CRYSTALLIZATION OF LOW SOLUBILITY CALCIUM-ARSENATE COMPOUNDS FOR ARSENIC REMOVAL FROM POLY(DIALLYLDIMETHYL AMMONIUM CHLORIDE)-ARSENATE SOLUTION

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Introduction

Arsenic contamination in water supplies is a serious problem in various parts of the world (Smedley and Kinniburgh, 2002; Mandal and Suzuki, 2002), and has long been a concern due to the carcinogenic, mutagenic, and teratogenic effect of arsenic on humans. In 2001 the USEPA set a new maximum concentration level (MCL) for arsenic in drinking water of 10 ppb which became effective in 2006 to replace the old MCL of 50 ppb, a level at which arsenic still exhibits chronic effects (USEPA, 2001). Compliance with this new MCL makes a serious problem, especially for small communities with less financial support, to reach the new standard since expensive technologies are often required.

The technology called polyelectrolyte-enhanced ultrafiltration (PEUF) (Figure 1.) is one technology being explored to remediate low level arsenic contamination to meet this new standard. Previous work using poly(diallyldimethyl ammonium chloride) (PDADMAC) cationic polyelectrolyte and a 10 kDa molecular weight cut-off (MWCO) ultrafiltration membrane achieved up to 99.95% arsenic removal from 100 ppb synthetic arsenic solution (Pookrod, et al., 2004). Scale-up of the PEUF process for arsenic removal using PDADMAC and a 10 kDa MWCO spiral wound ultrafiltration module demonstrated 95% arsenic removal from synthetic 50 ppb feed inlet solution (Gallo, et al., 2006), further demonstrating that PEUF is a useful technology to remove low concentration arsenic from water. They also performed cost analysis for using the PEUF process for arsenic removal. Their estimation based on the assumption of 95% polyelectrolyte recovery and recycle found that the PEUF technology has lower life cycle capital, operation, and maintenance cost compared to ion exchange (IX), granular ferric hydroxide adsorbents (GFH), coagulation/microfiltration (C/MF), coagulation/filtration (C/F), and nanofiltration (NF) technologies.
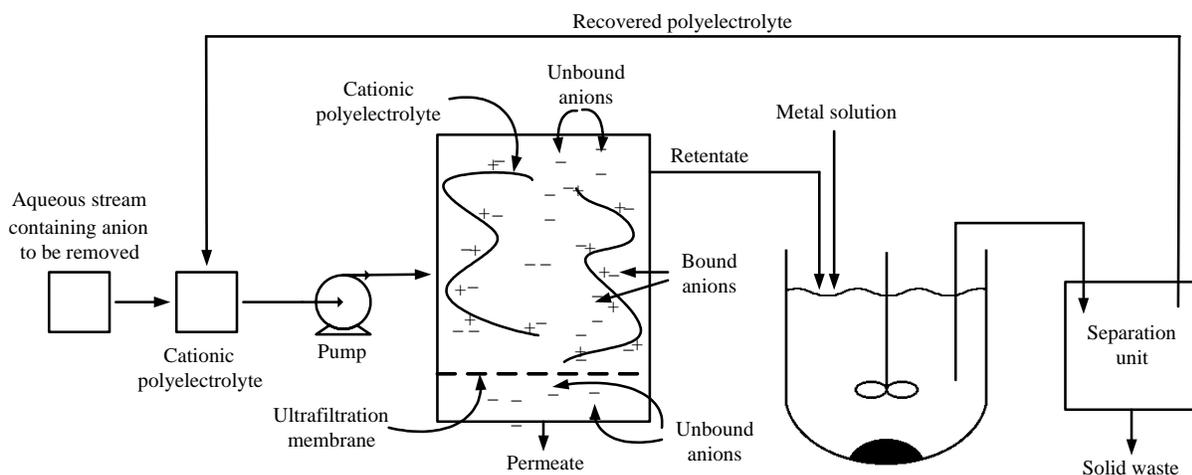
Figure 1. Schematic diagram of the PEUF process with polyelectrolyte recovery.

