ISSN 1411 - 3481

ADSORPTION BEHAVIOUR OF CADMIUM-(II) ON HYDROUS OXIDE INORGANIC RESINS

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ABSTRACT

ADSORPTION BEHAVIOUR OF CADMIUM-(II) ON HYDROUS OXIDE INORGANIC RESINS. Hydrous titanium oxide (HTO), hydrous zirconium oxide (HZO) and hydrous cerium oxide (HCO) resins were subjected to batch experiments on cadmium-(II) adsorption studies using standard solutions of Cd-(II)-nitrate. This was aimed to gain more experimental data in concern to choose inorganic resin for separation of Cd^{2+} - In^{3+} matrices in production technology of indium radioisotopes ($^{111/115m}In$) as well as for recovery of high-enriched cadmium-($^{112/114}Cd$) target. Series of cold Cd-(II)-nitrate standard solutions prepared from natural cadmium were treated by means of mixing and stirring with the resins at room temperature and then separated from the resin by centrifugation. The separating supernatants were then spectrophotometrically analyzed for Cd-(II) determination as compared to Cd-(II) content in the corresponding initial solutions. The results indicate that there was no Cd-(II) adsorption on Merck-produced titanium oxide pre-treated with neutral, acidic or basic condition. The Cd-(II) adsorption occured either on zirconium oxide or on cerium oxide. The self-synthesized HCO having molecule formula of $CeO_2.nH_2O$ ($n = 0.8868 \pm 0.0026$) showed higher Cd-(II)-adsorption capacity than self-synthesized HZO that was found to have molecule formula of $ZrO_2.qH_2O$ ($q = 1.7613 \pm 0.0836$), i.e. $(47.167 \pm 0.083) \times 10^{-3}$ mg/mg as compared to $(12.200 \pm 0.255) \times 10^{-3}$ mg/mg. The ready-used zirconium oxide produced by Atomergic Chem. Corp. showed significantly smaller, i.e. $(9.449 \pm 0.092) \times 10^{-3}$ mg/mg. The influence of hydrate content in the resins to the Cd-(II)-adsorption capacity was observed by comparing Cd-(II)-adsorption capacity of HCO heated up to 400°C (found as $CeO_2.0.1706H_2O$) and that of HCO heated up to 800°C (found as $CeO_2.0.0400H_2O$), i.e. $(116.567 \pm 0.839) \times 10^{-3}$ mg/mg and $(146.533 \pm 0.897) \times 10^{-3}$ mg/mg respectively.

Key words : hydrous oxide inorganic resin, cadmium-(II) adsorption, titanium oxide, zirconium oxide, cerium oxide, synthesis of zirconium oxide, synthesis of cerium oxide, spectrophotometric determination.

ABSTRAK

SIFAT PENYERAPAN KADMIUM-(II) PADA RESIN HIDRO-OKSIDA ANORGANIK. Penelitian ini mempelajari sifat penyerapan kadmium-(II) pada resin titanium oksida (hidro-titanium oksida, HTO), zirkonium oksida (hidro-zirkonium oksida, HZO) dan serium oksida (hidro-serium oksida, HCO) dengan menggunakan larutan standar kadmium-(II) nitrat. Penelitian dimaksudkan untuk mendapatkan tambahan data eksperimental yang mendasari pemilihan dan penggunaan resin anorganik untuk pemisahan matriks Cd^{2+} - In^{3+} dalam teknologi produksi radioisotop indium-($^{111/115m}In$) dan pemungutan ulang bahan sasaran kadmium-($^{112/114}Cd$) pengkayaan tinggi. Larutan standar kadmium-(II) nitrat yang dibuat dari kadmium alam diperlakukan melalui pencampuran dan pengadukan pada temperatur kamar dengan resin-resin tersebut dan kemudian dipisahkan kembali dengan cara sentrifuga. Kandungan Cd-(II)

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produced using BATAN's cyclotron and G.A. Siwabessy reactor respectively. The production of the former is based on ^{112}Cd (p,2n) ^{111}In nuclear reaction (in cyclotron) while the later is produced by ^{114}Cd (n,γ) $^{115}Cd \rightarrow {}^{115m}In$ nuclear reaction (in reactor, followed by separation in radioisotope generator system) [4,5]. The resulting radio-indium can be bound to suitable substrate molecules to produce radiopharmaceutical preparations used for diagnosis of various tumors and cancers [6,7], intravascular infection and inflammatory bowel disease [8,9] as well as for hematological damage detection [10]. Utilization as therapeutic radionuclide is also enable for ^{115m}In [11] due to its nuclear transition emitting β radiation of 0.84 MeV with an abundant of less than 10 %. However, domestic public services with those indium radioisotopes are not yet committed due to lack of experience and expertise on the production technology.

