Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Centrifugal Polyelectrolyte Enhanced Ultrafiltration for Removal of Copper-Citrate Complexes from Aqueous Solutions

Jung-Seok Yang[a]; Tae-Soon Kwon[a]; Kitae Baek[b]; Ji-Won Yang[a]
[a] Department of Chemical and Biomolecular Engineering, KAIST, Yuseong-gu, Daejeon, Republic of Korea [b] Department of Environmental Engineering, Kumoh National Institute of Technology, Gyeongbuk, Republic of Korea

To cite this Article Yang, Jung-Seok , Kwon, Tae-Soon , Baek, Kitae and Yang, Ji-Won(2006) 'Centrifugal Polyelectrolyte Enhanced Ultrafiltration for Removal of Copper-Citrate Complexes from Aqueous Solutions', Separation Science and Technology, 41: 8, 1583 — 1592

To link to this Article: DOI: 10.1080/01496390600675072

URL: http://dx.doi.org/10.1080/01496390600675072

Separation Science and Technology, 41: 1583–1592, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600675072

Centrifugal Polyelectrolyte Enhanced Ultrafiltration for Removal of Copper-Citrate Complexes from Aqueous Solutions

Jung-Seok Yang and Tae-Soon Kwon
Department of Chemical and Biomolecular Engineering, KAIST,
Yuseong-gu, Daejeon, Republic of Korea

Kitae Baek
Department of Environmental Engineering, Kumoh National Institute of
Technology, Gyeongbuk, Republic of Korea

Ji-Won Yang
Department of Chemical and Biomolecular Engineering, KAIST,
Yuseong-gu, Daejeon, Republic of Korea

Abstract: To replace the conventional dead-end polyelectrolyte enhanced filtration (PEUF), which is a time consuming process in the optimization of process variables, centrifugal polyelectrolyte enhanced ultrafiltration was investigated to remove copper-citrate complex in aqueous phase with a cationic polyelectrolyte, poly(diallydimethylammonium chloride) (PDADMAC). Effects of concentration ratios between polyelectrolyte, copper, and citrate and pH were observed. Below pH 3, copper was not removed by centrifugal PEUF. At the same concentration (1 mM) of citrate and copper, removal of copper at pH 5 was the highest value of 54%, 90%, and 98% with 5, 10, and 20 mM PDADMAC, respectively. Removal of copper decreased with the logarithmic ionic strength. Since the centrifugal PEUF is very economical in time compared with conventional dead-end PEUF, the present method should be a valuable tool in the optimization of process variables.

Keywords: Chelate, complexation, ligand, PDADMAC, PEUF

Received 12 December 2005, Accepted 21 February 2006

Address correspondence to Ji-Won Yang, Department of Chemical and Biomolecular Engineering, KAIST, Yuseong-gu, Daejeon 305-701, Republic of Korea; Tel.: +82 42 869 3924; Fax: +82 42 869 3910; E-mail: jwyang@kaist.ac.kr

INTRODUCTION

Various industrial wastewaters produced by industries, such as metal plating, metal finishing, mining, aerospace production, automotive manufacturing, and battery production, as well as by general chemical processes, contain toxic heavy metals. Conventional methods for the removal, concentration, and/or recovery of these heavy metals are precipitation, ion exchange, electro-deposition, crystallization, evaporation, and liquid-liquid extraction (1). Among these methods, precipitation is the most economical and common method. However, some industrial wastewaters and soil washing effluents contain chelating agents such as citrate, ethylenediaminetetraacetic acid (EDTA), and nitrilotriacetic acid (NTA) make the chemical precipitation ineffective due to the high buffering capacity of the solution (2).

To obtain high removal efficiency and low operating cost, ultrafiltration process combined with surfactant micelle (micellar-enhanced ultrafiltration, MEUF) (3, 4) or polyelectrolyte (polyelectrolyte-enhanced ultrafiltration, PEUF) (2,5–10) have been proposed. Many surfactants (3, 4), polyelectolytes (2,5–9), and organic matter (1–11) were used for the removal of heavy metals, radionuclides, or anionic metals with ultrafiltration. Among these, PEUF is one of the powerful processes to remove heavy metals from industrial effluents and contaminated soil treated water. This process also has been applied to remove ligand-heavy metals complexes. Although ligand-heavy metal complexes, in principle, can be removed by ultrafiltration with polyelectrolyte, conventional dead-end ultrafiltration is very time-consuming to optimize process variables. Thus an alternative method is needed to save time.

