.4 mg/L. The removal rate by FeSO_4 was only 80%, less than that by PFS and $\text{Fe}_2(\text{SO}_4)_3$, and the residual As(III) concentration was about 2 mg/L.

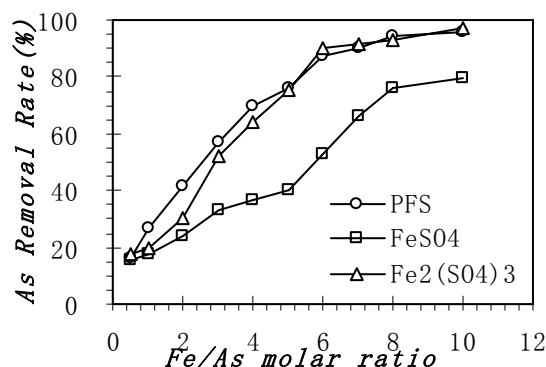
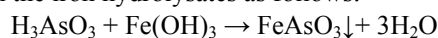


Fig.1 As(III) removal rate during coagulation with ferric

Trivalent arsenic exists in anionic form of H_3AsO_3 , H_2AsO_3^- or HASO_3^{2-} when pH was in the range of 5-12 typically encountered in water treatment. Hence, adding iron coagulant to water could facilitate the conversion of soluble arsenic species to insoluble reaction products. These products might form through three major mechanism: (i)

precipitation, forming $\text{Fe}(\text{AsO}_3)$ deposition; (ii) coprecipitation, soluble arsenic species were incorporated into a growing hydroxide phase via inclusion, occlusion, or adsorption; and (iii) adsorption, involving the formation of surface complexes between soluble arsenic and the solid hydroxide surface site. In terms of arsenic removal from drinking water, however, precipitation may not contribute significantly toward the overall performance. Solid FeAsO_3 could not be easily formed for thermodynamic calculation in arsenic contaminated water source. The polynuclear complexes of iron hydrolysis intensely adsorbed colloid particle as well as water-soluble As(III) from wastewater, thus As(III) was removed through the reactions such as adsorption, bridging, crossing linking of colloid particles, and formed the cotton-shape coagulation precipitation. Meanwhile, H_3AsO_3 could be removed effectively by iron ion and form FeAsO_3 precipitates, which deposited together with the iron hydrolysates as follows:



It could be seen that, there is a little difference for As(III) removal with the same amount of Fe added in form of PFS and $\text{Fe}_2(\text{SO}_4)_3$. It was possible related with the same quantity of final hydrolysates of PFS and $\text{Fe}_2(\text{SO}_4)_3$. Hence, As(III) removal was mainly affected by Fe hydrolysate, further suggesting that the main removal mechanism are adsorption and the co-precipitation. As the hydrolyzation of ferrous ion was weaker than that of ferric ion, and the stability of the complex produced with Fe^{2+} and As(III) was weaker than that of the later, the removal rate with ferrous was smaller than that of ferric.

B. Effects of As(III) initial concentration on arsenite removal

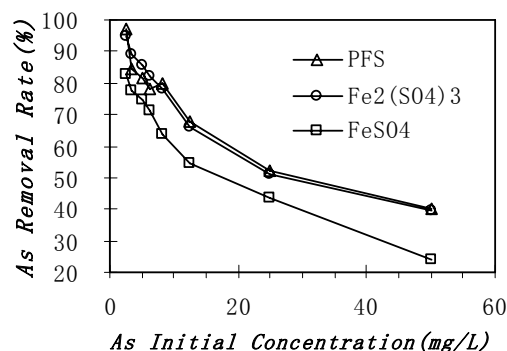


Fig.2 Relationship between As(III) initial concentration and As(III) removal rate

Figure 2 shows the relationship between As(III) initial concentration and As(III) removal rate by several kinds of molysite at pH 7.0. Each kind of molysite contains 5 mg Fe. As(III) removal rate reduced with increasing initial As(III) concentration. Presence of more than 20 mg/L has no pronounced effect. The overall As(III) removal rates were about 70%. The possible explanation is that the amount of adsorption sites or combine sites was not enough for As(III) adsorption or complexation as Fe was added in a little dosage,

