IJFAC

Indonesian Journal of
Fundamental and Applied Chemistry

Article http://ijfac.unsri.ac.id

Preconcentration of Cadmium assisted with Sonication using Dowex 50WX2-200 Resin

Siti Nuraini, Yuniar*

Department of Chemistry, Faculty of Mathematic and Natural Sciences, University of Sriwijaya, Indralaya, South Sumatera, Indonesia 30662

*Corresponding Author: yuniarhasani@gmail.com

Abstract

Preconcentration of Cd in water has been carried out using Dowex 50WX2-200 resin as a solid phase extractor. The extraction process was carried out with a sonicator. Elution of Cd which was adsorbed by the resin was released again using 1M HNO_3, then Cd was measured using Flame-Atomic Absorption Spectrophotometer. In this study, the effects of pH, sample solutian sonication time, elution time of Cd adsorbed and eluent volume were studied. The results of the optimization of preconcentration conditions were obtained at pH 3, the duration of the sonication process for Cd adsorption was 15 minutes and the elution time was 7.5 minutes and the eluent volume of 1M HNO_3 was 10 ml. Method validation was carried out using a Certificate Reference Material, CRM for clean water at optimum conditions. The Accuracy and precision measurement results were obtained 96% recovery and 11% RSD (n=3) which showed the accuracy still in the ranges of acceptance criteria according to the AOAC, between 70% -125 and precision with % RSD < CV Horwitz 14%. Finally, preconcentration of Cd metal in water was successfully with sonicator assisted.

Keywords: Cd, Dowex 50WX2-200, Flame-SSA

Abstrak

Prekonsentrasi logam Cd dalam air telah dilakukan menggunakan resin Dowex 50WX2-200 sebagai pengekstrak fase padat. Proses ekstraksi dilakukan dengan alat sonikator. Elusi logam Cd yang teradsorpsi oleh resin dilepaskan kembali menggunakan HNO_3 1M, kemudian logam Cd diukur menggunakan Spektrofotometer Serapan Atom-Nyala. Pada penelitian ini dipelajari pengaruh pH, waktu sonikasi larutan dan waktu elusi logam serta volume eluen. Hasil optimasi kondisi prekonsentrasi diperoleh pada pH 3, lama proses sonikasi untuk adsorpsi logam 15 menit dan waktu elusi 7,5 menit serta volume eluen HNO_3 1M 10 ml. Validasi metode dilakukan menggunakan Certificate Reference Material, CRM untuk air bersih pada kondisi optimum. Diperoleh rekoveri 96% dan RSD 11% (n=3) yang menunjukkan nilai akurasi masih memenuhi batas keberterimaan menurut AOAC antara 70%-125 dan presisi dengan % RSD lebih kecil dari CV Horwitz yaitu 14%. Kesimpilan hasil penelitian menunjukkan bahwa teknik prekonsentrasi logam Cd dalam air bisa dilakukan dengan bantuan alat sonikator.

Kata Kunci: Cd, Dowex 50WX2-200, SSA-nyala

Article Info

Received 29 October 2021
Received in revised 23 January 2022
Accepted 25 January 2022
Available online 20 February 2022

INTRODUCTION

Trace metals in environmental, food and chemical agriculture are generally found in complex form with ligands of biological systems containing sulfur, nitrogen and oxygen. This condition will cause changes in the structure of protein molecules, breaking hydrogen bonds or inhibiting enzyme activity. This is the main reason why some trace metals are seen as poisons and potential carcinogens [1]. Therefore, it is necessary to develop methods to detect trace metals.

It is known that the method is quite selective and sensitive to determine heavy metals such as Cd, Pb, Cr, Cu, Fe, etc. in samples using Atomic Spectrometry techniques such as Flame Atomic Absorption Spectrometry (FAAS), Electrothermal Atomic Absorption Spectrometry and Inductively Coupled Plasma Spectrometry (ICP).

Generally, the presence of heavy metals in the environment are very low concentration or below the detection limit of the instruments. Therefore it is necessary to develop the preparation technique to separate the target metal from the matrix and pre-concentrate the metal first in order to obtain accurate and precise results [2].

The preconcentration (enrichment) technique provides a solution to the limitations of the flame-AAS instrument in the measurement of heavy metals at very low concentrations. The preconcentration step with the sorption technique not only increases the analyte concentration but also eliminates the matrix effect that can interfere the analysis process. The metal preconcentration method using cation exchange resin has advantages over other preconcentration methods, it can minimize analyte loss, the amount of resin used is small (0.1-0.5 g), and can be used repeatedly for the same analysis or can be regenerated [3].

