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Arsenic Removal From Water Using Anion Exchange Resin Spectra/Gel

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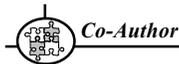
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ABSTRACT

Arsenic in drinking water is one of the most challenging health hazards facing mankind today. Arsenic is a naturally occurring carcinogenic element and creates epidemiological problems through chronic ingestion from drinking water. Arsenic is present in water primarily as As(III) or As(V). Removal of both As(III) and As(V) from water by adsorption on strong base anion-chloride form has been studied. Arsenic concentration was measured by inductive coupled plasma (ICP) analysis. The resin was regenerated and the adsorbed arsenic fractions were eluted by using 2M NaCl. The effect of different parameters that affect adsorption process, such as metal and resin concentration, retention time, and pH, was investigated. Results obtained revealed that As(III) was poorly adsorbed, whereas As(V) was retained on the resin. The adsorption process was optimized by using 0.5g resin for 100 ppm As(V) at pH 7 for 30 minutes. The removal efficiency of As(V) was 99.2%.   © 2007 Trade Science Inc. - INDIA

INTRODUCTION

Arsenic contamination of drinking water has been an environmental issue that requires serious attention in many parts of world. Although in certain situations it might be possible to switch the water supply source in the affected areas by a safer and easily available one, this solution is temporary at best and may only be possible during the part of the year when alternate water supplies are available. It may also be prohibitively expensive. Arsenic removal may be a more prudent option. In January 2001, EPA published a revised MCL for arsenic in drinking water that requires public water suppliers to lower the current arsenic concentrations standard from 50 microgram per liter (part-per-billion, or ppb) to 10 ppb by

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2006[1,2]. The revised standard may affect arsenic cleanup goals for groundwater. Based on information from EPA's CERCLIS 3 database through fiscal year (FY) 1999[3], arsenic is the second most common contaminant of concern (COC) cited in Records of Decision (RODs) for sites on the superfund National Priorities List (NPL). Mining activities are responsible for arsenic poisoning in Thailand, while natural sources cause or have caused poisoning of populations, as has happened in Bangladesh, where nearly 30 million people were affected[4]. Because arsenic readily changes valence state and reacts to form species with varying toxicity and mobility, effective treatment of arsenic could be challenging. As(III) is generally more toxic to humans and 4 -10 times more soluble in water than As(V)[5].

Most arsenic removal technologies are effective in removing the pentavalent form of arsenic. The trivalent form (arsenite) is predominantly non-charged below pH 9.2. Therefore, many treatment systems include an oxidation step to convert arsenite to arsenate. Various processes dealing with arsenic in hydrometallurgical treatments include; coagulation and filtration[6,7]; sorption onto metal oxides such as activated alumina[8], etc. Granular ferric hydroxides were also used with high removal efficiency and capacity[9,10]. Adsorption is one of the most commonly reported techniques for removal of As(V). This process regulates the fate and mobility of As in soil, and it is mainly linked to different environmental factors such as pH, redox potential, reaction time, oxidation state of arsenic, and type of the adsorbent. Synthetic ion exchange resins developed for removal of anions such as sulfate and nitrate have proven to be reasonably effective at removing arsenic from water[8]. Anion exchange resins (AER) offer an economical alternative to other As separation methods. The use of AER minimizes the adverse effects that samples preservatives can have on As species in environmental samples as the separation can be performed instantly[9]. Pawel and bartlomiej[10] used ion exchange column chromatography to speciate arsenic in solution. Different AER have been previously tested and evaluated for pentavalent arsenic removal[11-13]. Clifford, et al.[14] and Lesan et al.[15] used a conventional sulfate-selective

type 2 polystyrene strong-base-anion resin at pH of 7.5-8.0. Bissen et al.[16] used Amberlite IRA-93, while Dominguez et al.[17] synthesized anion exchange fibers from a vinylbenzyl chloride precursor. Benjamin and Kim, et al.[18-19] described an approach for operating an ion exchange process for separating As(V) selectively from sulfate or nitrate, respectively.

The aim of this work is to study the applicability of the anion-exchange (Spectra Gel IE 1X8) resin for the separation of the arsenic species As(III) and As(V). Different parameters affecting the adsorption process, such as solution pH, metal adsorption capacity, and time, are investigated in details.

