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メタデータ	言語: eng 出版者: 公開日: 2017-10-03 キーワード (Ja): キーワード (En): 作成者: メールアドレス: 所属:
URL	http://hdl.handle.net/2297/34164

A Silica Gel-Bound Macrocyclic System for the Selective Separation of Toxic Cadmium from Metal-affluent Aqueous Matrix

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Abstract

Selective separation of cadmium(II) on a macrocycle immobilized solid phase extraction (SPE) system namely AnaLig Cd-01, and commonly known as molecular recognition technology (MRT) gel, have been examined. The MRT-SPE able to retain the cadmium from the metal-affluent aqueous matrix at the pH range of 2 to 8, and the captured species can be recovered via elution with 1 and 6 M HNO₃. Besides the effects of solution pH and eluent concentration, the impacts of sample loading flow rates and coexisting matrix ions were also investigated and optimized. The Cd(II) retention capacity of the MRT-SPE was 0.26 mmol g⁻¹, and it can be reused for more than 100 loading and elution cycles. The Cd(II) recovery attained from the metal-spiked natural waters was satisfactory (95.3–98.1%). However, the Cd(II) retention ability of the MRT-SPE was significantly decreased when excess of chelant remain in the aqueous waste matrix.

Keywords

Cadmium; non-destructive removal; solid phase extraction; molecular recognition technology gel; wastewater treatment

1.0 Introduction

Heavy metal contamination of water resources is causing serious ecological problems in many parts around the world. Cadmium(II) is one of the 13 toxic metal species in the priority pollutant list of the Environmental Protection Agency [1, 2], and is one of six substances banned by the European Union's Restriction on Hazardous Substances directive [3]. Moreover, cadmium has been designated as a human carcinogen [4]. Cd(II) occurs naturally in rocks and soils, and the major route for cadmium intake is ingestion of trace cadmium in foodstuffs of natural origin or from the use of phosphate fertilizers and sludge on agricultural soils. Potential sources of cadmium exposure include emissions from the smelters, steel works and incinerators [5]. Although the levels of cadmium in the environmental samples are usually low, separation of trace cadmium from the metal-contaminated matrix is an issue of concern to avoid the potential health hazard associated with the exposure.

Coprecipitation [6], liquid–liquid extraction [7], cloud-point extraction [8], dispersive liquid–liquid microextraction [9] and solid-phase extraction (SPE) [10–12] have been used for the separation of cadmium from different matrices. SPE technique is preferentially used for the separation of heavy metal ions from aqueous solutions as compared to other separation techniques, mainly due to its simplicity, low cost, ease of recovery of the solid phase, and ability to attain a high concentration factor [10–12]. SPE systems having the capability to interact with a variety of metal ions, or fairly specific selectivity to one particular ion of interest are available [13–20].

One group of SPE materials includes the macrocyclic structures, such as crown ethers, immobilized on a silica or polymer support have been introduced as molecular recognition technology (MRT) gel [21, 22]. The retention of analytes on a macrocycle depends on the relative sizes and charges of analytes, the conformational flexibility of the macrocycle structure, and interaction of the macrocycle with solvent. Highly selective retention of the

target analyte can be achieved using macrocycles and the selectivity behavior of macrocycle can be modified by varying any of those factors [18, 19, 23-26]. Macrocycles are widely used in separation chemistry for solvent extraction, solid sorbent extraction, chromatographic separation and electrochemical analysis [27, 28].

The aim of the presented work is to establish a rapid, simple and selective separation process for the recovery of cadmium(II) ions from metal-rich waste aqueous matrix using the SPE system AnaLig Cd-01. To the best of our knowledge, it is the first report on the application of a SPE system containing Cd(II) ion-selective immobilized macrocycle in the solid phase.

2.0 Material and Methods

2.1 Instrumentation

An iCAP 6300 model inductively coupled plasma optical emission spectrometer (ICP-OES) from Thermo Fisher Scientific (Waltham, MA) was used for the metal analysis. The ICP-OES assembly was composed of an EMT duo quartz torch, glass spray chamber and concentric glass nebulizer. The RF power at the torch was 1.15 kW, the plasma gas flow was 12 L min⁻¹, the auxiliary gas flow was 1 L min⁻¹, the nebulizer gas flow was 0.5 L min⁻¹, and the integration time was 30 s.

