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Preconcentration of Cr(III) using Dowex 50WX2-200 Resin and Its Application to River Water

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Abstract

Cr(III) is one of the most stable chromium species in nature, Cr(III) species are not carcinogenic to humans, but if the levels in the body exceed 0.2 mg / day it is very dangerous for the body especially in the respiratory tract. The presence of chromium in the aquatic environment is so low that it is very difficult to detect it using instruments with various limitations to detect it, therefore preconcentration techniques are carried out to overcome the issue. In this study the water sample was adjusted pH using HNO_3 0.1 M or NaOH 0.1 M, after which it was passed in the dowex column 50WX2-200. Furthermore, an elution process was carried out using the 1 M HNO_3 eluent, the eluat was measured for absorbance with flame AAS. The results of Cr(III) preconcentration optimization are: resin weight 0.5 g, HNO_3 eluent concentration 1 M, solution pH 3 and sample volume 50 – 100 mL. The Cr(III) preconcentration technique using Dowex 50WX2-200 resin has been applied to river water samples with a detectable concentration of 0.0075 mg/L.

Keywords: AAS, preconcentration, Dowex 50WX2-200 resin

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Cr(III) adalah salah satu spesies kromium yang paling stabil di alam, spesies Cr(III) tidak karsinogenik bagi manusia, tetapi jika kadarnya didalam tubuh melebihi 0,2 mg/hari maka sangat berbahaya bagi tubuh terutama pada saluran pernapasan. Keberadaan kromium di lingkungan perairan sangat rendah sehingga sangat sulit untuk mendeteksinya menggunakan instrument dengan berbagai keterbatasan untuk mendeteksinya, oleh karena itu teknik prekonsentrasi dilakukan untuk mengatasi hal tersebut. Dalam penelitian ini sampel air diatur pHnya dengan menggunakan HNO_3 0,1 M atau NaOH 0,1 M, setelah itu dilewatkan pada kolom dowex 50WX2-200. Selanjutnya dilakukan proses elusi menggunakan eluen HNO_3 1 M, eluat diukur absorbansinya dengan SSA nyala. Hasil optimasi prekonsentrasi Cr(III) sebagai berikut : berat resin 0,5 g, konsentrasi eluen HNO_3 1 M, pH larutan 3 dan volume sampel 50 – 100 mL. Teknik prekonsentrasi Cr(III) menggunakan resin Dowex 50WX2-200 ini telah diaplikasikan pada sampel air sungai dengan konsentrasi terdeteksi yaitu 0,0075 mg/L.

Kata Kunci: SSA, prekonsentrasi, resin Dowex 50WX2-200

INTRODUCTION

Cr(III) is one of the most stable chromium species in nature, in small amounts Cr(III) is still needed by living organisms, which plays a role in metabolic processes by increasing the activity of certain enzymes and stimulating the synthesis of cholesterol and fatty acids. [1] Cr(III) is dominant in surface water at a lower pH of 5 - 7, as the pH of the water increases, Cr(III) can oxidize to form Cr(VI) chromate which is very harmful to the human body, the World Health Organization (WHO) reports that the level of Cr(VI) in drinking water should not exceed 50 µg/L. [2-3] Cr(III) species are not carcinogenic to humans, but if the levels in the body exceed 0.2 mg / day then it is very dangerous for the body, especially in the respiratory tract. [4] The presence of chromium in the aquatic environment is very low so it is very difficult to detect it using other instruments with various limitations, therefore preconcentration techniques are carried out to overcome this. [2, 5-6]

Ion exchange chromatography is a type of chromatography that is widely used in the separation of charged samples, both anions and cations and metal ion preconcentration. The Dowex is an example of a commercial ion exchange resin with a fine mesh size formed from microporous copolymers of styrene and divinylbenzene (DVB). Commercially available resins are the most commonly used cation exchangers for removing metal ions from solutions and contain functional groups for binding metal ions and are effective also for organic phase matrices.[7] The Dowex has advantages such as maximum resistance to oxidation, reduction, mechanical wear, and damage, in addition to the structure of this resin is also insoluble in general solvents.

In this paper, we will discuss the preconcentration of Cr(III) using Dowex WX2-200 cation exchange resin as a sorbent and study the effect of pH which plays a role in chromium preconcentration, besides that it will also study the effect of resin weight, eluent and sample volume.

MATERIALS AND METHODS

Materials

The material and tools used are Dowex 50WX2-200 resin (Sigma-Aldrich), stock standard solution was prepared by the standard solution of Cr traceable to SRM from NIST $Cr(NO_3)_3$ in HNO_3 0.5 mol/L 1000 mg/L Cr CertiPUR. F (Merck), HNO_3 65% (Merck), Merck NaOH, Ultrapure Water produced with MilliQ-system direct Q, river water samples from the Ogan River in the Kertapati Area of Palembang, a set of class A glassware pyrex from Iwaki, analytical balance brand Adam NBL-254, Atomic Absorption Spectrophotometer (AAS) Shimadzu Type AA7000, the pH determination use Hanna Instrument pH-meter HI 8010 of Hanna and chromatography columns pyrex from Iwaki with ID 1 cm and length 30 cm.