EXPERIMENTAL

Materials

Strong base anion exchange resin Spectra/Gel IE 1×8 (type 1) with bead size of 75-150 μm was used and evaluated for separation of As(III) and As(V) species. Specta/Gel resins are supplied in chloride form, and use a trimethylbenzylammonium group as the exchange site. Sodium arsenite ($NaAsO_2$) 0.1N standardized solution (Alfa Aesar) was used as precursors of As(III). Sodium hydrogen arsenate ($Na_2HAsO_4 \cdot 7H_2O$), ACS, 98.0-102.0% (Alfa Aesar) was used as precursors of As(V). All chemical used were of technically analytical grade.

Batch adsorption experiments

Batch adsorption experiments were conducted in a pyrex glass flasks, with 500 ml capacity, a magnetic rod was used for stirring. For each flask, 500 ml of a solution containing a specific amount of the resin was transferred. The pH values of the solutions were adjusted from 1 to 11 with 0.5M NaOH and 0.5M $HClO_4$ and measured with an Orion Model 801A pH meter. The pH was kept at a specific value during experiments using a pH controller (New Brunswick Scientific, Edison, NJ). The experiments were carried out for 180 minutes. A 10-ml sample was drawn every 15 minutes during the first hour, and then after every 30 minutes during the rest. The liquid samples were filtered for analysis through 0.2 μm syringe filters (Gelman acrodic syringe filter with 25 mm diameter, and Nylon membrane of 0.2 μm

pore size, PN4436T, pall gelman laboratory, Ann Arbor, Michigan). At the optimum adsorption conditions, a set of experiments were performed in a disposable polypropylene columns (with a 6 ml volume) packed with 2 g of the resin. The flow rate of the arsenic solution was adjusted to be 2 to 3 ml/minute. The adsorbed arsenic fractions were eluted from the resin using 2M NaCl. Finally, the resin was washed with bi-distilled water for reusing. Arsenic concentrations in solutions were analyzed by inductive coupled plasma (ICP) optical emission spectrometer (model optima 5300 DV Perkinelmer).

RESULTS AND DISCUSSION

The adsorption capability of As(III) on the spectra/gel resin was investigated at a wide pH range (pH 1-11). The results are shown in figure 1, As(III) concentration of 20 ppm was used with resin concentration of 1 g/l, for adsorption times of 1 and 3 h. It can be seen that As(III) was poorly adsorbed in general, the adsorption capability increases slowly with the increase of solution pH reaching a maximum As(III) removal of about 10 wt %. Increasing the adsorption time from 1 to 3 h did not greatly affect the removal efficiency. The adsorption behavior of As(V) on the spectra/gel resin and the effect of solution pH at different adsorption times is shown in figure 2. The pH of the solution has a strong effect

Figure 2: Adsorption behavior of As(V) on spectra/gel IE 1X8 at different pH values
As(V) conc. 16 ppm, resin conc. 1 g/L
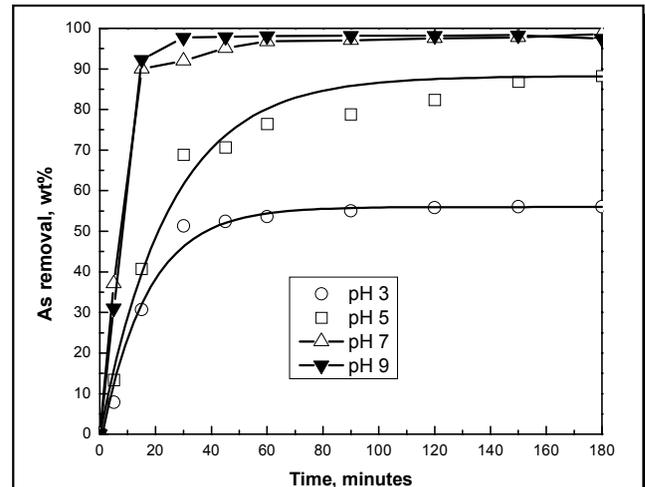
Figure 3: Adsorption behavior of As(V) on spectra/gel IE 1X8 at different pH values
As(V) conc. 16 ppm, resin conc. 1 g/L

on the adsorption and removing process of As(V) from solution. Better arsenic removal efficiencies were achieved with As(V) as compared with that of As(III). Removal efficiency of As(V) was not measured to be significant at low pH values but increased rapidly with increase of the pH, attaining a maximum value of 97.8 % at pH of 7 after adsorption time of 90 minutes. The removal % attained a maximum value of 99.2 % at pH 9 after treatment for 30 minutes only. Further increase in pH, beyond 9, showed only a small increase in the removal efficiency. Figure 3 shows the effect of adsorption time on the removal of As(V) by the spectra/gel resin at