A TOSOH 8020 model high-performance liquid chromatography (HPLC) system from Tosoh (Tokyo, Japan) was used for EDTA analysis. The HPLC system was fully automated with the following components: a DP-8020 pump, an AS-8021 auto sample injector, a CO-8020 column oven, a PD-8020 UV-VIS detector, PD-8020 data processing software, and TSK-gel ODS-80TM octadecylsilica columns (4.6 mm i.d. × 250 mm and 4.6 mm i.d. × 150 mm). Ammonium dihydrogenphosphate (5 mM, pH 2.4) was used as the mobile phase solution and was pumped at a flow rate of 0.5 mL min⁻¹ at 25°C. The injection volume was maintained at 20 µL, and the detection was performed at 254 nm.

A GL-SPE vacuum manifold kit (for 12 samples) from GL Sciences (Tokyo, Japan) combined with a CAS-1 air pump from AS ONE (Osaka, Japan) was used to perform the SPE. A Navi F-52 pH meter from Horiba Instruments (Kyoto, Japan) and a combination electrode were used for pH measurements.

Deionized water prepared with a Barnstead 4-housing E-Pure water purification system from Barnstead/Thermolyne (Dubuque, IA) was used throughout, and is referred to as EPW hereafter.

2.2 Materials

Analytical grade commercial products were used without further purification. Cd(II) stock solution (10 mM) was prepared using cadmium(II) nitrate tetrahydrate, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ from Wako Pure Chemical (Osaka, Japan). Disodium dihydrogen ethylenediamine tetraacetate dehydrate, $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ from Kanto Chemical (Tokyo, Japan) was used to prepare the 10 mM stock solution of EDTA. A PlasmaCAL multi-element solution from SCP Science (Québec, Canada) containing 21 metals (Al, Ba, Be, Bi, Ca, Cd, Co, Cu, Fe, Ga, In, Mg, Mn, Ni, Pb, Sc, Sr, Ti, V, Y, and Zn) in 5% HNO_3 was used to check the effects of diverse ions. Solutions of working standards were prepared from the stock solutions by dilution with EPW.

The experimental pH ranged from 2 to 10 and was adjusted using either 1 M HNO_3 or 1 M NaOH. MES (2-(*N*-morpholino) ethanesulfonic acid monohydrate, $\text{C}_6\text{H}_{13}\text{NO}_4\text{S} \cdot \text{H}_2\text{O}$) from Sigma–Aldrich (St. Louis, MO), HEPES (N-2-Hydroxyethylpiperazine-N'-2-ethanesulfonic acid, $\text{C}_8\text{H}_{18}\text{N}_2\text{O}_4\text{S}$) from Nacalai Tesque (Kyoto, Japan), and TAPS (N-Tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid, $\text{C}_7\text{H}_{17}\text{NO}_6\text{S}$) from MP Biomedicals (Solon, OH) were used as buffer reagents for pH 5, 6.5–8 and 10, respectively. HNO_3 solutions of 1.0, 0.1, 0.01, or 0.001 M were used for pH 2.

GL Sciences (Tokyo, Japan) provided AnaLig Cd-01 that manufactured commercially by the IBC Advanced Technologies, Inc. (American Fork, UT) with the following particle specifications: (a) mesh size – 60 to 100; (b) density – 0.4 g mL^{-1} ; (c) binding capacity – 0.1 to 0.3 mmol g^{-1} . The MRT-SPE systems from IBC Advanced Technologies, Inc. reported to contain proprietary polymeric organic material having selective separation aptitude attributable to molecular recognition and macrocyclic chemistry [29].

Low-density polyethylene bottles from Nalge Nunc (Rochester, NY), perfluoroalkoxy tubes and micropipette tips from Nichiryo (Tokyo, Japan) were used. Before use, laboratory wares were first soaked in Scat 20X-PF alkaline detergent from Nacalai Tesque (Kyoto, Japan) overnight, and then in 4 M HCl overnight, followed by rinsing with EPW after each step.

2.3 Experimental setup

SPE materials packed into 3 or 5 mL columns were used. Rinsing or cleaning of immobilized SPE materials was performed with 8 mL of 1 M HNO_3 and 6 mL of EPW. Conditioning treatment was conducted with 32 ~ 40 mL of either HNO_3 or buffer reagents (MES, HEPES or TAPS) to ensure the desired pH conditions within the SPE systems.

