

Non-destructive separation of metal ions from wastewater containing excess aminopolycarboxylate chelant in solution with an ion-selective immobilized macrocyclic material

著者	Hasegawa Hiroshi, Rahman Ismail M.M., Kinoshita Sanae, Maki Teruya, Furusho Yoshiaki
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1 **Non-Destructive Separation of Metal Ions from Wastewater**
2 **Containing Excess Aminopolycarboxylate Chelant in Solution with an**
3 **Ion-Selective Immobilized Macrocyclic Material**
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7 Hiroshi Hasegawa,*¹ Ismail M.M. Rahman,^{1,2} Sanae Kinoshita,¹ Teruya Maki,¹ and
8 Yoshiaki Furusho³
9

10 ¹*Graduate School of Natural Science and Technology, Kanazawa University, Kakuma,*
11 *Kanazawa 920-1192, Japan*

12 ²*Department of Chemistry, University of Chittagong, Chittagong 4331, Bangladesh*

13 ³*GL Science, Nishishinjuku 6-22-1, Shinjuku, Tokyo 163-1130, Japan*
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22 *Author(s) for correspondence.

23 E-mail: hhiroshi@t.kanazawa-u.ac.jp (H. Hasegawa). Tel/ Fax: +81-76-234-4792
24

25 **Abstract**

26 Although the excellent metal-binding capacities of aminopolycarboxylate chelants
27 (APCs) facilitate their extensive use, pre- and post-toxicity of APCs and their high
28 persistence in aquatic environments evoke concerns. Several treatment techniques with a
29 principal focus on the degradation of APCs at the pre-release step have been proposed. Here,
30 we report a technique for the separation of metal ions from waste solution containing excess
31 APCs using a solid phase extraction system with an ion-selective immobilized macrocyclic
32 material, commonly known as a molecular recognition technology (MRT) gel. Synthetic
33 metal solutions with 100-fold chelant content housed in H₂O matrices were used as samples.
34 The MRT gel showed a higher recovery rate compared with other SPE materials at 20 °C
35 using a flow rate of 0.2 mL min⁻¹. The effects of solution pH, metal-chelant stability
36 constants and ionic radii were assessed for 32 metals. Compared to the conventional
37 treatment options for such waste solutions, our proposed technique has the advantage of non-
38 destructive separation of both metal ions and chelants.

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40 *Keywords:* solid phase extraction; molecular recognition technology gel; metal-chelant
41 complexation, wastewater treatment, pH

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50 **1.0 Introduction**

51 Multidentate chelating agents (chelant) are receiving widespread acclaim for their
52 usefulness in a variety of industrial applications (Nowack and VanBriesen, 2005) including
53 the treatment of toxic metal-contaminated solid waste materials (Ayres, 1970; Bell, 1977;
54 Grasso, 1993; Roundhill, 2001). Since major elements (e.g., Ca^{2+} , Fe^{3+} , Mg^{2+} , Al^{3+}) compete
55 with toxic metals for the binding sites of chelating agents, an excess amount of chelant is
56 added to ensure the adequate separation of toxic metal-contaminants from solid wastes
57 (Leštan et al., 2008). Meanwhile, aminopolycarboxylate chelants (APCs), such as
58 nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) and
59 diethylenetriaminepentaacetic acid (DTPA), are commonly used to restrict metal ions from
60 playing their normal chemical roles, through the formation of stable and water-soluble metal
61 complexes. In particular, EDTA has most often been utilized among the APCs, since EDTA
62 forms strong water-soluble chelant complexes with most toxic metals (Egli, 2001; Nowack
63 and VanBriesen, 2005; Leštan et al., 2008).

64 While chelants are advantageous because of their powerful metal-binding properties, it is
65 this same characteristic that may have undesirable environmental consequences. Wherever
66 APCs have been introduced into the natural environment, the aqueous transport of metals,
67 which characteristically form stable complexes with chelates, can be expected to occur
68 (Means et al., 1980; Nowack and VanBriesen, 2005). Residence time of the metals is thus
69 extended, as they are remobilized from soils and sediments into the water phase. EDTA and
70 its homologs are poorly photo-, chemo- and biodegradable in the environment (Means et al.,
71 1980; Bolton Jr. et al., 1993; Kari and Giger, 1995; Kari et al., 1995; Egli, 2001; Nowack,
72 2002; Nörtemann, 2005) and, in most cases, metal complexation raises the threshold values
73 for toxic effects (Sillanpää and Oikari, 1996; Sorvari and Sillanpää, 1996; Sillanpää, 2005).
74 Excess chelant also increases the total nitrogen content and the phosphate solubility in

75 interstitial waters (Norvell, 1984; Horstmann and Gelpke, 1991; Erel and Morgan, 1992; Li
76 and Shuman, 1996; Hering and Morel, 2002).

