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Preconcentration of Ion Ni(II) using Ca-Alginate Modified Resin with Dimethylglyoxime as a Filler Material of Column

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Abstract

The research about preconcentration of Ni(II) ions using Ca-alginate resin modified with dimethylglyoxime (DMG) as a material filler of column has been done. The stage of preconcentration done by using the water sample was passed through the column, then eluted using HNO_3. The amount of Ni(II) in the eluate was measured using atomic absorption spectrophotometer (AAS). The several important parameters in the preconcentration stage have been studied. The optimal condition at the stage of preconcentration Ni(II) ions was retention at pH 4, the volume of sampel was 10 mL, volume of HNO_3 eluen was 4 mL at a concentration of 1.5 M, with the retention of capacity value was 2.4657 mg Ni(II)/g resin. The analytical performance of this method is good, showed with repeatability value as percentage of coefficient of variance value was 4.06%, and can increase the limit detection of Ni(II) ions was 3.94 times, if compared to direct measurements with AAS. The method can be applied to determination of Ni(II) ions in the water samples from Mahakam river at port Samarinda with recovery percentage value was > 95 %, indicating that the matrix of samples not affect the results of measurements.

Keywords: AAS, Ca-alginate-DMG, Ni(II), preconcentration.

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1. INTRODUCTION

Heavy metal is widely used both directly and indirectly can pollute the environment if it exceeds specified limits and has a negative impact on life organism. The hazardous of heavy metals that often pollute the environment include mercury (Hg), Lead (Pb), Arsenic (As), Cadmium (Cd), Chromium (Cr) and Nickel (Ni). These heavy metals are known to be able to accumulate in the body of a microorganism and remain long-term as a poison (Rapp *et al.*, 2017).

The preconcentration method most commonly used for trace metal ions is the solvent extraction method. The method has a disadvantage, because it requires expensive organic solvents, often has toxic properties and very dangerous (Naeemullah *et al.*, 2012; Suwarsa *et al.*, 2008). The preconcentration and separation techniques have a very important role in trace analysis of metal ions from various samples with very complex matrices. Preconcentration stages with sorption techniques not only increase the concentration of the analyte but also eliminate the matrix effect that can interfere with the analysis process (Miro and Frenzel, 2014).

Cation exchange resins can be used as a filler material of column in the preconcentration stages of heavy metal ions for sample analysis and provide solutions to the limitations of the sensitivity of instrument, in the determination of heavy metals at trace levels. The preconcentration method using cation exchange resins has advantages over other preconcentration methods, because the analyte loss factor can be minimized, the amount of resin used is small (0.1-0.5 g), can be regenerated and it can be used repeatedly for the same analysis (Panggabean *et al.*, 2014).

Several studies on the use of preconcentration techniques in determination of metal ion such as; the characterization of Ca-alginate based on ion exchange resins and the application toward Pb and Zn ions (Chen and Wang, 2001), transition metal ions (Fuks *et al.*, 2006), determination of Cu ions by using Ca-alginate microcapsules (Panggabean *et al.*, 2012) and modification of Ca-alginate microcapsules with EDTA chelating in the preconcentration stages of Pb(II) metal ions (Sari et al., 2016), chitosan-1,5-diphenyl carbazide resins for analysis of Cr(VI) (Panggabean and Bohari, 2015), PSDVB-PAN resins for analysis of Pb(II) ions (Panggabean *et al.*, 2010), and Cd(II) ions (Amran *et al.*, 2011). The preconcentration of Ni(II) ions has been reported about the use of modified DMG adsorbents in magnetic nanoparticles with solid phase extraction techniques (Karimi and Kaffi, 2015), coprecipitation with $Al(OH)_3$ (Thubkhum and Tangtreamjitmun, 2018), resins 1-(2-pyridylazo)-2-naphthol modified in SiO_2 nanoparticles (Kaur and Gupta, 2009), synthesis of PSDVB-DMG resins to adsorb Ni(II) ions (Darwin *et al.*, 2016), and preconcentration of Pb, Cd and Ni ions in the Cikapundung river Bandung samples by extraction methods using chelating reagents (Koesmawati *et al.*, 2017).

Based on the description above, in this research a Ca-alginate microcapsule resin modified with dimethylglyoxime (DMG) was made as a filler material of column in the preconcentration stage of Ni(II) ions, which had not been previously reported. In this research, several stages of determining the optimum composition of Ca-alginate-DMG were made, optimization in the preconcentration stage, the analytical performance, and it’s application in the determination of Ni(II) ions in water samples from nature.

