CHROMATOGRAPHIC BEHAVIOUR OF CADMIUM-(II) IN HYDROUS CERIC OXIDE COLUMN

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ABSTRACT.

CHROMATOGRAPHIC BEHAVIOUR OF CADMIUM-(II) IN HYDROUS CERIC OXIDE COLUMN. The potential of hydrous ceric oxide (HCO) in the immobilization of cadmium ions enables the compound to be used as an adsorbent for recovering ^{112}Cd target in the production of medical radioisotope ^{111}In. Since the enriched-^{112}Cd is very expensive, the dynamic sorption of ^{112}Cd in HCO column needs to be evaluated. In the presented work, the HCO was synthesized through the reaction of ceric sulphate and ammoniac solution. The reaction product was then heated and dried at 100°C to give HCO. A series of Cd(II) standard solutions was loaded onto HCO columns followed by fractional elution and determination of Cd(II)-content in each eluate fraction. The quantitative determination of Cd(II) content was performed by UV-spectrophotometry at 301 nm with a standard regression curve expressed as $A = 0.0001C - 0.0002$. The chromatographic behaviour of Cd(II) in HCO column was characterized by dynamic sorption capacity, elution profile, recovery yield and total volume of the eluent. It appears that the dynamic sorption of Cd(II) increases if the HCO was treated with ammoniac solution instead of with 0.1 M HCl solution. By using NH_4OH solutions (5 %, 10 % and 20 %) as eluents, it is shown that the concentration of NH_4OH does not significantly affect the Cd(II)-elution profile. The recovery yield was obtained in the range of 94 to 100 %, while most the eluted Cd(II) was collected in the first and second-2 mL fractions.

ABSTRAK.

PERILAKU KROMATOGRAFI KADMIUM-(II) DALAM KOLOM RESIN SERIUM OKSIDA. Potensi resin anorganik serium oksida (HCO) untuk mengikat ion kadmium mendorong kemungkinan pemanfaatan HCO dalam proses pemungutan ulang bahan sasaran ^{112}Cd diperkaya yang digunakan dalam proses produksi radioisotop medis ^{111}In. Karena mahalnya bahan sasaran ^{112}Cd tersebut, maka fenomena penyerapan dinamik ^{112}Cd pada kolom resin HCO dipelajari dengan menggunakan Cd alam. Di dalam percobaan ini HCO disintesis melalui reaksi antara serium sulfat dengan larutan amonia.

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Produk reaksi dipanaskan dan dikeringkan pada suhu 100°C untuk mengubahnya menjadi HCO. Larutan standard Cd(II) dengan variasi konsentrasi dimasukkan ke dalam kolom HCO dan kemudian dilakukan elusi berfraksi diikuti dengan pemeriksaan kandungan Cd(II) dalam masing-masing fraksi eluat. Penentuan kuantitatif Cd(II) dilakukan dengan metoda spektrofotometri UV pada panjang gelombang 301 nm dengan persamaan regresi standar yang dinyatakan sebagai $A = 0{,}0001C - 0{,}0002$. Sifat kromatografi Cd(II) dalam kolom HCO dipelajari melalui pengamatan terhadap 4 aspek yaitu kapasitas penyerapan dinamik, profil elusi, efisiensi elusi dan volume total eluen yang diperlukan. Didapatkan bahwa penyerapan dinamik Cd(II) pada kolom HCO yang diaktivasi dengan larutan HCL 0,1 M lebih rendah dibandingkan pada kolom HCO yang diaktivasi dengan larutan NH_4OH (5 %, 10 % dan 20 %). Hasil percobaan menunjukkan bahwa penggunaan eluen NH_4OH dengan konsentrasi 5 %, 10 % dan 20 % tidak memberikan perbedaan profil elusi Cd(II) yang signifikan. Dengan elusi berfraksi sebanyak 2 mL per fraksi eluat, didapatkan akumulasi Cd(II) terelusi pada 2 fraksi eluat pertama dengan efisiensi elusi antara 94 - 100 %.