77 Wastewater with excess APCs entails subsequent separation or degradation treatment
78 before it can be safely discharged. In Europe, treatment of EDTA-containing wastewaters is
79 increasingly required because of the increasingly stringent environmental regulations
80 (Grundler et al., 2005; van Ginkel and Geerts, 2005). Several processes have been proposed
81 for the degradation of APCs to restrict their intrusion to the environment (Sillanpää and
82 Oikari, 1996; Kagaya et al., 1997; Madden et al., 1997; Krapfenbauer and Getoff, 1999;
83 Muñoz and von Sonntag, 2000; Rämö et al., 2000; Bucheli-Witschel and Egli, 2001; Rämö
84 and Sillanpää, 2001; Sillanpää and Pirkanniemi, 2001; Sillanpää and Rämö, 2001;
85 Pirkanniemi et al., 2007). The cost of chelants is also an important issue surrounding their use
86 in metal ion sequestration. Methods that recycle not only the processed water, but also the
87 chelant, may therefore be economically feasible (Lim et al., 2005; Leštan et al., 2008).

88 Separation and pre-concentration of metal ions from aqueous solutions using solid
89 sorbent materials, known as solid phase extraction (SPE) systems, have increased in
90 popularity since the 1980s (Hosten and Welz, 1999). Some of the sorbent materials have the
91 capability to interact with a variety of metal ions, while others are fairly specific for a
92 particular ion (Ebdon et al., 1991; Carbonell et al., 1992; Nickson et al., 1995; Ghaedi et al.,
93 2006; Ghaedi et al., 2007; Ghaedi et al., 2008). Lately, there has been increasing interest in
94 developing more specific materials that can be used for the separation of particular ions from
95 solutions containing complex matrices with high concentrations of interfering ions. However,
96 there is no report of an SPE system for the removal of APCs in wastewaters. The extraction
97 efficiency of SPE materials remarkably decreases in aqueous solutions containing excess
98 chelant, since APCs compete with SPE materials for complexation of metal ions. One group
99 of SPE materials includes the macrocyclic chelants, such as crown ethers, immobilized on a

100 silica or polymer support (Hosten and Welz, 1999). Ion-selective behavior of SPE-type
101 systems with immobilized macrocyclic materials has been mentioned for pre-concentration
102 and separation of metals (Bradshaw et al., 1988; Izatt et al., 1988; Bruening et al., 1991; Izatt
103 et al., 1994; Izatt et al., 1995; Izatt et al., 1996; Izatt, 1997; Izatt et al., 2003).

104 In this study, we propose a method for the separation of metal ions from waste solutions
105 containing excess amount of APCs. Synthetic wastewater was treated with an ion-selective
106 immobilized macrocyclic material attached to a solid phase, commonly known as a molecular
107 recognition technology (MRT) gel. The performance of the separation process with the MRT
108 gel was studied in terms of metal-chelant stability constants, ionic radii of the metals and
109 solution pH.

110

111 **2.0 Materials and Methods**

112 *2.1 Reagents and instrumentation*

113 SPE materials (Table 1): AnaLig TE-01 and MetaSEP ME-1 from GL Science, Japan,
114 Chelex-100 from Bio-Rad, USA, and NOBIAS Chelate PA-1 from Hitachi High-
115 Technologies, Japan were used. APCs: NTA, EDTA, DTPA and GEDTA [O,O'-bis(2-
116 aminoethyl)ethyleneglycol-N,N,N',N'-tetraacetic acid] were used without further purification
117 as supplied by Dojindo Laboratories, Japan. Other chemicals were analytical grade
118 commercial products. Deionized water prepared using four housing E-Pure systems
119 (Barnstead, USA) was used throughout, and is referred to as EPW hereafter.

