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# TRACE ANALYSIS OF Cd(II) ION USING PSDVB-EDTA IN PRE-CONCENTRATION TECHNIQUE WITH OFF-LINE METHOD

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**Abstract:** The trace analysis of Cd(II) ion used polystyrene divinyl benzene-ethylene diamine tetraacetate (PSDVB-EDTA) as the material column filler in pre-concentration technique with off-line method has been done. The pre-concentration method was performed by using a column filled with PSDVB-EDTA activated at pH 6 the sodium acetate. The optimal conditions for the best analytical performed in pre-concentration steps were 9 mL injection volume of water samples and 3 mL of 1.0 M HCl as eluent. The obtained retention capacity was 6.43 mg.g<sup>-1</sup> Cd(II).g<sup>-1</sup> resin. The analytical performance of the method was very good; the limit of detection values was 3.85 µg.L<sup>-1</sup>. The reproducibility value expressed as percentage of coefficient variance was 4.12 % his method provided good accuracy in term of good recoveries in the range 5-100 µg.L<sup>-1</sup> without the effect of interferences in real water sample. *The proposed method can certainly analyze Cd(II) in water samples at the trace levels.*

## 1. Introduction

Cadmium has high toxicity to all living organisms because of the ability in making biotransformation and bioaccumulation [1]. The extensive use of cadmium compounds led the extent contamination impact. Nevertheless, these elements need to be determined quantitatively in food, water, and biological material [2]. Because Cd(II) is extremely low concentration in environmental or biological samples which is usually complicated matrices, so pre-concentration and separation techniques are often required [3].

The determination of low cadmium concentrations can be done by using sophisticated instruments, such as ; ICP-MS [4], ICP-AES [5], but in the development country, the instruments are still rarely found. Pre-concentration has two purposes, the first, to increase the concentration of solution. so it can be measured by the spectromeric method. The second, it can reduce the amount of solids which can affect the process of nebulization at the time of measurement by using spectrometric method [6].

In the pre-concentration stage, the use of resin-modified is very good because it has high selectivity. One of the supporting resins which can be used is Amberlite XAD-16 (PSDVB) [7]. This resin is a polystyrene polymer (PS) with divinyl benzene (DVB) as a cross linking and it has a functional groups that can not be ionized.

Many studies have been conducted for trace analysis metal ions with PSDVB and it is modified with

chelating agent, such as: Polystyrene divinyl benzene-1-(2)-pyridylazo 2 naphthol (PSDVB-PAN), Polystyrene divinyl benzene-4-(2)-pyridylazo resorsinol (PSDVB-PAR), Polystyrene divinylbenzene- $\alpha$ -nitroso- $\beta$ -naphthol (PSDVB-NN) [8-9].

In this research, it has been studied several conditions that affect for the result of pre-concentration Cd(II) ion in a samples, the influence of pH, retention capacity, analytical performance, and percent recovery. The concentration of Cd(II) ion is detected by using Flame-Atomic Absorption Spectrophotometer (FAAS).

## 2. Materials and Methods

### 2.1 Materials

Chelating resin polystyrene divinyl benzene-ethylene diamine tetra acetate (PSDVB-EDTA) is used as material column filler. All solutions were prepared with distilled water, and all chemicals were analytical reagent grade. Cadmium stock solutions were made with Cd (CH<sub>3</sub>COO)<sub>2</sub> (Merck). The pH solution was fixed by using HCl and acetate buffer solutions. The real water was taken from Karang Mumus river, and the cadmium detection used Flame-AAS Hitachi 170-130 Spectrometer.

### 2.2 Method

#### 2.2.1. Effect of pH

The batch method was used to determine the effect of pH to activate PSDVB-EDTA. In 0.05 g of PSDVB-EDTA soaked in the HCl or acetate buffer solutions with variations of pH 2-10 and allowed for 24 hours, it filtered and dried. In 10 mL of Cd(II) 1 mg.L<sup>-1</sup> is placed into a plastic bottle containing PSDVB-EDTA and stirred slowly, allowed for 24 hours.

#### 2.2.2 Retention Capacity

In 0.05 g of PSDVB-EDTA resin soaked in 10 mL solutions Cd(II) with variation of concentration of 1-100 mg.L<sup>-1</sup> at pH optimum conditions for 24 hours.

#### 2.2.3 Optimization of pre-concentration

The Effect of eluent concentration was studied by adding 10 mL of Cd(II) 0.5 mg.L<sup>-1</sup> into the column which contained PSDVB-EDTA resin. The retained Cd(II) ions were eluted with 5 mL of HCl with the variation concentration of 0.1-2.5 M, the eluent volume effect was studied by adding into the column and eluted at HCl to optimum concentrations obtained with



variation of volume of 1-10 mL, and the effect of volume Cd(II) was studied by adding standards solution of Cd(II) 0.5 mg.L<sup>-1</sup> with the variation of volume of 1-10 mL.