2. MATERIALS AND METHOD

Instrumentation and Materials

The instruments used in this research are Atomic Absorption Spectrophotometer (GBC Avanta 6000), laboratory glassware, analytical balance, hot plate, cuvette, spatula, micro pipette, glass beaker, stopwatch, plastic film bottle, clamps, stative and glass column (1 cm i.d x 30 cm length).

The materials used are $CaCl_2$, Na-alginate, dimethylglyoxime (DMG), $NiSO_4.6H_2O$, HNO_3 (E'Merck), Universal pH, filter paper, aquabides and samples water was taken from dam and the Mahakam river at port Samarinda, East Kalimantan.

Manufacturing of Ca-Alginate-Dimethylglyoxime (DMG) Resin

A total of 50 mL of 0.3M $CaCl_2$ solution was put into a glass beaker, added DMG powder as much as 0.05 g (0.1% w/v) and stirred until homogeneous. 1% Na-alginate solution (1 g Na-alginate dissolved in 100 mL aquabides) in the burette, added dropwise to $CaCl_2$ solution while stirring with magnetic stirrer to form Ca-alginate-DMG microcapsules. The Ca-alginate-DMG microcapsules obtained were dried at room temperature ± 24 hours. Furthermore, the resins can be determined that the retention toward Ni(II) ions (Sari *et al.,* 2016).

Optimization of Ca-Alginate-DMG Resin by Batch Method (Effects of pH)

0.1 g of Ca-alginate-DMG resin was immersed in aquabides, whose pH of solution was adjusted to a variation of 2-8. The resin was dried and added with a standard solution of Ni(II) 10 mg/L and soaked for ± 24 hours. Filtered and the filtrate was measured using AAS.

Determination of the Retention Capacity of Ca-Alginate-DMG Resin toward Ni(II) Ions

0.1 g of Ca-alginate-DMG resin was immersed in 10 mL of Ni(II) solution, that the concentration was varied 0.5-80 mg/L for ± 24 hours. Filtered and the filtrate was measured using AAS (Panggabean *et al.,* 2014).

Optimization of Ca-Alginate-DMG Resin Preconcentration by Column Method

Effects of Acid Concentration

Ca-Alginate-DMG resin that has been conditioned at the optimum pH was inserted into the column and added with 10 mL of 1 mg/L Ni(II) of standard solution, subsequently eluted with 5 mL of HNO_3 with a concentration variation of 0.5-3 M. The filtrate was measured using AAS.

Effects of Ni(II) Ion Volume

Ca-alginate-DMG resin that has been conditioned at the optimum pH was inserted into the column and added with 1 mg/L Ni(II) standard solution, that the volume varied 2-10 mL. The Ni(II) ion which is retained in each volume variation is then eluted with 5 mL HNO_3. The filtrate was measured using AAS.

Effect of Acid Volume

Ca-alginate-DMG resin that has been conditioned at the optimum pH was inserted into the column and added with to the optimum volume of 1 mg/L Ni(II) standard solution. The Ni(II) was retained subsequently eluted with HNO_3,at the varied of volume was 3-10 mL.The filtrate was measured using AAS (Panggabean and Bohari, 2015).

Analytical Performance

Linearity

In this research, linearity was determined by preparing a standard Ni(II) series solution with a concentration of 0.05-1 mg/L, with the optimum conditions and the same procedure as in the optimization of Ca-alginate-DMG resin by the batch method above. Each absorbance was determined using AAS. The regression line equation was obtained by plotting the absorbance against the concentration of Ni(II).

Precision (Repeatibility)

Repeatability was determined by measuring the absorbance of a 0.2 mg/L Ni(II) standard solution with AAS repeatedly (n = 10), at the optimum conditions and the same procedure as above.

Limit of detection (LOD)

LOD can be determined using a calibration curve equation obtained through a linear regression line from the calibration curve (Miller and Miller, 1991).

Application of Sample Waters from Nature

The Percentage of Recovery

Determinaton of the effect of the matrix on the measurement of Ni(II) ions in the water samples from nature, it is done by determining of the percentage of recovery (% recovery), using the spike method. In this spike method, a certain amount of the volume Ni(II) standard solution was pipetted and then added to the water sample. The absorbance of the spike solution was determined by using AAS with the optimum conditions and the same procedure as above.

3. RESULTS AND DISCUSSION

Optimization of Ca-Alginate-DMG Resin by Batch Method

Effects of pH

The retention of each metal ion against a particular resin is strongly influenced by the pH of the resin or sample solution. Each metal ion is optimum at only a certain pH (Panggabean *et al.*, 2010). Measurement of the effect of pH variations, of Ca-alginate-DMG resin by using batch method, can be seen in Fig. 1.