120 The stock solutions containing 10 mM chelants were prepared by dissolving appropriate
121 amounts of NTA, EDTA, DTPA and GEDTA in EPW. Metal-stock solutions (1000 ppm)
122 were purchased from GL Science, Japan. In total, 32 metals were used: five alkaline earth
123 metals (Be, Mg, Ca, Sr and Ba), 10 transition metals (Sc, Y, Ti, V, Mn, Fe, Co, Ni, Cu, Cd),
124 four post-transition metals (Al, Ga, In, Pb), 12 rare earth metals (Ce, Pr, Nd, Sm, Eu, Gd, Tb,

125 Ho, Er, Tm, Yb, Lu) and one radioactive metal (U). Sample solutions were prepared by
126 mixing the 10 mM chelant solutions in 0.1 M buffer ($\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ for pH 4–5,
127 and $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ for pH 6–8) and 50 ppm metals at a ratio of 99:1.

128 All laboratory glassware was soaked for 24 h in an alkaline detergent (Scat 20X-PF,
129 Nacali Tesque, Japan) and for 24 h in 4 M hydrochloric acid, followed by rinsing with EPW.

130 The pH of the sample solutions was measured with a Navi F-52 pH meter (Horiba
131 Instruments, Japan). A Perkin-Elmer Model 3300XL inductively coupled plasma atomic
132 emission spectrometer (ICP-AES) was used to determine the concentrations of metal ions in
133 aqueous solutions. Detection limits for the measurements were 0.01–6 ppb.

134

135 *2.2 Experimental procedure*

136 The SPE materials packed into 3 or 6 mL columns were used in this experiment. Figure 1
137 shows a comprehensive view of the experimental setup. Column cleaning was conducted
138 with 8 mL of 1 M HNO_3 and 6 mL of EPW. 0.1 M buffer solution (5 mL) was allowed to
139 pass through the column to ensure the desired pH condition. Solubility of APCs decrease at
140 low pH (Ueno et al., 1992), and silica gels of the AnaLig TE-01 column may dissolve due to
141 increased solubility at higher pH (Vogelsberger et al., 1992). Therefore, the study was
142 restricted to the selected pH range of 2–8. The pH values of the solutions were maintained by
143 using buffer solutions of 0.1 M $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ for pH 4–5 and 0.1 M
144 $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ for pH 6–8. For pH 2, 0.01 M HCl was used without the addition of
145 chelant.

146 Sample solutions were then treated with the pH-conditioned SPE columns at a controlled
147 flow rate. Studies were conducted on the sample loading flow rates adjusted in a range of
148 0.2–4.0 mL min^{-1} . Quantitative retention of metal ions was observed up to 0.25 mL min^{-1} ,
149 while the retention rate decrease gradually with increasing flow rates in the range of 0.3–1.0

150 mL min⁻¹. At high flow rates (2.0–4.0 mL min⁻¹), the recovery of analyte was about 60%
151 which indicates the constant retaining capability of the SPE columns at the initial loading
152 period. Since quantitative extraction of the analyte is desirable, 5 mL of the sample solutions
153 was passed through the SPE columns at a flow rate of 0.2 mL min⁻¹.

154 The ‘captured’ metal ions were eluted with 5 mL of 6 M HCl solution followed by
155 ICP-AES measurement. Effect of eluent concentration on the recovery percentage of analyte
156 with the SPE columns were conducted using 0.1–6.0 M HCl (analyte: Fe(III) – 0.1 mM,
157 chelant: EDTA – 10 mM, matrix: H₂O, pH: 8.0, volume: 5 mL, flow rate: 0.2 mL min⁻¹). The
158 recovery percentage increased with increasing concentrations of HCl until 0.5 M, and then
159 remained constant. Hence, 6 M HCl was selected as the eluent for the subsequent
160 experiments to ensure quantitative elution of the analyte. The recovery of metals via eluent
161 was calculated as follows:

$$162 \quad \text{Recovery(\%)} = \frac{\text{number of moles of metal recovered in all fractions}}{\text{number of moles of metal applied to the column}} \times 100 \quad (1)$$

163 For all mixture compositions, triplicate measurements were performed, and the average of
164 these values was considered in all calculations. The standard deviations and relative errors of
165 the measurements were within 3%.