#### 2.2.4 Analytical Performances

Linearity of the analytical method was determined by measuring the absorbance of Cd(II) in the range of concentration for 5-100 µg.L<sup>-1</sup> at the optimum conditions. The reproducibility was determined by measuring the absorbance of the 25 µg.L<sup>-1</sup> Cd(II) (n = 7) and the limit of detection was determined by using a linear regression equation of calibration curve.

#### 2.2.5 Determination of real samples

To determine the influence of matrix on the determination of Cd(II) ions in real water samples from Karang Mumus river was used the spike method at the optimum conditions. The Cd(II) ions in sample solutions were determined by Flame-Atomic Absorption Spectrophotometer at wavelength (λ) 228.8 nm.

### 3. Results and Discussion

#### 3.1 The effect of pH to activation PSDVB-EDTA

The determination of optimum pH was aimed to obtain the best conditions for the chelates formation, so the resin could optimally absorb Cd(II) ions. Figure 1 showed that the resin could completely absorb Cd(II) ions (95%) at pH 6. After that the retention of Cd(II) ions decreased slowly then it was used as optimum condition.

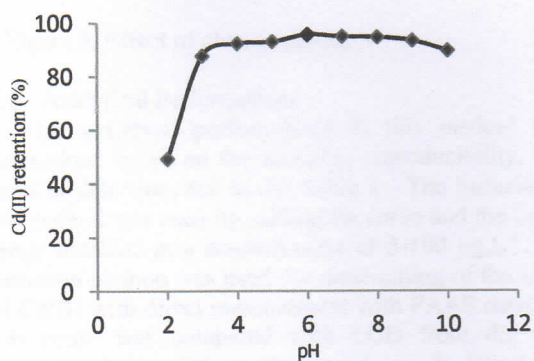


Figure 1. Effect of pH to activation PSDVB-EDTA

#### 3.2 Retention Capacity

The retention capacity is a quantity that indicates the ability of PSDVB-EDTA to absorb Cd(II) ions with the contact time during 24 hours. Figure 2 showed the retention capacity obtained are 6.43 mg Cd(II)/g PSDVB-EDTA resin, it means that every 1 g of resin can absorb optimally 6.43 mg Cd(II) ions. This value indicates the resin has a large adsorption capacity, so it can be used repeatedly to absorb Cd(II) ions and can be applied as filler material of column to pre-concentration technique for the determination of cadmium in trace level.

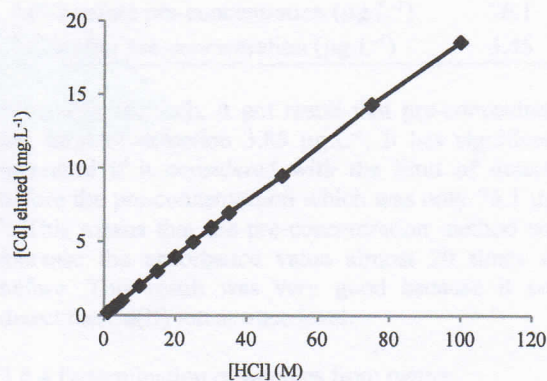


Figure 2. Retention Capacity of PSDVB-EDTA resin

#### 3.3 Optimization Pre-concentration

##### 3.3.1 Effect of eluent concentration

The effectivity of the elution was influenced by the type and concentration of eluent. HCl was used as an eluent with the consideration of the elution process, and it is expected that there is no damage resin in the column.

Figure 3 obtained Cd(II) ions completely eluted at 1 M HCl, whereas at the elution using concentration up and under 1 M HCl, the retained Cd(II) ions has not eluted totally. It was due to the high concentration of eluent, H<sup>+</sup> ions from the eluent made the competition effect with Cd(II) ions to fill the capacity resin so it made the broad of the concentration zone. The concentration of 1 M HCl was used as the optimum concentration for further work.

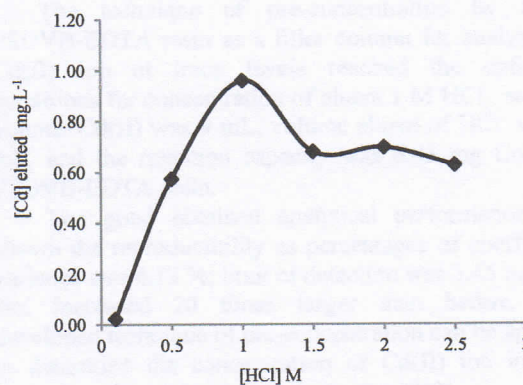


Figure 3. Effect of eluent concentration

##### 3.3.2 Effect of volume Cd(II)

Figure 4, it can be seen that the more volume of Cd(II) ions used, the higher concentration of ions were eluted by 1 M HCl until it reached the optimum volume at 9 mL. In the volume of 10 mL, the eluted ions decreased but it was not significantly, it was caused by the above of volume the population of the Cd(II) ions has been maximum absorbed by the resin. Furthermore, the optimum



volume of Cd(II) ions was 9 mL, and it was used for further work.