Sample solution (4 mL, pH pre-adjusted) was allowed to pass through the SPE column at the flow rate of 0.2 mL min^{-1} , and the column effluent was collected. The unretained analyte fraction was removed by washing the column with EPW in the next step. Lastly, the ‘captured’ analyte was eluted with HNO_3 (1 and 6 M) from the SPE system. The metal concentrations in the sample, column effluent, wash effluent and the elution effluent were measured using the ICP-OES. Corresponding analyte concentrations in each of the aforesaid fractions were used to elucidate the performance of the SPE systems in terms of extraction and recovery rates (%). The numbers of moles of analyte in the elution effluent was compared with the cumulative number of moles of analyte present in all the effluents to

estimate the extraction rate. The cumulative number of moles of analyte recovered from column, wash and elution effluents was compared with the numbers of moles of analyte in the sample for the computation of the recovery rate. A schematic diagram of the workflow sequence is shown in Fig. 1.

The behavior of the SPE systems with macrocycles attached to solid supports [23, 30, 31] is used to predict a schematic model as shown in Fig. 2, which illustrate the non-destructive selective separation process of the target Cd(II) ion in solution within the MRT-SPE system.

3.0 Results and discussion

3.1 Effect of matrix pH

Retention of Cd(II) on the AnaLig Cd-01 SPE column was studied as a function of pH. Cd(II)-fortified samples of different pH (2–10) were allowed to pass through the MRT-SPE column, and almost complete retention of Cd(II) was observed until pH 8 followed by a certain decrease at pH 10 (Fig. 3). The increasing solubility of silica gel with increasing pH [32], which may dissolve the silica gel base support of the MRT-SPE column, was a likely cause for such separation performance of the MRT-SPE at pH 10. The recovery rates remain optimum at all the studied pH. The Cd(II) extraction rates at pH 5, 6.5 and 8, respectively, were 94.9 ± 4.4 , 99.4 ± 3.9 and 97.8 ± 4.0 , and a sample pH of 6.5 was maintained for the subsequent experiments.

3.2 Effect of sample loading flow rate

The loading flow rates of metal-fortified sample solutions have a considerable influence on metal retention rates in SPE systems [33]. The effects of sample loading flow rates on the retention capacities of the MRT-SPE were studied in the range of 0.2–4 mL min⁻¹, and a gradual decrease was observed with increasing flow rates above 0.2 mL min⁻¹ (Fig. 4a). Such

behavior indicated a constant retaining capability of the MRT-SPE at the initial loading period. Hence, a flow rate of 0.2 mL min^{-1} was applied for following experiments.

3.3 Effect of eluent concentration

Quantitative separation of the target analyte should be achieved with the solvent used as eluent in a particular process [34]. A varying concentration of HNO_3 in the range of 0.3 to 6 M was used for the elution of analyte 'captured' within the MRT-SPE and compared in terms of the recovery yield. The sample solution (4 mL, pH 6.5) spiked with Cd(II) was first allowed to pass through the MRT-SPE at the rate of 0.2 mL min^{-1} followed by the elution of the retained analyte. An increase in the recovery rate (%) of Cd(II) was occurred until the 1 M HNO_3 dosing and remained constant afterwards (Fig. 4b). Hence, $\geq 1 \text{ M HNO}_3$ is required to accomplish optimum retrieval of Cd(II) retained within the Cd-01 MRT-SPE. However, there is a possibility of reduced recovery rate with the real samples if the eluent concentration is maintained to the borderline of 1 M due to the likely impeding effects from matrix components and operating conditions. Thus, a combination of 1 M HNO_3 (2 mL), 6 M HNO_3 (1 mL) and EPW (1 mL) was selected as eluent for subsequent experiments to ensure quantitative elution of the analyte.

3.4 Effect of diverse metal ions in matrix

The quantitative extraction of analytes is significantly hindered due to the interferences from coexisting matrix components [35]. Efficiency of MRT-SPE in the selective separation of Cd(II) was checked in the presence of various interfering metal ions using PlasmaCAL multi-element metal ion solutions. The extraction and recovery rates (%) were 99.2 ± 3.8 and 99.8 ± 2.0 , respectively, showed the superior ion selective separation performance of the MRT-SPE in the presence of $\geq 200 \text{ }\mu\text{M}$ of different ions in the matrix. The matrix was H_2O , the flow rate was 0.2 mL min^{-1} , and the elution solution consisted of 2 mL of 1 M HNO_3 , 1 mL of 6 M HNO_3 , and 1 mL of EPW.

