Preliminary Study on The Development of Preconcentration Method of Cu(II), Co(II), Ni(II), and Cr(III) Ions in Water Samples Using Nanomagnetite Coated by Carboxymethyl kappa-Carrageenan (CMKC)

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Abstract. Flame Atomic Absorption Spectrophotometry (FAAS) is one of the instruments that is often used to determine metal ion concentration in solution. FAAS uses simple operational procedure for metal ions concentration determination and produces accurate metal ion concentrations. Unfortunately, the accuracy of metal ion determination test decreases if the concentration of metal ions is too low, whereas the threshold for metal ions in drinking water is very low. Preconcentration is a method for increasing the concentration of metal ions in sample. An effective preconcentration method needs to be studied to improve the accuracy in the determination of metal ions concentration in water at low concentration using FAAS. This research aims to determine the effectiveness of metal ions preconcentration in water samples using nanomagnetite coated by CMKC. The research was conducted in four stages, 1) synthesis of nanomagnetite coated by CMKC; 2) preconcentration of samples containing Cu(II), Co(II), Ni(II), and Cr(III); 3) measurement of metal ion concentration with FAAS; 4) effectivity of preconcentration process and preconcentration optimum conditions. The result showed that nanomagnetite coated by CMKC can be used to preconcentration of metal ions Cu(II), Co(II), Ni(II), and Cr(III) in water samples by utilizing desorption-adsorption mechanism. Desorption was done using 0.1 N HNO₃ as a desorption solvent without variation in concentration and desorption time preconcentration optimum conditions for each metal ion were as follows, adsorption condition of Ni(II) was pH 7 and 60 minutes; Cr(III) was pH 7 and 40 minutes; Co(II) was pH 7 and 60 minutes; Cu(II) pH 6 and 40 minutes. The effectiveness of preconcentration at optimum conditions for each metal ions are: %Cr(III) > %Cu(II) > % Co(II) > %Ni(II), successively.

1. Introduction
Flame atomic absorption spectroscopy (FAAS) was very useful to determine a large number of elements, especially at trace levels. FAAS has widely used to analyze variety of sample matrices including water, soils, and biota. It is a reputable technique that is inexpensive and delivers accurate results even in a complex matrix [1]. In addition, this instrument is often accepted as a suitable
instrumental technique for the measurement of metal ion because of its speed and ease of operation [2]. Many researchers use FAAS to determine the concentration of metal ion because of its low cost, easy usage, and it is available in most of laboratories [3]. The test results of metal ions concentration determination have a high accuracy. Unfortunately, the accuracy of metal ion determination test decreases if the concentration of metal ions is at trace level. The widespread distribution of metal ion is a source of contamination problems, resulting in the low concentration. As a result, a treatment must be done when dealing with a very low-level sample. As in drinking water, the lower the concentration, the higher the risk of contamination.

The levels of heavy metal ions in drinking water are generally at µg/L level. There are many other method for precise and accurate analysis of heavy metal ions in drinking water, such as Neutron Activation Analysis (NAA), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), X-ray Fluorescence Spectrometry (XFS), and Graphite Furnace Atomic Absorption Spectrometry (GFAAS). The accuracy of those instruments are much better than FAAS, but those are only available in a few laboratories in Indonesia. It caused the sample testing costly and it would be processed in a long time, due to the lack of laboratories that provide those instruments. Beside that, laboratories have those instruments mostly, so it would be better that we optimize the use of FAAS to determine levels of heavy metal ions in drinking water. The use of FAAS is more ideal for routine use in laboratories to produce an accurate and precise measurements. However, the sensitivity of FAAS is not high enough to determine metals at trace levels. Hence, its sensitivity should be firstly increased using either simple modified systems or some preconcentration procedures [4].

Preconcentration is a method for increasing the concentration of metal ions in water due to its-low concentration. There are variety of procedures for preconcentration of metal ions, such as solid phase extraction (SPE), liquid-liquid extraction (LLE), coprecipitation, and cloud point extraction (CPE) which have been developed [5]. Among them, SPE is one of the most reliable and simple preconcentration methods for the enrichment of trace metal ions in water. SPE method is based on the contact of a homogeneous liquid sample through a flask containing a selective absorber holds metal ions [6].

The absorber that used in this research is nanomagnetite coated by carboxymethyl kappa carrageenan. Magnetite (Fe₃O₄) is one of many magnetic materials that widely investigated because of their unique properties, inexpensive, and easy to synthesize for MRI, sensor, and adsorbent. Nanomagnetite has a high surface area that produces numerous active sites. However, nanoparticle Fe₃O₄ preparation is a problematic since Fe₃O₄ could agglomerate and leads to the decrease in the active sites [7]. Therefore, coating them with organic surfactants (polymer) such as carboxymethyl kappa-carrageenan could prevent the agglomeration [8].

