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Virolainen Sami, Suppula Ilkka, Sainio Tuomo

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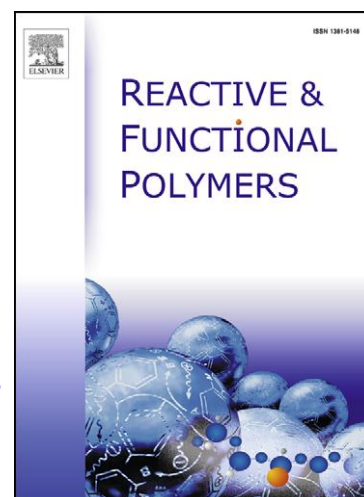
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Controlled Partial Neutralization of Amphoteric Ion Exchange Resin for Improved Metals Separation

Submitted by

Sami Virolainen, Ilkka Suppula, and Tuomo Sainio[*]

from Lappeenranta University of Technology, Laboratory of Industrial Chemistry, P.O. Box 20, FI-53851 Lappeenranta, Finland

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*) Corresponding author. Tel.: +358 40 3578683; e-mail address: tuomo.sainio@lut.fi

1   **Abstract**

2   Controlled partial neutralization of an amphoteric aminomethylphosphonium

3   functional ion exchange resin (Lewatit TP–260) was investigated. The particular goal of

4   controlled neutralization was to replace H^+ in the acidic phosphonium groups with Na^+

5   ions but leave the basic amino groups protonated. In this manner, metals' sorption is

6   enhanced and undesired pH changes during the metal separation process are avoided. The

7   conjugate bases of organic weak acids (sodium formiate, sodium acetate and sodium

8   citrate), sodium phosphate and NaOH were studied as neutralizing agents. The organic acid

9   salts and sodium phosphate were all found to be suitable. Lengthening the neutralization

10   cycle and using more concentrated neutralization agents were found to yield higher extents

11   of neutralization and more uniform profiles along a resin bed. Concentrated NaOH also

12   neutralized the amine group from the resin. With dilute NaOH, desired extent of

13   neutralization was not achieved within a reasonable time. The effect of partial

14   neutralization on metal sorption was tested with dynamic single column experiments. 5.5

15   BV of Ag-NaCl solution could be purified from Ca, Mg, Pb and Zn when the resin was

16   partially neutralized with 2.0 M NaAc. With the acid form resin, the impurity metals broke

17   through at 1.0 BV.

18

19   Keywords: amphoteric resin, chelating resin, aminomethylphosphonium, silver chloride,

20   sodium acetate

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23   1.   Introduction

24   Chelating ion exchangers are known to be effective adsorbents for base metals and

25   heavy metals in the form of divalent cations [1,2]. Consequently, they have potential for

26   purification of hydrometallurgical solutions of many rare and valuable metals, which are

27   often in form of complexes, oxoanions, monovalent cations, etc.

28   When working with solutions having pH near the neutral range and with ion

29   exchangers that have functional groups with both acid and base properties, it is important

30   to modify the functional groups to the desired form before the actual adsorption stage. This

31 step is required because functional groups may bind or release H^+ ions and cause pH

32 changes in the column. Such changes may lead to decreased metal sorption, if the pH

33 decreases, or precipitation problems, if it increases.

34   A usual pretreatment or regeneration of amphoteric resins is to totally convert the

35 resin either into acid or base form by using a concentrated acid or base. An iminodiacetate

36 resin, for example, is usually regenerated with concentrated acid to remove bound metals.

37 Maximal dynamic metal binding capacity is obtained by subsequently neutralizing the

38 resin with a strong base. The drawback is that the amine group becomes converted to the

39 free base form and will capture H^+ ions from the solution to be purified, increasing its pH

40 and causing a risk of precipitation. A method is needed to neutralize in a controlled manner

41 only the carboxylic groups while leaving the amine group protonated.

42   Although weak acids or bases have been used in regeneration instead of strong acids

43 and bases, controlled partial neutralization of ion exchange resins has not been studied

44 systematically in the available literature. For example, CO_2 regeneration has been proposed

45 for weak acid resins by Kiehling and Hoell [3], Kunin and Vasillou [4] and Larsen [5], and

46 the resulting HCO_3^- solutions were used for regenerating weak base resins. Greenleaf and

47 Sengupta [6] have used CO_2 (in rainwater or snowmelt) regeneration for ion exchange

48 fibers with weak acid functionality as a part of a water softening process. Bayard et al. [7]

49 describe a procedure for preparing a packed bed of an iminodiacetic acid resin where part

50 of the resin particles are completely in acid form and part in half neutralized form. 20% of

51 the resin volume is moved into a separate column where it is treated with 2 N HCl

52 followed by water elution to pH 4.5. This fraction is then mixed with particles that have

53 previously been converted to monosodium iminodiacetate form (most probably by

54 titration). Such a complicated procedure is hardly suitable for high throughput industrial

55 processes.

