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Application of ion chromatography for the assessment of cadmium adsorption in simulated wastewater by activated carbon

Mutah Musa[a], Akira Kikuchi[a,*], Nor Eman Ismail[a], Jafariah Jaafar[b], Zaiton Abdul Majid[b], Mohd R. Salim[a], Kazuhiko Tanaka[c]

[a]*Institute of Environmental and Water Resources Management, Universiti Teknologi Malaysia, Johor Bahru, Malaysia*
Tel. +6075531725; email: akira@utm.my
[b]*Faculty of Science, Department of Chemistry, Universiti Teknologi Malaysia, Johor Bahru, Malaysia*
[c]*Graduate School for International Development and Cooperation, Hiroshima University, Hiroshima, Japan*

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ABSTRACT

A separation for Cd^{2+} and its interferences of common cations (Na^+, NH^+, K^+, Mg^{2+}, and Ca^{2+}) was performed. Cation-exchange ion chromatography for Cd^{2+} and common cations separation on a weakly acidic H^+ forming cation-exchange resin was investigated and applied to test the efficacy of activated carbon in the removal of Cd^{2+} from simulated wastewater. The difference of retention volumes between Ca^{2+} and Cd^{2+} was 0.45 mL for oxalic acid with a concentration of 1.75 mM, and the retention volume drastically decreased when the oxalic acid concentration increased in the eluent. Considering the prevailing conditions for TOSOH TSK gel Super IC A/C at 40°C with a least pH limit of 2.0, 1.75 mM of oxalic acid was selected for rapid analysis with pH of 2.3. Applying 50 µL sample injection, the calibration curve was linear for tested standard samples ranging from 0.05 to 2.0 mg/L, the detection limit ($S/N = 3$) was 0.066 mg/L (0.583 µM), and the analysis was applicable with coexisting Ca^{2+} up to 10.0 mg/L (250 µM) while other cations did not interfere. It was possible to analyze three samples within an hour. The application of this method on Cd^{2+} adsorption indicated the effectiveness of the method for heavy metals' analysis.

Keywords: Activated carbon; Cadmium; Cation-exchange; Ion chromatography; Oxalic acid

1. Introduction

Heavy metals comprise a wide range of elements with varying industrial applications; this ranges from essential elements like iron to toxic metals like cadmium and mercury. Their toxicity to living species makes them to be considered among the most harmful of the pollutants in the environment [1]. Most heavy metals have affinity to sulfur and disrupt enzyme function through bonds formed with sulfur groups in enzymes while cadmium, copper, lead, and mercury ions also bind to cell membranes hindering proper cell wall function in tissues [1,2]. Heavy metals' concentrations are frequently elevated as a result of contamination in the ecosystem, among which the most hazardous and frequently occurring incidences are those of Cu, Zn, Ni, Co, Cr, Fe, Cd, and As [3]. Cd^{2+} is one of the toxic elements found in effluents of electroplating, mining, painting, battery, and electronic industries and landfill leachates and is harmful to both

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*Corresponding author.

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humans and the environment [2–6]. Heavy metals are associated with both reproduction and development problems in humans [7]. It is carcinogenic and is a causal factor for other cardiovascular illnesses [8,9]. Thus, because of its inherent toxicity and existence above the allowable limit of 0.01 mg/L in some Malaysian rivers [10], Cd^{2+} was selected for analysis in this study.

Recent concerns in the area of environmental contamination have led to the development of appropriate technologies to assess the presence and mobility of metals in soil, water, and wastewater [4,11,12]. In order to assess and evaluate the effect of heavy metals on the environment, a robust monitoring system is required [13,14]. Currently, IC-AES, ICP-MS, and AAS are trends for heavy metals' analysis, including Cd^{2+} [15–17]. However, these analysis demand high cost and large equipment; thereby, ion chromatography has another unique analytical role in terms of simple, low cost, convenient simultaneous analysis for anions/cations separation [17–19]. The application of IC for environmental monitoring has known advantages of being effective, easy to control, and rapid [20,21]. The development of a simple analytical method which is convenient with sufficient sensitivity is important for determining the concentration of Cd^{2+} in aqueous samples. For example, in Malaysia, industries dealing in electroplating, electronics, batteries, and metal treatment/fabrication are the major sources of heavy metal contamination, with many such industries located in the west coast of peninsular Malaysia, including the Klang valley, Malacca, Johor Bahru, and Penang areas [22]. Over the years, various treatment technologies have been developed for its removal, such as chemical precipitation, ion exchange, membrane separation, electrocoagulation, solvent extraction, reduction, reverse osmosis, and adsorption [23–25]. Among these treatment methods, adsorption has been described as one of the easiest and most effective methods of heavy metals removal from environmental water [26].