In this study, centrifugal force was applied to the polyelectrolyte enhanced ultrafiltration in the removal of copper-citrate complex as a model system in aqueous phase with a cationic polyelectrolyte, poly(diallydimethylammonium chloride). The purpose of applying centrifugal force was to see whether we could save time compared with conventional PEUF. We also observed the effect of the concentration of polyelectrolyte, citrate, and copper in PEUF by centrifugal method.

MATERIALS AND METHODS

Chemicals

Poly(diallydimethylammonium chloride), PDADMAC, with an average molecular weight 100,000–200,000 (Aldrich, USA) was used as a 20 wt% aqueous solution, and the concentration of PDADMAC was expressed as the concentration of monomer unit which is the molecular weight of

161.7 g/mol. Trisodium citrate, copper nitrate, and other inorganic chemicals were supplied by Sigma-Aldrich. The aqueous phase was prepared by dissolving copper nitrate, citrate, and PDADMAC in deionized water at the required concentration, in which the pH was adjusted by adding a small amount of HCl and NaOH. Prior to use, the solutions were mixed for minimum 1 day at 25 ± 1°C to reach equilibrium state. All chemicals were used as received without further purification.

Ultrafiltration

The centrifugal ultrafiltration experiments were operated with Amicon Ultra-4 centrifugal filter device (Millipore, USA). Regenerated cellulose membrane with an effective area of 3 cm^2 and a molecular weight cut-off (MWCO) of 10,000 was used. The centrifugal filter device was initially filled with 3.5 ml feed solution. The filter unit was centrifuged by 5000 rpm and spin time was 10 min. The retentate volume was reduced below 20% of initial feed volume after centrifugation.

The conventional ultrafiltration experiments were conducted with the regenerated cellulose membrane (YM10, Millipore, USA) with an effective area of 45 cm^2 and MWCO of 10,000. Initial feed volume was 100 ml and applied pressure was maintained at 2 bars. To minimize the membrane fouling, the solution was stirred with 200 rpm. At desired time interval, permeate was collected and analyzed. Average water flux was 45.6 L/h · m^2. Filtration time was 30 min and final feed volume was different by PDADMAC concentration, but generally below 25% of initial feed volume. The relative flux was calculated by the following equation:

$$J_R = J_S/J_W \tag{1}$$

where J_R, J_S, and J_W are the relative flux, solution flux, and water flux, respectively.

Analysis

Samples were pretreated by the method of acid digestion to analyze copper. Concentrated nitric acid and hydrogen peroxide were inserted in the permeate sample and the solution was heated at 110°C during 2 h to remove residual citrate and PDADMAC. The concentration of copper in the sample was analyzed by anodic stripping voltammetry (TEA-3000V, MTI, Australia). The removal efficiency of copper was calculated by the following equation:

$$R = 1 - C_p/C_i \tag{2}$$

where R is the removal efficiency and C_i and C_p represent the copper concentration in the initial feed and in the permeate, respectively. Theoretical distribution of copper and citrate in aqueous solutions was simulated by MINEQL+ (12).

RESULTS

Effect of PDADMAC Concentration

Figure 1 showed the effect of PDADMAC concentration on the removal of copper citrate complexes under 1 mM citrate (L) and 1 mM copper (Cu) in various pH. Copper has several forms by complexation with citrate. The dominant form of copper is Cu(II) ion (Cu^{2+}) below pH 3 and Cu(II)-citrate complexed ion (CuL^-) above pH 4 (Fig. 2). Because PDADMAC is a cationic polyelectrolyte, Cu(II), a plus charged ion, does not bind PDADMAC and Cu(II)-citrate complex, a minus charged ion, can bind PDADMAC. As shown in Fig. 1, removal of copper was 54%, 90%, and 98% with 5, 10, and 20 mM PDADMAC, respectively, with 1 mM citrate and 1 mM copper at pH 5. Although cloudy solutions due to the hydroxide formation were obtained at high pH (>5.5) and low PDADMAC concentration, removal of copper was still high. Copper hydroxide formation and precipitation is a serious disadvantage of membrane filtration, as it is related to membrane fouling (6). This problem can be solved by addition of more citrate or PDADMAC.