Several studies have been conducted on metal preconcentration, among others, using a column using Dowex 50WX2-200 resin [4]. Various solid phase extraction methods have been applied for pre-concentration of Cd metal, including using modified multiwalled Carbon nanotubes [5, 6] modified nanographene [7, 8], various types of Dowex resins [1], [9], Amberlite XAD resins [10, 11] vortex [12] and using ultrasonic with 1-nitroso-2-naphthol [13], zeolite MWCNTFe_3O_4@Zeo [14] have been reported.

Preconcentration using the ultrasonic wave-assisted method with a frequency > 20 KHz has advantages such as more active substances, safer, and faster extraction process. This is because the extraction process with the help of ultrasonic waves can increase cell wall permeability [15]. This research is a continuation of previous research with pre concentration using column. Pre-concentration using a column takes a long time, it was 50 minutes, it is expected that by using ultrasonic the time used for preconcentration will be shorter and the results obtained are more optimal.

MATERIALS AND METHODS

Materials

The main Equipment involved in this study such as: SSA-Flame Shimadzu model AA-7000F with deuterium lamp as background correction lamp, irradiation source Hollow cathode lamp Cd (228.8 nm), flame air-Acetylene. The procedure to determination of Cd follow the instruction manual.

The pH determination use Hanna Instrument pH-meter HI 8014. Ultrasonic, merck Wiggens UE03SFD used for extraction, Analytical balance, capacity 250g d=0,0001g, merck Adams.

The materials used are ion-free water (Millipore-Milli-Q purification system). High quality HNO_3 (65%) and NaOH from Merck, Germany. The standard solution of Cd traceable to the SRM of NIST $Cd(NO_3)_2$ in HNO_3 0.5 mol/L 1000 mg/L Cd CertiPUR. For the validation method, it is used a solution of CRM Metals, PotableWatR (cat.697), ERA a Waters Company. Adjusting the pH of the solution using a 1 mol/L HNO_3 solution and 1 mol/L NaOH.

Methods

The preconditioning of the resin was carried out by adding 500 mg Dowex 50WX2 resin in 50 ml of a blank solution which has been set at pH 3 using 0.1 mol/L HNO_3 or NaOH solution, then sonicated using ultrasonic for 20 minutes and continued with the filtration process.

The extraction for preconcentration was observed by sonication of 50 ml solution containing 100 µg Cd added with 500 mg Dowex 50WX2 resin then sonication using ultrasonic with variations below:
interval times observed ranges from 5 to 20 minutes, pH ranges 3 to 7, elution time 1 to 5 minutes, sample volume ranges from 50 mL to 150 mL (n=3). The results measured with Flame-AAS.

Data Analysis

Data evaluation use equation as follows:

$$\% R = \frac{\bar{x}}{\mu} \times 100\% \quad (1)$$

where is:
$\bar{x}$= evarage result test
µ = target value of model or sample solution

$$\% RSD = \frac{SD}{\bar{x}} \times 100\% \quad (2)$$

Requirement: RSD ≤ 0.5 x $2^{1-0.5 \log C}$

RESULT AND DISCUSSION

Effect of pH in extraction of Cd with sonication observed with pH ranges from 3 to 7 (n=3). The pH optimum condition at pH 4 as shown in Figure 1.

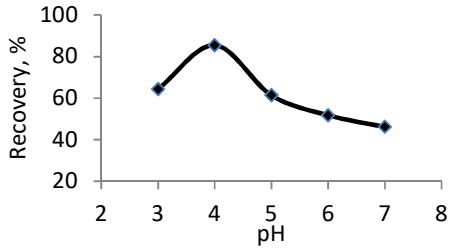

Figure 1. Effect of pH on the recoveries of Cd (n=3)

Times Effect

The effect of times sonication for Cd to be adsorbed by Dowex 50WX2-200 Resin were observed with ranges times from 10 minutes to 30 minutes. The optimum times result was 15 minutes (Figure 2).

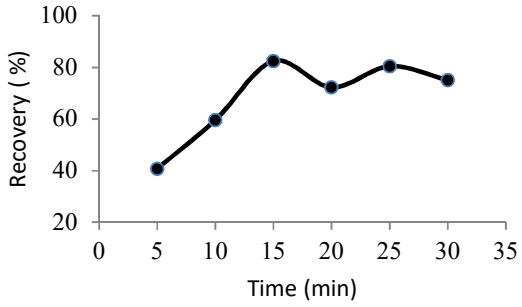

Figure 2. Effect of times sonication on the recoveries of Cd (n=3)

The sonication times below 15 minutes, the resin not effective yet for adsorption of Cd. At the times 15 minutes, the dowex resin had interacted optimally for adsorption Cd, while at times above 15 minutes the capitation effect of the ultrasonic caused the Cd adsorbed in the resin to be released again in the solution [15].