56   A different approach to eliminate pH variations was employed by Trochimczuk et al.

57 [8,9], who used an acetate buffer in the feed when studying adsorption of metals into

58 chelating resins that were used in H^+ form. This method introduces an additional chemical

59 to the target metal solution, which may be undesirable. Moreover, sorption of metals by the

60 resin is greatly reduced if they form complexes with the organic acids in the solution

61 phase.

62   Citrate, tartrate and complexing agents in general (e.g. EDTA) have been used to

63 improve stripping of metals from ion exchange resins. They also have a strong tendency to

64 capture species that they have affinity to associate with, such as H^+ ions, from resins [10].

65   If partial neutralization is needed in a dynamic column operation, it is important to

66 have as even a neutralization profile along the column as possible to ensure good

67 performance. For example, if a stoichiometric amount of a strong acid or a strong base is

68 used for partial neutralization of a bed, the extent of neutralization averaged over the

69 column length may be appropriate, but there may be a steep gradient in the concentration

70 of protonated functional groups near the column inlet.

71   The purpose of this work was to find suitable chemicals and conditions for controlled

72 partial neutralization of an amphoteric aminomethylphosphonium resin in order to prevent

73 precipitations while maintaining good removal capacity for impurity metals in dynamic

74 column operation. The conjugate bases of organic weak acids (sodium formiate NaFo,

75 sodium acetate NaAc, and sodium citrate Na_3Ci), sodium phosphate (Na_2HPO_3) and NaOH

76 were studied as neutralizing agents. The influence of partial neutralization on metals'

77 sorption was tested in a single column for purification of Ag(I) from divalent impurity

78 metals in concentrated chloride medium. Process performance was evaluated based on the

79 volume of purified AgCl solution obtained before the breakthrough of the impurity metals.

80 Only a single flow rate was used and the influence of extent of neutralization on mass

81 transfer rates was thus not investigated in detail.

82

83

84 2.   Experimental

85 *2.1. Materials*

86   All the chemicals used were of analytical grade, except NaCl, which was of technical

87 grade. The chemicals were supplied by VWR Prolabo (NaCl, AgCl, citric acid H_3Ci), Alfa

88 Aesar ($PbCl_2$), Merck ($ZnCl_2$, acetic acid HAc, HCl, formic acid HFo, NaOH), Riedel de

89 Haën ($MgCl_2 \cdot 6H_2O$, Na_2HPO_4) and J.T. Baker($CaCl_2 \cdot 2H_2O$).

90   Lewatit TP-260 (supplied by Lanxess) is a macroporous aminomethylphosphonic

91 acid –functional resin that has a crosslinked polystyrene divinylbenzene matrix (Fig. 1)

92 [11]. Physical properties given by manufacturer [11] of the resin are following: total

93 capacity 2.3 eq/L, particle size 0.4-1.25 mm (>90%), water retention 58-62%, volume

94 change from Na^+ to H^+ form max. 25%. The density of the resin was determined as 1.19

95 g/mL in 4.8 M NaCl in this work. Before the experiments the resin was subjected to two

4

96   four-stage pretreatment cycles where 10 to 20 bed volumes of 1 M NaOH, water, 1 M HCl,
97   and water were passed through a resin bed.

98

99   << Figure 1 about here >>
100

101   *2.2   Titration of resin*

102   Titrations of the Lewatit TP-260 resin with and without NaCl background were done
103   batchwise in test tubes. Wet free base form resin, 0.5 M NaOH, 1 M HCl and purified
104   water were weighed into the test tube. The total liquid volume was 10 mL. Test tubes were
105   shaken for two days at $50^{\circ}C$ and solution pH was measured after separation of the phases.
106   Calibration curves were constructed to both acidic and base side to convert the pH readings
107   to H^+ and OH^- concentrations.

108   *2.3   Neutralization and separation experiments*

109   Neutralization of the resin and removal of divalent impurity metals from an Ag(I)
110   solution were investigated in laboratory scale columns. The experiments were done at 50
111    $^{\circ}C$ in 15 mm diameter columns (Kronlab ECO15/120M3K-K) with a 24.0-27.6 mL resin
112   bed. All feed solutions were placed on scales to monitor flow rates. Air was removed from
113   the solutions with a vacuum pump before experiments and the solutions were passed
114   through a degassing unit (Phenomenex Degassex DG-4400) before the column to remove
115   traces of dissolved gases.

