

Removal of arsenic from contaminated water by foam flotation

Z. Pan, L. Zhang and P. Somasundaran*

NSF-Industry/University Cooperative Research Center for Advanced Studies in Novel Surfactants, Langmuir Center for Colloids and Interfaces, Columbia University, New York, N Y 10027, U.S.A.

Received 23 January 2002; accepted 18 June 2003

ABSTRACT

Foam flotation has been employed in this work for enhanced removal of arsenic species from water. The method involves interactions between arsenic species or arsenic-hydrolyzable multi-cation complexes and surfactants, and removal of the hydrophobic complexes formed by air bubbles under quiescent conditions. The system in our experiments consisted of arsenic(V) oxide hydrate, aluminum chloride, sodium dodecyl sulfate ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$), dodecylamine ($\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$), and frothers. It was found that as much as 99% removal of arsenic species can be obtained by adsorbing colloid flotation, the removal being depended upon the solution pH, the ratio of arsenic to aluminum chloride and the interactions between the arsenic-multication species and the surfactants used as collectors. The low removal (less than 10%) of arsenic species by ion flotation in our experiments suggests that the interactions between arsenic species and oppositely charged surfactants may be weak, and therefore an activator is needed to transform arsenic species into more ionic forms for the ionic flotation of arsenic species. These results show that flotation based on the interactions between arsenic-multication species and surfactants is a new effective method either by itself or in combination with other techniques for the removal of arsenic from effluents. © 2003 SDU. All rights reserved.

Keywords: Arsenic removal; Foam flotation; Aluminum chloride; Surfactants

1. INTRODUCTION

Because of its toxicity, arsenic is of considerable environmental concern. Arsenic generally exists in the inorganic form in water supplies. The stability and the predominance of arsenic species in aquatic environment at different pH ranges are shown in Table 1 (Gupta and Chen, 1978). Arsenic in soluble form generally occurs in its +3 and +5 oxidation states.

Table 1
Stability and predominance of arsenic species in different pH ranges

pH	0-9	10-12	13	14
As(III)	H_3AsO_3	H_2AsO_3^-	HAsO_3^{2-}	AsO_3^{3-}
pH	0-2	3-6	7-11	12-14
As(V)	H_3AsO_4	H_2AsO_4^-	HAsO_4^{2-}	AsO_4^{3-}

Various methods have been proposed and adopted to remove arsenic from water (Viraraghavan *et al.*, 1999; Kartinen and Martin, 1995). These methods include: (1) adsorption and co-precipitation (2) membrane process and electrodialysis; (3) ion exchange and (4) oxidation followed by filtration. Sometimes, these conventional methods have not been successful to meet the new effluent standard for arsenic due to the solubility of the resultant product. Foam flotation techniques have proven to be very effective in removing various heavy metal ions such as Cr(VI), Cu(II), Pb(II) and Zn(II) from dilute aqueous solutions (Huang *et al.*, 1982; Lin and Huang, 1989-1990; Choi and Ihm, 1988; Robertson *et al.*, 1976). These techniques are also getting increasing attention and applications in removal of arsenic from aqueous solutions since they are not only effective but also have several advantages, including the ability to treat low metal concentration, rapid operation, need of less surfactant and low cost (Peng and Di, 1994; Huang *et al.*, 1984-1985; Zhao *et al.*, 1996a; Matis *et al.*, 1987; Zhao *et al.*, 1996b). Studies on the removal of

* Corresponding author. E-mail: ps24@columbia.edu

arsenic involving adsorbing colloid flotation (one of the foam flotation techniques) have used ferric hydroxide as co-precipitator (or sorbent), and anionic surfactants such as sodium dodecyl sulfate (SDS) as the collector so far. However, little information is available concerning aluminum hydroxide as the co-precipitator (or sorbent) in the adsorbing colloid flotation. Al(III) can be an activator or accelerator. For example, addition of Al(III) makes $\text{Fe}(\text{OH})_3$ floc more positive, which presumably increases the affinity of the floc for anionic surfactant adsorption (Peng and Di, 1994; Huang *et al.*, 1984-1985). Therefore, Al(III) could be effective both as sorbent and as activator for removal of arsenic in adsorbing colloid flotation. There is also little information available on removal of arsenic from water by ion flotation (one of the foam flotation techniques) even though this method has been used for selective separation of molybdenum and arsenic or germanium (Matis *et al.*, 1987; Zhao *et al.*, 1996a). In this paper, two foam flotation techniques were studied: adsorbing colloid flotation with aluminum(III) both as a sorbent (or co-precipitate) and as an activator, sodium dodecyl sulfate as collector; and ion flotation with dodecylamine as the collector. The objective of this work was to investigate the optimum conditions for enhanced removal of arsenic from water using ion flotation techniques and to better understand the mechanisms involved in these processes.