166

167 **3.0 Results and discussion**

168 *3.1 Recovery (%) with different SPE materials and APCs*

169 To investigate the comparative affinities of the different SPE materials with the APCs,
170 the sorption experiments were first carried out in a non-competitive environment.
171 Performance of the solution of Fe(III) in excess EDTA was first checked as a representative
172 metal species, because Fe(III)-EDTA solution is the main EDTA species released from solid
173 waste treatment processes and comprises 20–90% of total EDTA in the effluents (Kari and
174 Giger, 1996; Nowack, 2002). Similar experiments were repeated with aqueous solutions

175 containing excesses of NTA, GEDTA and DTPA. Figure 2 shows the recovery performance
176 comparison of different SPE materials from aqueous metal solutions containing excess APCs.
177 The recovery efficiency of AnaLig TE-01 was much better, compared with Chelex-100,
178 MetaSEP ME-1 and NOBIAS Chelate PA-1. Possible maximum percentage recovery of
179 metals was achieved with the NTA-, GEDTA- and EDTA-metal mixed feed solutions. On the
180 contrary, the recovery efficiency was reduced to half with the DTPA-enriched waste solution.

181

182 *3.2 Effect of metal-chelant stability constants and ionic Radii of metals*

183 The advantages of using chelating agents in the treatment of metal-containing wastes
184 include the high efficiency of metal extraction and high thermodynamic stabilities of the
185 metal complexes formed (Fischer et al., 1998; Lim et al., 2005). Figure 3 shows the effect of
186 the metal-chelant stability constant on the performance of SPE materials during column-
187 extraction of Fe(III) from the Fe(III)EDTA aqueous solution containing 100-fold
188 concentrations of EDTA. Better efficiency of AnaLig TE-01 was observed compared to the
189 other SPE materials for the metal-chelant complexes. Thus, considering the high stability
190 constants and chemical forms of the metal-DTPA complexes, better performance of AnaLig
191 TE-01 is expected with the following APCs: NTA, GEDTA and EDTA.

192 Metal-chelant stability constants are pH-dependent. Therefore, pH plays a key role in
193 the separation of metals from metal-chelant solutions using SPE-type systems. The effects on
194 metal separation efficiency of solution pH, in the range of pH 5–8, were examined using the
195 AnaLig TE-01 and the excess chelant containing waste solutions for all 32 metals (Fig. 4).
196 The treated metal-contaminated waste solutions at pH 2 were without chelant due to the
197 minimal solubility of chelant at low pH. Most of the transition and post-transition elements
198 were extracted with TE-01 quantitatively at pH 5–6.5, and the recoveries decreased at pH 8.0.
199 The rare earth and radioactive elements showed the highest recovery rate at pH 8. The

200 recovery efficiency of TE-01 with the alkaline earth metals was not remarkable. Quantitative
201 retention in the entire experimental pH range of 5–8 was observed for some metals such as,
202 Be, Sc, Fe, Cu, Pb, Sm, Eu, Gd and Tb.

203 The effect of the metal-EDTA stability constants and ionic radii of the metals on the
204 metal separation efficiency of the AnaLig TE-01 at pH 8.0 are shown in Fig. 5. Although the
205 oxidation states were used to identify the metals, no correlation was observed between the
206 change in oxidation states and percentage recoveries. Izatt et al. (1994) reported that ionic
207 radii of the metals govern the separation behavior of some MRT-type SPE systems. However,
208 no such patterns were observed in the present study with AnaLig TE-01 (Fig. 5b). The metal
209 separation efficiency of the MRT gel was instead related to the stability constant of the metal-
210 chelant complex with EDTA within the studied pH region (Fig. 5a). A positive correlation
211 with the percentage recovery and metal-chelant stability constants was notable for the studied
212 metals with the exception of Be and V.

213

214 *3.3 Non-destructive separation of metals and APCs*

215 Systems with macrocycles attached to solid supports (Bradshaw et al., 1988; Horwitz et
216 al., 1992; Izatt, 1997) allow the non-destructive separation of metals from APCs. They also
217 facilitate the repeated use of macrocycles, since the material can be regenerated after each use.

218 The separation mechanism of the AnaLig TE-01 is still unknown and requires extensive
219 study. However, based on the behavior of the SPE systems with macrocycles attached to solid
220 supports (Bradshaw et al., 1988; Horwitz et al., 1992; Izatt, 1997), we predicted a schematic
221 model, as shown in Fig. 6, to show how the non-destructive selective separation of metal and
222 APCs occurred within the system. Such selective separation ensures the minimization of both
223 macrocycle loss to the environment and the use of diluents (Favre-Réguillon et al., 1997).