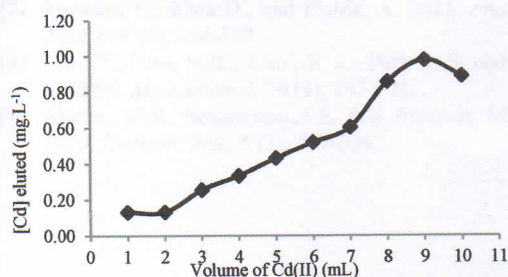


Figure 4. Effect of Cd(II) volume

### 2.2.3.3 Effect of eluent volume

The effect of the HCl eluent volume was determined by varying the eluent volume at the optimum concentration. Figure 5 shows that the using 3 mL of 1 M HCl was able to elute 0.48 mg.L<sup>-1</sup> of Cd(II) ions in the resin. Nevertheless, 3 mL was used in the optimum volume of 1 M HCl for further work.

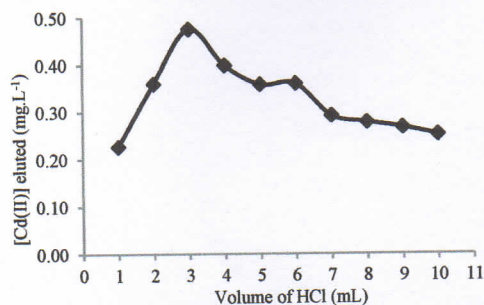


Figure 5. Effect of eluent volume

### 3.4 Analytical Performances

The analytical performances in this method was determined based on the linearity, reproducibility, and limit of detection, see in the Table 1. The linearity of the method was used by calibration curve and the linear range obtained at a concentration of 5-100  $\mu\text{g.L}^{-1}$ . the detection method was used by determining of the LOD of Cd(II) with direct measurement with FAAS detector. this result was compared with LOD from the pre-concentration technique developed, so it found the analytical performance of measurement. The concentration of Cd(II) ions that was used 10  $\mu\text{g.L}^{-1}$ .

The reproducibility of the method was examined under the optimum experimental conditions. The calculated results showed coefficient of variance (CV) 4.12% for the measurements of Cd(II) ions 0.025 mg.L<sup>-1</sup> (n = 7). This method provided good accuracy without interferences.

Table 1: Result of Analytical Performances

Analytical Performance	Result
Linearity ( $\mu\text{g.L}^{-1}$ )	5-100
Reproducibility (n = 7) (% CV)	4.12

LOD before pre-concentration ( $\mu\text{g.L}^{-1}$ )	76.1
LOD after pre-concentration ( $\mu\text{g.L}^{-1}$ )	3.45

From this research, it got result that pre-concentration has limit of detection 3.85  $\mu\text{g.L}^{-1}$ . It has significantly increased if it considered with the limit of detection before the pre-concentration which was only 76.1  $\mu\text{g.L}^{-1}$ . This means that the pre-concentration method could increase the absorbance value almost 20 times than before. This result was very good because it could detect the Cd(II) ion at trace level.

### 3.4.4 Determination of samples from nature

The resin PSDVB-EDTA has been used for the pre-concentration and analysis of Cd(II) ion in Karang Mumus river as the real water samples. The result of the determination of ion's concentrations in the real samples had shown that the recovery of the method could reach 97.95%. These data indicate that the accuracy of the method developed is very good and the water sample matrix did not effect for the measurement results. The results of the determination of Cd(II) ion's concentration in the real sample shows in the Table 2.

Table 2 : Cd(II) ions in water samples

Real Sample	Cd(II) ( $\text{mg.L}^{-1}$ )		
	Added	Found	Recovery (%)
A	0	0.033	-
B	0.05	0.081	97.59

### 4. Conclusions

The technique of pre-concentration by using PSDVB-EDTA resin as a filler column for analysis of Cd(II) ion at trace levels reached the optimum conditions for concentration of eluent 1 M HCl, sample volume Cd(II) was 9 mL, volume eluent of HCl was 3 mL, and the retention capacity was 6.43 mg Cd(II)/g PSDVB-EDTA resin.

The good obtained analytical performance had shown the reproducibility as percentages of coefficient variance was 4.12 %, limit of detection was 3.45 mg.L<sup>-1</sup>, and increased 20 times larger than before. The developed technique of pre-concentration can be applied to determine the concentration of Cd(II) ion in real water samples with recovery more than 95%.

### References

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