2. EXPERIMENTAL

2.1. Materials

All the solutions were prepared by dissolving the powder or crystals in distilled water. Arsenic solution was made from Arsenic(V) oxide hydrate ($\text{As}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$, Aldrich); AlCl_3 solution was made from $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Fisher); solutions of dodecylamine and sodium dodecyl sulfate were made from dodecylamine ($\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$, Eastman) and sodium dodecyl sulfate ($(\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$, Fluka), respectively. A frother (mixture of polyglycols, Cytac Inc.) was used for generating more foam in the flotation.

2.2. Procedure

The removal of arsenic from water was studied using a laboratory-scale Hallimond flotation cell (Figure 1). The Hallimond cell setup was composed of a 30mm - diameter and 30cm-high Pyrex glass tubing with a fritted glass disk. The fritted glass disk with fine porosity was used to generate the gas bubbles for flotation. 220ml of mixed solution of As, AlCl_3 and sodium dodecyl sulfate (for adsorbing colloid flotation), or As and dodecylamine (for ion flotation) at different mixture ratios was prepared in a beaker. The initial As concentration in both the cases was chosen to be 70ppm.

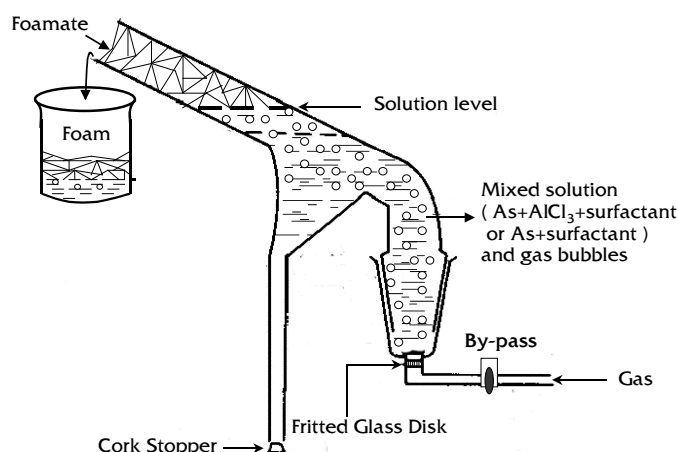


Figure 1. Schematic diagram of Hallimond cell for foam flotation

For the adsorbing colloid flotation, mixed solutions of As with AlCl_3 were stirred for 5 minutes after pH was adjusted, then a predetermined amount of sodium dodecyl sulfate (SDS) was added, and the solution was stirred for another 2 minutes after pH was adjusted. For the ion flotation, mixed solutions of As with dodecylamine were stirred for 5 minutes with pH adjustment. 5-10ml of the mixed solutions were taken for measuring the initial arsenic concentration and then 2-3 drops of the frother was added to the mixed solutions in both the adsorbing colloid flotation and the ion flotation. The solutions were then transferred to the Hallimond cell for flotation. Nitrogen was used at a flow rate adjusted to generate fine bubbles for

flotation under quiescent conditions. At the top of the Hallimond cell, a thin layer of foam, which contains As-Al-SDS complexes or As-dodecylamine complexes, was formed (Figure 1). This foam flowed continuously via a foam discharge and was collected in a beaker. The foam product was a small portion of the original solution volume. The flotation time was 20 minutes.

The analysis of arsenic in the solutions was carried out using Perkin-Elmer ICP/6500 emission spectrometer. The results are expressed in removal efficiency (As removal %) as follows:

$$\text{As removal (\%)} = (1 - C_r/C_i) \times 100\%$$

Where C_i and C_r are the initial and residual arsenic concentration, respectively.