Figure 1: Adsorption behavior of As(III) on spectra/gel IE 1X8 at different pH values
As(III) conc. 20 ppm, resin conc. 1 g/L

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Arsenate   Arsenite

Figure 4: Differences in the molecular configuration of arsenate and arsenite in water
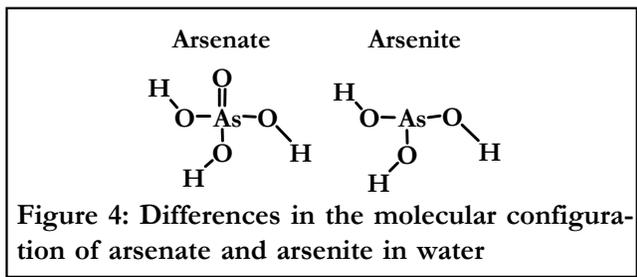
different pH values. A fast removal of As(V) was achieved in a short time. About 93.2 and 99.2 % of As(V) was removed after 30 minutes of treatment at pH values of 7 and 9, respectively. However increasing the time beyond 30 minutes did not affect the AS(V) removal at low pH in which case the removal efficiency values were about 51 and 85 % at pH values of 3 and 5, respectively.

The difference in the adsorption capability of both As(III) and As(V) may be attributed to the difference in molecular structure between arsenite and arsenate, as shown in figure 4[20]. The double bond oxygen in the arsenate molecule influences its ability to become ionized through the loss of hydrogen ions, the process is termed dissociation. A negative charge develops on the molecule when dissociation occurs. The double bond oxygen increases the capacity to delocalize that charge, easing the loss of hydrogen ions. The propensity for ionization is expressed by pK_a the constant of dissociation. For arsenate and arsenite pK_a values are as follows[20]:

Arsenate (H_3AsO_4), pK_1= 2.19, pK_2= 6.94, pK_3= 11.5   (1)
Arsenite (H_3AsO_3), pK_1= 9.20, pK_2= 14.22, pK_3= 19.22   (2)

Where, pK_1 is 1st ionization constant, pK_2 is 2nd ionization constant, pK_3 is 3rd ionization constant. The pH at which these ionization steps occur is significantly different between arsenate and arsenite, as illustrated in figure 5 (Robins[21] and Welch[22]). (We need to describe what is presented in figure 5) Figure 4 also shows the control of redox potential (Eh) on the arsenate/arsenite transition. This Eh/pH relationship is the key to understand arsenic mobility in water and the effectiveness of arsenic water treatment systems.

Figure 6 shows the effect of the resin dosage on the As(V) removal. The removal efficiency increased by increasing the resin concentration. The As(V) removal reached a maximum value of 99.2% with resin dosage of 1 g/l after 90 minutes. Although further
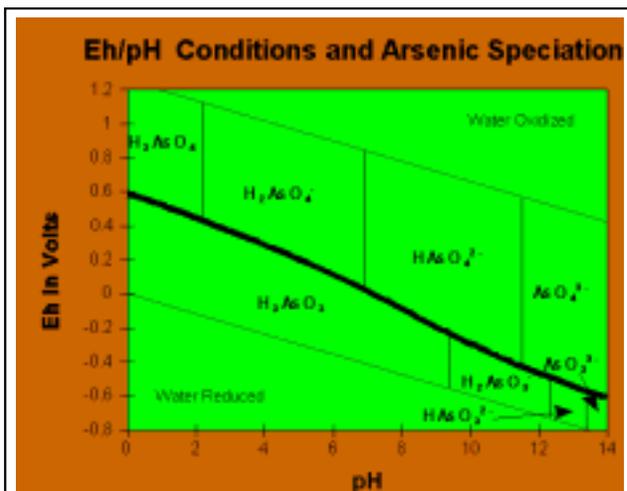
Figure 5: Control of arsenic speciation by Eh and pH conditions
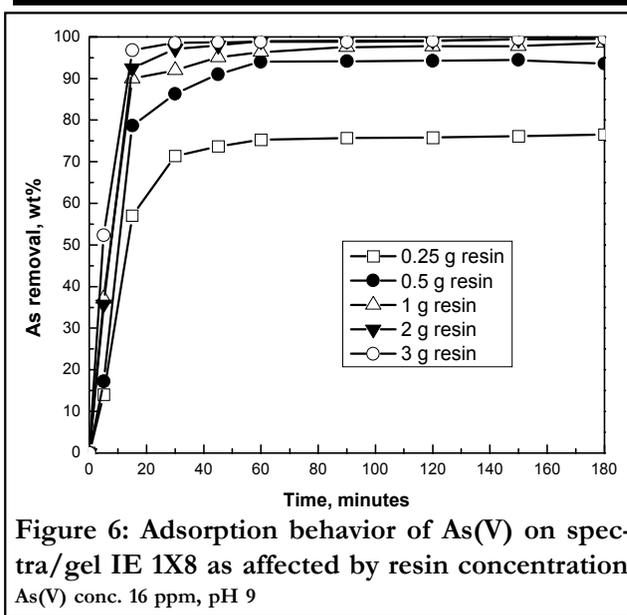
Figure 6: Adsorption behavior of As(V) on spectra/gel IE 1X8 as affected by resin concentration
As(V) conc. 16 ppm, pH 9