INTRODUCTION

During the last decade, the use of hydrous ceric oxide (HCO) as an inorganic resin has been studied and developed [1-4]. It was even reported that the resin has been used in some parent-daughter radionuclidic separations, e.g. in separation of ^{99}Mo - ^{99m}Tc [5] and of ^{68}Ge - ^{68}Ga [6]. A study on the immobilization of Cd and other metal ions on ceric oxide [3,4] leads to a possibility that the HCO can be used as adsorbent in the sorption and recovery of enriched-^{112}Cd target used for production of ^{111}In .

The production of ^{111}In is being developed at the CDRR (Centre for Development of Radioisotopes and Radiopharmaceuticals), BATAN Serpong, through ^{112}Cd (p,2n) ^{111}In nuclear reaction [7] in cyclotron with proton energy ranging between 24 – 27 Mev [8]. Because the enriched-^{112}Cd target is very expensive and still has to be imported, the recovery of the target is necessary and important to be done. It was expected that cadmium will be trapped in an HCO-column and can be eluted efficiently from the column using a suitable solvent.

Related to that expectation, the sorption and chromatographic behaviors of cadmium in HCO column were studied using natural-Cd instead of enriched-^{112}Cd. The reported work is aimed as a basis for developing enriched-^{112}Cd recovery technique.

EXPERIMENTAL

Material and Equipment.

Reagent-grade (p.a.) $Ce(SO_4)_2$. 4 H_2O, H_2SO_4 and NH_4OH for the synthesis of HCO and Cd metal powder for the preparation of Cd(II) standard solutions were purchased from Merck, Germany, and used as received. Demineralized water was obtained from G.A. Siwabessy Reactor Facility (CDRRT, the Centre for Development of Research Reactor Technology), BATAN, Serpong.

A JASCO UV/Vis-Spectrophotometer (V-550) equipped with a Spectra Manager software for Windows (961105 version) was used for Cd(II) measurement. The analysis of synthesized ceric oxide was performed by means of Infra Red (IR)-Spectrophotometer (JASCO FT/IR-410) and X-Ray Diffractometer (Shimadzu VG-108R).

Synthesis of HCO.

The synthesis of HCO was based on the method reported by MISHRA [4]. An approximately 80 g of $Ce(SO_4)_2$. 4 H_2O was dissolved with stirring in 250 mL of 0.05 M H_2SO_4. Concentrated NH_4OH (150 mL) was added dropwise to the stirred solution. The reaction mixture was continuously stirred for about 15 minutes and then kept overnight at room temperature. The precipitated ceric hydroxide was filtered and washed with 4 x 25 mL of dilute ammonia, then with water until the pH was neutral. Finally the solid product was dried at about 100^0C for a few hours to give a constant weight of HCO.

For sorption experiments, the resulting HCO was carefully ground in a mortar and sifted to get particle size ranging between 80 - 100 meshes.

Analysis of HCO.

An appropriate amount of HCO was mixed, ground with KBr powder and pressed in a mold to give CeO_2-KBr pellet suitable for IR-spectrophotometry. An HCO sample for X-Ray diffraction analysis was sent to the Centre for Research and Development of Material Science and Technology (CRDMST, BATAN). The X-Ray diffraction analysis was performed in a range of diffraction angle between 5 - 70^0 using Cu-K_α at 1.542 A^o.

Chromatographic Behaviour of Cd(II) in HCO Column.

An approximately 2 g of HCO resin (80 - 100 meshes) was washed with water and treated with 0.1 M HCl or NH_4OH solution (5 %, 10 % or 20 %) for about 1 hour with occasionally stirring. The floating fraction was removed by decantation. The wet resin was then loaded onto chromatographic column (i.d. 1 cm) up to a height of 1 mL-volume. The HCO upper surface was covered by glass wool and kept to be soaked.

A 2 mL Cd(II) standard solution was loaded onto the column. The effluent (2 mL) was collected in a 10-mL vial marked as F0. The following fractional elution was carried out using ammoniac solution as eluent. The eluate fractions (10 fractions, each 2 mL) were collected separately as F1 to F10 and submitted for spot analysis of Cd(II) by using Na_2S solution in the presence of NH_4OH. The fractions giving positive test result, indicated by the appearance of yellow solution or precipitate, were then submitted to UV-spectrophotometric determination of Cd(II) content.