3.5 Analytical characteristics

The Cd(II)-fortified aqueous standards were treated with Cd-01 MRT-SPE system, and the concentration of the target analyte in the treated samples was measured with ICP-OES. The calibration curve was linear for 1 to 20 $\mu\text{g L}^{-1}$ Cd(II) in solution with the correlation coefficient of 0.9916 under optimum conditions. The method detection limit was 0.004 $\mu\text{g L}^{-1}$ as calculated from three times higher standard deviation ($n = 15$) of the blank. The precision of the method for aqueous standards was evaluated by analyzing 10 replicates containing 10 $\mu\text{g L}^{-1}$ Cd(II) in solution, and the relative standard deviation was 2.1%.

3.6 Retention capacity

Retention capacity of the SPE material provides estimation about the stability of the system during the separation process. The breakthrough volume, *i.e.* the sample volume required for the elution of the target analyte from SPE system, and the analyte concentration is used to calculate the retention capacity of the SPE material [36]. Cd(II)-spiked sample solutions were allowed to pass through the Cd-01 MRT-SPE system, eluted and subjected to ICP-OES analysis, and the retention capacity at pH 6.5 was 0.26 mmol g^{-1} (matrix– H_2O , flow rate– 0.2 mL min^{-1} , elution– 2 mL of HNO_3 + 1 mL of 6 M HNO_3 + 1 mL of EPW).

3.7 Reusability

The reusability of the MRT-SPE system was examined with sample solutions spiked with 200 μM of Cd(II) ions in aqueous matrix. Again, the flow rate was 0.2 mL min^{-1} , and the elution solution contained 2 mL of 1 M HNO_3 , 1 mL of 6 M HNO_3 , and 1 mL of EPW. The extraction rates (%) with fresh column was 99.1 ± 3.2 and after 100 cycles was 96.6 ± 2.1 . Therefore, the MRT-SPE system was capable to perform at least 100 loading and elution cycles without any loss of analytical performance.

3.8 Applications

3.8.1 Recovery of Cd(II) from metal-contaminated natural waters

The proposed separation process was applied to the analysis of local natural water samples (tap, lake and river waters). Tap water was collected from our laboratory at Kakuma campus of Kanazawa University (Kanazawa, Japan), lake water was from Lake Biwa (Shiga, Japan) and river water was from Asano River (Kanazawa, Japan). Cellulose membrane filters of 0.45 μm pore size (Advantec; Tokyo, Japan) were used for the pre-separation step filtration treatment of the raw samples. A total 100 mL volume of each sample type was filter-treated and then spiked with the calculated amount of Cd(II) stock solution (10 mM) to achieve the target concentration of 50 $\mu\text{g L}^{-1}$. The Cd(II)-spiked sample then passed through the MRT-SPE, followed by elution recovery and analysis of the eluent using ICP-OES (Table 1). The Cd(II) recovery rates from the spiked samples were 95.3 to 98.1%, which can be termed as satisfactory.

3.8.2 Recovery of Cd(II) from contaminated effluent containing excess EDTA in matrix

Washing effluents from the metal-contaminated solid-waste treatment process often characterized by a large excess of free EDTA in solution, or combined with other competitive ions in the waste [37-39]. The recovery and reuse of both EDTA and metals is considered useful when the concentration is above 5 mM in solution [40, 41]. The selective Cd(II) collection capability of the MRT-SPE system was investigated as a function of pH using simulated washing effluent containing Cd(II) and EDTA of 1:50 molar ratio in H_2O matrix (Fig. 5a). The objective was to propose an option for simultaneous recovery of EDTA and Cd(II). The study was restricted to the pH range of 5 to 10 because of the insufficient solubility of EDTA at very low pH in aqueous medium [42]. The samples were treated at the flow rate of 0.2 mL min^{-1} and the ‘captured’ ions in the SPE system were quantitatively eluted with HNO_3 . A significant change in the Cd(II) retention behavior of the MRT-SPE