The recovery of polyelectrolyte from PEUF retentate solution has been studied using the easy and inexpensive precipitation process. Cations that able to form low K_{sp} compounds with arsenate are of interest since the arsenic concentration in the PEUF retentate solution is quite low (about 25 ppm). Barium cation was studied (Pookrod, 2003; Dungkaew, et al, 2006), but does not appear to be suitable due to the very low initial arsenate concentration, and the fact that barium itself may effect to human health (USEPA, 1998). The calcium cation is an interesting candidate since it is friendly to human health and also forms low K_{sp} calcium arsenate compounds (Bothe and Brown, 1999a and 1999b). One problem is that calcium arsenate compounds are not stable under atmospheric conditions due to the transformation of calcium-arsenate compounds to calcium carbonate and the subsequent release of arsenic back into the solution.

Calcium phosphate apatite has been used as the host for cations such as Cd^{2+} and Zn^{2+} (Peld, et al., 2004; Marchat, et al., 2006), and Pb^{2+} (Chen, et al., 1997). The incorporation can occur at the surface (sorption) or in the apatite structure (substitution) resulting in the toxic substances being removed into a chemically very stable structure form. Moreover, these compounds appear to be stable under atmospheric conditions and calcium carbonate does not form. The present study examines arsenic removal from arsenate containing PEUF retentate solution with the aim of polyelectrolyte recovery. The method is to form arsenate substituted calcium phosphate hydroxyapatite compounds based on the similarity of phosphate and arsenate allowing formation of stable calcium phosphate arsenate hydroxyapatite structures.

Experimental

Chemicals

All chemicals except PDADMAC were analytical grade and used without further purification. Disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$) and disodium hydrogen arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) from Carlo Erba (Milan, Italy) and Fluka (Buchs, Switzerland), respectively, were used as the source of phosphate and arsenate anion. Calcium cation was from calcium hydroxide ($Ca(OH)_2$) from Carlo Erba. Sodium hydroxide used for pH adjustment is a product of EKA Chemicals (Bohus, Sweden).

The cationic polyelectrolyte, PDADMAC, with the average molecular weight of 240 kDa was purchased from Calgon Corp. (Pittsburgh, PA) under the trade name MERQUAT. Short chain polyelectrolyte was removed before use using 10 kDa ultrafiltration membranes from Osmonic (Minnetonka, MN) as filter. PDADMAC concentrations were determined by a LECO CNS-2000 analyzer using Leco soil standard. The concentration of carbon and nitrogen corresponds to PDADMAC concentration based on the polymer repeating unit formula. Deionized water was used for all experiments.

Crystallization of calcium phosphate arsenate hydroxyapatite

The continuous crystallization experiments were performed using a 500 mL mixed-suspension mixed-product removal (MSMPR) borosilicate crystallizer equipped with MasterFlex L/S peristaltic pump and CAT R50D overhead stirrer. A schematic diagram of experimental set up is shown in Figure 2. 500 mL of anion and cation solutions were prepared in separate storage and adjusted to the desired pH (anion solution only) with NaOH before being introduced simultaneously into the crystallizer by peristaltic pump with equal flow rates of 8.3 mL/min. The agitation speed was fixed at 100 RPM throughout the experiment. The solution level in the crystallizer was maintained at 500 mL by setting the outlet line to remove the mixed-product solution to the product storage at this level. The reaction time in the crystallizer was 30 min from start until the mixed product started to be removed to the product storage, and the reaction finished within 60 min of the start (aging time = 0 at this point). The mixed products were filtered at different aging times of 0 and 60 min before characterization. Initial arsenic concentration was fixed at about 25 ppm, PDADMAC/As mol ratio was 100, P/As mol ratio vary to no phosphorus, 1/5, 3/3, 5/1, and no arsenic, and Ca/(P+As) used in this experiment was 1.67.
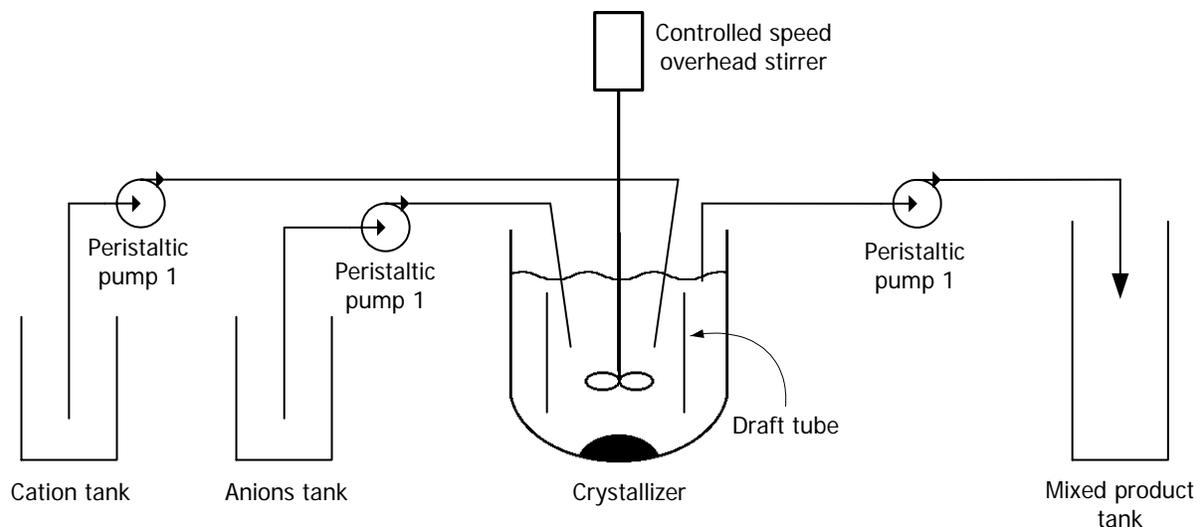