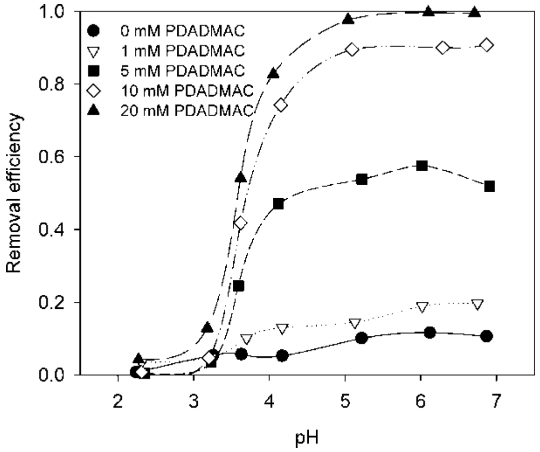

Figure 1. Effect of PDADMAC concentration with 1 mM copper and 1 mM citrate on the centrifugal PEUF.

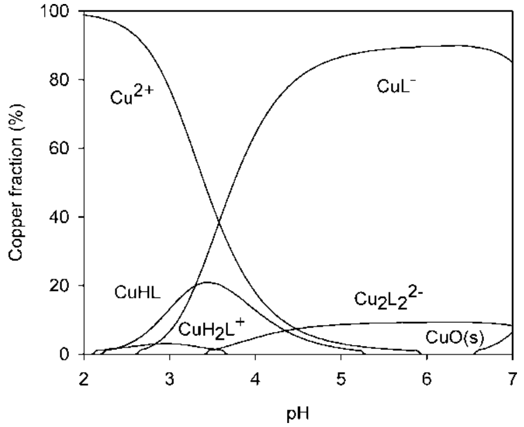

Figure 2. Distribution of copper fraction according to pH by MINEQL+ simulation with 1 mM copper and 1 mM citrate.

Effect of Citrate and Initial Copper Concentration

When the citrate concentration increased at fixed copper concentration (1 mM) and PDADMAC concentration (10 mM), the removal of copper was the highest at the same ratio of citrate and copper at pH 5 (Fig. 3). In model simulation results with MINEQL+, dominant citrate form in 1 mM citrate (L) was CuL^- and $Cu_2L_2^{2-}$. With 4 mM citrate, HL^{2-} and H_2L^- are the dominant species and these two species can bind PDADMAC. It means that competitive binding to PDADMAC occurred between copper-citrate complexes (CuL^- and $Cu_2L_2^{2-}$) and citrates (HL^{2-} and H_2L^-). The removal of copper was 31%, 53%, 90%, 83%, and 75% with 0.25, 0.5, 1.0, 2.0, and 4.0 mM citrate, respectively. If binding affinities are in the same level between citrate-copper complexes and citrate ions, the removal of copper is theoretically 94% with 1 mM citrate, and 18% with 4 mM citrate. However, the removal of copper with 4 mM citrate was 70% and the magnitudes of decrease in the removal efficiency by increase of citrate concentration were smaller than the theoretical value. This results show the binding affinities of CuL^- and $Cu_2L_2^{2-}$ to PDADMAC are higher than those of HL^{2-} and H_2L^-.

Figure 4 shows the effect of initial copper concentration on the removal of copper-citrate complexes by PEUF. At pH 5, the removal efficiencies were 0.99, 0.98, 0.90, 0.49, and 0.20 with 0.25, 0.5, 1.0, 2.0, and 4.0 mM of initial copper concentration, respectively, with 1 mM citrate and 10 mM PDADMAC. The removal efficiency of copper decreased with initial copper concentration because of the limitation of binding site of PDADMAC.