Table1 Coefficients of Langmuir equation fitting of As(III) removal

Coagulant	$C_e/q = a/q_{max} + C_e/q_{max}$	R	Se	q_{max} mg/g
PFS	$C_e/q = 0.002 C_e + 0.010$	0.977	0.006	434.8
Fe ₂ (SO ₄) ₃	$C_e/q = 0.002 C_e + 0.009$	0.976	0.006	416.7
FeSO ₄	$C_e/q = 0.004 C_e + 0.013$	0.997	0.004	263.2

Where q is the uptake capacity, q_{max} is the maximum uptake capacity, C_e is the equilibrium concentration, a , binding constant(L/mg), R , correlation coefficient and Se is the standard deviation.

whereas the amount of As(III) in water was relatively too large.

Along with the increasing residual As(III) concentration, As(III) adsorptive capacity increased markedly first, then the amplitude decreased and gradually reach to the equilibrium state (Figure 3). The Langmuir adsorption model was employed to fit the adsorption data. As shown in Table 1, As(III) removal data fit Langmuir adsorption equation model well ($P < 0.05$). It was further suggested that the dominant mechanism of As(III) removal in coagulation process was As(III) adsorption reaction, and the surface coverage degree of adsorbent was the important factor for As(III) adsorption removal. The apparent maximum As(III) uptake capacity of PFS was a little more than that of Fe₂(SO₄)₃ and FeSO₄. The uptake capacity by FeSO₄ was only 263.2 mg/g and it's the minimum in PFS, Fe₂(SO₄)₃ and FeSO₄.

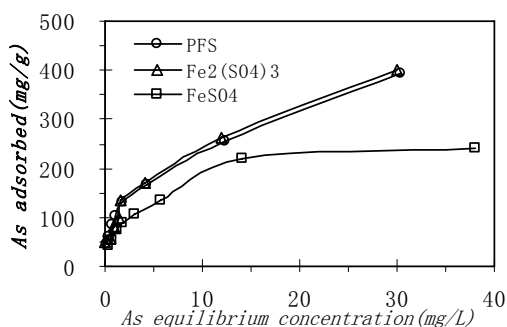


Fig. 3 As(III) isothermal adsorption curve

C. Effects of pH on arsenite removal

The results of coagulation experiments performed on the pH range 3 to 10 were shown in Figure 4 with As(III) initial concentration of 10 mg/L and the molar ratio of Fe/As(III) of 8. Increasing pH gives rise to similar effects on As(III) removal rates by three kinds of molysite. The removal rate increased observably with pH increasing from 3 to 7. The increased extent was about 40%, it maintained stable basically at solution pH 7~9, and then decreased with solution pH increasing at pH>9, the maximum removal rate achieved 99.3%.

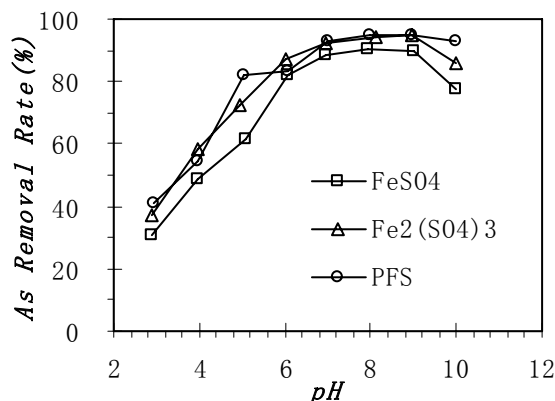
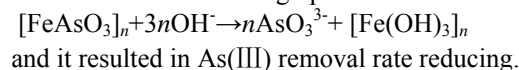