Methods

Preconditioning of Dowex 50WX2-200 resin is done by passing 50 ml of blank solution that has been set at pH 3 using 0.1 M HNO_3 or 0.1 M NaOH solution with a flow rate of 1 ml per minute. [6], [8]

The preconcentration was studied by making a solution containing 100 µg Cr. The solution was then passed in a Dowex column of 50WX2-200. After that, the elution process was carried out using HNO_3 eluent solution, eluate was measured by AAS, 3 repetitions for each of these procedures with variations below: resin weight at 0.25 g, 0.5 g, 1 g and 1.5 g, eluent solution with concentration variations of 0.5 M, 1 M, 1.5 M and 2 M, pH ranges 2 to 10, sample volume ranges from 50 ml to 200 ml.

The optimum conditions obtained in the preconcentration of Cr(III) were applied to Ogan River water samples in the Kertapati Palembang Area, 3 river water samples were taken with locations including: location 1 which is a riverside location close to residential areas, location 2 is a riverside location far from residential areas and location 3 is the middle of the river. The sample is then filtered using Whatman filter paper No 589/3 and Then preserved with HNO_3 to pH below 2 to preserve it before taking measurements.

Data Analysis

Data analysis of the effect of pH, eluent concentration, resin weight and sample volume was carried out based on the recovery of Cr(III), calculated based on the following equation:

$$\text{Cr from AAS}\left(\frac{\text{mg}}{\text{L}}\right) = \bar{x} \times \text{Enrichment Factor} \quad (1)$$

$$\%\ \text{R} = \frac{\bar{x}}{\mu} 100\% \quad (2)$$

$$\text{Enrichment Factor} = \frac{\text{Sample volume}}{\text{eluate volume}} \quad (3)$$

Notes:
$\bar{x}$ = average concentration from AAS (mg/L)
µ = target concentration (mg/L)
%R = recovery of Cr(III)

RESULTS AND DISCUSSION

Effects of Resin Weight

The general condition of resin weight variation was studied at resin weight variations of 0.25 g, 1 g, 1.5 g and 2 g against the recovery of Cr(III).

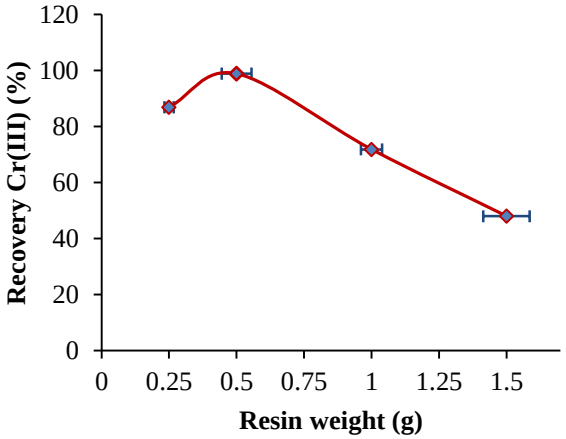

Figure 1. Effect of Resin Weight on Recoveries of Cr(III)

The measurement results presented in **Figure** 1 show the optimum condition at a resin weight of 0.5 g,

at this weight Cr(III) is optimally absorbed in the resin, but weighing more than 0.5 g the position of the resin particles is squeezed together so that the surface area is reduced besides that the analyte is not perfectly eluted by the eluent, this is in line with research [9-10] where the weight of Dowex resin 50WX2-200 0.5 g is the most optimal recovery.

Effect of Eluent Concentration

The optimum conditions for variation in eluent concentration aim to determine the appropriate eluent concentration to release Cr(III) bound to the resin. HNO_3 is used as an eluent because HNO_3 is better and sharper for the Cr(III) desorption process [11], because HNO_3 can dissolve almost all metals, except gold and platinum. **Figure** 2 shows the optimum conditions for variation in eluent concentration aim to determine the appropriate eluent concentration to release Cr(III) bound to the resin. HNO_3 is used as an eluent because HNO_3 is better and sharper for the Cr(III) desorption process.