increase in the resin dosage only slightly increased the removal efficiency, it facilitated the As(V) removal by decreasing the treatment time. About 99.2 % of the As(V) was removed after 30 minutes of treatment with 2g resin, but it took only 20 minutes with 3g resin to reach the same 99.2% removal efficiency.

The effect of varying As(V) concentration on its removal rate is shown in figure 7. The lower the As(V) concentration, the higher the efficiency of it's removal. A Langmuir-Hinshelwood type[23] of relationship can be used to describe the effect of As(V) concentration on its adsorption on the resin surface. The limitation of surface sites for the reaction may con-

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Figure 7: Adsorption behavior of different concentrations of As(V) on spectra/Gel IE 1X8
pH 9, resin conc. 1 g/L

Figure 8: Kinetics of As(V) adsorption on spectra/gel IE 1X8
As(V) conc. 16 ppm, resin conc. 1 g/L, pH 9

Figure 9: As(V) equilibrium isotherms for spectra/gel IE 1X8
As(V) initial conc. 16 ppm, pH 9
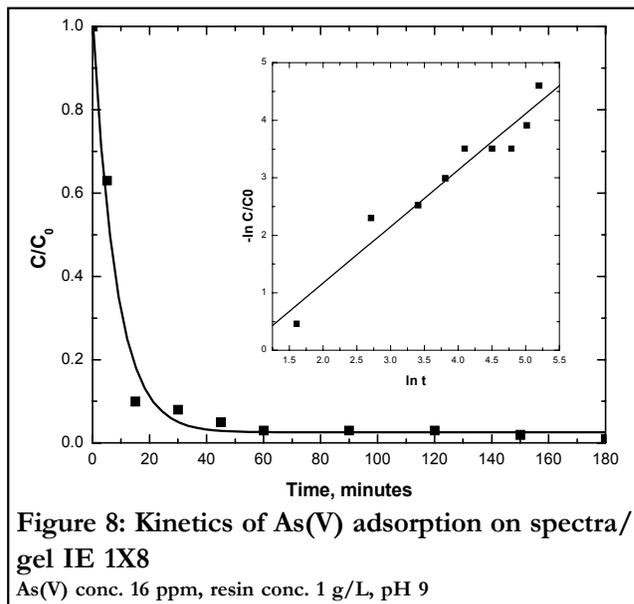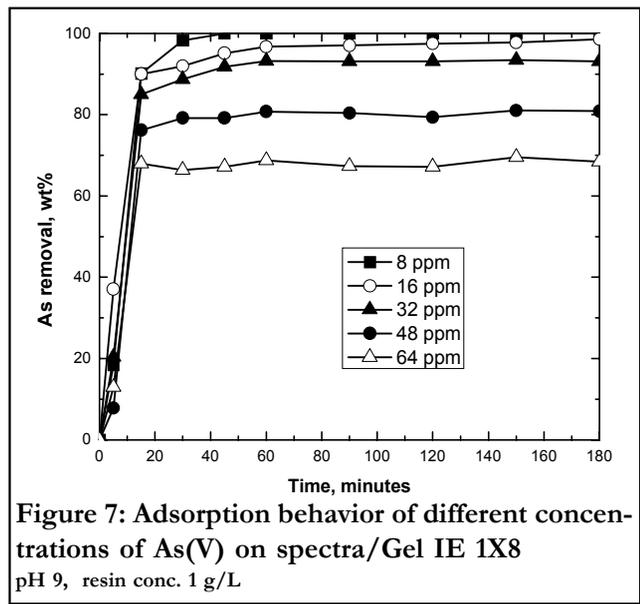
trol the As(V) adsorption. At a concentration of 8 ppm, As(V) can be totally adsorbed (complete removal) within 30 minutes. The As(V) removal decreased with increasing concentration and the reaction was time independent. The removal attained it's maximum after 90 minutes of treatment at any As(V) concentration. Maximum removal efficiency values of 99.2, 96, 78.8, and 68.5% were achieved for As(V) concentration values of 16, 32, 48, and 64 ppm, respectively. The results clearly demonstrate that the As(V) adsorption process is promising at low concentrations of the pollutant. This is also typical for heterogeneous catalytic systems where the reaction occurs at the interface between two phases.