Fig.4 Effects of pH on As(III) removal rate

It is most likely that the species of Fe(III) and As(III) in water were affected strongly by pH. H₃AsO₃ was the primary As(III) species at pH<9, and H₂AsO₃⁻ was the primary As(III) species when pH was over 9 for As(III) in water. The amount of Fe(OH)₃ or Fe(OH)₂ produced by Fe hydrolysis increased with pH elevating, and the tendency of ferric arsenite precipitates produced enhanced, that resulted in the As(III) removal efficiency increased. Ferric hydroxide is produced fast by Fe(III) hydrolysis at pH 3 -7, and As(III) can be removed by the adsorption of fresh colloid due to its large surface area and adsorptive capacity. Most of the Fe ions were hydrolyzed when pH was over 7. Therefore, the extent of As(III) removal rate changed a little at pH 7~9. With continuously increasing pH and OH⁻ quantity at pH>9, the negative charge of ferric hydroxide colloid surface by adsorption OH⁻ increased, and the repel function to H₂AsO₃⁻ was enhanced. The adsorption site position competed by OH⁻ and As(III) was strengthened too, the adsorptive capacity of Fe(OH)₃ for As(III) reduced. In addition, ferric arsenite would also dissolve at high pH as below:

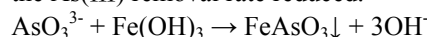


and it resulted in As(III) removal rate reducing.

Meanwhile, H₃AsO₃ was an amphoteric meta-acid compound although it's easier to hydrolysis at pH>9, there was a balanced reaction in water as follows:



The amount of As(III) in ionic form increased with the pH increasing, and the reversion of the reaction increasing, thus the As(III) removal rate reduced.



As the hydrolysis speed of Fe^{3+} was quick, and it was completed nearly instantaneously in microsecond level, but that of Fe^{2+} was slow, especially at low pH. The oxidation process also progressed with difficulty, so As(III) removal efficiency was low. A elevated pH levels the ferrous hydrolysis sped up, which promoted the ferrous oxidation, and As(III) removal rate increased fast, but always less than that of Fe^{3+} .

D. Effects of polyacrylamide (PAM) on arsenite removal

Being a linear structure, the high polymer flocculant may form polymer bridge between each solid pellet with long distance, namely, it adsorbs some solid phase pellet in an end and another solid phase pellet in another end in water, and that the pellets combine with the high polymer material bridging function increased gradually to form big flocculation finally, which accelerated the coagulation formation and precipitation. Thus, a little polymer flocculation added during coagulation can lead to a strong co-precipitated reaction and an elevated As(III) removal.

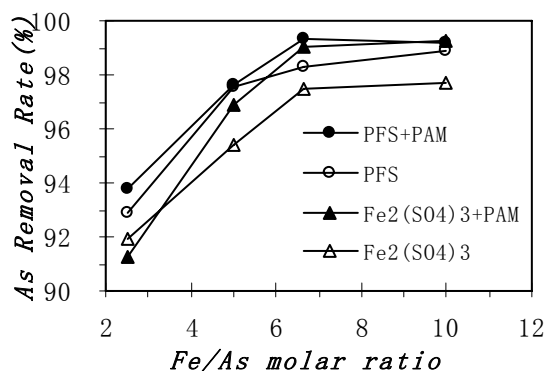


Fig.5 Effects of PAM on As(III) removal rate

Figure 5 shows relationship between As(III) removal rate and PAM addition at pH7.0, Fe dosage being 10 mg, the molar ratio of Fe and As(III) being distributed 2.5~10. As illustrated in Figure 5, different As(III) removal rates by several kind of molysite were observed after the addition of PAM. Big flocculation pellets could be rapidly formed after PAM addition with rapid subsidence and obvious lamination. Only small flocculence particles were formed and the subsidence was relatively slow without adding PAM, indicating that PAM might speed up the coagulation sedimentation rate, but could not enhance As(III) removal rate, and As(III) was removed mainly by Fe (III) adsorption. The PAM could not combine with As(III) to form a complex but only functions as a bridge, net catch to the colloidal particle in water, which accelerated the colloidal particle subsidence.