224

225 **4.0 Conclusions**

226 In the present work, an MRT gel-SPE system was used to treat metal-contaminated
227 wastewater containing 100-fold APCs in solution. The MRT-SPE system was tested using 32
228 metals with a number of APCs (NTA, EDTA, DTPA and GEDTA) in the pH range of 5–8.
229 The recovery rate was discussed in terms of solution pH, metal-chelant stability constants and
230 ionic radii of metals. Maximum separation (~100%) of metals was observed in the pH region
231 of 5–6.5. Quantitative maximum extraction of the analyte from the pH adjusted sample
232 solution was attained using a flow rate of 0.2 mL min⁻¹. Metal-chelant stability constants
233 influenced the metal recovery to some extent; whereas metal ionic radii seem to produce no
234 significant effect. AnaLig TE-01 was found to be stable in the operation process, and enabled
235 more than 100 loading and elution cycles to be performed without the loss of analytical
236 performance. Thus, the initial high cost of synthesis can be amortized over time. Our survey
237 of the literature shows that the idea of using an MRT gel-type SPE material for non-
238 destructive treatment of chelant-enriched metal-contaminated waste solution is rather new.
239 More work is required to investigate the ion-selective property of MRT gels, the behavior of
240 the MRT-SPE system in the presence of competing ions and the real mechanism of the ion-
241 separation technique using an MRT gel.

242

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399 Table 1: Different solid phase extraction (SPE) materials used in the study

SPE material type	SPE	Base Support	Functional group
MRT Gel	AnaLig TE-01	Silica gel	Crown ether
Chelate resin	Chelex-100	Styrene divinylbenzene	Iminodiacetic acid
	MetaSEP ME-1	Methacrylate polymer	Iminodiacetic acid
	NOBIAS Chelate PA-1	Hydrophilic methacrylate	Polyamino- polycarboxylic acid

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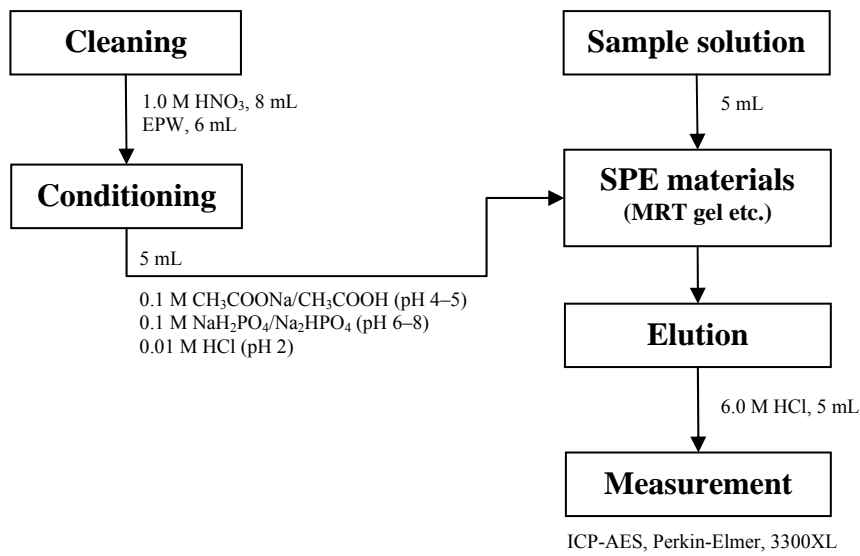
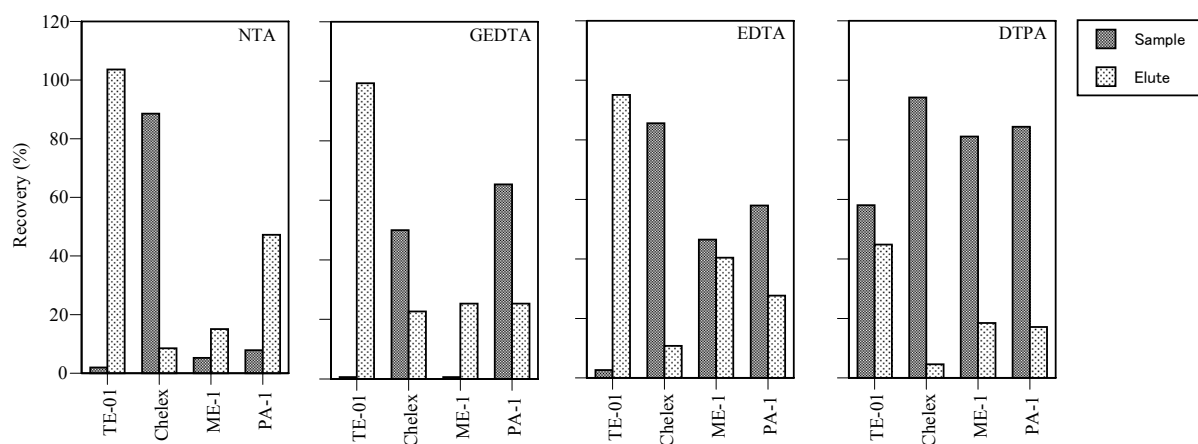