116   Partial neutralization of the resin was carried out in five consecutive steps as
117   described in Table 1. The procedure was otherwise identical in all runs but the
118   neutralization solution in step 3 was varied. A high salt concentration was used in all steps
119   to maintain the ionic strength, and thus the extent of resin swelling, at approximately the
120   same level as in the Ag solution to be purified. After the final rinse with H_2O, the resin bed
121   was divided into five or six sections of approximately equal height that were removed from
122   the column and titrated with NaOH to determine the H^+ content. The H^+ content was then
123   compared to the H^+ content of completely protonated resin to calculate the extent of
124   neutralization.

125   The influence of partial neutralization on the purification of divalent impurity metals

126   from an AgCl solution was investigated by determining breakthrough curves. Details of the

127   procedure are given in Table 2. Metal analyses of aqueous samples from the column

128   effluent for Ca, Mg, Pb and Zn were carried out from 10% HNO_3 media and for Ag from 2

129   M NaCl + 2 M HCl media using inductively coupled plasma atomic emission spectroscopy

130   (ICP-AES, device: IRIS Intrepid Duo, Thermo Electron Corporation).

131

132

133   << Table 1 about here >>

134

135

136   << Table 2 about here >>

137

138   3.   Results and discussion

139   *3.1   Titration curves*

140   According to literature, an aminomethylphosphonium group has three pK_a values:

141   1.45 and 5.4 for the phosphonium group, and 11.0 for the amino group [12]. As can be

142   observed in Fig. 2, Lewatit TP-260 was found to have a remarkably flat titration curve,

143   which is typical for weak acid and weak base resins [2,10]. Such flatness is mostly because

144   the three different groups have different H^+ binding behavior but also partly because of

145   heterogeneity of the polymer. The individual pK_a values for phosphonium groups cannot

146   be distinguished from the experimental titration curve. Consequently, totally neutralizing

147   the acidic phosphonium groups while leaving all of the amino groups protonated in the

148   controlled partial neutralization experiments may be challenging.

149   The titration curves obtained with and without an electrolyte background differ

150   remarkably. Generally, the resin is neutralized more easily in the presence of NaCl,

151   because Na^+ replaces some H^+ from the cation exchange group [2,10]. The curves in pure

152   H_2O and 0.5 M NaCl cross at around log c_{H+} = −6 and at higher acidity the resin was

153   protonated more easily in 0.5 M NaCl than in H_2O. Increasing the salt concentration from

154   0.5 to 4.5 M also had a remarkable diminishing effect on the protonation.

155   Based on the titration curves, the H^+ capacity of phosphonium groups in Lewatit TP-

156   260 in every background electrolyte concentration used is around 2.3 mmol/mL resin,

157   which corresponds to the value given by the manufacturer [11]. The titration curves in the

158   NaCl background are in correspondence with the results of Vaaramaa and Lehto [13] and

159   without background NaCl the curve corresponds to the pK_a 11.0 for the amino group (in

160   0.1 M KNO_3) given by Nesterenko et al. [8]. The protonation behavior of the amine group

161   is seen mostly in the negative side of the titration curves because the amine group is in

162   protonated form after the pretreatment, in which the last stage is a water wash. In water and

163   0.5 M NaCl the amine group part of the curve is more abrupt than in 4.5 M NaCl.

164   Consequently, it might be challenging to achieve the desired extent of neutralization in

165   controlled partial neutralization experiments. The H^+ capacity of the amine group in every

166   background was ~1.1 mmol/mL, which is approximately half the H^+ capacity in the

167   phosphonium groups, as would be expected based on the chemical structure of the

168   functional group (Fig. 1).

169

170   << Figure 2 about here >>

171

172   *3.2   Neutralization profiles*

173   The ideal level of neutralization of the resin would be 67%, meaning that the two

174   protons in each phosphonium group would be completely neutralized while each amino

175   group would still be in protonated form. In such a state, the neutralized phosphonium parts

176   of the functional groups will prevent loss of metal uptake capacity caused by competition

177   of protons with metals. The protonated amine parts in turn, will prevent potential

178   precipitation problems caused by pH increase that occurs if protons are taken up by the

179   amine part.

