Separation and Recovery of Lead by Cation Exchange Process Combined with Precipitation

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Wastewater generated by circuit board industries contain high levels of toxic heavy metals such as lead, nickel, chromium, cadmium, copper, as well as other components (Haas and Tare, 1984). The recovery of these metals is very important not only in the aspect of environmental protection but also in that they are valuable raw materials. The most common methods for the treatment of wastewater containing heavy metals include precipitation and adsorption (Patterson, 1975). A new application of ion exchange combined with precipitation for recovery and concentration of toxic heavy metals, in particular, lead, is presented in this article.

The combined process consisted of the saturation of a cation-exchange column with a mixture of Pb^{2+}, Ni^{2+}, or Cd^{2+} and elution with a NaCl solution. Precipitation of lead salt ($PbCl_2$) was caused purposely by introducing the NaCl solution containing anions (Cl^-) that formed $PbCl_2$ of very low solubility in the cation-exchange column. The unprecipitated ions (Ni^{2+} or Cd^{2+}) were eluted whereas the precipitated lead salt stayed in the column. After the complete precipitation of the lead salt and the elution of nickel or cadmium ions, a solubilizing reagent solution (CH_3COONa or methane sulfonic acid) was fed to the column to dissolve and elute the lead precipitate. The combined process was demonstrated to be efficient in the separation and concentration of lead.

Materials and Methods

Ion-exchange resin and fixed-bed operation

An acidic cation-exchange resin Dowex 50W-X8 in hydrogen form was purchased from the Dow Chemical Co. (Midland, MI) as 100–200 mesh beads. A single lot of the commercial resin was vacuum dried in an oven at 110°C. After 20 h drying, the water content was determined to be about 49%. Its dry resin capacity was determined as 5.0 meq/gram by a batch equilibrium study. Averaged separation factors (α_{ij}) were determined from plots of binary ion-exchange isotherms (20°C) according to the method developed by Clifford (1982). The separation factors for Ni^{2+}, Cd^{2+}, Pb^{2+}, and Na^+ with respect to H^+ were determined to be 3.1, 3.0, 7.7, and 1.5, respectively. A glass column of 1.4 cm ID × 7.8 cm was slurry packed with 4.9 grams of H^+-form Dowex 50W-X8 resin. The total capacity of the cation-exchange column was determined from the breakthrough curve analysis. The total bed capacity Q was determined to be 24.3 meq. The void fraction of the bed was determined to be 0.42 when the resin was saturated with Na^+ ions at 1.0 M sodium hydroxide.

Chemicals and analysis methods

All chemicals used in this study, except methane sulfonic acid, were ACS reagent grade purchased from Fisher Scientific (Pittsburgh, PA). Methane sulfonic acid (MSA) was provided by Elf Atochem North America (Riverview, MI). Concentrations of metal ions were determined by atomic absorption spectrophotometry (Perkin Elmer 430) for routine analysis of the column effluent. Ion selective electrodes and chemical colorimetric method were also used for continuous measurement in batch experiments. The ion selective electrodes used in this study were Model 94-82 from Orion (Boston, MA) for Pb^{2+} and FK1502Cd from Radiometer (Westlake, OH) for Cd^{2+}. The concentration of Ni^{2+} was determined colorimetrically by forming a blue complex with ammonium citrate (Thomas and Chamberlin, 1980). A conductivity meter (Varian Model CM-2) was connected to the column to monitor the total ion concentration in the effluent stream.

Theoretical Analysis

We will consider the separation of Pb^{2+} and Ni^{2+}. A fixed-bed operation consists of three steps: (1) saturation of the Na^+-form bed with a feed containing Pb^{2+} and Ni^{2+}; (2) precipitation of Pb^{2+} as $PbCl_2$ and elution of Ni^{2+} by introducing NaCl solution; and (3) solubilization of the $PbCl_2$ precipitate by feeding a NaAc solution. The feed stream is at concentrations of 0.2 meq/mL Pb^{2+} and 0.2 meq/mL Ni^{2+}. The total bed capacity and the volume of the bed are $Q = 24.3$ meq and $V_{bed} = 12.0$ cm^3, respectively. The bed capacity per unit volume q is 2.03 meq per cm^3 of bed volume. The separation factors are $\alpha_{Pb/Na} = 5.13$ and $\alpha_{Ni/Na} = 2.07$. The void fraction of the bed is $\epsilon = 0.42$.