The times to released Cd from Dowex 50WX2-200 Resin used HNO_3 1M was 7,5 minutes (Figure 3) with the optimum volume 10 mL (Figure 4).

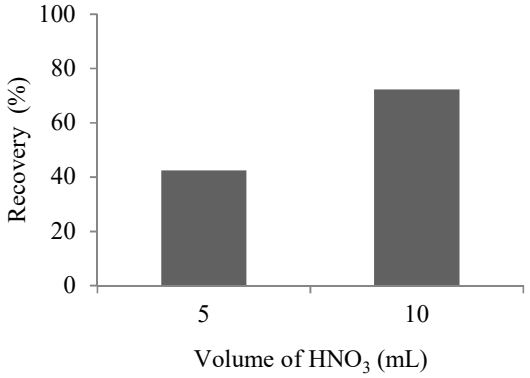

Figure 4. Effect of volume HNO_3 1M on the recoveries of Cd (n=3)

Effect Of Sample Volume

The effect of samples volume for Cd to be adsorbed by Dowex 50WX2-200 Resin were observed with ranges volume from 50 to 200 mL. The recoveries of Cd higher than 90% up to 150 mL (Figure 5). The recoveries decrease in sample volume above 150 mL, due to the resin surface being unable for further adsorption [11]. The preconcentration factor in this study achieved was 15.

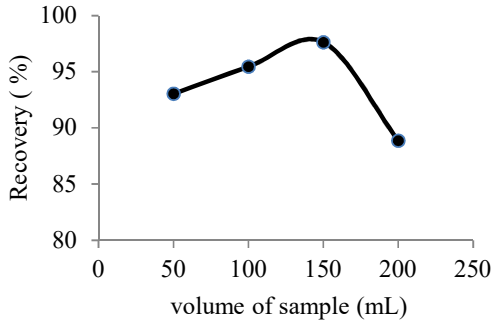

Figure 5. Effect of sample volume on the recoveries of Cd (n=3)

Methods Validation With CRM

Using the optimum conditions obtained in this research, validation of the method was carried out using CRM Metals, PotableWatR (cat.697), ERA a Waters Company. Before determining the accuracy and precision of the CRM, a calibration curve profile is made first. The concentration of calibration curve of Cd was in the ranges from 0.01 mg/L to 0.2 mg/L. Linear regression equation was obtained Y = 0,286x - 0,000 with $R^2 = 0.999$

Table 1. The results of Accuracy and precision of Certtified Refernce Material, CRM (n=3)

Analyte	PotableWatR (cat.697), ERA a Waters Company, µ/L			
	Certificate value	Result	%R	%RSD
Cd	13.2±2.12	12.69±1.42	96	8.4

The Results showed the accuracy still in the ranges of acceptance criteria according to the AOAC, between 70%-125 [17] and precision with % RSD < CV Horwitz 14% [18]. These results indicate the developed methods assisted with sonicator for preconcentration of Cd applicable for determination of Cd in very law concentration in water and free of interferencee.

CONCLUSION

The results of optimum conditions were obtained at pH 3, the duration of the sonication process for Cd adsorption was 15 minutes and the elution time was 7.5 minutes and the eluent volume of 1M HNO_3 was 10 mL. The validation method was carried out using a Certificate Reference Material, CRM for clean water at

optimum conditions were obtained 96% recovery and 11% RSD (n=3). Finally, preconcentration of Cd metal in water was successfully with sonicator assisted.

ACKNOWLEDGMENT

The authors are grateful to Direktorat Sumber Daya Direktorat Jenderal Pendidikan Tinggi, Kemeneterian Pendidikan, Kebudayaan, Riset, dan Teknologi for financing the project with contract number 179.13/E4.3/TA.03.01/2021.

REFERENCES

[1] A. S. Gugushe, A. Mpupa, and P. N. Nomngongo, "Ultrasound-assisted magnetic solid phase extraction of lead and thallium in complex environmental samples using magnetic multi-walled carbon nanotubes/ zeolite nanocomposite," *Microchem. J.*, vol. 149, p. 103960, 2019.

[2] V. Kazantzi, E. Drosaki, A. Skok, A. B. Vishnikin, and A. Anthemidis, "Evaluation of polypropylene and polyethylene as sorbent packing materials in on-line preconcentration columns for trace Pb (II) and Cd (II) determination by FAAS," *Microchem. J.*, vol. 148, pp. 514–520, 2019.

[3] A. S. Panggabean, S. P. Pasaribu, and I. Y. L. Sari, "Prakonsentrasi Ion Cu (II) Menggunakan Resin Berbasis Mikrokapsul Ca-Alginat Secara Off-Line Pembuatan Mikro Kapsul Ca-Alginat," *Chem. Prog.*, vol. 5, no. 2, pp. 70–76, 2012.