180   Different types of neutralization agents in a concentrated NaCl background were

181   tested for controlled partial neutralization: neutral salt solution (NaCl), dilute and

182   concentrated bases (NaOH), phosphate buffer (Na_2HPO_4) and salts of monoprotic and

183   triprotic weak organic acids. The total concentration of Na^+ in the neutralization solution

184   was between 4.5 M and 4.8 M in all cases. As shown in Fig. 3, the best neutralization

185   agents are the buffer type solutions, such as 0.5 M NaAc and 0.2 M Na_2HPO_4. This is due

186   to the fact that they have the ability to capture and bind H^+ from the phosphate groups of

187   the resin in the neutral or slightly acidic pH range.

188   As observed in Fig. 3, there is an undesired gradient in the extent of neutralization
189   along the bed when these concentration levels of neutralization agents were used. The
190   extents of neutralization obtained with 0.5 M NaAc and 0.2 M Na_2HPO_4 were 55% and
191   59% near the column inlet and 31% and 36% near the outlet.

192   According to the titration curve (Fig. 2), the desired extent of neutralization would
193   eventually be achieved also with 4.5 M NaCl at neutral pH or with 0.001 M NaOH in
194   absence of salt. However, the capability of neutral or slightly basic solutions to remove H^+
195   from the phosphonium groups is so small that neutralization up to the desired extent would
196   require excessive solution volumes and time. In these experiments, the extent of
197   neutralization remained under 30% with 4.8 M NaCl and 0.001 M NaOH through the
198   whole column.

199   Finally, it is observed in Fig. 3 that concentrated NaOH is too strong a neutralizing
200   agent, converting also the amino group to unprotonated form. This is not acceptable
201   because the pH of the metal solution to be purified would increase significantly as the
202   amino group captures H^+ from the liquid phase.

203

204   << Figure 3 about here >>

205

206   NaAc was found to be a more effective neutralizing agent than NaFo, leading to 15-
207   25 percentage units higher extent of neutralization along the resin bed (Fig. 4). The
208   difference between the inlet and outlet was about 20 percentage units with both salts. This
209   result is readily explained by the acid strength of the substances. For HAc and HFo, the
210   pK_a values are respectively 4.48 (45°C, 0.7 M NaCl) and 3.78 (50°C, KCl) [14]. The top of
211   the bed meets fresh neutralization solution that captures H^+ from the resin. The higher the
212   pK_a of the acid, the more H^+ it can bind before the system reaches a local equilibrium.
213   When the solution reaches the bottom of the bed, the weak acids are already carrying a
214   large amount of H^+ and the pH of the solution is much lower than near the inlet. The
215   degree of neutralization therefore increases more slowly near the outlet of the column than
216   at the inlet.

217   Na$_3$Ci gave similar neutralization results as NaAc, although it gave a higher extent of

218   neutralization near the column outlet and thus a smoother neutralization profile (Fig. 4).

219   H$_3$Ci is a triprotic acid with pK_a values 3.05, 4.40 and 5.52 (35°C, KNO$_3$) [15]. The third

220   hydroxyl in citrate is a stronger proton acceptor than the acetate anion, the second is rather

221   similar to acetate, and the third one is a weaker proton acceptor than acetate. All of these

222   are in the range that they can be effective in a partial neutralization process, so it is

223   reasonable that citrate has a higher capacity per mole to take H$^+$ than the salts of

224   monoprotic carboxylic acids. However, it can be concluded from the neutralization profiles

225   in Fig. 4 that the higher proton acceptor capacity and the one unit higher third pK_a value do

226   not yield a significantly higher extent of neutralization in the inlet side of the column. This

227   finding implies that mass transfer phenomena also had some effect at these experimental

228   conditions.

229

230   << Figure 4 about here >>

231

232   The effect of the amount of NaAc on neutralization is displayed in Fig. 5, which

233   shows axial profiles obtained with different acetate concentrations and with different

234   neutralization times. Increasing the acetate concentration from 0.2 M to 2.0 M resulted in a

235   15 percentage units higher extent of neutralization at the column inlet and 35 percentage

236   units higher extent of neutralization at the outlet. The gradient in the bed was thus

237   shallower with the more concentrated solution. As expected, increasing the length of the

238   neutralization cycle had a positive effect on the extent of neutralization. A significantly

239   higher level was reached when 0.2 M NaAc was fed into the column for 20 minutes instead

240   of 10 minutes. The increase was highest near the column outlet (17 percentage units) than

241   near the inlet (8 percentage units), meaning that the profile was also shallower. With the

242   longer neutralization cycle the extent of neutralization varied between 58 % (inlet) and 39

243   % (outlet).