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The method of characteristics (Rhee et al., 1989; Page et al., 1975) is used to determine concentration profiles during the breakthrough, precipitation, and solubilization steps. C_i is in meq per mL of solution phase and q_i is in meq per mL of bed volume. In the saturation step with a feed mixture of $C_{Pb} = 0.2$ meq/mL and $C_{Ni} = 0.2$ meq/mL, Na^+ ions initially in the resin phase are eluted first and the breakthrough of Ni^{2+} and Pb^{2+} follow step 1. When the column is saturated with the Pb-Ni mixture, the bed composition is $q_{Pb} = 1.45$ meq/cm^3 and $q_{Ni} = 0.58$ meq/cm^3.

If a sodium acetate (NaAc) solution is fed to the saturated column, Ni^{2+} and Pb^{2+} will elute without precipitation. If a sodium chloride (NaCl) solution is fed to displace the adsorbed Pb^{2+} and Ni^{2+} (step 2), the precipitation of lead chloride ($PbCl_2$) will take place. For either of the cases, the following local conditions have to be satisfied:

Cation-Exchange Equilibrium (Separation Factors):

$$\alpha_{Pb/Na} = \frac{q_{Pb}C_{Na}}{C_{Pb}q_{Na}} = 5.13 \qquad (1)$$

$$\alpha_{Ni/Na} = \frac{q_{Ni}C_{Na}}{C_{Ni}q_{Na}} = 2.07 \qquad (2)$$

Constant Bed Capacity:

$$q_{Na} + q_{Ni} + q_{Pb} = q \qquad (3)$$

Electroneutrality in Liquid Phase:

$$C_{Na} + C_{Ni} + C_{Pb} = C_{Cl} \qquad (4)$$

For the case of the precipitation of lead with NaCl, in addition to the above equations, the concentrations of C_{Pb} and C_{Cl} should satisfy the following solubility product:

Solubility Product:

$$K_{sp} = C_{Pb}C_{Cl}^2 = 1.6 \times 10^{-5} \qquad (5)$$

Without precipitation with NaAc as a displacer, Eq. 4 is substituted with:

$$C_{Na} + C_{Ni} + C_{Pb} = C_o \qquad (6)$$

where C_o is the total cation concentration in the mobile phase.

To determine the concentrations of Na^+, Ni^{2+}, and Pb^{2+} with respect to time t and distance measured from the inlet of the column z, the following material balance equations for Na^+ and Ni^{2+} have to be solved with the local conditions described above:

$$u\frac{\partial C_{Na}}{\partial z} + \epsilon\frac{\partial C_{Na}}{\partial t} + \frac{\partial q_{Na}}{\partial t} = 0 \qquad (7)$$

$$u\frac{\partial C_{Ni}}{\partial z} + \epsilon\frac{\partial C_{Ni}}{\partial t} + \frac{\partial q_{Ni}}{\partial t} = 0 \qquad (8)$$

The material balance equation for Pb is not necessary, because it is not independent of Eqs. 3, 4 or 6, 7, and 8. Rearranging the Eqs. 1–8 describing the local conditions, we obtain q_{Na} and q_{Ni} as a function of C_{Na} and C_{Ni}: $q_{Na} = q_{Na}(C_{Na}, C_{Ni})$ and $q_{Ni} = q_{Ni}(C_{Na}, C_{Ni})$.

A general procedure for determining the trajectories for the concentration profile or history in the hodographic plane (C_{Na} vs. C_{Ni}) is as follows:

(1) For a given initial bed state of $B(C_{Na}, C_{Ni})$ and a given feed state of $F(C_{Na}, C_{Ni})$, the following values are determined:

$$A = \left(\frac{\partial q_{Na}}{\partial C_{Na}}\right)_{Ni}, \quad B = \left(\frac{\partial q_{Ni}}{\partial C_{Ni}}\right)_{Na}, \quad C = \left(\frac{\partial q_{Na}}{\partial C_{Ni}}\right)_{Na}, \quad \text{and} \quad D = \left(\frac{\partial q_{Ni}}{\partial C_{Na}}\right)_{Ni} \qquad (9)$$

(2) Two eigenvalues and the corresponding eigenvector directions are determined from:

$$\lambda_{\pm} = \frac{1}{2}\left\{(A+B) \pm \sqrt{(A+B)^2 - 4(AB - CD)}\right\} \qquad (10)$$

$$\frac{dC_{Na}}{dC_{Ni}} = \frac{C}{\lambda - A} = \frac{\lambda - B}{D} \qquad (11)$$

With the initial bed B as a starting point, the eigenvector determined with λ_- is chosen. With the feed state F as a starting point, the eigenvector determined with λ_+ is chosen.