Based on the need for a simplified technique, ion chromatography application for Cd^{2+} and its interferences of common cation simultaneous analysis was considered in this study. A cation-exchange ion chromatography method for Cd^{2+} separation and common cations on a weakly acidic H^+ form cation-exchange resin with conductimetric detection of electrons was examined, and was applied to test the efficacy of activated carbon (AC) in the removal of Cd^{2+} from simulated Cd^{2+} wastewater. In the separation process, the ion exchange resin attracts positively charged molecules of the analytes, while on the other hand complexing agents in the eluent attract the analytes simultaneously; this effect occurring in opposition is an important process in separation phenomena. Wherefore, the difference in ion exchange interaction and the difference of stability constant between heavy metal ion and the common cations were used as the principles for this analysis. The objective of this study was to optimize the analysis of Cd^{2+} by using cation-exchange chromatography and to test the effectiveness of the optimized method on simulated Cd^{2+} wastewater for Cd^{2+} adsorption by AC.

2. Materials and methods

2.1. Analytical instruments

An ion chromatograph TOSOH (Tokyo, Japan) model IC2010 equipped with vacuum degasser, double plunger pump, column oven, auto sampler with 500 µL sample loop, and conductivity detector was employed for analysis, data collection, and processing. An analytical TOSOH TSK gel Super-IC-A/C (3-µm particle size, 0.2 meq/mL cationic exchange capacity, and 150 mm × 6.0 mm ID) H^+ formed at 40°C was used for the simultaneous separation for cations in ion exchange chromatography. A Cyberscan 510 pH meter was used for the pH measurement of eluent and samples. An Eyela MMS 210 orbital shaker was used for agitation during adsorption test.

2.2. Reagents

All reagents used in this study were of analytical reagent grade purchased from Sigma Aldrich and Merck, and ultra pure water (UPW) system (Millipore Direct Q3) was used to prepare stock and standard solutions, washing solvents, and eluents. An analytical balance (0.2 µg), ATY 224 (Shimadzu, Tokyo, Japan), was used to weigh the reagents. Stock solutions were prepared by solving $CaCl_2$ (0.2775 g) in 25 mL UPW to make stock solution of 100 mM (solution A) and solving Na_2SO_4 (0.3551 g), $MgSO_4$ (0.3009 g), KNO_3 (0.2528 g), and NH_4NO_3 (0.2001 g) in 25 mL UPW (solution B). A stock solution of 8.89 mM (1,000 mg/L) Cd^{2+} was obtained from VWR International Ltd., England. These stock solutions were mixed and then diluted for calibration purpose. Oxalic acid (1.0–2.0 mM) was applied for elution in optimizing the analytical condition. Preparation of standard solutions from stock followed the methods employed by Mori and Tanaka [27].

2.3. Adsorption test

Adsorption tests using AC were carried out in batch mode at an ambient temperature of 28 ± 1°C for 1 h. Commercial AC powder, from Fluka chemicals, was applied for the experiment. A 17.78 μM (2.0 mg/L) standard solution was prepared as simulated Cd^{2+} wastewater (adsorbate), and the solution pH was adjusted to 4.5 using 0.1 M NaOH solution. A 50 mL volume of the adsorbate was put into a 100-mL conical flask and agitated at a speed of 150 rpm for 2, 4, 8, 12, 15, 30, 45, 60, 120, 180, 360, and 720 min in different trials on an Eyela MM 210 mechanical shaker after dosing with a known quantity of the adsorbent. The removal percentage of Cd^{2+} ($R\%$) is defined as the ratio of decrease in Cd^{2+} concentration to the initial concentration of Cd^{2+} in the adsorbate, which is represented by the formula:

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{1}$$

where C_0 is the initial concentration of the adsorbate in mg/L and C_t is the residual Cd^{2+} concentration in the adsorbate after adsorption has taken place over a period of time t in mg/L [22]. The adsorption tests in batch mode were carried out in duplicate and the mean values were taken.

2.4. Sample pretreatment

Five milli-litre of sample was taken from each conical flask using a syringe upon withdrawal of experimental flasks from the mechanical shaker. The sample was then filtered with a 0.45 μm polypropylene membrane filter and taken for residual Cd^{2+} concentration analysis using ion chromatography.