was observed for the treatment of excess EDTA containing effluent. Maximum Cd(II) retention (%) of 73.3 ± 4.8 was observed at pH 5 while for metal-contaminated matrix it was occurred at pH 6.5 (Fig. 5b). The quantitative maximum performance was also not achieved in terms of either extraction or recovery. Based on the HPLC analysis data, we assumed the possible occurrence of competitive extraction of EDTA and Cd(II) within the SPE system during the treatment of excess EDTA containing effluent sample. Possibly, Cd(II) extracted at higher rates compared to EDTA at low pH while at near neutral pH region or at high pH the EDTA complexation rate with the SPE predominated. Therefore, the use of AnaLig Cd-01 MRT-SPE system is not recommended for the selective removal of Cd(II) from the excess EDTA containing effluent considering the low efficiency of the system, and to avoid the possible risk of pre-mature breakdown.

4.0 Conclusion

An immobilized macrocyclic material containing SPE system, AnaLig Cd-01, was used for the selective recovery of Cd(II) from metal-contaminated aqueous matrix and simulated washing effluents containing excess of EDTA. Cd(II) was quantitatively recovered from metal-contaminated aqueous matrix with the MRT-SPE system in the pH range of 2 to 8. However, the performance of the MRT-SPE system was significantly altered when it was applied for the separation of Cd(II) from excess EDTA containing simulated washing effluents, and was not suggested for such separation. A sample loading flow rate of 0.2 mL min^{-1} was used to achieve the quantitative extraction and a mixture of 1 and 6 M HNO_3 was used for the elution of the 'captured' metal ions. More than 100 loading and elution cycles was performed without any loss of analytical performance of the MRT-SPE. The method is rapid and simple, and has good potential for use in the selective Cd(II) separation from high metal containing aqueous waste solutions.

Acknowledgement

This research was partially supported by the Grants-in-Aid for Scientific Research (24310056 and 24-02029) from the Japan Society for the Promotion of Science.

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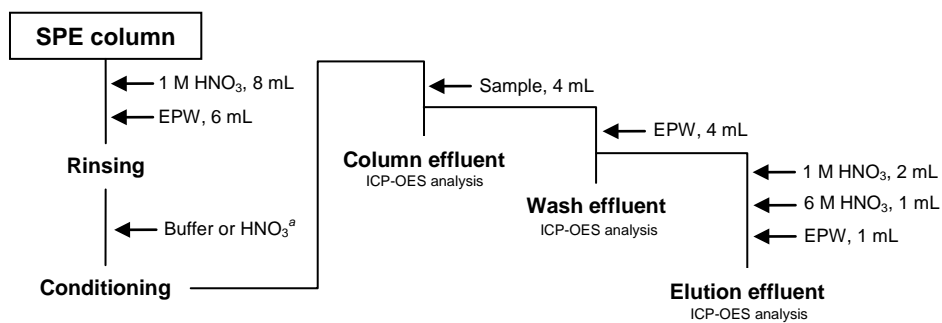
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Table 1. Performance of MRT-SPE for recovery of Cd(II) from natural waters ($n = 3$)

Sample	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water	0	BDL ^a	–
	50	47.7 ± 1.5	95.3 ± 3.1
Lake water	0	0.61 ± 0.17	–
	50	49.1 ± 0.8	98.1 ± 1.6
River water	0	1.11 ± 0.13	–
	50	48.2 ± 1.3	96.4 ± 2.5

^a BDL– Below Detectable Limit



^a 20~40 mL, 0.001- 1 M HNO₃ (pH 2), MES buffer (pH 5), HEPES buffer (pH 6.5–8), TAPS buffer (pH 10)