(3) q_{Na} and q_{Ni} along the eigenvectors are determined from:

$$\lambda = \frac{dq_{Na}}{dC_{Na}} = \frac{dq_{Ni}}{dC_{Ni}} \qquad (12)$$

(4) The solute velocity defined as:

$$u_s = \frac{dz}{dt} = \frac{u}{\epsilon + \lambda} \qquad (13)$$

is determined along the eigenvectors.

(5) Steps 1 through 4 are repeated until the two eigenvectors intersect at point P in the hodographic plane. The intersection point represents a plateau in the concentration profile C_i vs. z and the concentration history C_i vs. t.

(6) If the eigenvalue increases along the trajectory from the bed to feed state, the concentration change along the trajectory represents diffusive waves flanking the plateau. If the eigenvalues decreases, a shock wave should exist and the following jump condition will be used instead of Eq. 12:

$$\lambda = \frac{[q_{Na}]}{[C_{Na}]} = \frac{[q_{Ni}]}{[C_{Ni}]} \qquad (14)$$

Experimental Results

Separation of Pb^{2+} and Ni^{2+} from a Pb-Ni mixture

A mixture of 0.1 M lead nitrate (0.2 meq/mL Pb^{2+}) and 0.1 M nickel nitrate (0.2 meq/mL Ni^{2+}) was fed to the Na^+-

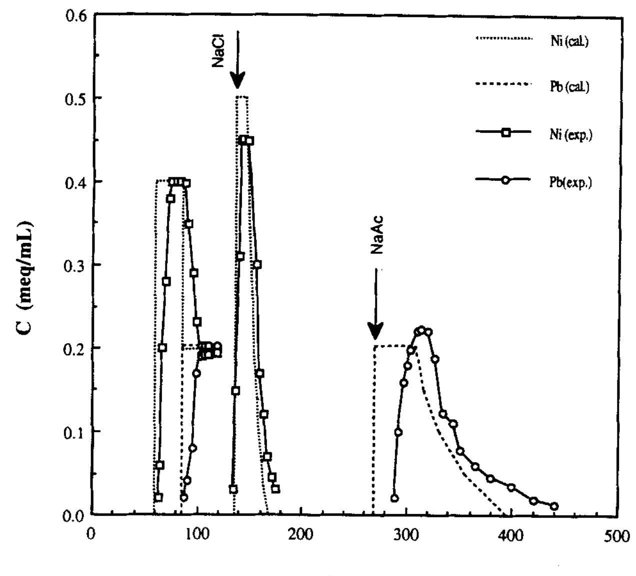

Figure 1. Separation of Ni^{2+} and Pb^{2+} with precipitation and solubilization.

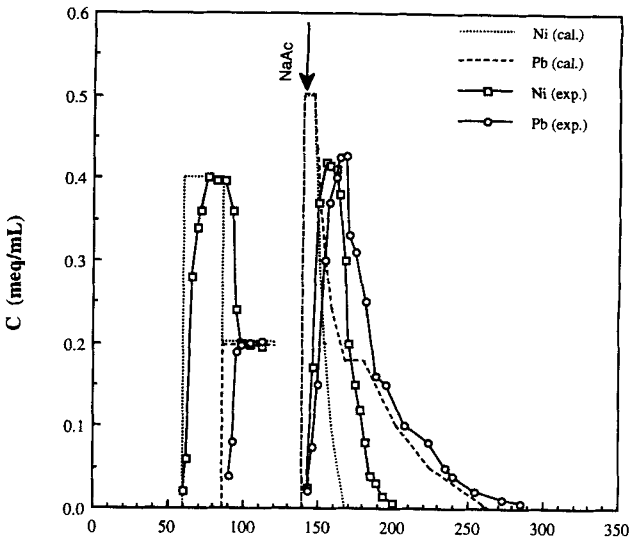

Figure 2. Separation of Ni^{2+} and Pb^{2+} without precipitation.