Figure 2. Schematic diagram of the online crystallization of calcium-arsenate-phosphate compounds.

Characterization

The filtrate was analyzed for arsenic concentration using flow injection hydride generation atomic absorption spectrophotometer (Perkin-Elmer AAnalyst 100 equiped with FIAS-400 system). The solid precipitates were characterized by powder X-ray diffraction using

a Bruker Analytical X-ray Systems model D5005 X-ray diffractometer equipped with a Cu K_α sealed tube X-ray source operating at 40 kV and 35 mA. The data were collected in the range of 5.0-60.0° two theta in steps of 0.02° and a scan speed of 0.4 sec/step. Infrared spectra were recorded on a Biorad model FTS175C FTIR for the region 400-4000 cm^{-1} (KBr technique). A scanning electron microscope (Jeol model JSM-6400 SEM) equipped with an energy dispersive X-ray fluorescence unit (Microspec model WDX-100 EDX) was used to examine morphology and to verify heavy element composition in the precipitates, and a transmission electron microscope was used to examine the extremely small size particle morphologies.

Results and Discussion

Formation of calcium phosphate arsenate hydroxyapatite

In the absence of PDADMAC the precipitation immediately occurs when the two feed solutions are mixed, resulting in a turbid solution then particles agglomerating and falling to the bottom of the tank. In contrast, in the presence of PDADMAC, the particles remain dispersed in the solution and no precipitate falls to the bottom of the tank even after 24 hours. The white precipitates are characterized