Fig. 1: Schematic workflow diagram of the separation process

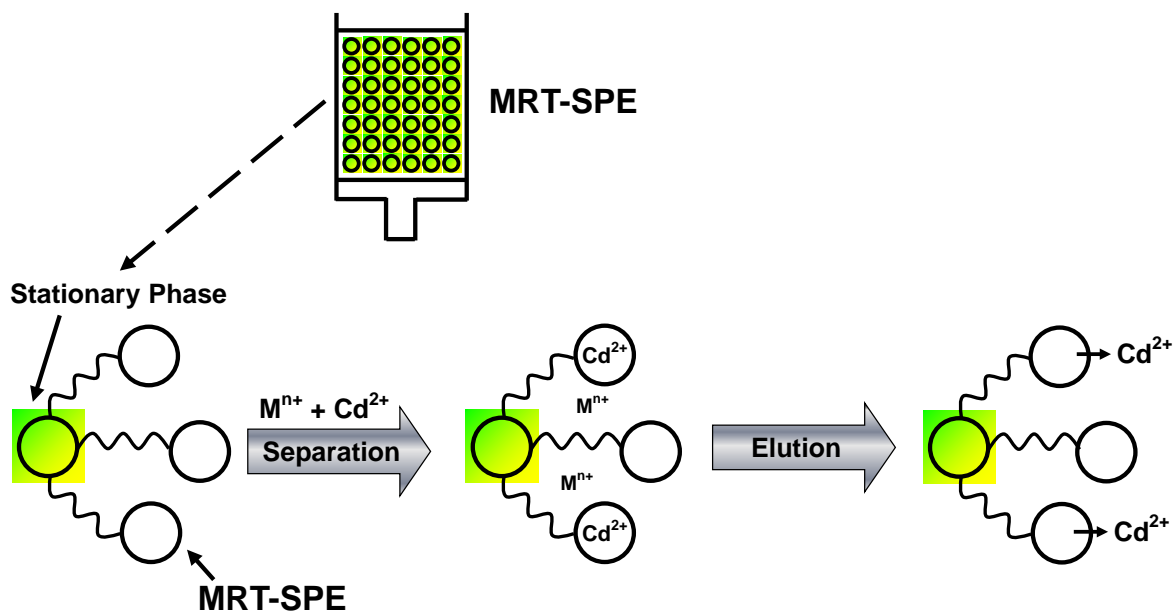


Fig. 2: A schematic illustration of the selective separation of Cd(II) by AnaLig Cd-01 MRT-SPE system.

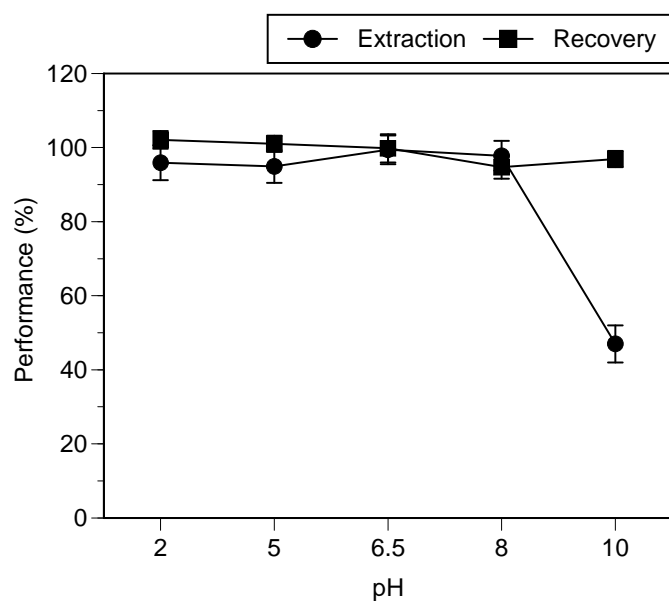


Fig. 3: Effect of matrix pH on the separation performance of the MRT-SPE. Sample solution– Cd(II) (200 μ M), pH– 2 to 10, volume– 4 mL, flow rate– 0.2 mL min⁻¹, elution– 1 M HNO₃ (2 mL) + 6 M HNO₃ (1 mL) + EPW (1 mL) ($n = 3$).