The removal of As(V) by spectra/gel anion exchange resin can be explained as follows; the water containing As(V) passes through a bed of the chloride form resin (designated by RCl), during which the chloride arsenate ion exchange reaction (equation 3), takes place to yield resin in the arsenate form (R_2HAsO_4). When the column capacity for arsenic is exhausted, the reaction is easily reversed and regeneration returns the resin to the chloride form according to equation 4[8].

$$2RCl + HAsO_4^{-2} = R_2HAsO_4 + 2Cl^- \qquad (3)$$
$$R_2HAsO_4 + 2NaCl = 2RCl + Na_2HAsO_4 \qquad (4)$$
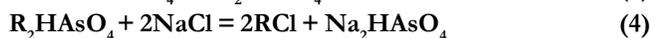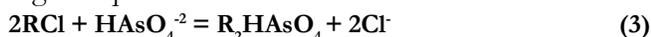
The rate of the reaction was calculated by plotting ln C/C_0, for As(V) concentration of 16 ppm with 1g resin at pH of 9, as a function of ln time, as shown in figure 8. Here C_0 and C are the initial and remaining As(V) concentrations in the solution, respectively. The plot gave a straight line which confirmed that the adsorption process follows a pseudo-first order reaction. Figure 9 shows the As(V) equilibrium isotherm for the resin at the same experimental conditions of figure 8. In the lower concentration regime, the resin exhibits a higher exchange capacity, followed by a crossover. Although the resin is classified as strongly basic anionic, these systems may posses a combination of strong and weak groups due to side reactions that occur during resin synthesis[17]. It is possible that as the concentration increases, these weaker groups begin to exert exchange capacity thus resulting in a crossover point.
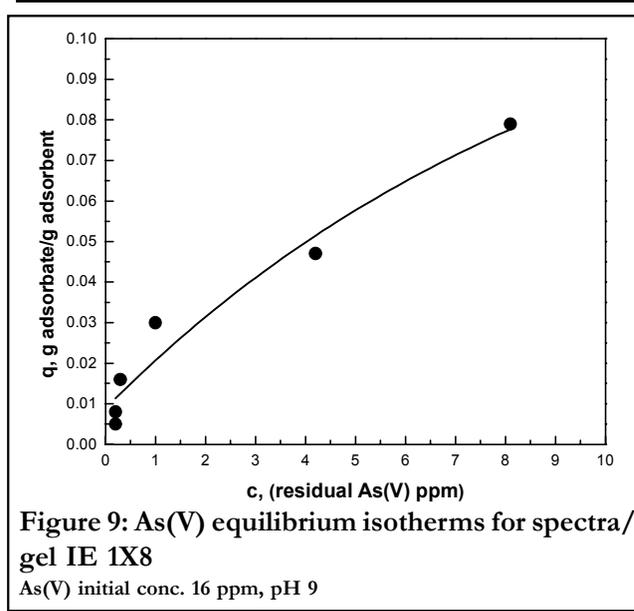
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At the optimum adsorption conditions, a run of experiments was performed in the disposable polypropylene columns packed with 2 g of the resin. The flow rate of the arsenic solution was adjusted to be 2 to 3 ml/minute. The adsorbed arsenic fractions were eluted from the resin using 2M NaCl. Finally, the resin was washed with bi-distilled water for re-using.