Figure 1: Schematic diagram of the experimental setup

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441 Figure 2: Comparative performance of SPE materials with the aqueous metal solution

442 containing an excess of APCs (n = 3). Sample solution: Fe(III) – 0.1 mM, Chelant: EDTA –

443 10 mM, matrix: H₂O, pH: 8.0, sample volume: 5 mL, flow rate: 0.2 mL min⁻¹, elution: 6 M

444 HCl – 5 mL.

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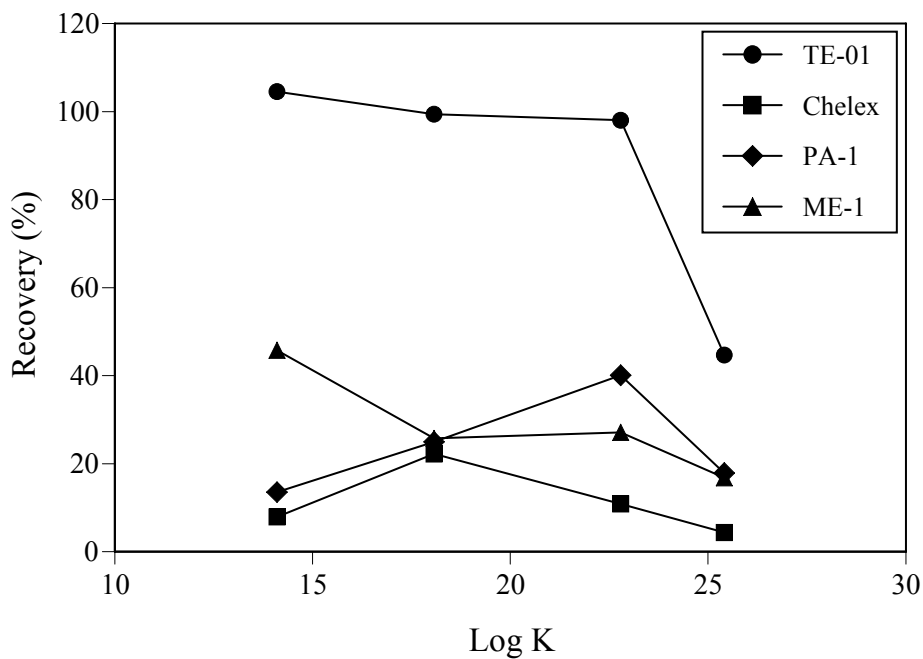
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466 Figure 3: Effect of metal-chelant stability constants on the performance of SPE materials.

467 Sample solution: Fe(III) – 0.1 mM, Chelant: EDTA – 10 mM, matrix: H₂O, pH: 8.0, sample

468 volume: 5 mL, flow rate: 0.2 mL min⁻¹, elution: 6 M HCl – 5 mL.