3. Results and discussion

3.1. Effect of oxalic acid concentration

In optimizing the simultaneous separation of Cd^{2+} and common cations using weakly acidic H^+ form ion-exchange resin column and weak acid eluent, the effect of eluent concentration was investigated. Ion exchange chromatography for heavy metal has generally been applied by a combination between cation-exchange column and acid eluent. In a process where the retention volume (V_R) of bivalent and trivalent heavy metal ions for ion exchange resins are similar, strong acid eluent (e.g. nitric acid) cannot be used to achieve heavy metal separation [28,29]. Thus, the effect of oxalic acid concentration on V_R for Ca^{2+} and Cd^{2+} were tested for 1.25, 1.6, and 2.0 mM. V_R of Ca^{2+} and Cd^{2+} greatly decreased upon increase of the oxalic acid concentration in the eluent (Fig. 1). It was observed that increasing hydrogen ion concentration in the eluent greatly decreased the degree of cation-exchange reaction to the carboxylic group on ion exchange regime in the analytical column. For cation-exchange chromatography separation, the higher and lower cation-exchange affinity reveal small and large V_R, respectively [21]. On the other hand, another affinity of chelating effect between complexing agent in eluent and cations was used, whereby difference of stability constants between complexing agent and cations resulted in different V_R for Ca^{2+} and Cd^{2+} [30]. Thus, the difference of V_R is influenced by both the difference of affinity between carboxyl group on cation-exchange resin and the analyte of cations, and difference of stability constant between complexing agent in eluent and the analyte cations, respectively. The difference of V_R between Ca^{2+} and Cd^{2+} was 0.45 mL for oxalic acid with a concentration of 1.75 mM with an increase to 1.02 mL at a concentration of 1.0 mM, and the V_R drastically decreased by increasing oxalic acid concentration in eluent (Fig. 2). From the result, it was clear that the separation between Ca^{2+} and Cd^{2+} is only slightly influenced by oxalic acid concentration variation, but the analysis duration for Ca^{2+} and Cd^{2+} can significantly be shortened with continuous increasing of concentration of oxalic acid in the eluent. As there was only a slight difference in the separation for Ca^{2+} and Cd^{2+} with varying oxalic acid concentrations (Fig. 1), consideration was given to the available operation condition for TSK gel Super IC A/C for pH ($2.0 < pH < 12$), and oxalic acid concentration of 1.75 mM was selected for rapid analysis with a pH of 2.3.

3.2. Effect of Ca^{2+} concentration on Cd^{2+} determination

The effect of Ca^{2+} over Cd^{2+} was investigated to confirm the degree of influence. Cd^{2+} concentration was maintained constant at 25×10^{-3} μM, while that of

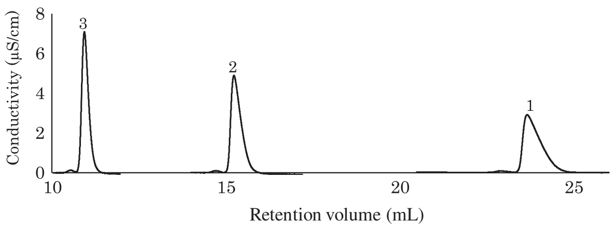

Fig. 1. Effect of oxalic acid concentration on retention volume of Cd^{2+} and Ca^{2+} chromatogram. Eluent: oxalic acid, 1: 1.25 mM, 2: 1.6 mM, 3: 2 mM, column: TOSOH TSK gel Super-IC-A/C resin (150 × 6.0 mm I.D.), column oven temperature: 40℃, flow rate: 0.80 mL/min, and injection volume: 50 μL.

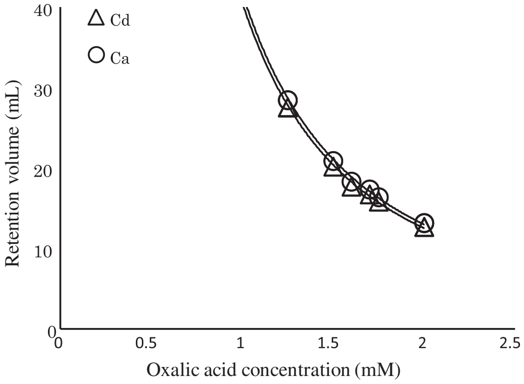

Fig. 2. Effect of oxalic acid concentration on the retention volume of Cd^{2+} and Ca^{2+} ions. Column: TOSOH TSK gel Super-IC-A/C resin (150 × 6.0 mm I.D.), column oven temperature: 40℃, flow rate: 0.80 mL/min, eluent concentration: 1.75 mM oxalic acid, and injection volume: 50 µL.