CONCLUSION

Strong base anion exchange resin spectra/gel IE 1×8 (type 1) with bead size of 75-150 μm was used and evaluated for removal of As(III) and As(V) species from water. As(III) was poorly adsorbed, whereas As(V) was retained on the resin. The adsorption process was optimized by using 0.5g resin for 100 ppm As(V) at pH 7 for 30 minutes. The maximum removal efficiency of As(V) was 99.2%. The adsorption process follows a pseudo-first order reaction. The resin was regenerated and the adsorbed arsenic fractions were eluted by using 2M NaCl.

ACKNOWLEDGEMENTS

REFERENCES

[1] U.S.EPA. National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring; Proposed Rule. Federal Register, **65**, 38888, June 22, **(2000)**. http://www.epa.gov/safewater/ars/arsenic.pdf.

[2] U.S.EPA. Fact Sheet: Drinking Water Standard for Arsenic. Office of Water. EPA 815-F-00-015, January **(2001)**. http://www.epa.gov/safewater/ars/ars_rule_factsheet.html.

[3] U.S.EPA Office of Water. Fact Sheet: EPA to Implement 10ppb Standard for Arsenic in Drinking Water. EPA 815-F-01-010, October, **(2001)**. http://www.epa.gov/safewater/ars/

[4] P.L.Smedley, D.G.Kinniburgh; A review of the source, behavior and distribution of arsenic in natural waters. Applied Geochemistry, **17**, 517-568 **(2002)**.

[5] U.S.Occupational Safety and Health Administration. Occupational Safety and Health Guidelines for Arsenic, Organic Compounds (as As). November, **(2001)**. http://www.osha-slc.gov/SLTC/healthguidelines/arsenic/recognition.html.

[6] R.C.Cheng, S.Liang, H.C.Wang, M.D.Beuhler; Journal of the American Water Works Association, **86(9)**, 79-90 **(1994)**.

[7] M.Kang, H.Chen, Y.Sato, T.Kamei, Y.Magara; Water Research, **37**, 4599-4604 **(2003)**.

[8] D.Clifford; Ion exchange and inorganic adsorption. In: A. Letterman [Ed.] 'Water Quality and Treatment', American Water Works Association, McGraw Hill, New York, **(1999)**.

[9] A.I.Christopher; Water Research, **38**, 1207-1214 **(2004)**.

[10] P.Pawel, P.Bartlomiej; Trends in Analytical Chemistry, **23(1)**, 63-69 **(2004)**.

[11] G.Thomas, S.Uwe, U.Erhard, F.Lothar; Chemische Technik (Leipzig), **48(4)**, 203-211 **(1996)**.

[12] D.A.Clifford, G.L.Ghurye; Jr. Environmental Chemistry of Arsenic, 217-245 **(2002)**.

[13] P.Pawel, P.Bartlomiej; Trends in Analytical Chemistry, **23(1)**, 63-69 **(2004)**.

[14] D.A.Clifford, G.L.Ghurye, A.R.Tripp; Journal American Water Works Association, **95(6)**, 119-130 **(2003)**.

[15] C.Iesan, S.B.Satish, B.Fries, D.Coman, D.Florea; Environmental Engineering and Management Journal, **3(3)**, 283-291 **(2004)**.

[16] M.Bissen, T.Gremm, U.Koklu, F.H.Frimmel; Acta Hydrochim.Hydrobiol., **28(1)**, 41-46 **(2000)**.

[17] L.Dominguez, J.Economy, K.Benak, C.L.Mangun; Polymers for Advanced Technologies, **14**, 632-637 **(2003)**.

[18] J.Kim, M.M.Benjamin, P.Kwan, Y.Chang; Journal - American Water Works Association, **95(3)**, 77-85 **(2003)**.

[19] J.Kim, M.M.Benjamin; Water Research, **38**, 2053-2062 **(2004)**.

[20] L.Pauling; 'General Chemistry', Dover Publications, Mineola, NY, 499 **(1970)**.

[21] R.G.Robins; The aqueous chemistry of arsenic in relation to hydrometallurgical processes, impurity control and disposal, In: Proceedings of CIM Metallurgical Society, 15th Annual Hydrometallurgical Meeting, 1-1 to 1-26 **(1985)**.

[22] A.A.Welch, S.L.Michael, J.L.Hughes; Groundwater, **26(3)**, 333-347 **(1988)**.

[23] Y.Ku, I.L.Jung; Water Res., **35(1)**, 135-142 **(2001)**.