In both nuclear reactions mentioned above, the immobilization of cadmium-(II) is important related to the separation and purification of the indium radioisotopes as well as to the recovery of the enriched cadmium-($^{112/114}Cd$) targets. This present paper is to report adsorption study of cadmium-(II) on various hydrous oxide resins, e.g. those based on titanium, zirconium and cerium oxides structure. The hydrous oxides of titanium, zirconium and cerium have been known to be used as separating agents in immobilization or production of some radioisotopes [12-18].

This presented experiment was performed using natural cadmium, instead of enriched material, in cold condition and exploiting spectrophotometric behaviour of cadmium in ultra violet region for quantitative determination [19,20]. The aim of the present study is to gain more experimental data in concern to choose inorganic resin for separation of Cd^{2+} - In^{3+} matrices as well as for recovery of high enriched cadmium-($^{112/114}Cd$) target in production technology of indium radioisotopes ($^{111/115m}In$).

EXPERIMENTAL METHODS

Preparation of materials and equipments

The cadmium metal (Merck, A617501.2001.0250) was used for the preparation of stock and standard solutions of cadmium-(II), TiO_2 from Merck (K21853008.1.00808.1000) and ZrO_2 (Atomergic Chem. Corp., L0626) were used for ready-used-resins, $ZrOCl_2.8H_2O$ (Merck, B.372317.1.08917.0100) and $Ce(SO_4)_2.4H_2O$ (Merck, B896674.1.02274.0250) were used as raw materials for synthetic hydrous zirconium oxide (HZO) and hydrous cerium oxide (HCO) respectively. Other chemical materials were p.a. reagent grade and purchased from Merck sole agent, dissolved or

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being standed overnight, the formed precipitate was filtered and washed to remove the excess sulphate. The solid product was dried at about 100°C for a few hours to give relatively constant weight and then was grinded and sieved to get fraction of smaller than 100 mesh.

Each of the resulting oxide compounds was analyzed by means of infrared spectrophotometry and was closely stored in desiccator until used. The yield of the synthesis based on the stoichiometric formation of MO_2 (M = Zr and Ce) was calculated by comparing the weight of resulting products to the chemical reaction to determine the number of hydrate bound in the oxide molecules.

Adsorption studies of Cd-(II) on the hydrous oxide resins

Certain amounts of resins were mixed and stirred with 10 mL of Cd-(II) standard solution for about 30 minutes. The mixture was then centrifuged and the supernatant was cited and, in case necessary, accurately diluted for determination of its Cd-(II) content. The determination of Cd-(II) in solution was performed by UV spectrophotometry as has been previously reported [19,20] and was corrected with corresponding dilution factor, whereas that of Cd-(II) adsorbed on the resin was calculated by subtracting Cd-(II) content in the initial solution with residual amount in the corresponding supernatant. Experiments were performed with ready-used titanium oxide and zirconium oxide as well as self-synthesized zirconium oxide and cerium oxide. The variables and repetition of the experiments are presented in Tabel 1.

Effect of heating treatment on Cd-(II)-adsorption capacity

The effect of heating was conducted with self-synthesized HCO resin. A weighed-amount of HCO produced by above synthesis procedure was heated at 400°C and 800°C for one hour. In this case, the time consumed to achieve the setting temperature was not taken into consideration. After one hour of heating treatment at the setting temperatures, the system was kept back to room temperature without taking time consumed into consideration. The resin was then closely stored in desiccator until used. The retained hydrate content after heating was determined by means of weight calculation. Adsorption capacity of Cd-(II) on the heat-treated resin was studied as formerly described.