UV-Spectrophotometric Determination of Cd(II).

The eluate fractions giving positive test for Cd(II) were properly diluted with water and measured spectrophotometrically for the total cadmium content. Prior to the determination, the UV-absorbance spectrum of each solution was run and compared to that of the Cd(II) standard solution. The Cd(II)-contents were calculated by means of regression equation obtained from the standard solutions.

RESULTS AND DISCUSSION.

The IR-spectra of the synthesized HCO show significant absorption bands in the range of 3000 - 3500 cm^{-1} corresponding to the sum of the contributions from interstitial water and hydroxyl groups [4]. The absorption bands at 1630 - 1650 cm^{-1} is due to the bending vibration of water molecule [4]. A typical band shown at 900 - 1050 cm^{-1} indicates the presence of Ce-O-H group in the structure of HCO [4,9]. The presence of water in the synthesized HCO is also shown in Fig. 1 indicating that it was easily liberated at the beginning of heating. However, a small amount of water is still left as hydrate or interstitial water with respect to the following chemical reactions :

$$Ce(SO_4)_2 + 4\,NH_4OH + x\,H_2O \rightarrow Ce(OH)_4.\,x\,H_2O + 2\,(NH_4)_2SO_4$$
$$Ce(OH)_4.\,x\,H_2O \rightarrow x\,H_2O + CeO_2.\,y\,H_2O + (2 - y)\,H_2O$$

where y was found, in average, to be 0.885, calculated from the weight of the resulting HCO as compared to the reaction stoichiometry.

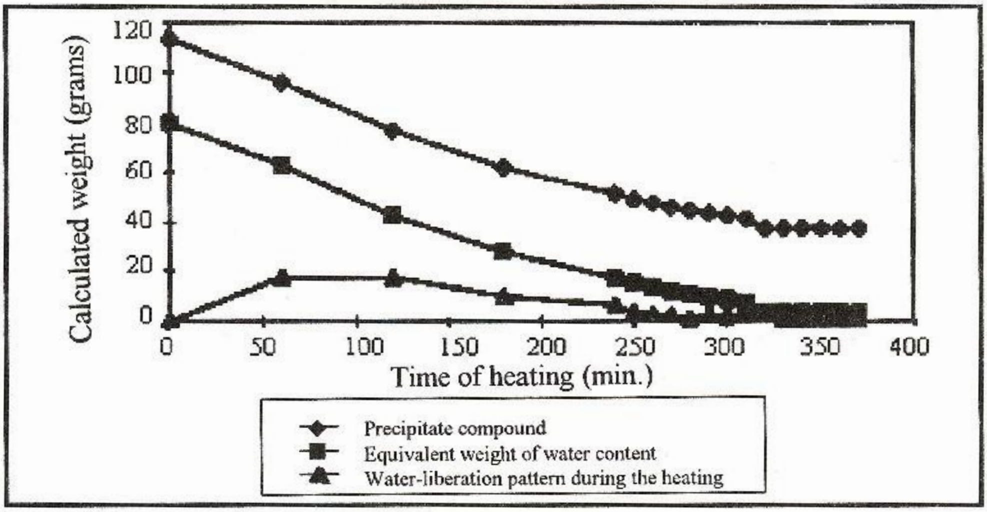

Fig. 1. Illustration on water-content in the resulting HCO

Table 1 shows that the X-ray diffraction data of the synthesized HCO are comparable to that of the literatures [4,10] as indicated by the RMS values which are less than 2.5 %. The values reveal that the sample has microcrystalline behaviour similar with that of cerianite (cerium[IV] oxide) [4,10]. Considering the equipment available at the CDRR, BATAN, the UV/Vis-spectrophotometric method was used for the quantitative determination of Cd(II). It appears in Fig. 2 that the maximum absorbances in the region of 250 - 330 nm, i.e. at 301 nm, are proportional to the concentration of Cd(II).