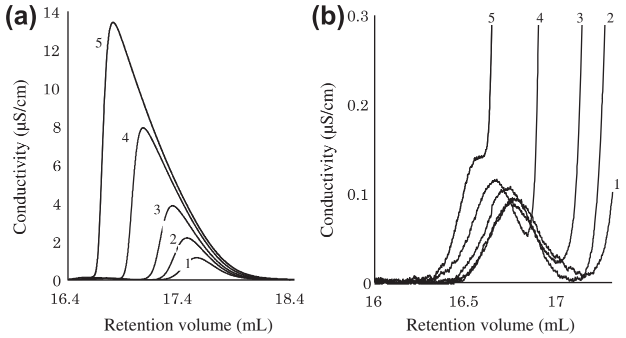

Fig. 3. Ca^{2+} peak shape (a) for concentrations of sample and its overlap on Cd^{2+} peak. (b) Sample: Cd^{2+}: 2.5×10^{-3} µM; Ca^{2+}, 1: 25 µM, 2: 50 µM, 3: 100 µM, 4: 250 µM, 5: 500 µM, column: TOSOH TSK gel Super-IC-A/C resin (150 × 6.0 mm I.D.), column oven temperature: 40℃, flow-rate: 0.8 mL/min, eluent concentration: 1.75 mM oxalic acid, and injection volume: 50 µL.

Ca^{2+} was varied at 25, 50, 100, 250, and 500 µM. It was observed that at higher concentration Ca^{2+} peak had continuously increased in size as shown in Fig. 3(a). Further increase in the concentration of Ca^{2+} in the samples analyzed showed a broadening in peak size and subsequent overlap with Cd^{2+}. The overlapping effect was insignificant at 25 µM of Ca^{2+} but became pronounced at 100 µM of Ca^{2+}, and at 500 µM the Ca^{2+} overlap was almost completely over the Cd^{2+} peaks (Fig. 3(b)). From the data, it was deduced that Cd^{2+} analyzability of Ca^{2+} concentration of up to 250 µM was possible. Furthermore, decreasing sample injection volume reduced peak size which in turn improved Ca^{2+} and Cd^{2+} separation. This, however, reduced sensitivity, and consequently for this study an injection volume of 50 µL was applied and this was similar to conditions applied in other works [31]. Fig. 4 shows the optimum IC simultaneous separation for Cd^{2+} and other common cations, indicating that Cd^{2+} is well separated from Ca^{2+} and other common cations.

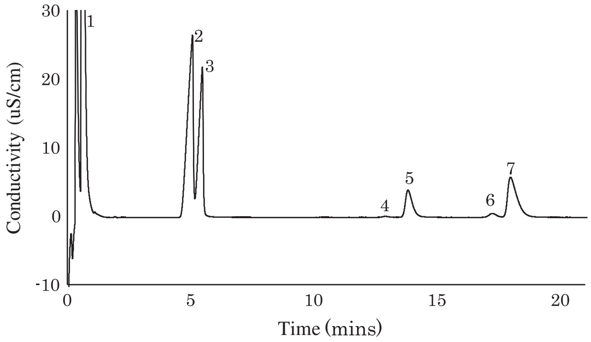

Fig. 4. Simultaneous cation-exchange chromatogram of common cations and Cd^{2+}. Peak identity, 1: elution dip, 2: Na^+, 3: NH_4^+ and K^+, 4: unknown, 5: Mg^{2+}, 6: Cd^{2+}, and 7: Ca^{2+}, column oven temperature: 40℃, runtime: 20 min, flow-rate: 0.80 mL/min, eluent concentration: 1.75 mM oxalic acid, and injection volume: 50 µL.

3.3. *Analytical performance and reproducibility*

Multi-parameter analysis of ions is convenient using a conductivity detection method within a single sample injection (50 µL). A conductimetric detector measures the electric conductivity of ions, which is a property attributed to all ions in a solution. This characteristic (conductivity) relates ionic concentration of the constituents in a solution. Calibration curve was obtained by plotting peak areas of concentration at the earlier optimized eluent concentration for Cd^{2+} and common anions and cations standard solutions. Cd^{2+} standard solutions were used for calibration with concentrations of 0.05, 0.075, 0.1, 0.25, 0.5, 1.0, and 2.0 mg/L. Linear calibration curve was obtained from the predetermined conditions with $r^2 = 0.998$. Detection limit ($S/N = 3$) calculated at 1.25 µM (0.14 mg/L) was 0.583 µM (0.066 mg/L) for Cd^{2+}. Recovery test was run to show the reproducibility of the cation-exchange chromatographic peaks for Cd^{2+} for repeated chromatographic runs ($n = 5$) and the results gave a recovery value of 99.5 ± 1.54%.