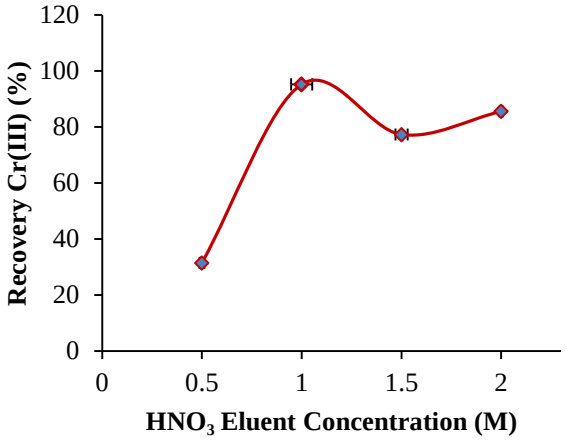

Figure 2. Effect of Eluent Concentration on ecoveries of Cr(III)

Variations of pH

pH is a very important factor for quantitative analyte recovery [12], changes in the shape of Cr species occur depending on the pH of the solution. [13] pH variations were carried out at pH 2 – 12 with the results shown in **Figure** 3 where pH 3 and 4 are the most pH, these results are in line with research [10, 13-14] where the most optimal recovery results at pH 3 – 4, the more alkaline the solution, the Cr(III) will form a precipitate of $Cr(OH)_3$ and $Cr(OH)_4$ so that the solution recovery decreases, according to the following reaction:

$$Cr^{3+}_{(aq)} + 3OH^-_{(aq)} \Leftrightarrow Cr(OH)_{3(s)} \quad (4)$$

$$Cr(OH)_{3(s)} + OH^-_{(aq)} \Leftrightarrow Cr(OH)_{4(aq)} \quad (5)$$

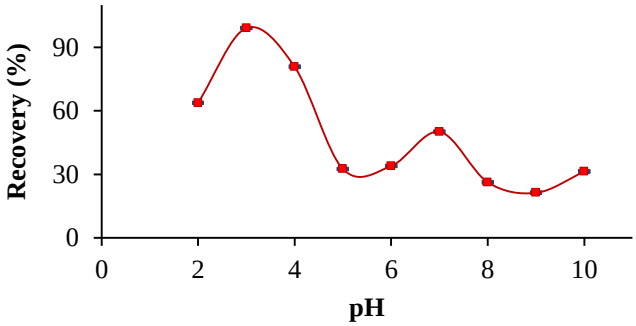

Figure 3. Effect of pH on Recoveries of Cr(III)

Effect of Sample Volume

Volume is one of the most important factors to see the extraction ability of sorbents on analytes at low concentrations.[15] The optimum conditions of sample volume variation are studied with volume variations of 50 mL, 100 mL, 150 mL and 200 mL. The results obtained in **Figure** 4 are that the sample volume of 50 mL - 100 mL is the most optimal condition. Selection of a sample volume of 50 mL can save preconcentration time, but the larger the volume of 100 mL, the enrichment factor increases and the target compound adsorbed into the sorbent increases [15].

For volumes greater than this, the Cr(III) recovery obtained decreases, this is because the pores of the resin have been saturated so that excessive analytes cannot stick to the resin, this is in line with research. [15-16] namely too much volume can reduce recovery from analytes.

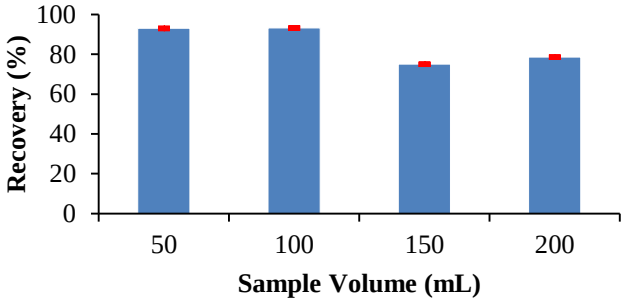

Figure 4. Effect of Sample Volume on Recoveries of Cr(III)

Determination of Cr(III) Concentration in River Water Samples

The results of measurement of Cr(III) concentration in river water samples are shown in **Table** 1 where Cr(III) concentration in river water at location 1, namely the riverbank close to residential areas, Cr(III) is detected at 0.0749 mg/L with an enrichment factor of 10, as for locations far from waste sources, the results are smaller, even below the instrument detection limit [17].

Table 1. Cr(III) Concentration in River Water Samples

Area	Cr(III) Concentration from Preconcentration Results (mg/L)	Enrichment Factor	Actual Cr(III) Concentration (mg/L)
1	0,0749	10	0,0075
2	< 0,0130*	10	< 0,0130*
3	< 0,0130*	10	< 0,0130*

Remarks: * Measurement results below the detection limit of AAS

CONCLUSION

Based on the results of the research that has been done, it can be concluded that Dowex 50WX2-200 resin can be used for Cr(III) preconcentration techniques, the optimum conditions obtained in this study are 0.5 g resin weight, HNO_3 eluent concentration is 1 M, solution pH 3 and sample volume 50 – 100 mL.

Preconcentration of Cr(III) using Dowex 50WX2-200 resin can be utilized in the implementation of Cr(III) testing in water samples that have very low levels, but in the future it is necessary to redevelop this research so as to produce greater enrichment factors and Cr(III) levels below the detection limit of the instrument can be detected.

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