by XRD, typical XRD patterns are shown in Figure 3. Calcium phosphate hydroxyapatite (HAP) is formed in the no arsenate system. In solutions containing arsenate anion, the arsenate is incorporated into the calcium phosphate hydroxyapatite is detected. Calcium arsenate hydroxyapatite (AHAP) was formed in the preliminary study of calcium arsenate precipitation at high arsenic concentration. This phase disappears in these low arsenic concentration experiments. As show in Figure 3, it is difficult to distinguish between the various forms since they have low crystallinity. The precipitates were heat treated at 600 °C for 4 hr to improve crystallinity before comparing the shift of d-spacing as shown in Figure 4. Arsenate incorporation in calcium phosphate hydroxyapatite results in expansion of the d-spacing of HAP due to the larger radius of arsenic compared to phosphorus.
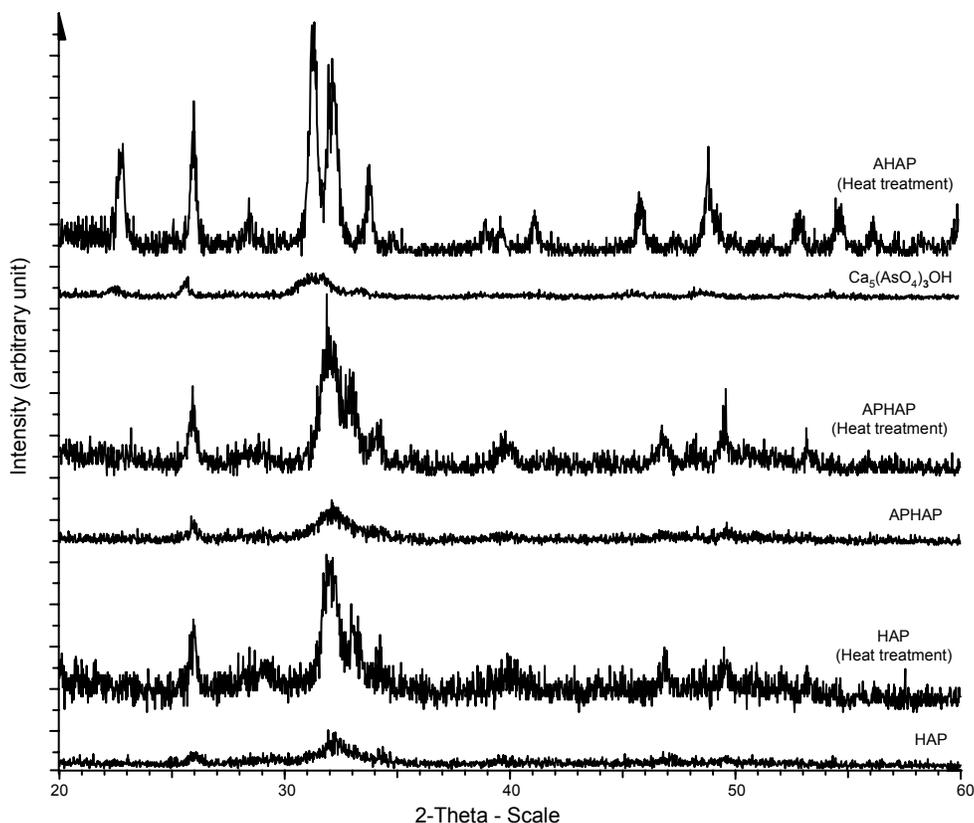
Figure 3. Typical XRD patterns of calcium phosphate hydroxyapatite (HAP), arsenate incorporated calcium phosphate hydroxyapatite (APHAP), and calcium arsenate hydroxyapatite (AHAP).
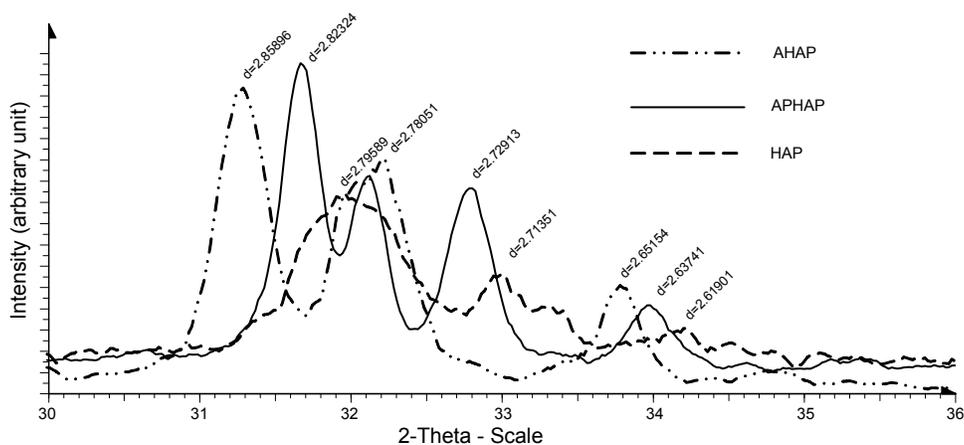

Figure 4. Comparison of d-spacing of HAP, APHAP, and AHAP.

IR spectrometry is simple and useful for characterization of the incorporation of arsenate into HAP (Figure 5). The arsenate anion in precipitates is detected by the As–O stretch at about 870 cm^{-1}. The 874.2 cm^{-1} from HAP in Figure 6 may from the contamination of during the experiment.
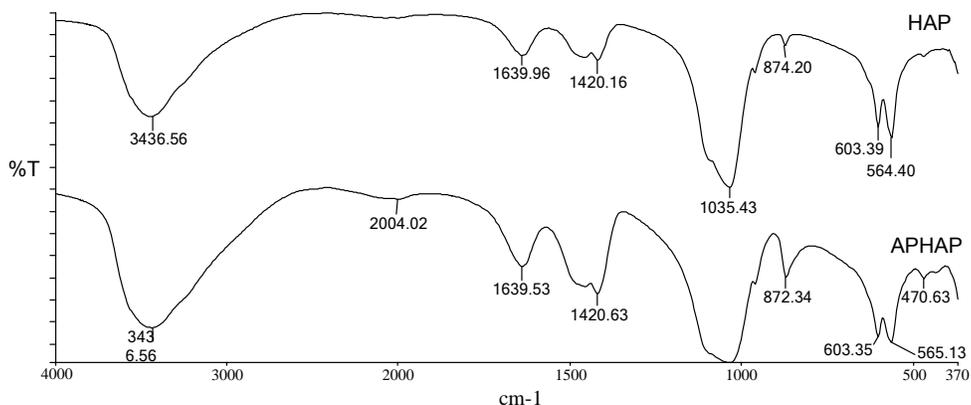
Figure 5. IR spectra of HAP, APHAP.