Ca-alginate-DMG resin has been conditioned with a good pH absorption results at pH 3-5 (Fig. 1), can absorb Ni(II) ions above 98%. While the pH greater than 5 and less than pH 3, a greater number of H^+ and OH^- ions (very acidic or very base) will damage Ca-alginate because the resin will return forming back to gel, and the retention is not optimal (Mørch *et al.*, 2006). The optimum pH used in further work was pH 4.

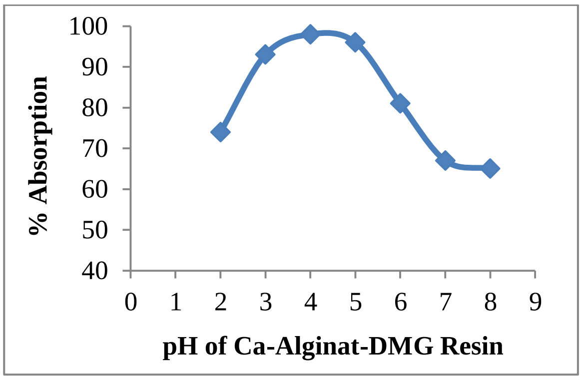

Figure 1. Effect of pH of Ca-alginate-DMG resin in the absorption of Ni (II).

Ca-Alginate-DMG Retention Capacity

Retention capacity is a measure of the ability of the Ca-alginate-DMG resin to retain Ni(II) ions (Amran *et al.*, 2011). The more amount of Ni(II) ions absorbed, produce the higher value of retention capacity. Retention capacity analysis can be done by batch method, the measurement results can be seen in Fig. 2.

The retention capacity of Ca-alginate-DMG for Ni(II) metal ions can be determined using line intersection of two curves (Fig 2.), where the meeting point is the retention capacity of Ca-alginate-DMG resin (Panggabean et al., 2012). The intersection of the two lines is the retention capacity of Ca-alginate-DMG was 2.4657 mg/g resin. The result of this amount was means that every 1 g of Ca-alginate-DMG resin can retain 2.4657 mg of Ni(II) ion.

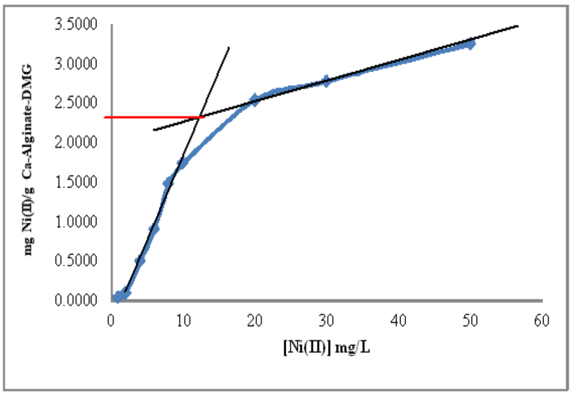

Figure 2. Retention capacity of Ca-Alginate-DMG resins toward Ni(II) ions

Optimization of Ca-Alginate-DMG Resin Preconcentration by Column Method

Effects of Concentration and Volume of Acid as Eluent

The next preconcentration stage is effect of concentration and volume of acid as eluent. HNO_3 was used as an eluent to release the Ni(II) ion that is retained in the Ca-alginate-DMG resin. The concentration and volume of the eluent must be optimized because it greatly influences the analytical performance of the measurement results and was expected to not damage the resin in the column (Panggabean *et al.*, 2014). The measurement results can be seen in Fig 3.

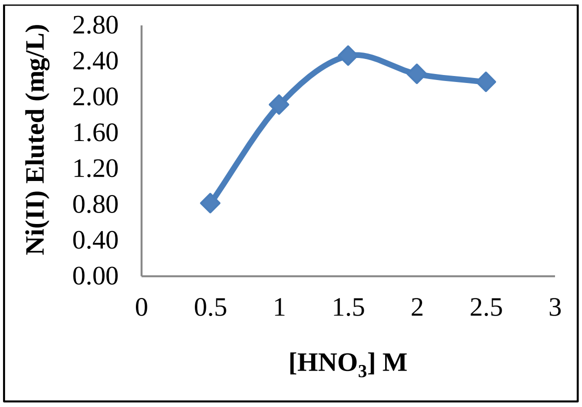

Figure 3. Effect of HNO_3 concentration as eluent

The optimum concentration of HNO_3 as eluent was 1.5 M (Fig. 3). While the concentration of HNO_3 eluent above 2M, Ni(II) ion which eluted will be decrease. This is due to the higher concentration of HNO_3, will be able the damage of Ca-alginate DMG resin, and the retention of the resin is not optimal. For the next stage the optimum volume of the 1.5 M HNO_3 eluent was determined, with used the same conditions as determining the optimum eluent concentration. The measurement results can be seen in Fig 4.