Table 1. X-Ray diffraction data of HCO (Cu-K_α, $\lambda = 1.542$ A°).

DIFFRACTION ANGLE (°)	PRESENTED WORK		H.E. SWANSON [10]		S.P. MISHRA [4]		RMS VALUE OF d	
	I/I_0	d(A°)	I/I_0	d(A°)	I/I_0	d(A°)	(A°)	(%)
± 28	100	3,153	100	3,124	100	3,124	0.017	0.54
± 33	39	2,820	29	2,706	31	2,714	0.064	2.33
± 47	47	1,943	51	1,913	52	1,912	0.017	0.88
± 56	37	1,626	44	1,632	38	1,624	0.004	0.25
± 60	18	1,562	5	1,562	14	1,552	0.005	0.32
± 70	--- *)	---	5	1,353	10	1,352	--	--

Note : *). Not clearly detected.

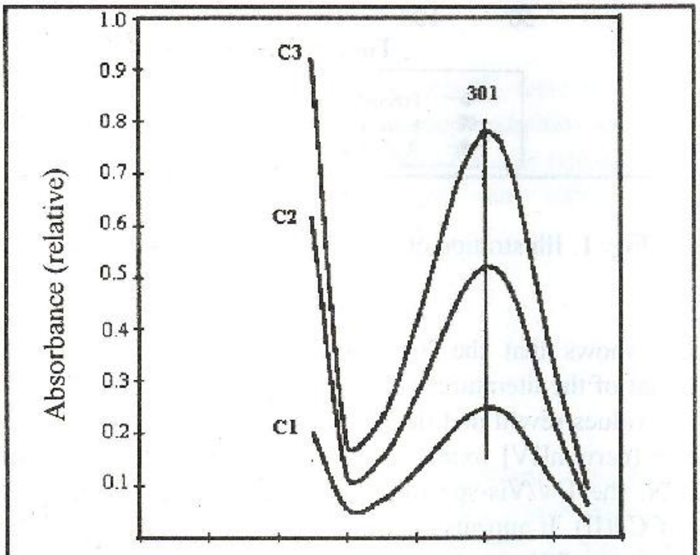

Fig. 2. UV-spectra pattern of Cd(II) standard solution.
C1 : 2004 ppm, C2 : 4008 ppm, C3 : 6013 ppm

The maximum absorbances were observed to be stable within 24 hours, giving a good prospect for the determination of Cd(II) by UV-spectrophotometry. The regression curve of Cd(II) standard solution was found to have mathematical relationship of $A = 0.0001\ C - 0.0002$, where A is absorbance and C is Cd(II) concentration (ppm), while the correlation coefficient R was 0.99997. The accuracy and precision of the method was examined by using standard addition method. The results in Table 2 show that the method used is reliable for quantitative determination of Cd(II).

Table 2. Reliability test of UV-spectrophotometric determination of Cd(II).

NO	Cd(II) CONTENT IN SAMPLE (mg)	Cd(II) ADDED TO SAMPLE (mg)	TOTAL Cd(II) MEASURED (mg)	Cd(II)-ADDED RECOVERY [R] ([d] - [b])		RECOVERY IN AVERAGE (%)	T-TEST VALUE *	
				(mg)	(%)		T_{CAL}	T_{TAB}
[a]	[b]	[c]	[d]	[e]	[f]	[g]	[h]	[i]
I	44.3	8.9	53.2	8.9	100.0			- 4.303
	59.3	12.0	71.1	11.8	98.3	99.9 ± 1.4	0.124	to
	70.6	15.2	86.0	15.4	101.3			4.303
II	44.3	17.8	62.1	17.8	100.0			- 4.303
	59.3	23.8	82.9	23.6	99.2	100.0 ± 0.8	0.000	to
	70.6	28.3	99.1	28.5	100.7			4.303

Note : *). T_{TAB} was found from Reference [11] for a two-tailed test with degrees of freedom (n-1) = 2 and probability level $P = 0.05$.

