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**Non-Destructive Separation of Metal Ions from Wastewater
Containing Excess Aminopolycarboxylate Chelant in Solution with an
Ion-Selective Immobilized Macrocyclic Material**

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Abstract

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

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

1.0 Introduction

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

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

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

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

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

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

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

2.0 Materials and Methods

2.1 Reagents and instrumentation

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

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

Ho, Er, Tm, Yb, Lu) and one radioactive metal (U). Sample solutions were prepared by 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, 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.

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

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

2.2 Experimental procedure

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

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

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

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

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

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

3.0 Results and discussion

3.1 Recovery (%) with different SPE materials and APCs

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

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

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

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

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

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

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

3.3 Non-destructive separation of metals and APCs

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

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

4.0 Conclusions

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

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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

Figure 2: Comparative performance of SPE materials with the aqueous metal solution containing an excess of APCs ($n = 3$). Sample solution: Fe(III) – 0.1 mM, Chelant: EDTA – 10 mM, matrix: H₂O, pH: 8.0, sample volume: 5 mL, flow rate: 0.2 mL min⁻¹, elution: 6 M HCl – 5 mL.

Figure 3: Effect of metal-chelant stability constants on the performance of SPE materials.
Sample solution: Fe(III) – 0.1 mM, Chelant: EDTA – 10 mM, matrix: H₂O, pH: 8.0, sample
volume: 5 mL, flow rate: 0.2 mL min⁻¹, elution: 6 M HCl – 5 mL.

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

Figure 5: Effect of (a) metal-chelant stability constants and, (b) ionic radii of the metals on the performance of AnaLig TE-01 with chelant. Sample solution: 0.1 mM, Chelant: EDTA – 10 mM, matrix: H₂O, pH: 8.0, sample volume: 5 mL, flow rate: 0.2 mL min⁻¹, elution: 6 M HCl – 5 mL.

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