IV.CONCLUSION

For As(III) removal by coagulation, Fe(III) was more effective than Fe(II), and the equilibrium removal rate exceed 90% by both PFS and Fe₂(SO₄)₃, and that by PFS was more than that by Fe₂(SO₄)₃. As(III) removal by Fe(II) coagulant in water was the least as it had strong hydrolyzation ability and weak stability for the complex produced by the

reaction of iron and As(III). The equilibrium removal rate is only 80%. The experimental conditions used and compatibility of the results with the isothermal adsorption equation model indicates that As(III) adsorption on iron hydrolysate and co-precipitation process were the dominant mechanism of As(III) removal. As(III) removal was effected by pH, Fe/As molar ratio, high polymer flocculant. pH is important for the wastewater disposal effect, and the optimal pH value should be controlled in the range of 7~9. Fe/As molar ratio was also important for the removal efficiency. When Fe/As molar ratio was more than 5, pH was controlled at 7.0, the residual As(III) concentration in treated wastewater may drop to below 0.4 mg/L. PAM might effectively enhance As(III) sedimentation, but only had a little influence on As(III) removal.

ACKNOWLEDGMENT

We thank Prof.Hefei Zhang and Dr. Lixi Zhang, Institute of Environmental Engineering, School of Dynamics and Energy, Northwestern Polytechnical University, China, for their warmhearted help and advice in revising this paper. Comments from anonymous reviewers significantly improved the manuscript too.

REFERENCES

- [1] D.K. Bhumbra, R.F. Keefer, in: J.O. Nriagu (Ed.), 1994, *Arsenic in the Environment*. Part I: Cycling and Characterization, John Wiley & Sons, New York, pp. 51–82.
- [2] Morales, K.H.; Ryan, L.; Kuo, T.L.; Wu, M.M.; Chen, C.J, 2000. Risk of internal cancers from arsenic in drinking water. *Environ. Health Perspect.* 108(7), pp. 655–661.
- [3] Kaltreider, R.C.; Davis, A.M.; Lariviere, J.P.; Hamilton, J.W, 2001. Arsenic alters the function of the glucocorticoid receptor as a transcription factor. *Environ. Health Perspec.* 109(2), pp. 245–251.
- [4] Shen, Y.S, 1973. Study of arsenic removal from drinking water. *J. Am. Water Works Assoc.* 65(8), pp. 543–547.
- [5] Arienzo, M., Adamo, P., Chiazzelli, J., Bianco, M.R., de Martino, A., 2002. Retention of arsenic on hydrous ferric oxides generated by electrochemical peroxidation. *Chemosphere* 48, pp. 1009–1018.
- [6] Hering, J.G., Chen, P.Y., Wilkie, J.A., Elimelech, M., Liang, S., 1996. Arsenic removal by ferric chloride. *J. AWWA* 88 (4), pp. 155–167.
- [7] Katsoyiannis, I.A., Zouboulis, A.I., 2004. Application of biological processes for the removal of arsenic from groundwaters. *Water Res.* 38, pp. 17–26.
- [8] Korngold, E., Belayev, N., Aronov, L., 2001. Removal of arsenic from drinking water by anion exchange. *Desalination* 141, pp. 81–84.
- [9] Kumar, P.R., Chaudhari, S., Khilar, K.C., Mahajan, S.P., 2004. Removal of arsenic from water by electrocoagulation. *Chemosphere* 55, pp. 1245–1252.
- [10] Sato, Y., Kang, M., Kamei, T., Magara, Y., 2002. Performance of nanofiltration for arsenic removal. *Water Res.* 36, pp. 3371–3377.
- [11] Wickramasinghe, S.R., Han, B., Zimbron, J., Shen, Z., Karim, M.N., 2004. Arsenic removal by coagulation and filtration: comparison of groundwaters from the United States and Bangladesh. *Desalination* 169, pp. 224–231.
- [12] Johnson, D.L., Pilson, M.E.Q. 1972. Spectrophotometric determination of arsenite, arsenate and phosphate in natural waters. *Anal. Chim. Acta* 58, pp. 289–299.
- [13] APHA-AWWA, 1985. *Standard Methods for the Examination of Water and Wastewater*, 16th ed. Am. Publ. Hlth. Assoc. Am. Wat. Works Assoc., Washington, DC, USA.