3. RESULTS AND DISCUSSION

3.1. Adsorbing colloid flotation

Effects of pH and the mixture ratios on the removal efficiency of arsenic are shown in Figure 2. It can be seen that the removal efficiency increased with increase in the mixture ratio of AlCl_3 to As. The maximum removal efficiency at all the three mixture ratios tested was obtained in the neutral pH range: at pH 7, as much as 99% removal efficiency was achieved at the mixture ratio of 3 to 1. It is noted that as much as 98% removal efficiency was achieved even at low pH (e.g. at pH 4) when the mixture ratio of AlCl_3 to As was increased to 5 to 1. These results suggest that the optimum conditions for removal of arsenic in the adsorbing colloid flotation are medium mixture ratios of AlCl_3 to As (e.g. 3 to 1) and neutral pH (e.g. pH 7). Effects of pH and the mixture ratios of AlCl_3 to As on the removal efficiency are attributed to the behavior of trivalent aluminum at different pH. In the pH range of 4~10, the predominant Al species are $\text{Al}(\text{OH})_3$ (floc), $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})^{2+}$ and Al^{3+} . Negatively charged As(V) oxyanion species in this pH range, such as H_2AsO_4^- and HAsO_4^{2-} , will adsorb on or incorporated into the $\text{Al}(\text{OH})_3$ flocs and complex with $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})^{2+}$ and Al^{3+} . The amount of adsorbed or incorporated arsenic species could increase with increase in amounts of $\text{Al}(\text{OH})_3$ flocs, the latter increasing with increase in the mixture ratio of AlCl_3 to As at neutral pH range. Interactions between anionic surfactants (e.g. SDS) and As-Al complexes or As-Al flocs make these flocs and/or complexes hydrophobic. These hydrophobic flocs and complexes are then removed via the gas bubbles. Mechanism involved in the adsorbing colloid flotation is shown in Figure 3(a).

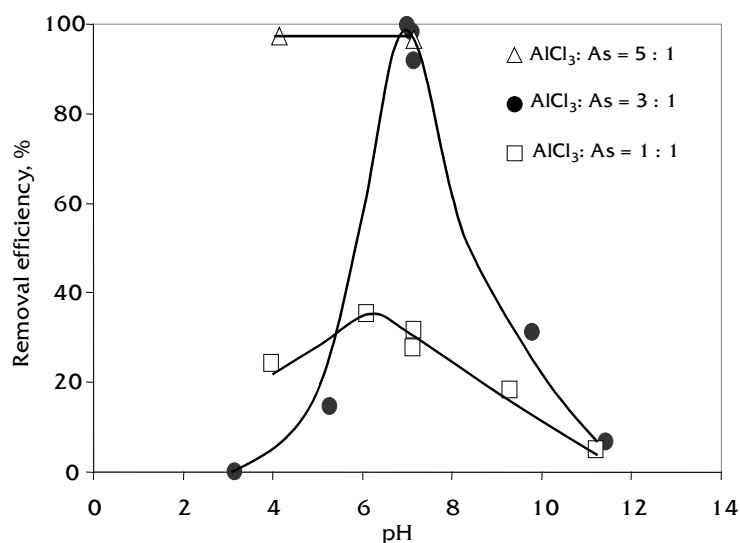


Figure 2. Removal efficiency of arsenic by adsorbing colloid flotation

3.2. Ion flotation

The removal efficiency of arsenic by ion flotation is presented in Figure 4. The lower removal efficiency of arsenic in the pH range of 3~10 by this method in our experiments suggest that the interactions between anionic arsenic species and cationic dodecylamine (as collector) might be weak, and therefore an activator is possibly needed to enhance such interactions for effective removal of arsenic. Mechanism involved in the ion flotation is shown in Figure 3(b).

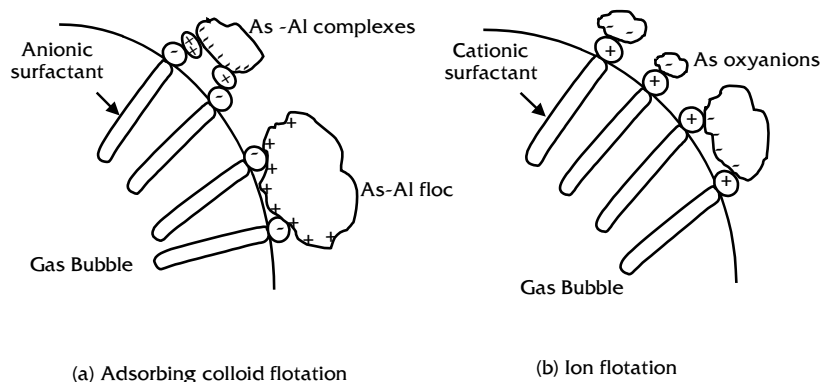


Figure 3. Interactions among arsenic species, multivalent cations, surfactants and gas bubbles in the foam flotation for removal of arsenic from water, (a) Anionic As species are incorporated into Al flocs or complexes with Al species. Anionic surfactant interacts with these positively charged As-Al floc and/or complexes, making them hydrophobic for flotation via gas bubbles; (b) Cationic surfactant interacts with negatively charged As species, making them hydrophobic for flotation via gas bubbles