saturated column with the total capacity of 24.3 meq. The flow rate was 0.34 mL/min. The development of green nickel front could be observed. The entire elution profiles including the breakthrough curve are plotted in Figure 1. The dotted lines represent the theoretical prediction described previously. A concentrated solution of Ni^{2+} eluted at $64 < V_e < 90$. Saturation of the bed with Pb^{2+} and Ni^{2+} was achieved at an elution volume of $V_e = 97$ mL. The total amount of Pb^{2+} and Ni^{2+} fed to the column was 17.4 meq each. The feed was then switched to 1.0 M NaCl at $V_e = 134$ mL. The precipitation of $PbCl_2$ took place from the inlet and the precipitation front moved along the column. The difference in pressure drop with and without precipitates was negligible. During the precipitation step, the concentration of Pb^{2+} in the effluent stream was measured to be below 10^{-6} meq/mL, whereas the concentration of Ni^{2+} ($134 < V_e < 200$) was as high as 0.44 meq/mL. The total Ni^{2+} collected was about 6.9 meq. The recovery of concentrated pure Ni^{2+} was achieved in this step. When the elution of nickel was completed, 1.0 M NaAc was fed at $V_e = 270$ mL to dissolve the lead precipitate in the column. The white precipitate began to dissolve from the inlet of the bed, and the total 16.8 meq of pure Pb^{2+} was recovered at an elution volume of $286 < V_e < 470$. The recovery of Pb^{2+} was 96.5%. The maximum concentration of Pb^{2+} was 0.24 meq/mL. During the elution with NaAc, the resin was simultaneously regenerated to the Na^+-form. The predicted concentration profiles for the saturation, precipitation, and dissolution steps agreed reasonably well with the experimental results. The solubilization of $PbCl_2$ and elution of Pb^{2+} with NaAc gave an elution profile with a lag in Pb^{2+} appearance and a broader diffusive tail than the predicted concentration profile. This discrepancy is because the actual dissolution is not instantaneous, as assumed in the theoretical analysis.

For a direct elution without precipitation, 1.0 M NaAc solution was fed at an elution volume of $V_e = 140$ mL to the bed saturated with Pb-Ni mixture (Figure 2). The elution profiles of Pb^{2+} and Ni^{2+} were overlapped and complete separation was not achieved. The total Ni^{2+} and Pb^{2+} collected were 6.9 meq and 17.3 meq, respectively.

For a successful operation of the cycle of saturation-precipitation-solubilization, a judicious selection of a precipitating agent is important, because the salt of Pb^{2+} with the anion of the precipitating agent should have an optimally low solubility. We may use anions other than chloride, such as hydroxide and carbonate. They can form salts of much lower solubility than that of $PbCl_2$. However, the reasons for using chloride instead of hydroxide or carbonate ions in this study are (i) chloride ions form a precipitate with lead ions; (ii) $Pb(OH)_2$ and $Pb(CO_3)_2$ salts may not be solubilized easily by NaAc or methane sulfonic acid due to their extremely low solubility products. The solubility products of $Pb(OH)_2$ and $Pb(CO_3)_2$ are as low as 1.40×10^{-20} and 1.48×10^{-13}, respectively; (iii) OH^- and CO_3^- can form precipitates with Ni^{2+} and Cd^{2+} as well as with Pb^{2+}.

Separation of Pb^{2+} and Cd^{2+} from a Pb-Cd mixture

Similar experiments were carried out with Pb-Cd mixtures. The feed mixture of 0.1 M lead nitrate and 0.1 M cadmium acetate was fed to the Na^+-saturated column. The flow rate was 0.40 mL/min. The experimental and theoretical concentration profiles for the steps of breakthrough, precipitation by NaCl, and solubilization of $PbCl_2$ by NaAc are shown in Figure 3. Direct elution without precipitation was also carried out with NaAc as a displacer, and the experimental and theoretical results are shown in Figure 4.