244   On the other hand, nearly the same extent of neutralization was achieved with 20 min

245   neutralization time and 0.2 M NaAc (*i.e.*, in total 0.04 mol of NaAc) as with 10 min cycle

246   and 0.5 M NaAc (*i.e.*, in total 0.05 mol of NaAc). The main difference in the profiles was

247   observed near the outlet of the column, where a higher level was reached with the longer

248   residence time. This finding indicates that the role of mass transfer effects cannot be

249   neglected under these experimental conditions. From the practical process design point of

250   view, it would be preferable to use as concentrated a solution as possible to shorten the

251   time required for achieving certain extent of neutralization, which is in accordance with the

252   theory of ion exchange column dynamics that predicts shorter regeneration cycles with

253   highly concentrated regeneration solutions [2]. It should be noted that an almost uniform

254   neutralization profile with near optimal extent of neutralization (64-70%) was achieved

255   with 2.0 M NaAc and a 20 min regeneration step.

256

257   << Figure 5 about here >>

258

259   *3.3   Purification of a multimetal solution*

260   The influence of controlled partial neutralization on the adsorption of metals to an

261   aminomethylphosphonic acid resin is shown in Fig. 6. For example, in the case of

262   neutralization with 2.0 M NaAc (Run 6 in Table 2), the breakthroughs of Pb, Mg, Ca, and

263   Zn occurred at 6.0, 6.5, 8.0, and 15.2 BV, respectively. Without neutralization, they

264   occurred at 0.8, 2.6, 3.8 and 3.2 BV, respectively. It can further be observed in Fig. 6 that

265   the breakthrough order of the metals was not affected except for Zn, which broke through

266   before Ca without neutralization and after all other metals with neutralization. As expected,

267   the target product, AgCl, was not affected by neutralization because the resin has much

268   higher affinity towards H^+ than Ag^+.

269   When comparing different neutralization agents by considering the breakthrough

270   curves of the four divalent metals (Fig. 7), NaFo was found to show the worst performance

271   (except for the experiment without neutralization). The differences between the other

272   neutralization agents were relatively small. 2.0 M NaAc and 0.5 M Na_3Ci resulted in a

273   slightly higher dynamic uptake capacity for all the metals than 0.5 M NaAc or 0.2 M

274   Na_2HPO_4. It is noteworthy that the adsorbed amount of all metals except Ca increased with

275   increasing extent of neutralization. This is particularly clear from the breakthrough curve

276   of Pb, where the displacement effect is much more pronounced when higher extent of

277   neutralization was reached.

278   The effect of controlled partial neutralization on metal sorption can also be explained
279   by considering the pH values at the column outlet (see Fig. 7). The pH of the column
280   effluent at the beginning of the metals loading step gives an indication of the extent of
281   neutralization in the column. A low pH stems from displacement of H^+ by Na^+ during the
282   washing step (with 4.8 M NaCl at pH 6.5) that follows the neutralization step (see Table
283   2). In all cases, the pH changed fairly little for a duration of several bed volumes at the
284   beginning of the loading step, which means that there was no steep pH gradient in the bed
285   after the washing step. Without neutralization (Run 1 in Table 2), the pH dropped below
286   unity as the metals were taken up by the resin. The pH rose slowly towards a value of 2 by
287   the end of the experiment (approximately 35 BV feed). Considering the titration curve
288   displayed in Fig. 2, it is obvious that the resin is nearly completely in H^+ form at such low
289   pH. With 2.0 M NaAc neutralization (Run 6), the outlet pH was approximately 6 in the
290   beginning of the feeding step and started to decrease after approximately 8 BV of feed,
291   remaining just below 4 at the end of the run (approximately 50 BV of feed).

292   To describe the comparison of the neutralization agents numerically, the 5%
293   breakthrough points ($c/c^0 = 0.05$) for all the metals and for each neutralization agent are
294   given in Table 3. It should first be noted that Ag was practically not adsorbed at all. The
295   breakthrough sequence was the same in every experiment where neutralization was
296   applied: Zn > Ca > Mg > Pb > Ag. From Table 3 it can also be seen that when
297   neutralization was not applied, Pb breaks through almost immediately (at 1.4 BV) and thus
298   only a very small amount of the AgCl solution could be purified. If the required product
299   quality is defined such that none of the impurity metals can exceed 5% of its initial
300   concentration at column outlet, the productivity of the separation process proportional to
301   the difference between the breakthrough volumes of Pb and Ag (the latter is always
302   approximately 1 BV). 2.0 M NaAc neutralization was found to be most effective (Pb
303   breakthrough at 6.5 BV), while productivities obtained with 0.5 M Na_3Ci, 0.2 M $NaHPO_4$,
304   0.5 M NaAc, 0.5 M NaFo and pure NaCl were 84%, 84%, 69%, 36% and 7% of that value.