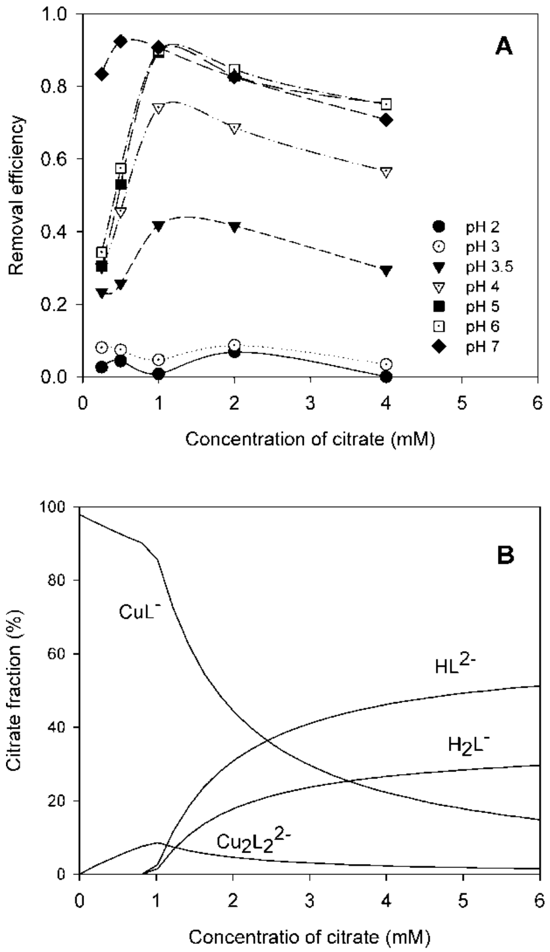

Figure 3. Effect of citrate concentration with 1 mM copper and 10 mM PDADMAC on the centrifugal PEUF. (a) Experimental result and (b) model by MINEQL+.

Effect of Salt Concentration

It is well known that the ionic strength of aqueous solutions affect the effectiveness of binding in ultrafiltration processes (2). Removal of copper decreased with increasing salt concentration and the magnitude was in the order NaCl < $NaNO_3$ << $MgCl_2$ ≈ Na_2SO_4 < $CaCl_2$ (Fig. 5). As the salt concentration increases, the electrical double layer of PDADMAC is compressed. It means that many molecules of salts locate in the surface of PDADMAC. The salts also have a chance to bind with PDAMAC. Hence electrostatic attraction between PDADMAC and citrate-copper complexes is

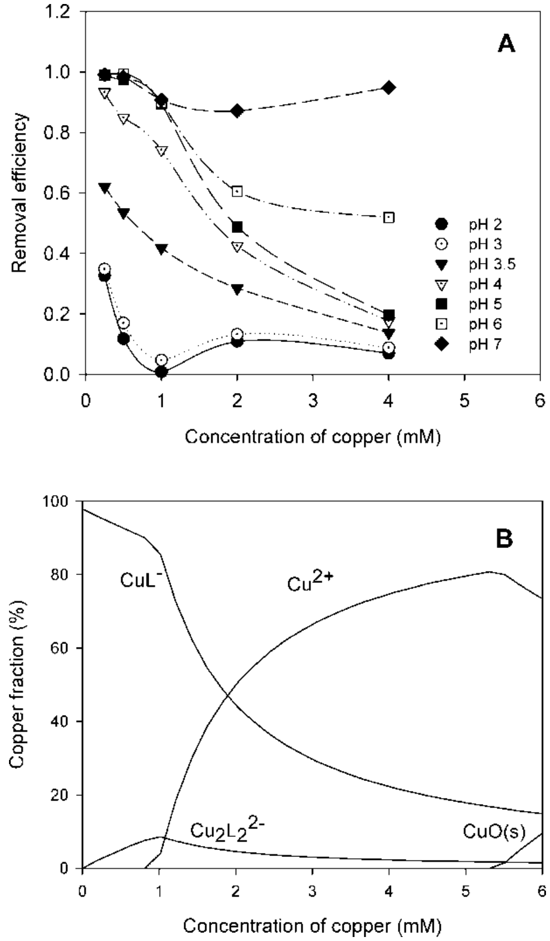

Figure 4. Effect of initial copper concentration with 1 mM citrate and 10 mM PDADMAC on the centrifugal PEUF. (a) Experimental result and (b) model by MINEQL+.

reduced. The results occurred in the phenomena that cations of salts compete with copper for binding citrate, and anions of salts compete with citrate for binding PDADMAC. Although the binding affinities in each case are slightly different, the influence on the removal efficiency is generally the same in equal ionic strength.