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The batches of experiment shown in Table 1, however, were performed due to the difference of results on preliminary study in which there was no cadmium-(II) adsorbed on titanium oxide but there was on either zirconium oxide or cerium oxide. As the ready-used titanium oxide (Merck K21853008.548) showed no adsorption of Cd-(II), then no experiment with self-synthesized hydrous titanium oxide was carried out. Heating treatments on the cerium oxide were performed to further observe how was the Cd(II)-adsorption capacity influenced by pre-heating of the resin.

Table 1. Experiment batches on adsorption studies of Cd-(II)

Hydrous oxide resin	**W_r [a] (mg)**	**C_0 [b] (mg)**	**Dilution factor [c]**	**Number of batches**
Titanium oxide, Merck (K21853008.548)	500	210	10 ×	3 [d]
Zirconium oxide (Atomergic Chem. Corp., L0626)	500	40	No dilution factor (the solution was directly measured)	3
Synthesized Zirconium oxide (dried up to 100°C)	500	40	No dilution factor (the solution was directly measured)	3
Synthesized Cerium oxide (dried up to 100°C)	600	400	10 ×	1
		480	10 ×	1
		560	10 ×	1
Synthesized Cerium oxide (dried up to 400°C)	600	400	10 ×	1
		480	10 ×	1
		560	10 ×	1
Synthesized Cerium oxide (dried up to 800°C)	600	400	10 ×	1
		480	10 ×	1
		560	10 ×	1

a). W_r = The amount of resin with precision weight of ± 1,0 mg

b). C_0 = The amount of Cd-(II) content in 10 mL standard solution. The precision content based on preparation and dilution of the stock solution was ± 0.025 %.

c). Dilution factor was used for UV-Spectrophotometric determination of Cd-(II) in order to have absorbance values between 0.20 to 0.90

d). Three batches were respectively involving titanium oxide pre-treated with water (neutral condition), NaOH 1M (basic condition) and HCl 1 M (acidic condition).

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oxide based on the method reported by Misrha and Singh [17] was adopted to be applied for self-synthesis of cerium oxide and zirconium oxide. The products were assumed as hydrous oxide compounds having typical formula as $MO_2.x\ H_2O$ (M = Ce or Zr), which were formed through the following reactions :

$$Ce(SO_4)_2.\ 4\ H_2O + 4\ NH_4OH \rightarrow CeO_2.n\ H_2O + 2\ (NH_4)_2SO_4 + (6 - n)\ H_2O$$

$$ZrOCl_2.8H_2O + 2\ NH_4OH \rightarrow ZrO_2.qH_2O + 2\ NH_4Cl + (9 - q)\ H_2O$$

The formation of $CeO_2.nH_2O$ and $ZrO_2.qH_2O$ was respectively determined by repeatedly weighing the corresponding intermediate products which were assumed as $Ce(OH)_4.mH_2O$ and $Zr(OH)_4.pH_2O$ respectively during heating treatment up to about 100°C. The typical pattern of water liberation and the retained water bound in the products are shown in Figure 3 following the reactions below :