305

306   << Figure 6 about here >>
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308
309   << Figure 7 about here >>

310

311   << Table 3 about here >>

4.   Conclusions

313   The aim of this study was to find suitable reagents and conditions to partially
314   neutralize an aminomethylphosphonium functional resin (Lewatit TP-260). More precisely,
315   the goal was to leave the amine group protonated while completely neutralizing the
316   phosphonium group, thus preventing undesired pH changes while permitting adsorption of
317   metals from neutral solutions. A concentrated strong base (NaOH) by itself was found to
318   be too strong a neutralizing agent, converting the nitrogen group into free base form. 4.8 M
319   NaCl at neutral pH or 0.001 M NaOH was found to result in too low extent of
320   neutralization within a reasonable time. However, both sodium salts of organic acids and a
321   phosphate buffer were found to be suitable neutralizing agents.
322   The length of the neutralization step and the concentration of the neutralizing agent
323   were found to be more important factors in controlled partial neutralization than the choice
324   of organic acid salt. The most favourable neutralization profile was achieved with 7.5 BV
325   of 2.0 M NaAc, which yielded 63-70% extent of neutralizationalong the column, while the
326   desired extent is 67%.
327   Purification of an Ag-NaCl solution from Ca, Mg, Pb and Zn in a single column
328   operation was used as a model system. Practically no separation was achieved with the
329   resin in acid form resin since Pb broke through almost immediately. By employing the
330   controlled partial neutralization procedure with 2.0 M NaAc, up to 5.5 BV of the Ag-NaCl
331   solution could be purified before regeneration of the resin was required.
332   The main benefit of the controlled partial neutralization method over the use of
333   buffered feed solutions is that no additional chemicals are introduced into the purified
334   solution.
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343   References

[1]   J. Wyethe, M. Kotze, B. Van Hege, R. Bell, The Use of Selective Ion Exchange for the Recovery of Base Metals from Effluent Streams, in: South African Institute of Mining and Metallurgy, Zambia, 2005.

[2]   F. Helfferich, Ion Exchange, Dover Publications, Inc., 1995.

[3]   B. Kiehling, W. Hoell, Partially desalinating water with ion exchanger materials which are subsequently regenerated, IL66421A, 1985.

[4]   R. Kunin, B. Vassiliou, Regeneration of carboxylic cation-exchange resins with carbon dioxide, Ind. Eng. Chem. Prod. Res. Dev. 2 (1963) 1–3.

[5]   A.L. Larsen, Regenerating resins of deionization systems, US3691109A, 1972.

[6]   J.E. Greenleaf, A.K. Sengupta, Environmentally benign hardness removal using ion-exchange fibers and snowmelt, Environ Sci Technol. 40 (2006) 370–376.

[7]   J.P. Bayard, G. Bayard, Water free of heavy metals for medical use and ion exchange resin used in its preparation, FR2506286A1, 1982.

[8]   A.W. Trochimczuk, M. Streat, Novel chelating resins with aminothiophosphonate ligands, Reactive and Functional Polymers 40 (1999) 205–213.

[9]   A.W. Trochimczuk, Chelating resins with N-substituted diamides of malonic acid as ligands, European Polymer Journal 34 (1998) 1657–1662.

[10] K. Dorfner, Ion exchangers, Walter de Gruyter, Berlin, 1991.

[11] Lewatit TP-260 Product information, (2010).

[12] P.N. Nesterenko, M.J. Shaw, S.J. Hill, P. Jones, Aminophosphonate-Functionalized Silica: A Versatile Chromatographic Stationary Phase for High-Performance Chelation Ion Chromatography, Microchemical Journal 62 (1999) 58–69.

[13] K. Vaaramaa, J. Lehto, H+Na+ exchange in an aminophosphonate-chelating resin, Reactive and Functional Polymers 33 (1997) 19–24.

[14] Harned, Embree, Journal of the American Chemical Society 56 (1934) 1042.

[15] L.A. Kochergina, V.P. Vasil'ev, D.V. Krutov, O.N. Krutova, The influence of temperature on the heat effects of acid-base interaction in aqueous solutions of citric acid, Russian Journal of Physical Chemistry 82 (2008) 565 – 570.