Based on Fig. 4, it can be seen in the HNO_3 eluent volume at the begining from 2 mL, it has been able to optimally elucidate the Ni(II) ion which was retented by Ca-alginate-DMG resin. Furthermore, at the volumes higher than 4 mL, the Ni(II) ions retain did indeed increase, but the amount obtained was not significantly different from the 4 mL eluent volume. This is due to the maximum amount of Ni (II) eluted at the 4 mL eluent volume. For the next stage of the research used 4 mL of HNO_3 volume as eluent.

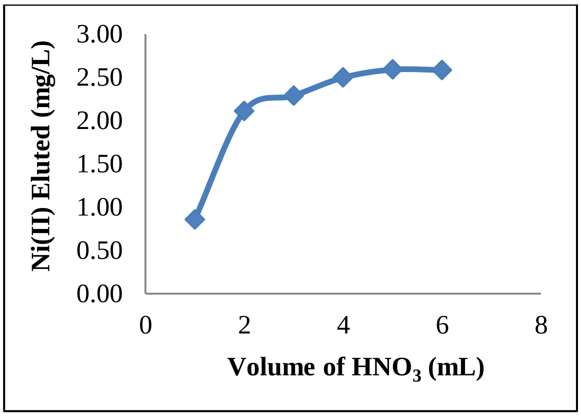

Figure 4. Effect of volume HNO_3 as eluent

Effects of Ni(II) Volume

The number of sample volumes of Ni(II) ions needs to be determined to find out the optimum volume of Ni(II) ions that are retain by resins. The concentration of Ni(II) ions used remains 1 mg/L, where the volume of Ni(II) ions is varied from 1-10 mL and the concentration eluent HNO_3 was 1.5 M with volume was 4 ml. Furthermore, the elution results are measured by AAS. The measurement results can be seen in Fig 5.

Based on Fig 5. it can be seen that the eluted Ni(II) ion increases with increasing volume of Ni(II) ions which are inserted into the column. This means that the increase in measurement of the number of Ni(II) ions which was retained is directly proportional to the increasing volume of the sample standard solution. For the effectiveness of the preconcentration stage, the volume of the 10 mL

Ni(II) ions solution is used for the next stage of this research.

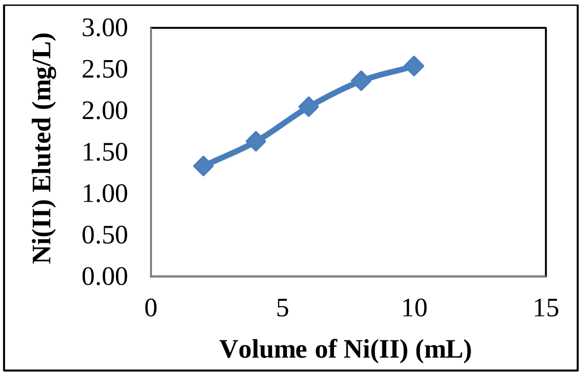

Figure 5. Effect of Ni(II) ions volume

Analytical Performance

Linearity

Linearity of analytical methods is the ability to find out the results of the analysis directly and in proportion to the concentration of analytes in a sample with a predetermined range aimed at proving a linear relationship between the actual (theoretical) substance concentration and the instrument response. Linearity or the correlation tendency between two variables is usually expressed in the correlation coefficient (r) and was said to be good if the value is ≈ 1 (Garfield, 1991; Miller and Miller, 1991).

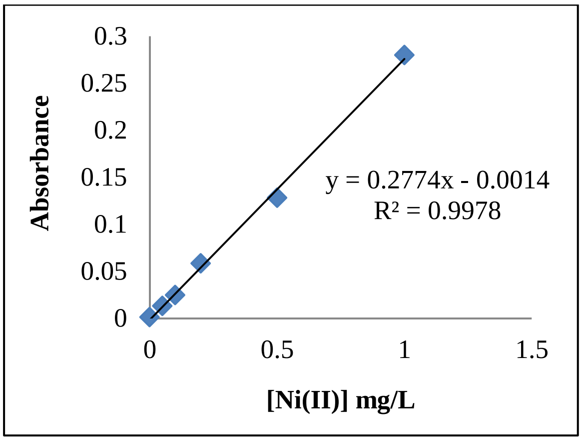

Figure 6. Calibration curve of Ni(II) standard.