The effectiveness of preconcentration method needs to be studied to improve the accuracy of the measurement using FAAS. This research aims to determine the effectiveness of preconcentration of metal ions in water samples using CMKC coated nanomagnetite. This research was conducted in four stages, 1) synthesis and characterisation of nanomagnetite coated by CMKC; 2) preconcentration of samples containing Cu(II), Co(II), Ni(II), and Cr(III) ions using CMKC coated nanomagnetite; 3) measurement of metal ion concentration with FAAS; 4) determination of the effectivity of preconcentration process and optimum preconcentration condition.

2. Experimental Procedure

2.1. Materials, Equipments and Intrumentations

2.1.1. Material. Kappa-carrageenan was obtained from CV Makmur Sejati, Malang, Indonesia. Sodium hydroxide, ethanol 96%, isopropyl alcohol, acetic acid (glacial, 96%), sodium chloride, nitric acid were bought from Merck. Iron(III) chloride hexadryate, iron(II) sulphate hexahydrate, and trichloroacetic acid were bought from Sigma Aldrich. Distilled water, demineralized water, and
The powder of metal ions (e.g. Cu(II), Co(II), Ni(II), and Cr(III)) were provided by Chemistry Department of Universitas Negeri Malang.

Equipment and Instrumentation. In this study was used analytical balance (Ohaus PA224), laboratory glassware, hotplate with magnetic stirrer (IKA C-MAG HS 7), oven, a set of vacuum pump and buchner funnel. Instruments used to characterization nanomagnetite by CMKC. Fourier Transform Infrared spectrophotometer (Shimadzu Irrestige 21) was conducted between 400 - 4000 cm\(^{-1}\). Scanning Electron Microscopy (FEI Inspect-S50) used to determine morphology and particle size. Magnetic properties of nanomagnetite were determined by Vibrating Sample Magnetometer (Oxford 1.2H). Crystallinity of nanomagnetite was determined by X-Ray Diffraction (Pananalytical E’xpert Pro).

2.2. Synthesis and Characterisation of Nanomagnetite Coated by CMKC

Nanomagnetite was synthesized by firstly mixing FeCl\(_2\) 0.5M (10 mL) and FeSO\(_4\) 0.25 (10 mL) which then precipitated by slow addition of 40 mL of NaOH 2M. Then, the mixture was stirred for 30 minutes, filtered off, neutralized with distilled water until pH 7 was reached and dried in the oven for 5 hours at 50 °C [9]. Study about optimization of synthesis of CMKC was done [8], the optimum condition of synthesis of CMKC from 1 g of kappa-carragenan need 7.2 g of sodium hydroxide for alkalization step and 1.5 g of trichloroacetic acid for etherification step due to their mol ratio. To coating nanomagnetite with CMKC, first step is preparing CMKC suspension by dissolved 1 g of CMKC in 500 mL of water and stirred for 3 hours. 1 g of nanomagnetite that dissolved in 100 mL of water was added into CMKC suspension and stirred for 2 hours at room temperature and filtered. The residue was neutralized by distilled water until pH 7 was reached and dried in the oven at 50 °C for 5 hours [10]. Fourier transform infrared spectroscopy (FTIR) operated from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) at room temperature used KBr pellet method. SEM machine working at EHT 25kV of accelerating voltage was used to determine morphology and particle size of nanomagnetite, whereas, accelerating voltage for nanomagnetite coated by CMKC was 20kV. XRD pattern of nanomagnetite crystal was obtained at 2\(\theta\) range of 10-90° by a Philips, X’pert, Cu K\(\alpha\) radiation (\(\lambda\) = 0.154 nm) source operated at 35 mA and 40 kV. Sampling technique to select nanomagnetite and nanomagnetite coated by CMKC done by magnetic bar. Selected sample was measured using VSM at room temperature.