The morphologies of HAP and AHAP were studied by SEM (Figure 6A), which shows the particle size of HAP and AHAP to be very small, making the SEM technique unsuitable for morphological studies of these samples. However, the EDX which is coupled with the SEM is useful to determine the heavy element composition in the sample (results not shown). The morphological study of HAP by TEM technique (Figure 6B), which operates at higher energy than SEM, providing higher resolution, shows APHAP forms needle-like crystals with about 100 nm lengths. The very small crystal size leads to poor diffraction of HAP and APHAP.
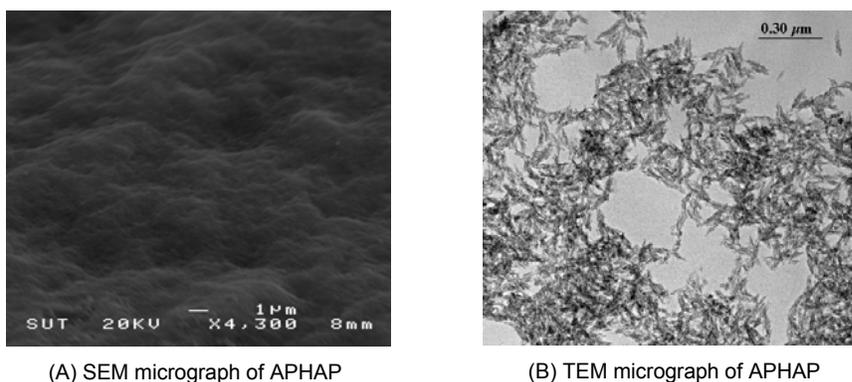
(A) SEM micrograph of APHAP   (B) TEM micrograph of APHAP

Figure 6. SEM and TEM micrograph of APHAP.

Arsenic removal

The mixed product was filtered at aging times of 0 and 60 min, and the filtrate was analyzed for arsenic concentration. The results, Figure 7A, show that high initial pH, and high P/As mol ratio provide better arsenic removal efficiency. There is no significant difference between no aging and 60 min aging time, indicating rapid reaction and no time requirement for arsenic to incorporate into the HAP. The HAP crystallization in the PDADMAC-phosphate-arsenate system is inhibited by PDADMAC. Poor arsenic removal in the presence of PDADMAC can be observed by comparing Figures 7B and 7B. The PDADMAC can enhance the phosphate and arsenate solubilization via electrostatic binding with cations sites on the polyelectrolyte resulting in crystallization inhibition of HAP.
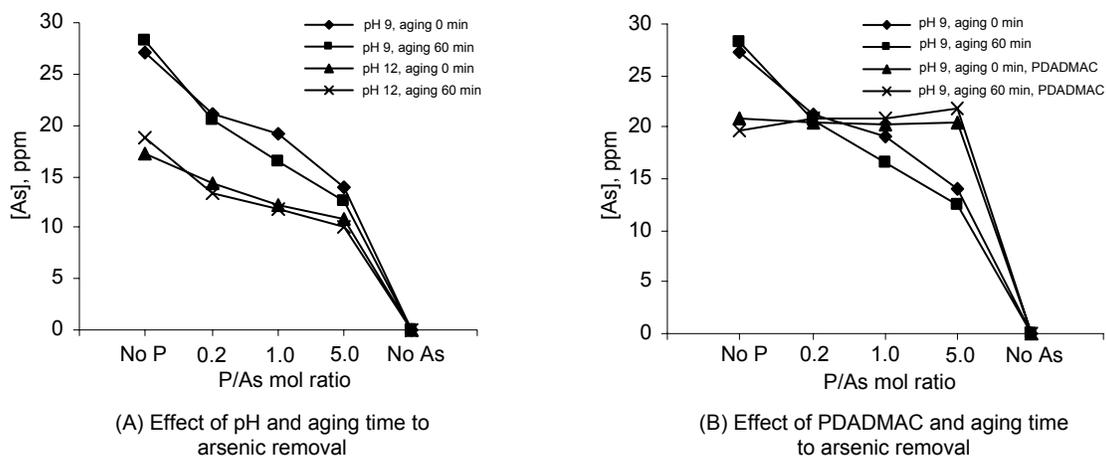
(A) Effect of pH and aging time to arsenic removal