3.4. *Analysis of Cd^{2+} adsorption by AC*

The synthetic wastewater was prepared in the laboratory by diluting stock solution containing Cd^{2+} with UPW to obtain the desired initial concentration of 2 mg/L; this falls within the range of Cd^{2+} concentrations applied in previous works [32,33].

The solution pH was adjusted to 4.5 by adding 0.1 M NaOH solution dropwise as required [22,33]. The effect of increasing adsorbent dosage on amount of Cd^{2+} adsorbed is shown in Fig. 5. A gradual increasing trend in adsorption capacity with increment in adsorbent dosage was observed from 1 to 12 g/L, whereas drastic results were recorded between 20 and 60 g/L. The initial increase in adsorption capacity with increasing adsorbent dosage was expected, since the number of adsorbent particles increases, and thus more surface areas were available for Cd^{2+} attachment. The results represented similar trends in previous adsorption studies and the progressive increase in adsorption could be related to limited mass transfer of the adsorbate molecules in the system from the bulk liquid to the external surface of AC. Adsorption test by batch mode was applied using an adsorbent dosage of 6.0 g/L. The effect of this relationship with time was observed and indicated increase in removal with increase in agitation time for in this experiment (Fig. 6). The detection limit of the method developed was 0.066 mg/L, which could be comparatively suitable with limits applied in other studies [34,35] to test the ability of AC in Cd^{2+} adsorption. The advantage ion chromatography offers [20,21] was demonstrated in analyzing the Cd^{2+} as well as its interferences. In the preliminary experiments, the analytical method developed was sufficiently tested in its applicability for testing of simulated wastewater samples and can be confirmed as suitable and of adequate sensitivity in determining the concentration of Cd^{2+} in aqueous samples.

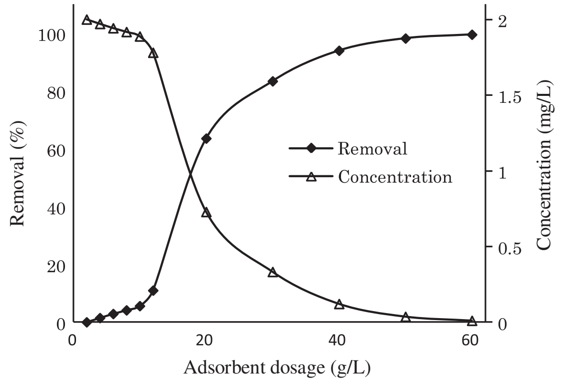

Fig. 5. Effect of adsorbent dosage (g/L) variation on metals adsorption at pH 4.5 with removal and residual Cd^{2+} concentration, agitation period of 60 min at 150 rpm with experimental condition: temperature of 28 ± 1°C for 1 h, pH 4.5, and 50 mL volume in 100 mL conical flask.

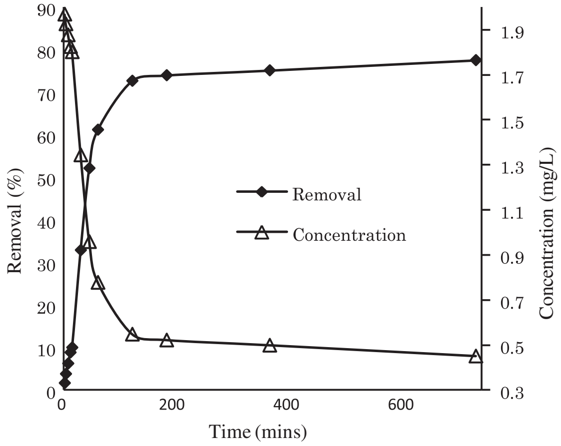

Fig. 6. Effect of contact time on adsorption with removal and residual Cd^{2+} concentration at ambient temperature of 28 ± 1°C, adsorbent dose of 6 g/L, and pH of 4.5.

4. Conclusion

A simultaneous determination of Cd^{2+} and its interferences of common cations in aqueous solution by cation-exchange ion chromatography was applied by using TOSOH TSK gel Super-IC-A/C at 40°C and 1.75 mM oxalic acid with 50 µL sample injection. The linear calibration curve for Cd^{2+} was obtained from 0.05 to 2.0 mg/L, and the detection limit (S/N = 3) was 0.066 mg/L (0.583 µM). It was possible to complete the analysis of three samples within an hour. The analysis was applicable with coexisting Ca^{2+} up to 10.0 mg/L (250 µM). This technique is practically suitable for experimental purposes in the analysis of Cd^{2+} and has a potential of being applied for water quality monitoring in wastewater with high concentration of Cd^{2+}. The result of Cd^{2+} adsorption tests by AC has indicated the effectiveness of the technique on the assessment of Cd^{2+} carried out in this study.

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