Conventional Dead-End Filtration

Figure 6 shows the removal efficiency and relative flux in a conventional dead-end ultrafiltration. The removal efficiency by dead-end filtration with

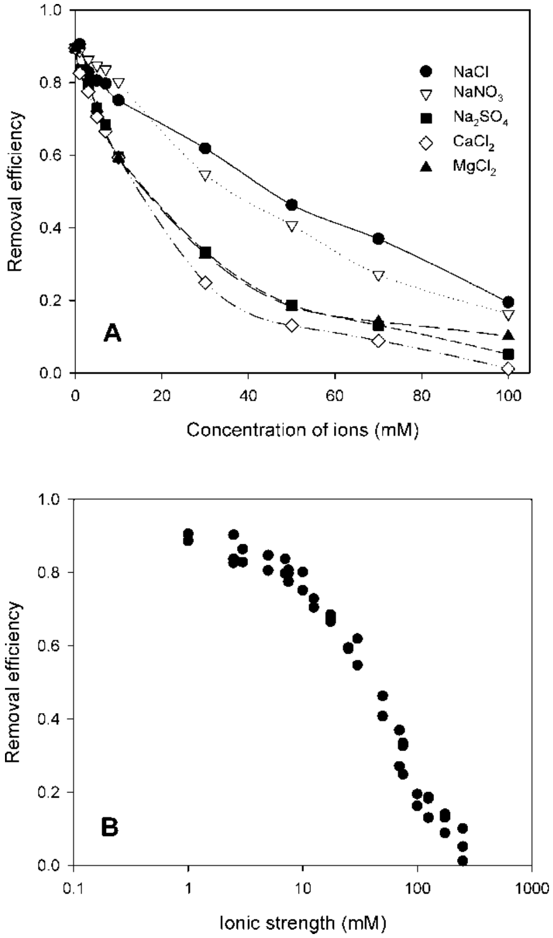

Figure 5. Effect of electrolyte with 1 mM copper, 1 mM citrate, and 10 mM PDADMAC on the centrifugal PEUF. Removal efficiency of copper according to (a) electrolytes and (b) ionic strength.

1 mM citrate and 1 mM copper at pH 5 was similar to centrifugal method and relative flux approached 0.7 regardless of the PDADMAC concentration. It means that centrifugal PEUF can be applied to the optimization of process variables.

CONCLUSION

Centrifugal PEUF was applied to replace the conventional dead-end ultrafiltration in optimization of process variable; the concentration of citrate, initial

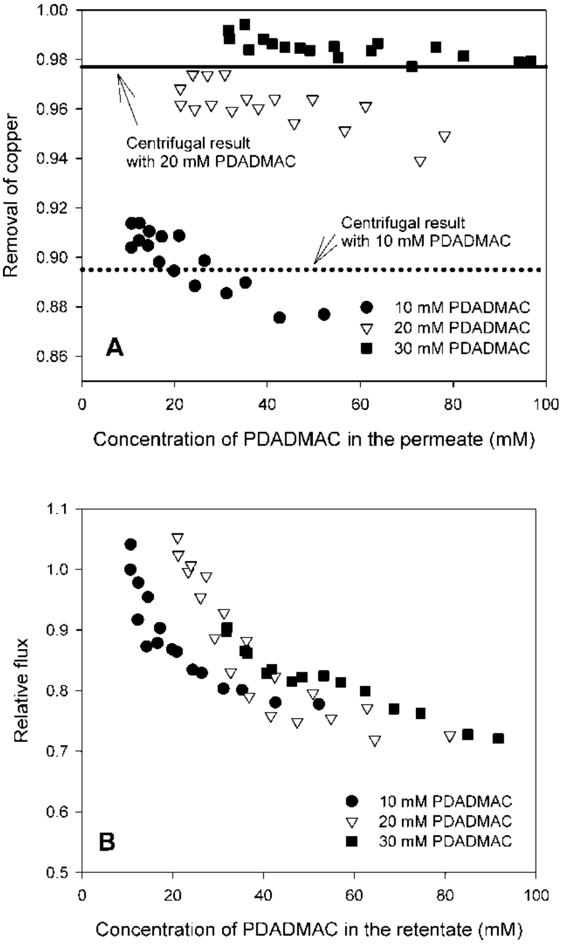

Figure 6. Comparison of centrifugal PEUF with conventional dead-end PEUF with 1 mM citrate and 1 mM copper at pH 5. Symbols indicate dead-end PEUF results and lines indicate centrifugal PEUF results. (a) Removal of copper and (b) relative flux.