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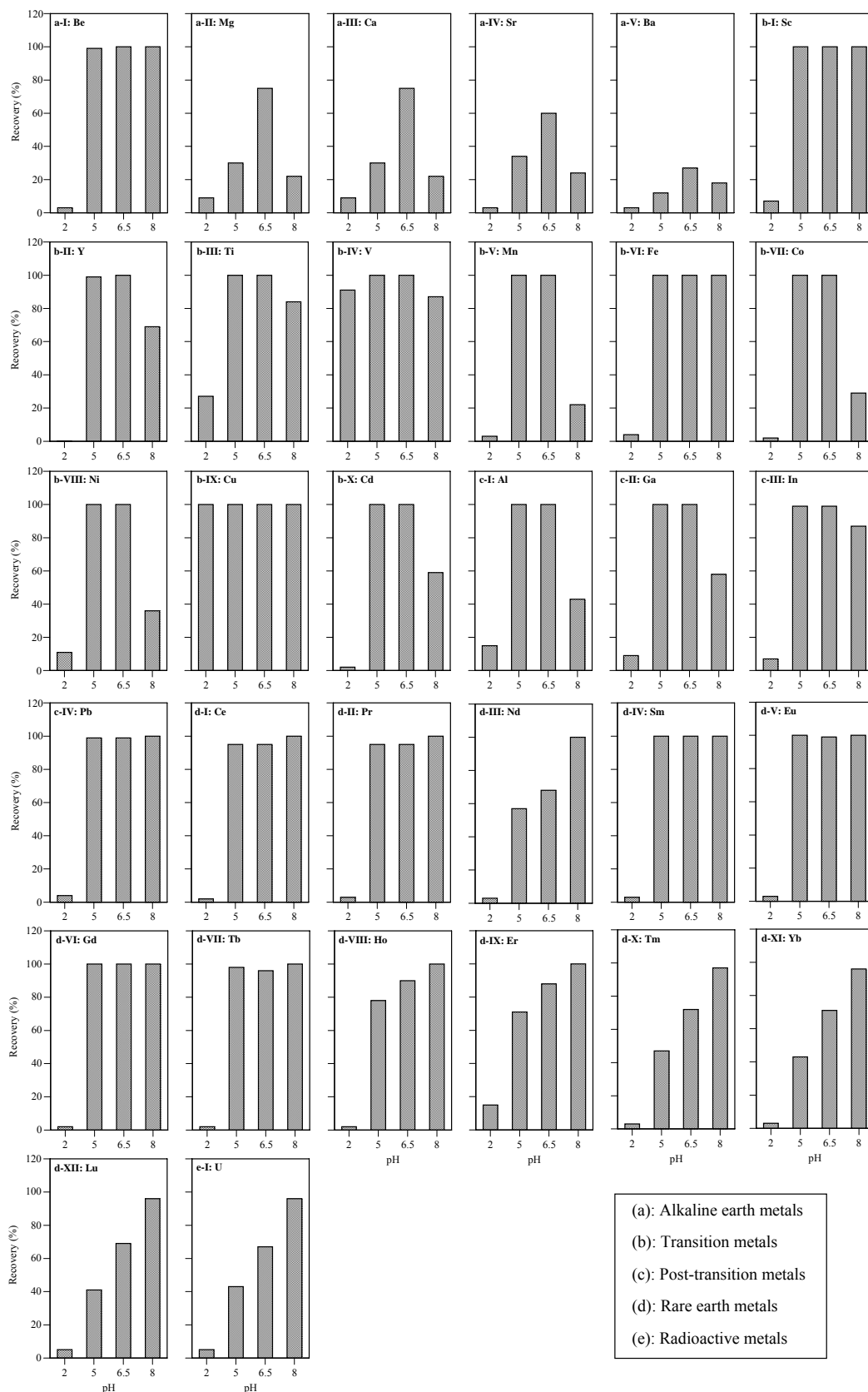
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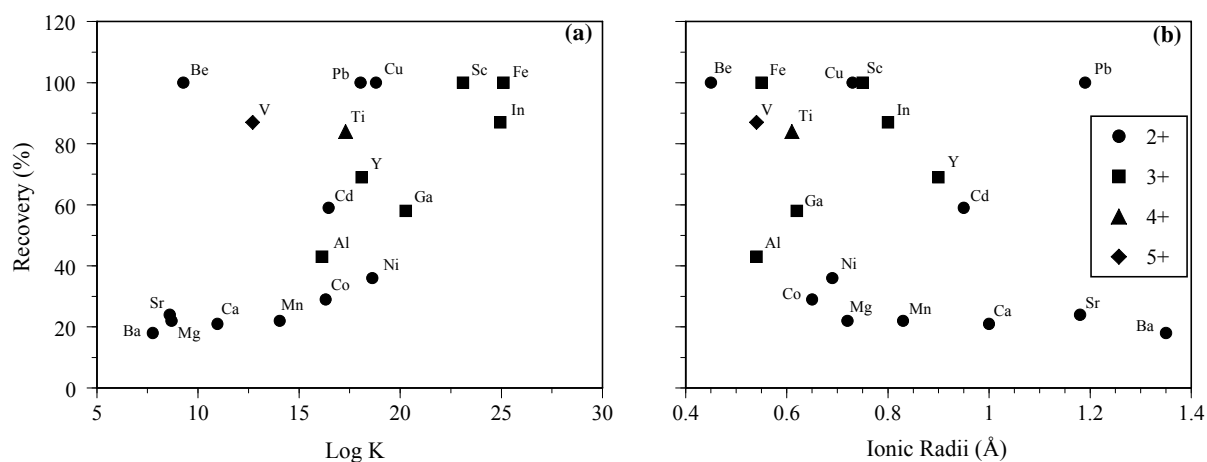
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483 Figure 4: The effect of pH on the metal separation efficiency of the AnaLig TE-01. Sample
 484 solution: 500 ppb, Chelant: EDTA – 10 mM, matrix: H₂O, pH: 2.0, 5.0, 6.5, 8.0, sample
 485 volume: 5 mL, flow rate: 0.2 mL min⁻¹, elution: 6 M HCl – 5 mL.