For the ion-exchange process combined with precipitation (Figure 3), Cd^{2+} eluted first at a higher concentration ($60 < V_e < 86$) in the saturation step. When the bed was saturated with Pb^{2+} and Cd^{2+} at $V_e = 86$ mL, the concentrations in the effluent stream were the same as those in the feed stream (0.2 meq/mL). The total amount of Pb^{2+} and Cd^{2+} fed to the column was 17.4 meq each. The elution of Cd^{2+} and the

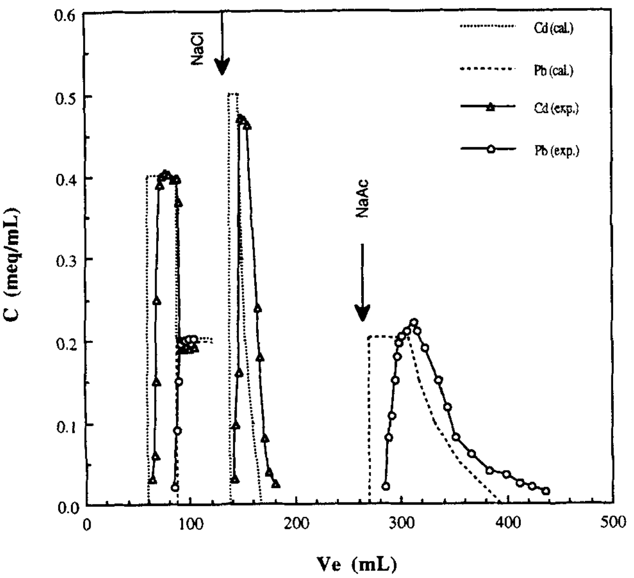

Figure 3. Separation of Cd^{2+} and Pb^{2+} with precipitation and solubilization.

precipitation of Pb^{2+} started at $V_e = 1.34$ mL by feeding 1.0 M NaCl. Cd^{2+} was eluted ($138 < V_e < 188$) while the $PbCl_2$ precipitate stayed in the column. About 6.9 meq of Cd^{2+} was collected and the peak concentration was 0.46 meq/mL. At an elution volume of $V_e = 270$ mL, the feed stream was switched to 1.0 M NaAc solution to dissolve the lead precipitate. The total 16.4 meq of Pb^{2+} was recovered ($280 < V_e < 460$), and the column was regenerated concurrently to the Na^+-form. The recovery of Pb^{2+} was 94%. The maximum concentration was 0.24 meq/mL. When the Pb-Cd saturated column was eluted with the NaAc solution without precipitation (Figure 4), Cd^{2+} and Pb^{2+} could not be separated. The total Cd^{2+} and Pb^{2+} collected were 6.9 meq and 17.2 meq, respectively. The concentration profiles were similar to those in Figure 2 obtained for the Pb-Ni mixture because the separation factor of Cd^{2+} ($\alpha_{Cd/Na} = 2.0$) is close to that of Ni^{2+} ($\alpha_{Ni/Na} = 2.07$).

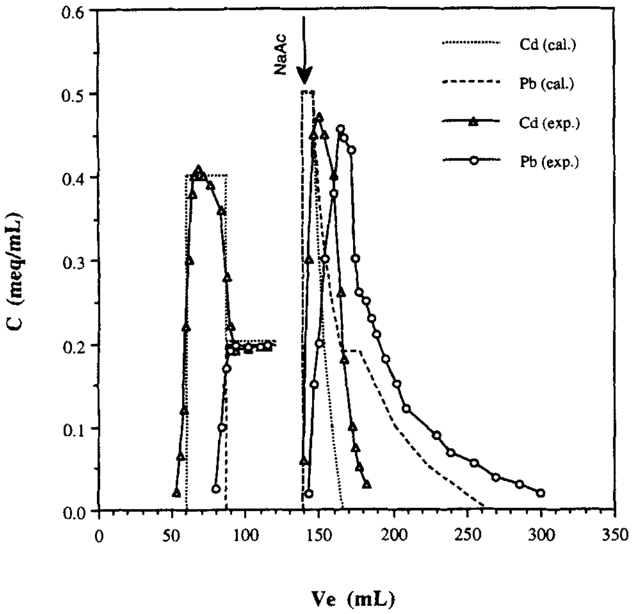

Figure 4. Separation of Cd^{2+} and Pb^{2+} without precipitation.

Use of methane sulfonic acid (MSA) as a solubilizing reagent

For the cycle of saturation, precipitation, and dissolution (Figures 1 and 3), the recovery of Pb^{2+} after the dissolution of $PbCl_2$ with NaAc was not complete. The objective of the next set of experiments involving repeated use of the column for five cycles was to determine if the incomplete recovery is due to a formation of precipitate in the resin, which is not easily dissolved by NaAc, resulting in a decrease in the bed capacity.