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375 **List of Figure Captions**
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378 Figure 1.   Chemical structure of the aminomethylphosphonic acid functional group of

379 Lewatit TP-260.

380

381 Figure 2.   Titration curves of aminomethylphosphonium functional Lewatit TP-260 resin
382   in NaCl solutions of different concentrations.

383

384 Figure 3.   Controlled   partial   neutralization   profiles   of   aminomethylphosphonium
385   functional resin (Lewatit TP-260). Comparison of different type neutralization
386   agents.

387

388 Figure 4.   Controlled   partial   neutralization   profiles   of   aminomethylphosphonium
389   functional resin (Lewatit TP-260). Comparison of different organic acid salts.

390

391 Figure 5.   Controlled   partial   neutralization   profiles   of   aminomethylphosphonium
392   functional resin (Lewatit TP-260). Influence of NaAc concentration and cycle
393   length.

394 Figure 6.   Single column adsorption of divalent metals to aminomethylphosphonium
395   functional resin (Lewatit TP-260) from an Ag bearing solution. Breakthrough
396   curves without (left) and with (right) controlled partial neutralization (2.0 M
397   NaAc + 2.8 M NaCl).

398
399
400 Figure 7.   Single column adsorption of divalent metals to aminomethylphosphonium
401   functional resin (Lewatit TP-260) from Ag bearing solution. Breakthrough
402   curves for individual metals and pH curves (from multimetal feed) with
403   different neutralization agents.
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408 **List of Tables**
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Table 1

Step description	Feed solution	Duration, min	Flow rate, mL/min
Conversion to acid form	2.0 M HCl + 2.0 M NaCl	30	6
Washing	4.8 M NaCl, pH 6.5	5	10
Partial neutralization			
Run 1	4.8 M NaCl, pH 6.5	10	5
Run 2	0.001 M NaOH + 4.8 M NaCl, pH 9.2	10	5
Run 3	1.5 M NaOH + 3.0 M NaCl	10	5
Run 4	0.2 M NaAc + 4.5 M NaCl, pH 7.1	10	10
Run 5	0.2 M NaFo + 4.5 M NaCl, pH 8.8	10	10
Run 6	0.2 M Na_2HPO_4 + 4.5 M NaCl, pH 7.9	10	10
Run 7	0.5 M NaAc + 4.5 M NaCl, pH 6.1	10	10
Run 8	0.5 M NaFo + 4.5 M NaCl, pH 9.0	10	10
Run 9	0.5 M Na_3Ci + 4.5 M NaCl, pH 8.7	10	10
Run 10	2.0 M NaAc + 2.8 M NaCl, pH 9.0	10	10
Run 11	0.2 M NaAc + 4.5 M NaCl, pH 8.9	20	10
Run 12	0.2 M NaFo + 4.5 M NaCl, pH 8.6	20	10
Run 13	2.0 M NaAc + 4.5 M NaCl, pH 9.0	20	10
Washing	4.8 M NaCl	5	10
Rinse	Deionized water	15	4