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488 Figure 5: Effect of (a) metal-chelant stability constants and, (b) ionic radii of the metals on

489 the performance of AnaLig TE-01 with chelant. Sample solution: 0.1 mM, Chelant: EDTA –

490 10 mM, matrix: H₂O, pH: 8.0, sample volume: 5 mL, flow rate: 0.2 mL min⁻¹, elution: 6 M

491 HCl – 5 mL.

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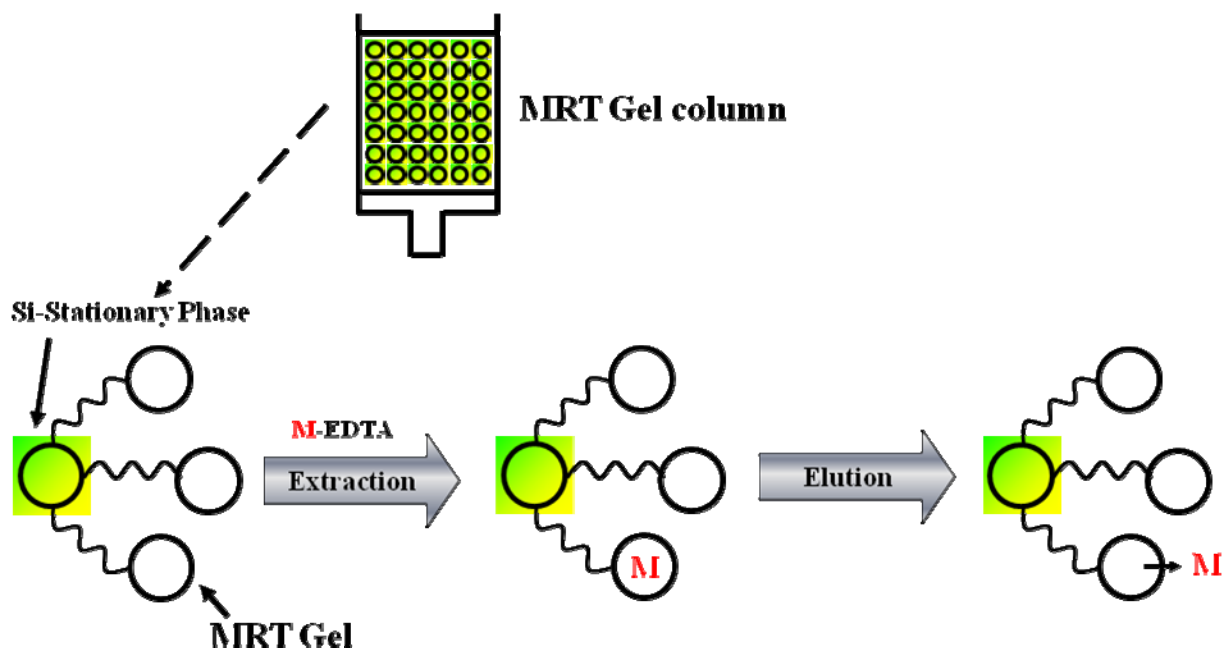
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Figure 6: Selective separation of metal ions by MRT Gel (TE-01): schematic model.