[4] Y. Yuniar and H. Yanti, "Peningkatan limit deteksi metode pengujian logam Pb secara kolom ekstraksi fase padat menggunakan resin DOWEX 50WX2: pengaruh pH, laju alir dan volume eluen," *J. Penelit. Sains*, vol. 23, no. 1, pp. 46–51, 2021.

[5] D. Kamaş, A. Karatepe, and M. Soylak, "Vortex-assisted magnetic solid phase extraction of Pb and Cu in some herb samples on magnetic multiwalled carbon nanotubes," *Turkish J. Chem.*, vol. 45, no. 1, pp. 210–218, 2021.

[6] A. A. Gouda and W. A. Zordok, "Solid-phase extraction method for preconcentration of cadmium and lead in environmental samples using multiwalled carbon nanotubes," *Turkish J. Chem.*, vol. 42, no. 4, pp. 1018–1031, 2018.

[7] A. Moghimi, "Extraction sorbent with nanographene with amino propyl-triethoxysilane (APTES) on surfactant coated C 18 for the preconcentration of Cd (II)," *Int. J. Bio-Inorg. Hybr. Nanomater*, vol. 7, no. 2, pp. 127–143, 2018.

[8] A. Moghimi and M. Yari, "Fabrication method of extracting Cadmium (II) and Lead (II) in water samples using Nano Graphene modified 2-propyl-piperidine- carbodithioate," *Int. J. Bio-Inorg. Hybr. Nanomater*, vol. 7, no. 3, pp. 241–253, 2018.

[9] P. N. Nomngongo, J. C. Ngila, J. N. Kamau, T. A. M. Msagati, and B. Moodley, "Preconcentration of molybdenum, antimony and vanadium in gasolsine samples using Dowex 1-x8 resin and their determination with inductively coupled plasma-optical emission spectrometry," *Talanta*, vol. 110, pp. 153–159, 2013.

[10] B. Enez, E. Varhan Oral, S. Aguloglu Fincan, and B. Ziyadanogullari, "Comparison of Methods for the Preconcentration of Cadmium (II) Using Amberlite XAD-16 Resin Modified with Anoxybacillus caldiproteolyticus and Geobacillus stearothermophilus as Novel Biosorbents," *Anal. Lett.*, vol. 53, no. 2, pp. 322–342, 2020.

[11] Baig, J. A., Memon, H. D., Bukhari, S. A. I., Kazi, T. G., Afridi, H. I., Naseer, H. M., & Elci, L. "Solid phase extraction preconcentration method for simultaneous determination of cadmium, lead, and nickel in poultry supplements," *Journal of AOAC International*, 100(4), 1062-1069, 2017.

[12] F. Tokay, R. Günaydin, and S. Bağdat, "A novel vortex assisted dispersive solid phase extraction of some trace elements in essential oils and fish oil," *Talanta*, vol. 230, p. 122312, 2021.

[13] M. Soylak and R. Maulana, "Ultrasound assisted magnetic solid phase extraction of copper(II) and lead(II) in environmental samples on Magnetic Activated Carbon Cloth," *Int. J. Environ. Anal. Chem.*, vol. 00, no. 00, pp. 1–13, 2021.

[14] M. Tavakoli, M. R. Jamali, and A. Nezhadali, "Ultrasound-Assisted Dispersive Liquid–Liquid Microextraction (DLLME) Based on Solidification of Floating Organic Drop Using a Deep Eutectic Solvent for Simultaneous Preconcentration and Determination of Nickel and Cobalt in Food and Water Samples," *Anal. Lett.*, vol. 54, no. 18, pp. 2863–2873, 2021.

[15] M. Andriani, I. D. Gde Mayun Permana, and I. W. Rai Widarta, "Pengaruh Suhu Dan Waktu Ekstraksi Daun Belimbing Wuluh (Averrhoa

bilimbi l.) Terhadap Aktivitas Antioksidan Dengan Metode Ultrasonic Assisted Extraction (UAE) Method," *J. Ilmu dan Teknol. Pangan*, vol. 8, no. 3, pp. 330–340, 2019.

[16] Y. Yuniar and S. Nuraini, "Cadmium in Water Samples determined by Atomic Absorption Spectrometry after Solid Phase Extraction using DOWEX 50WX2 resin," *Indones. J. Fundam. Appl. Chem.*, vol. 6, no. 1, pp. 14-19, 2021.

[17] S. V. Work, "AOAC Guidelines for Single Laboratory Validation of Chemical Methods for Dietary Supplements and Botanicals," pp. 1–38, 2002, Gaithersburg, MD, USA.

[18] Rivera, Carlos, and Rosario Rodriguez. "Horwitz equation as quality benchmark in ISO/IEC 17025 testing laboratory." Private communication, 2014.