2.3. Preconcentration of Samples Containing Cu(II), Co(II), Ni(II), and Cr(III)

Standard solution of each metal ion has different concentration due to lack of metal powder stock in laboratory. Metal ions weighed and made in to solution with concentration 5 ppm for Cu(II), 20 ppm for Cr(III), 30 ppm for Ni(II), and 50 ppm for Co(II). Preconcentration procedure of this research was done by adding 0.1 g of nanomagnetite coated by CMKC into 50 mL of sample solution that contain each metals ion. There are three stages for preconcentration procedure, first preconcentration was conducted at room temperature by varying pH of metal ion solution (e.g. pH 3, 5, 7) to determine the optimum condition of preconcentration. Standard solution of 0.1 M NaOH and 0.1 M HCl were used for pH adjustment. Once the optimum pH was determined, this pH was used for the second preconcentration at different adsorption time to determine the effect of time at metal ions adsorption by put them on the shaker for 20, 40 and 60 minutes at room temperature. The third preconcentration aimed to determine effectivity of preconcentration procedure at the optimum pH and contact time. After nanomagnetite added into the sample solution, nanomagnetite was filtered and the filtrate (filtrate 1) was kept for the further analysis. Nanomagnetite washed with 15 mL demineralization water, filtered, and the filtrate was thrown. Then, for the desorption, nanomagnetite eluted with 20 mL of 1 M HNO\(_3\) and the filtrate (filtrate 2) kept for further analysis [11]. These procedures conducted only once as preliminary study for further research to develop preconcentration method of metal ions in drinking water.
2.4. Measurement of Metal Ion Concentration With FAAS

Initial concentration measurement of standard solution before adsorption was needed to determine the real concentration of metal ion in the solution. Filtrate 1 is meant to be a filtrate after nano magnetite-CMKC adsorb metal ion, measurement of filtrate 1 would determine the concentration of metal ion that still remain in solution. Meanwhile, filtrate 2 is meant to determine metal ion concentration after metal ion un-attached from nanomagnetite-CMKC in 20 mL of 0.1N HNO₃. Standard solution, filtrate 1, and filtrate 2 was measured by using Flame Atomic Absorption Spectroscopy (Shimadzu, AA7000). This procedure conducted only once without any repetition, so there would be no statistical data in this study.

2.5. Determination of The Effectivity of Preconcentration Process and Optimal Preconcentration Condition

The effectivity of preconcentration process was determined by analysing the concentration that was obtained from the third preconcentration procedure, which conducted at the optimum pH and contact time of each metal ion. The adsorption capacity of nanomagnetite-CMKC was calculated using Equation (1), the percentage of metal ion removal was calculated using Equation (2), the desorption capacity was calculated using Equation (3), and concentration increasing was calculated using Equation (4):

\[
Q_{\text{adsorption}} \left( \frac{mg}{g} \right) = \frac{c_{\text{initial}} - c_{\text{remain}}}{m_1} \cdot V_1
\]

\[
\%\text{removal} = \left( 1 - \frac{c_{\text{initial}}}{c_{\text{remain}}} \right) \cdot 100
\]

\[
Q_{\text{desorption}} \left( \frac{mg}{g} \right) = \frac{c_{\text{desorption}}}{m_2} \cdot V_2
\]

\[
\text{Concentration Increasing} = \frac{c_{\text{desorption}}}{c_{\text{initial}}}
\]

where \( V_1 \) is the volume of metal ion solution (L), \( m_1 \) is the weight of nanomagnetite-CMKC used to adsorb (g), \( V_2 \) is the volume of HNO₃ as releasing media of metal ion (L), and \( m_2 \) is the weight of nanomagnetite-CMKC after adsorption. The adsorption capacity is the amount of metal ion that attached to per gram of nanomagnetite-CMKC. The desorption capacity is the amount of metal ion that desorbed or un-attached from per gram of nanomagnetite-CMKC.

3. Result and Discussion

3.1. Synthesis and Characterisation of Nanomagnetite Coated by CMKC

Nanomagnetite coated by CMKC is one of surface modifications to prevent nanomagnetite from agglomeration. Agglomeration could decrease the active site in nanomagnetite that could be binding with metal ions. Coating them with carboxymethyl kappa-carrageenan is not only to prevent agglomeration, but also to increase their ability to bind to the metal ions, because CMKC has negative charge to charge-balance the metal ions. Nanomagnetite was synthesized by co-precipitation method and dried it in the oven for several hours at 50°C. Meanwhile, CMKC was synthesized in two steps, alkalization and etherification steps. FTIR analysis was done to nanomagnetite coated by CMKC, nanomagnetite, and CMKC itself. FTIR analysis aimed to make sure that carboxyl groups in kappa-carrageenan was converted into hydroxyl groups and formed carboxymethyl kappa-carrageenan. The carboxylic groups formation can be seen through the comparison between FTIR analysis of kappa-carrageenan as shown in Figure 1 and carboxymethyl kappa-carrageenan as shown in Figure 2.