A mixture of 0.1 M lead nitrate and 0.1 M nickel nitrate was fed to the Na^+-saturated column with the total capacity of 24.3 meq. The flow rate was 0.34 mL/min. When the bed was saturated with Pb^{2+} and Ni^{2+}, the feed was switched to 1.0 M NaCl. The precipitation of $PbCl_2$ took place from the inlet, and the precipitation front moved along the column. During the precipitation step, Ni^{2+} was collected from the effluent stream. When the elution of nickel was completed, 1.0 M NaAc was fed to dissolve the lead precipitate in the column. The white precipitate began to dissolve from the inlet of the bed, and the total amount of pure Pb^{2+} was recovered. The percent recovery of Pb^{2+} was determined. During the elution with NaAc, the resin was regenerated to the Na^+-form for the next cycle of saturation, precipitation, and dissolution. Five cycles of operation were carried out and the recovery yield of Pb^{2+} gradually decreased as the number of cycle increased. The recovery yield fell down below 80% after five cycles. This recovery reduction was relatively significant compared with the recovery of Pb^{2+} without precipitation, which was consistently above 98%. The precipitate of $PbCl_2$ inside the column partly formed firm aggregates after repeated cycles. Once this happened, it was very difficult to redissolve the aggregate. The aggregates gradually occupied the interstitial space and reduced the resin capacity.

To enhance the dissolution of $PbCl_2$, methane sulfonic acid (MSA) was used as a solubilizing agent instead of NaAc. Most of the MSA metal salts commonly found in the waste streams are highly soluble in water. Anhydrous salts of MSA ($CH_3SO_3^-$) with divalent metal ions, such as Pb^{2+} Ag^{2+}, Hg^{2+}, Sn^{2+}, and Ba^{2+}, have high solubilities (Elf Atochem, 1992). The solubilities of Pb^{2+}, Ni^{2+}, and Cd^{2+} at 25°C are 143, 66, and 150 grams per 100 gram water, respectively. MSA is less corrosive than common acids such as acetic acid, sulfuric acid, hydrochloric acid, and fluoroboric acid.

The solubilization of $PbCl_2$ using MSA was carried out for Pb-Ni separation. The $PbCl_2$ precipitation occurred by flowing 1.0 M NaCl through the column saturated with Pb-Ni. The flow rate was 0.4 mL/min. After the complete precipitation of $PbCl_2$ and the elution of nickel, 2.94 M MSA was fed to dissolve the precipitate. Methane sulfonic acid (2.94 M) had a comparable efficiency with 1.0 M NaAc in terms of peak concentration and band broadening. During the dissolution, the bed was concurrently regenerated to the H^+ form ready for the next cycle of saturation, precipitation, and dissolution. Five cycles of operation were carried out and the recovery yield of Pb^{2+} were consistently about 99% with MSA as a solubilizing agent. These high yields were comparable with those obtained for the recovery of Pb^{2+} without precipitation, which was consistently above 98%.

Conclusions

The proposed ion-exchange process combined with precipitation resulted in efficient separation, concentration, and recovery of lead. Cyclic fixed-bed operation with saturation-precipitation-solubilization steps showed improvement in separation and concentration. During the precipitation step, concentrated metal ions (Ni^{2+} or Cd^{2+}) elute from the column while the precipitate of $PbCl_2$ stayed inside the column. The precipitates were solubilized by NaAc or methane sulfonic acid (MSA). The resin was concurrently regenerated to the Na^+-form and H^+-form using NaAc and MSA, respectively. The recovery yield of Pb^{2+} obtained with 2.94 M MSA in the solubilization step was comparable with that without precipitation. The solubilization of $PbCl_2$ by MSA reduced the accumulation of insoluble salts in the resin and, thus, the bed could be utilized to its maximum capacity for at least five cycles of saturation, precipitation, and solubilization.

Acknowledgments

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Notation

C_i = concentration of ion i in liquid phase, meq/mL
C_o = total concentration of ions in liquid phase, meq/mL
K_i = solubility product constant
q_i = concentration of ion i in resin phase, meq/cm^3 of bed volume
t = time, min
u = superficial velocity of mobile phase, cm/min
u_s = solute velocity, cm/min
V_{bed} = bed volume, mL
z = distance measured from the column inlet, cm

Greek letter

ϵ = void fraction of bed

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