Table 2

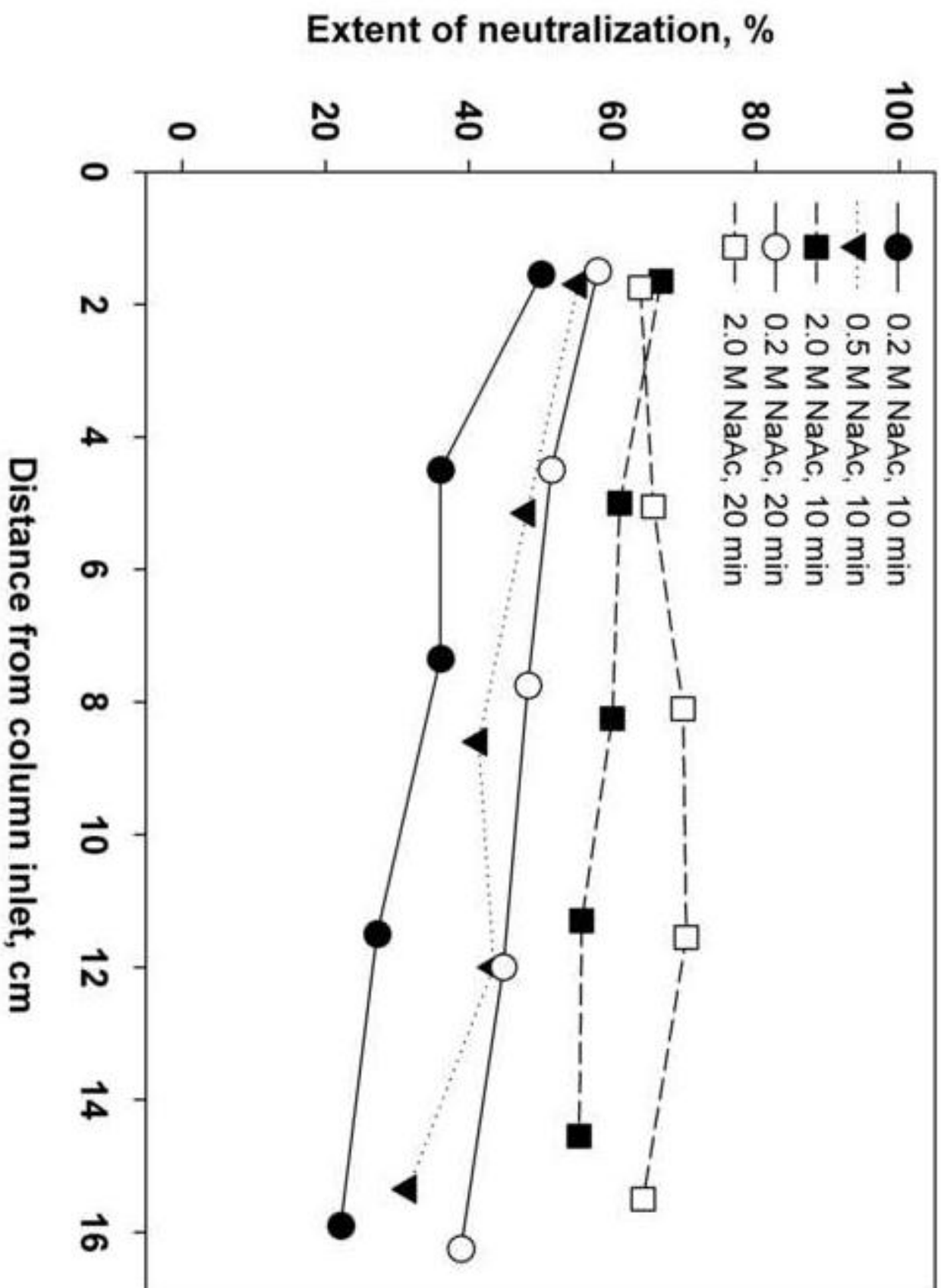| Step description	Feed solution	Duration, mL/min	Flow rate, mL/min
Conversion to acid form	2.0 M HCl + 2.0 M NaCl	30	6
Washing	4.8 M NaCl, pH 6.5	5	10
Partial neutralization			
Run 1	4.8 M NaCl, pH 6.5	10	10
Run 2	0.2 M Na_2HPO_4 + 4.5 M NaCl, pH 8.7	10	10
Run 3	0.5 M NaAc + 4.5 M NaCl, pH 8.4	10	10
Run 4	0.5 M NaFo + 4.5 M NaCl, pH 8.7	10	10
Run 5	0.5 M Na_3Ci + 4.5 M NaCl, pH 8.9	10	10
Run 6	2.0 M NaAc + 2.8 M NaCl, pH 8.4	10	10
Washing	4.8 M NaCl, pH 6.5	5	10
Loading	Metals (Ag, Ca, Mg, Pb, Zn) 537 - 887 mg/L 4.5 M NaCl, pH 6.26-6.35	ca. 100 BV	4
Elution	2.0 M HCl + 2.0 M NaCl	25	6
Rinse	Deionized water	5	10

Table 3

Metal	5% Breakthrough, BV					
	4.8 M NaCl	0.5 M NaFo	0.5 M NaAc	2.0 M NaAc	0.5 M Na$_3$Ci	0.2 M Na$_2$HPO$_4$
Ag	1.1	1.1	1.1	1.0	1.1	1.1
Ca	8.8	6.8	7.3	8.0	8.1	8.2
Mg	2.6	5.6	6.7	8.0	6.8	7.6
Pb	1.4	3.0	4.8	6.5	5.6	5.6
Zn	3.2	11.3	15.7	19.5	17.6	16.2

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 5

Legend:
- ● 0.2 M NaAc, 10 min
- ◀ 0.5 M NaAc, 10 min
- ■ 2.0 M NaAc, 10 min
- ○ 0.2 M NaAc, 20 min
- □ 2.0 M NaAc, 20 min

Y-axis: Extent of neutralization, %
X-axis: Distance from column inlet, cm

Figure 6

Figure 7