$$Ce(OH)_4.mH_2O \rightarrow Ce(OH)_4 + m\ H_2O$$

$$Ce(OH)_4 \rightarrow CeO_2.nH_2O + (2 - n)\ H_2O$$

$$Zr(OH)_4.pH_2O \rightarrow Zr(OH)_4 + p\ H_2O$$

$$Zr(OH)_4 \rightarrow ZrO_2.qH_2O + (2 - q)\ H_2O$$

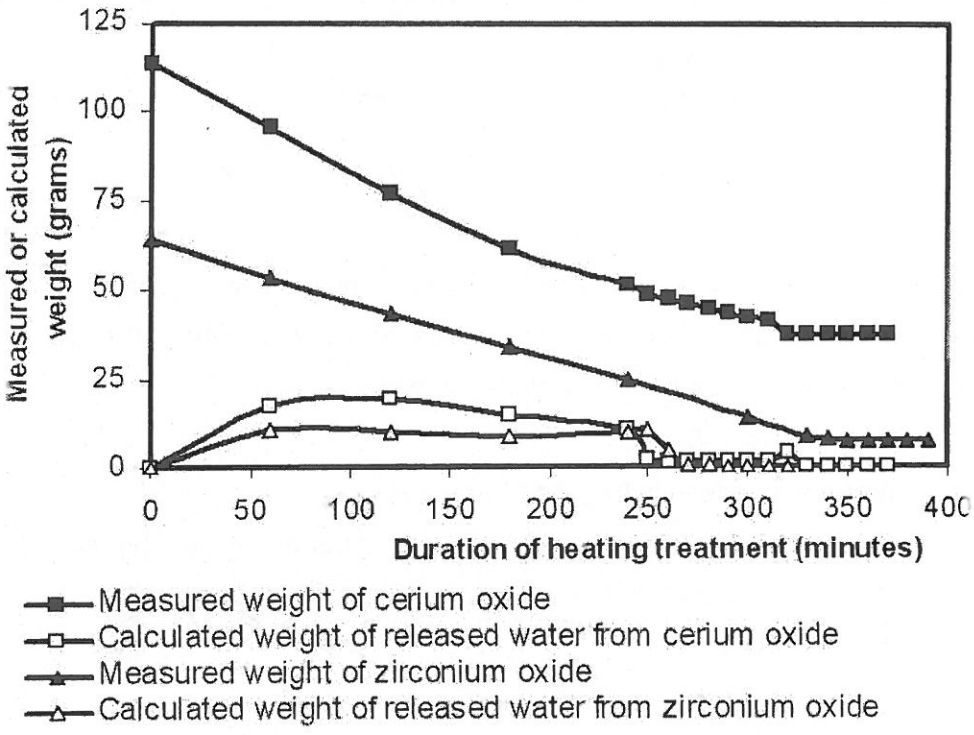

Figure 3. Typical pattern of water release from synthesized zirconium oxide and cerium oxide on heating treatment at 100°C.

$CeO_2.0.1706H_2O$ with Cd-(II)-adsorption capacity of $(116.567 \pm 0.839) \times 10^{-3}$ mg/mg. After heating at 800°C the formulation was changed to $CeO_2.0.0400H_2O$ showing Cd-(II)-adsorption capacity of $(146.533 \pm 0.897) \times 10^{-3}$ mg/mg.

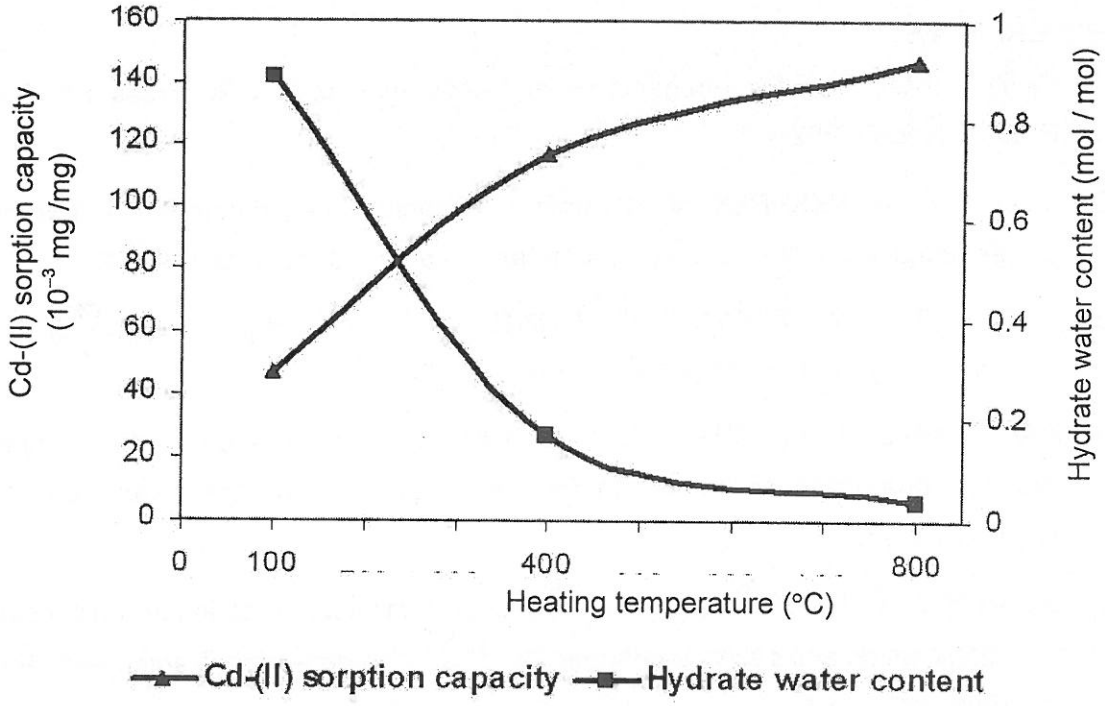

Figure 4. Correlation of hydrate content and Cd-(II)-adsorption capacity of HCO with temperature of heating treated to the HCO.