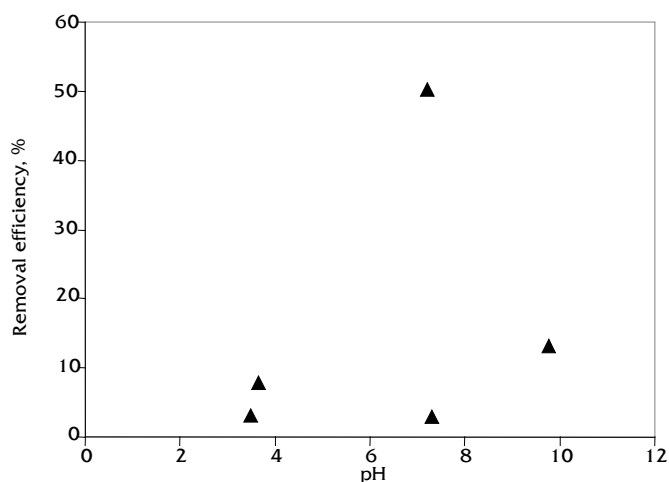


Figure 4. Removal efficiency of arsenic by ion flotation

4. CONCLUSIONS

- As much as 99% removal efficiency of arsenic was obtained by adsorbing colloid flotation using Al(III) as activator and sorbent and sodium dodecyl sulfate as the collector. This efficiency increased with increase in the ratio of Al(III) to As concentration. Maximum removal efficiency was obtained in the neutral pH range. The optimum conditions for removal of arsenic in the adsorbing colloid flotation are medium mixture ratios of $AlCl_3$ to As (e.g. 3 to 1) and neutral pH (e.g. pH 7).
- Low removal efficiency of arsenic (less than 10%) in the ion flotation suggests weak interactions between anionic arsenic species and the oppositely charged surfactants, e.g. dodecylamine, and therefore an activator is needed to increase such interactions for enhanced removal of arsenic.
- These results show that foam flotation based on interactions among arsenic species, multivalent cations and surfactants is an effective method either by itself or in combination with other techniques for enhanced removal of arsenic from water.

ACKNOWLEDGEMENTS

The authors acknowledge the support of NIH Grant 1 P42 ES10349 and the industrial partners of the Industry/University Cooperative Research Center (IUCRC) at Columbia University. Thanks also due to Dr. K. A. Matis and Dr. A. I. Zouboulis at Aristotle University in Greece for their suggestions.

REFERENCES

- Choi, S.J. and Ihm, S.K., Removal of Cu(II) from aqueous solutions by foam separation techniques of precipitate and adsorbing colloid flotation. *Separation Science and Technology*, 1988, **23**(4-5), 363-374.
- Gupta, S.K. and Chen, K.Y., Arsenic removal by adsorption. *Journal Water Pollution Control Federation*, 1978, **50**(3), 493-506.
- Huang, S.D., Fann, C.F., Hsieh, H.S., Foam separation of chromium(VI) from aqueous solution. *Journal of Colloid and Interface Science*, 1982, **89**(2), 504-513.
- Huang, S.D., Tzuoo, J.J., Gau, J.Y., Hsieh, H.S., Fann, C.F., Effect of Al(III) as an activator for adsorbing colloid flotation. *Separation Science and Technology*, 1984-1985, **19**(13-15), 1061-1072.
- Kartinen, E.O., Jr. and Martin, C.J., An overview of arsenic removal processes. *Desalination*, 1995, **103**, 79-88.
- Lin, J. and Huang, S.D., Floc foam flotation of chromium(VI) with polyelectrolyte. *Separation Science and Technology*, 1989-1990, **24**, 1377-1391.
- Matis, K.A., Papadoyannis, I.N., Zouboulis, A.I., Separation of Germanium and arsenic from solutions by flotation. *International Journal of Mineral Processing*, 1987, **21**, 92-93.
- Peng, F.F. and Di, P., Removal of arsenic from aqueous solution by adsorbing colloid flotation. *Industrial Engineering Chemical Research*, 1994, **33**, 922-928.
- Robertson, R.P., Wilson, D.J., Wilson, C.S., The adsorbing colloid flotation of Pb(II) and Zn(II) by hydroxides. *Separation Science*, 1976, **11**, 569-580.
- Viraraghavan, T., Subramanian, K.S., Aruldoss, J.A., Arsenic in drinking water – Problems and solutions. *Water Science and Technology*, 1999, **40**(2), 69-76.
- Zhao, Y.C., Zouboulis, A.I., Matis, K.A., Removal of Molybdate and arsenate from aqueous solution by flotation. *Separation Science and Technology*, 1996a, **31**(6), 769-785.
- Zhao, Y.C., Zouboulis, A.I., Matis, K.A., Flotation of molybdate oxyanions in dilute solutions. Part 1. Selective separation from arsenate. *Hydrometallurgy*, 1996b, **43**, 143-154.