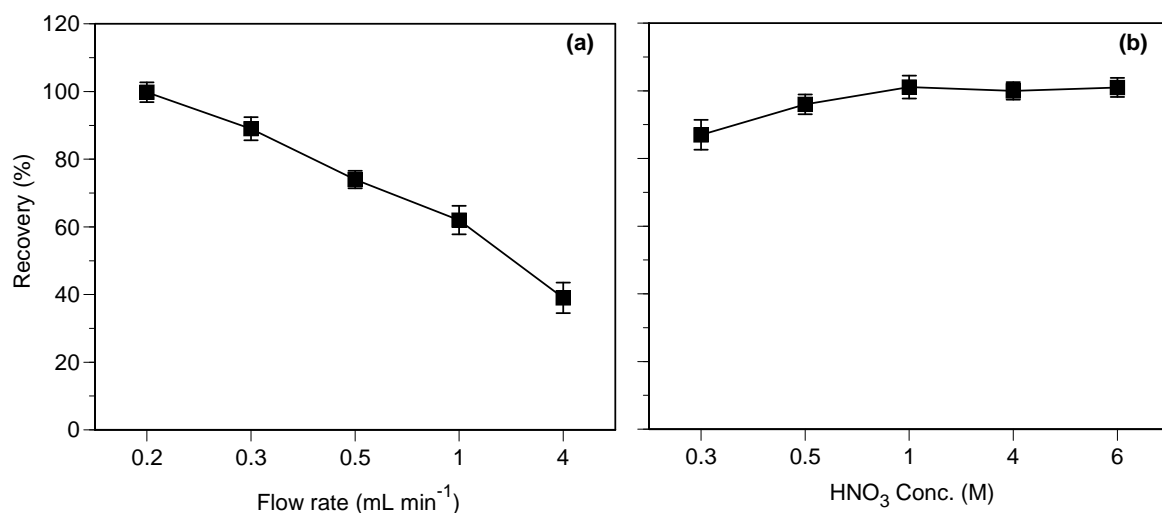


Fig. 4: Effect of (a) sample loading flow rates (b) eluent concentrations on the separation performance of the MRT-SPE. Sample solution– Cd(II) (200 μ M), pH– 6.5, volume– 4 mL, flow rate– (a) 0.2–4 mL min⁻¹, (b) 0.2 mL min⁻¹, elution– (a) 1 M HNO₃ (2 mL) + 6 M HNO₃ (1 mL) + EPW (1 mL) (b) 0.3–6 M HNO₃ (4 mL) ($n = 3$).

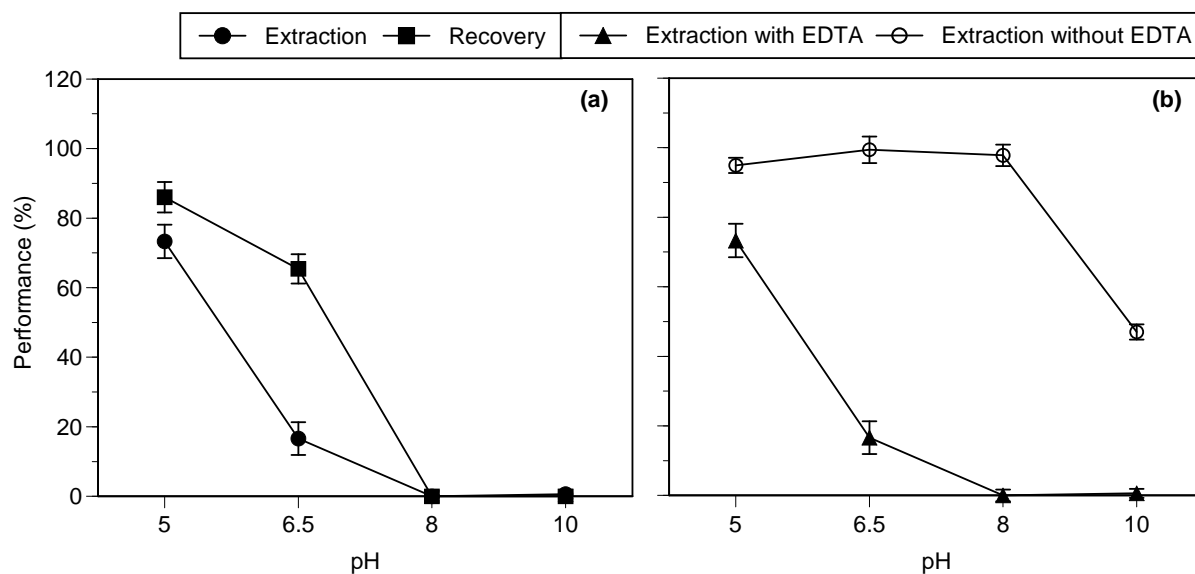


Fig. 5: (a) Cd(II) separation behavior of the MRT-SPE from effluent containing excess of EDTA as a function of pH, (b) comparative Cd(II) extraction performance from solutions containing excess of EDTA or no EDTA. Sample solution– Cd(II) (200 μ M), EDTA– 10 mM, pH– 5 to 10, volume– 4 mL, flow rate– 0.2 mL min⁻¹, elution– 1 M HNO₃ (2 mL) + 6 M HNO₃ (1 mL) + EPW (1 mL) ($n = 3$).