copper, and PDADMAC. Below pH 3, the removal of copper was very low because Cu^{2+} ion was a dominant species. Removal of copper in the centrifugal PEUF with 1 mM citrate and 1 mM copper at pH 5 was 54%, 90%, and 98% with 5, 10, and 20 mM PDADMAC, respectively. The highest removal of copper was obtained at the same ratio of citrate and copper. Removal of copper decreased with logarithmic ionic strength of aqueous solutions. These results could also be obtained in a conventional dead-end PEUF. Because the centrifugal PEUF is very time economical, it can be utilized in the optimization of process variables in various ultrafiltration processes.

ACKNOWLEDGEMENTS

This research was partially supported by a grant (M1-0412-00-0001) from the Korea Ministry of Science and Technology through the National Research Laboratory program and by a grant from KOSEF through the Advanced Environmental Monitoring Research Center (ADEMRC) at the Gwangju Institute of Science and Technology (GIST).

REFERENCES

1. Baek, K. and Yang, J.-W. (2005) Humic-subtance-enhanced ultrafiltration for removal of heavy metals. *Sep. Sci. Technol.*, 40: 699–708.
2. Juang, R.-S. and Chen, M.-N. (1997) Removal of copper(II) chelates of EDTA and NTA from dilute aqueous solutions by membrane filtration. *Ind. Eng. Chem. Res.*, 36: 179–186.
3. Liu, C.-K., Li, C.-W., and Lin, C.-Y. (2004) Micellar-enhanced ultrafiltration process (MEUF) for removing copper from synthetic wastewater containing ligands. *Chemosphere*, 57: 629–634.
4. Fillipi, B.R., Scamehorn, J.F., Taylor, R.W., and Christian, S.D. (1997) Selective removal of copper from an aqueous solution using ligand-modified micellar enhanced ultrafiltration using an alkyl-ketone ligand. *Sep. Sci. Technol.*, 32: 2401–2424.
5. Tunçay, M., Christian, S.D., Tucker, E.E., Taylor, R.W., and Scamehorn, J.F. (1994) Ligand-modified polyelectrolyte-enhanced ultrafiltration with electrostatic attachment of ligands. 1. Removal of Cu(II) and Pb(II) with expulsion of Ca(II). *Langmuir*, 10: 4688–4692.
6. Molinari, R., Poerio, T., and Argurio, T. (2005) Polymer assisted ultrafiltration for copper-citrate acid chelate removal from wash solutions of contaminated soil. *J. Appl. Electrochem.*, 35: 375–380.
7. Roach, J.D., Christian, S.D., Tucker, E.E., Taylor, R.W., and Scamehorn, R.W. (2003) Ligand-modified colloid enhanced ultrafiltration. Use of nitrilotriacetic acid derivatives for the selective removal of lead from aqueous solutions. *Sep. Sci. Technol.*, 38: 1925–1947.
8. Pookrod, P., Haller, K.J., and Scamehorn, J.F. (2004) Removal of arsenic anions from water using polyelectrolyte-enhanced ultrafiltration. *Sep. Sci. Technol.*, 39: 811–831.
9. Baticle, P., Kiefer, C., Lakhchaf, N., Leclerc, O., Persin, M., and Sarrazin, J. (2000) Treatment of nickel containing industrial effluents with a hybrid process comprising of polymer complexation-ultrafiltration-electrolysis. *Sep. Purif. Technol.*, 18: 195–207.
10. Korus, I., Bodzek, M., and Loska, K. (1999) Removal of zinc and nickel ions from aqueous solutions by means of the hybrid complexation-ultrafiltration process. *Sep. Purif. Technol.*, 17: 111–116.
11. Alpatova, A., Verbych, S., Bryk, M., Nigmatullin, R., and Hilal, N. (2004) Ultrafiltration of water containing natural organic matter: heavy metal removing in the hybrid complexation-ultrafiltration process. *Sep. Purif. Technol.*, 40: 155–162.
12. Schecher, W.D. and McAvoy, D.C. (2003) *Mineql+: A Chemical Equilibrium Modeling System, Version 4.5 for Windows, User's Manual*; Environmental Research Software: Hallowell, Maine.