Based on the results of measurements, the calibration curve obtained for the Ni(II) ions after being passed into a column containing Ca-alginate-DMG resin, the line equation $y = 0.277x - 0.001$ with a correlation coefficient (R^2) = 0.997 was obtained (**Fig. 6**). The results of this study shows, the measurements can be made in the trace level area (µg/L), because the linearity range obtained is at intervals of 50-1000 µg/L. The concentration range can be used as a measurement work area in determinination of Ni(II) ion concentrations in in the sample solution. Furthermore, this regression equation is used to measure sample concentration.

Precision

Precision illustrates the repeatibility of measurements, namely the closeness between one data value with another data obtained using the same of solution, equipment, method, time and analyst. In this research, the repeated of measurements of a concentration of Ni(II) ion has been done, at the under optimum conditions. Repetition of measurements taken 10 times, and expressed in a percentage of coefficient of variance (% CV). The % CV obtained in this research was 4.06%, for the concentration of 0.2 mg/L Ni(II) standard solution. The method was said to have good precision if the % CV wass ≤ 5% (Garfield, 1991; Miller and Miller, 1991).

The value of % CV obtained was compared with 2/3 % CV Horwitz. The precision of a method will qualify if the % CV obtained from the experiment is less than 2/3 CV Horwitz. The % CV of the experimental was 4.06% is smaller than the value of 2/3 % CV Horwitz are 17.52%, and it can be said the method of developed has a good precision (Garfield, 1991).

Limit of Detection (LOD)

The limit of detection states the smallest minimum concentration or mass that can still be detected by an analysis method with a high level of confidence (Miller and Miller, 1991). The value of LOD can be estimated the minimum number of sample concentrations needed in an analysis process as well as the search for new methods or the development of the old methods by comparing the detection limit with the previous method.

Determination of the LOD value is done by the linearity method by using the intercept line regression equation (Garfield, 1991; Miller and Miller, 1991). Based on the result of this research obtained, to determine the linearity measurement of Ni(II) directly with AAS obtained a regression line $y = 0.091x + 0.0076$, the LOD value obtained was 0.1781 mg/L. After preconcentration, the regression line of measurements are $y = 0.227x - 0.001$, and obtained the LOD value was 0.0451 mg/L. It can be concluded that the preconcentration technique developed can increased the LOD measurement of 3.94 times, when compared with direct measurement of Ni(II) with AAS.

Application of natural samples and the influence of matrices

The final of the aims of this research is to apply the preconcentration technique developed for the analysis of Ni(II) ions in water samples taken from nature, using Ca-alginate-DMG resin as a filler material of column. In this research, the determination of % recovery, performed by the spike method. In this method, water samples and blank are added with a certain amount of standard analyte solution whose concentration is known (Panggabean et al., 2014). The concentration of the analyte is determined in both the water samples and blank, and % recovery was obtained. The results of the research were obtained in the sample from Mahakan River and dam water, and can be seen in Table 1.

Table 1. % Recovery value of Ni(II) ions

Sample	**Ni(II), $\mu g\ L^{-1}$**		**% Recovery**
	Added	**Found**	
Mahakam river	0	148.4±16.5	-
	200	339.8±31.6	96.26±1.16
Dam	0	91.34±1.04	-
	100	195.28±0.83	97.98±0.87

The % recovery results obtained for the analysis of the water samples from dam and Mahakam river at port of Samarinda gave a value > 95%, indicating that the accuracy of the method developed was good (Miller and Miller, 1991). Based on this results, can be concluded the preconcentration technique was developed can be used for the analysis of Ni(II) ions for water samples in nature, because the influence of the matrix contained in the sample can be simplified and does not interfere with the measurement results.

4. CONCLUSION

Dimethylglyoxime (DMG) can be modified to form Ca-alginate-DMG microcapsules and can be used as a filler material of column in the preconcentration stages of Ni(II) ions in water samples. The optimum conditions of the preconcentration technique obtained were Ni(II) ions which could be retained at pH 4, retention capacity was 2.4657 mg Ni(II)/g resin, the concentrations and volumes of HNO_3 as eluents were 1.5 M and 4 mL respectively, and the volume of Ni(II) was 10 mL. The analytical performance obtained is very good which is shown the measurement of parameters such as precision with a % CV value was 4.06%. The LOD value was 0.0541 mg/L and can increase the LOD of Ni(II) ions of 3.94 times, if compared to direct measurements with AAS. The preconcentration technique has been applied for the analysis of Ni(II) ions in water samples from the environment with a % recovery value of > 95%, indicating the method can be used for analysis of Ni(II) ions in the sample at the trace levels.

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