The chromatographic behaviour of Cd(II) in HCO column was characterized by dynamic sorption capacity, elution profile, recovery yield and total volume of the eluent needed. The dynamic sorption capacity of Cd(II) on HCO was studied by comparing Cd(II)-content of the F0 fraction to that of the Cd(II) standard solution loaded onto the HCO column. Table 3 shows that there are significant differences between pretreated of HCO with 0.1 M HCl and that with NH_4OH (5 %, 10 % and 20 %).

It was presumed that by using 0.1 M HCl solution, the loaded Cd(II) tends to form $[CdCl_4]^{2-}$ instead of $[Cd(NH_3)_4]^{2+}$ if NH_4OH solution is used. The UV-spectrum of the chloro-complex was observed to be different from that of the Cd(II) standard solution, so that the recovered Cd(II) as $[CdCl_4]^{2-}$ was not determined. However, Table 3 shows that the dynamic sorption capacity of Cd(II) as $[CdCl_4]^{2-}$ is smaller than that of Cd(II) as $[Cd(NH_3)_4]^{2+}$. The dynamic sorption capacity of Cd(II) as $[Cd(NH_3)_4]^{2+}$ could be quantitatively determined because the UV-spectrum of $[Cd(NH_3)_4]^{2+}$ was similar to that of Cd(II) standard solution.

Table 3. Dynamic sorption of Cd(II) on HCO treated with various solutions.

TREATMENT SOLUTION	Cd(II) LOADED TO COLUMN (mg)	RECOVERED Cd(II) IN F0 FRACTION		DYNAMIC SORPTION [mg Cd(II)/cm^3 HCO]
		Spot test	Amount (mg)	
5 % NH_4OH	$29.8^{a)}$	+	3.5 ± 0.1	26.3 ± 0.1
	$22.6^{a)}$	-	-	$22.6^{e)}$
	$11.9^{a)}$	-	-	$11.9^{e)}$
10 % NH_4OH	$29.8^{b)}$	+	5.5 ± 0.2	24.3 ± 0.2
	$22.6^{b)}$	-	-	$22.6^{e)}$
20 % NH_4OH	$29.8^{c)}$	+	8.6	21.2
	$20.5^{c)}$	-	-	20.5
0.1 M HCl	$22.6^{b)}$	+	n.d. $^{d)}$	n.d.
	$17.4^{b)}$	+	n.d.	n.d.
	$1.1^{b)}$	+	n.d.	n.d.

Notes : a). Number of experimental work : n = 3.
b). Number of experimental work : n = 2.
c). Number of experimental work : n = 1.
d). The Cd(II)-content of F0 fraction was not determined because the UV-spectrum pattern is not similar to that of the Cd(II) standard solution (see text).
e). Standard deviation is not calculated because the amount of loaded Cd(II) was totally adsorbed in the HCO column.

Based on the dynamic sorption results (Table 3), the NH_4OH solutions (5 %, 10 % and 20 %) were used as eluents. It was observed that the Cd(II)-elution profiles are typically similar, in which the recovery yields are in a range of 94 - 100 %. The eluted Cd(II) was mostly collected in the first and second-2 mL fractions as shown in Fig.3.

It means that a small volume of eluent is capable of eluting Cd(II) sorbed in the HCO column. The concentration of NH_4OH used as eluent does not significantly affect the elution profile, although it affects the sorption capacity of Cd(II), as indicated in Table 3. Therefore, it can be expected that an ammoniac solution is suitable to be used as eluent for ^{112}Cd recovery using HCO column.

CONCLUSION.

The dynamic sorption capacity of Cd(II) in HCO pretreated with 0.1 M HCl is smaller than that of using ammoniac solution. The concentration of ammoniac solutions slightly affects the Cd(II)-sorption capacity but does not significantly affect the elution profile of Cd(II) in the HCO column.

By using ammoniac solution (5 %, 10 % and 20 %), the adsorbed Cd(II) in the HCO column can be eluted quantitatively (94 - 100 % of recovery). The recovered Cd(II) was mostly collected in the first and second-2 mL fractions. The experiment results indicate that ammoniac solution is suitable to be used as eluent in the recovery of enriched-^{112}Cd using HCO column.