CONCLUSION

Cadmium-(II) was not adsorbed on hydrous titanium oxide (HTO) resin but it was on hydrous zirconium oxide (HZO) and hydrous cerium oxide (HCO) resins. Self-synthesized HCO showed highest Cd-(II)-adsorption capacity as compared to self-synthesized or ready-used HZO, i.e. $(47.167 \pm 0.083) \times 10^{-3}$ mg/mg as compared to $(12.200 \pm 0.255) \times 10^{-3}$ mg/mg and $(9.449 \pm 0.092) \times 10^{-3}$ mg/mg respectively.

Pre-heating treatments at 400°C and 800°C on HCO could increase its Cd-(II)-adsorption capacity up to $(116.567 \pm 0.839) \times 10^{-3}$ mg/mg and $(146.533 \pm 0.897) \times 10^{-3}$ mg/mg respectively. It was presumed due to decreasing hydrate content as indicated by resulting structure of pre-heated HCO, i.e. $CeO_2.0.1706H_2O$ and $CeO_2.0.0400H_2O$ respectively as compared to the initial structure of $CeO_2.0.8868H_2O$.

It can be concluded that among the hydrous oxides studied (HTO, HZO and

12. BILEWICZ, A., et al, Ion exchange of alkali metal on hydrous titanium dioxide in neutral and alkali solution, J. of Radioanal. and Nucl. Chem., 148 [2], 1991, 357 – 371.

13. HASANY, S.M., Sorption of hafnium on hydrous titanium oxide using radiotracer technique, J. of Radioanal. and Nucl. Chem., 219 [1], 1997, 51 – 54.

14. BHATTACHARYYA, D.K., DUTTA, N.C., Immobilization of barium, cadmium and antimony cations over zirkonia, J. Nucl. Sci. and Technol., 28[11], 1991, 1014-1018.

15. DAS, S.K., GUIN, R., SAHA, S.K., Study of adsorption of zinc ions on hydrous zirconium oxide surface, Radiochimica Acta, 88 [2], 2000, 107 – 110.

16. BHATTACHARYYA, D.K., DUTTA, N.C., Separation of carrier free ^{99m}Tc from ^{99}Mo over ceria column, International Symposium on Radiochemistry and Radiation Chemistry, Bombay, February 4 – 7, 1991.

17. MISHRA, S.P., SINGH, V.K., Radiotracer technique in adsorption study. XI. Adsorption of barium and strontium ions on hydrous cerium oxide, Appl. Radiat. Isot., 46 [2], 1995, 75 – 81.

18. BAO, B., SONG, M., A new $^{68}Ge/^{68}Ga$ generator based on CeO_2, J. Radioanal. Nucl. Chem., Letters, 213 [4], 1996, 233 – 238.

19. SOENARJO, S., YANTIH, N., SINAMBELA, J., et al, Chromatographic behaviour of cadmium-(II) in hydrous cerium oxide column, J. of Radioisot. and Radiopharm., 3 [1], 2000, 43 – 53.

20. SOENARJO, S., RAHMAN, F., YANTIH, N., et al, Serapan Cd(II) pada resin CeO_2 dan pola pelepasannya melalui proses elusi pelarut, Prosiding Seminar Sains dan Teknologi Nuklir, P3TkN, BATAN, Bandung, 2000, 341 – 352.

21. GLADSDEN, J.A., "Infrared spectra of minerals and related compounds", Butterworths, London, 1975.

22. Website http://www.webelements.com/Web elements periodic table, April 2006.

23. SOENARJO, S., WIJAYA, C., ELZAN, R., et al., Effect of heating treatment on synthetic ceric oxide as inorganic resin for immobilization of cadmium-(II), Atom Indonesia, 31 [1], 2005, 13 – 25.