(B) Effect of PDADMAC and aging time to arsenic removal

Figure 7. Effect of pH, aging time, and PDADMAC on arsenic removal by APHAP crystallization

Conclusion

Low concentration arsenic in solution can be successfully removed by the formation of low solubility calcium phosphate hydroxyapatite at basic pH. The arsenic in form of arsenate can be incorporated into the calcium phosphate hydroxyapatite structure forming stable calcium phosphate arsenate hydroxyapatite. The advantage of this material is the very low solubility means that crystallization can occur even in low concentration systems, implying an easy and inexpensive process for arsenic removal could be based on this compound. However, the PDADMAC is a strong crystallization inhibitor since it can solubilize both phosphate and arsenate anions through electrostatic interaction on the molecular surface. Moreover, it is also able to disperse small particles in the solution resulting in settling retardation of precipitates. In the absence of PDADMAC arsenic removal via this approach is very attractive, but in the presence of PDADMAC more research is required to solve the problems of crystallization inhibition and settling retardation by PDADMAC.

Acknowledgements

References

1. Bothe, J. V. and Brown, P. W. (1999a), "Arsenic Immobilization by Calcium Arsenate Formation," *Environmental Science & Technology*, 33, 3806-3811.
2. Bothe, J. V. and Brown, P. W. (1999b), "The Stabilities of Calcium Arsenates at 23±1 °C," *Journal of Hazardous Materials*, B69, 197-207.
3. Chen, X., Wright, J. V., Conca, J. L. and Peurrung, L. M. (1997), "Effects of pH on Heavy Metal Sorption on Mineral Apatite," *Environmental Science & Technology*, 31, 624-631.

4. Dungkaew, W., Haller, K. J., Flood, A. E., and Scamehorn, J. F. (2006), "Barium-Arsenate Phase Precipitation and Solubilization Study," Proceeding of The International Conference on Hazardous Waste Management for a Sustainable Future, Bangkok, Thailand.

5. Gallo, D., Acosta, E., Scamehorn, J. F. and Sabatini, D. A. (2006), "Pilot Scale Study of Polyelectrolyte Enhanced Ultrafiltration for Arsenic Removal," *Journal AWWA,* 98(1), 106-116.

6. Mandal, B.K. and Suzuki, K.T. (2002), "Arsenic Round the World: A Review," *Talanta*, 58, 201-235.

7. Marchat, D., Bernache-Assollant, D. and Champion, E. (2006), "Cadmium Fixation by synthetic Hydroxyapatite in Aqueous Solution–Thermal Behaviour," *Journal of Hazardous Materials*, in press.

8. Peld, M., Tonsuaadu, K. and Bender, V. (2004), "Sorption and Desorption of Cd^{2+} and Zn^{2+} Ions in Apatite-Aqueous Systems," *Environmental Science & Technology*, 33, 5626-5631.

9. Pookrod, P. (2003), "Polyelectrolyte-enhanced Ultrafiltration for removal of arsenic from aqueous solutions," Thesis dissertation, Suranaree University of Technology, Nakhon Ratchasima, Thailand.

10. Pookrod, P., Haller, K. J. and Scamehorn, J. F. (2004), "Removal of Arsenic Anions from Water using Polyelectrolyte-Enhanced Ultrafiltration," *Separation Science and Technology*, 39(4), 811-831.

11. Smedley, P. L. and Kinniburgh, D. G. (2002), "A Review of the Source, Behavior and Distribution of Arsenic in Natural Waters," *Applied Geochemistry*, 17, 517-568.

12. United States Environmental Protection Agency. (1998), "Toxicological Review of Barium and Compounds," EPA/635/R-05/001

13. United States Environmental Protection Agency. (2001), "EPA to Implement 10 ppb Standard for Arsenic in Drinking Water," EPA 815-F-01-010.