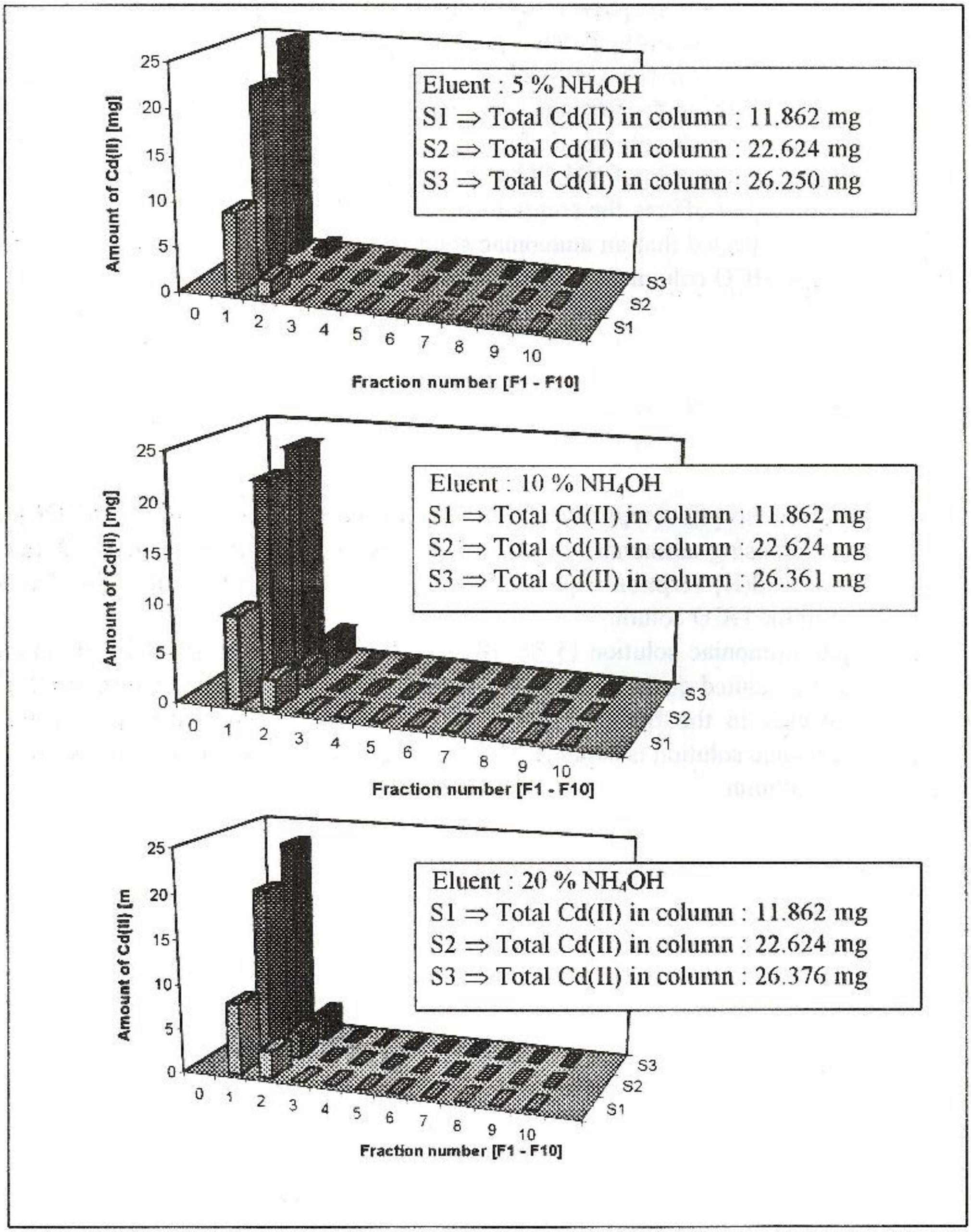

Fig. 3. Elution profiles of Cd(II) in HCO column

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