Figure 1 showed the hydroxyl groups (O-H) absorption peak appeared at 3205.69 cm⁻¹ in kappa-carrageenan with high intensity. The O-H absorption peak was shifted at 3197.98 cm⁻¹ in CMKC spectra, while the intensity of hydroxyl groups in CMKC was decreased and converted into carboxyl groups as shown from a new absorption peaks appeared at 1774 cm⁻¹ and 1417 cm⁻¹ in Figure 2. These two peaks indicate that C=O groups was formed, in which these peaks were not observed in the kappa-carrageenan spectra. Hence, the carboxymethyl kappa-carrageenan was successfully synthesized.
FTIR analysis was also done to determine the functional groups contained in magnetite (Fe$_3$O$_4$) as shown in Figure 3. According to specific peaks appeared in Figure 3, it is indicated that there was a bonding between iron (Fe) and oxygen (O), observed at 441 cm$^{-1}$ and 586 cm$^{-1}$ which is a signature peak of Fe-O. In similar to Fajaroh (2011) research, a signature peaks of Fe-O at 580 cm$^{-1}$ and 442 cm$^{-1}$ was resulted [12].

![Figure 1. FTIR Analysis of kappa-carrageenan.](image1)

![Figure 2. FTIR Analysis of CMKC.](image2)

![Figure 3. FTIR Analysis of Nanomagnetite.](image3)
Figure 4. XRD Analysis of Nanomagnetite.

Structure of nanomagnetite Fe₃O₄ has to be crystalline, to obtain a pure nanomagnetite [13] To determine the crystallinity of nanomagnetite, powder X-ray diffraction (XRD) analysis has been conducted and shown in Figure 4. The results showed that the synthesized nanomagnetite has peak intensity and 2θ angles that identical to X-ray diffraction pattern of standard nanomagnetite Fe₃O₄ of JCPDS (Joint Committee for Powder Diffraction Standard - Number 19-0629) which were: 8.2°, 30.1°, 35.4°, 37.1°, 53.4°, 56.9°, 62.5°, 65.7°, 70.9°, and 73.9°. High intensity that resulted from θ to 2θ angle because of impurities existed. Nanomagnetite made from mixture of iron(II) sulfate and iron(III) chloride that precipitated by sodium hydroxide. The existance of sodium(I) in nanomagnetite could possibly made diffraction pattern in below 2θ has high intensity. Amplitudes would be scattered by an electron from the donation of Sodium(I). The standards were used as comparison to confirm the product was truly the synthesized nanomagnetite. The data showed that the 2θ angles were appeared at 30º, 35º, 42º, 57º, 63º, and 74º, these peaks almost identical to the result reported by Fajaroh (2011) in which the nanomagnetite has 2θ angles from 30.5º to 63.1º, which correspond to crystalline nanomagnetite [12].

Iron has a strong magnetic moment due to four unpaired electrons in its 3d orbitals, when crystals were formed from iron, different magnetic states could happen [14]. Magnetization value is important to make sure that nano magnetite has magnetic ability to attract metal ions. Figure 5 showed VSM analysis result of nanomagnetite Fe₃O₄ at 25 °C. The saturation of nanomagnetite Fe₃O₄ magnetization was 59 emu/g and for nanomagnetite coated by CMKC was 23.5 emu/g. An excellent magnetic response was necessary for preconcentration metal ions in water. From the previous research [15], the saturation magnetization is about 22 emu/g, indicating an enough magnetic response to attract metal ions in preconcentration procedures.

The SEM analysis of nanomagnetite Fe₃O₄ is represented in Figure 6. As can be seen, the particles have relatively uniform structure. The nanomagnetite was agglomerate of a cluster, it was the reason that nanomagnetite has to be coated with CMKC. The diameter mean is about 31 nm, meanwhile for nanomagnetic coated by CMKC has diameter mean of about 51 nm. The diameter of nanomagnetic coated by CMKC was bigger and was not agglomerated into a cluster. Instead, it is smoother and more separated than the uncoated nanomagnetite. Both type of nanomagnetite are still categorized in nano size. Magnetite would categorized as nanomagnetite if the diameter was under 100 nm [16].
3.2. Preconcentration of Samples Containing Cu(II), Co(II), Ni(II), and Cr(III)

pH of aqueous solution is an important parameter that controlled in metal ion adsorption processes as reported by several authors in the literature. The effect of solution pH (e.g. pH 3, 5, 7) on the adsorption of Cu(II), Co(II), Ni(II), and Cr(III) ions from aqueous solutions use nanomagnetite coated by CMKC as shown in Table 1. Experiments were carried out at 298 K with a contacting time of 40 minutes. The results demonstrate that adsorption of metal ions dependent on the pH. The adsorption capacity increased by increasing the pH. The most optimum pH of this experiment is 7 and used for the next preconcentration procedure.

Contact time was the second important parameter to determine the effectivity of preconcentration procedures. pH 7 was the most optimum condition to be used in the second preconcentration. Contact time were varied: 20, 40, and 60 minutes. The results showed that each metal has their own optimum contact time. According to Table 2, 40 minutes is the optimum contact time for Cu(II) and Cr(III), meanwhile 60 minutes is the optimum contact time for Co(II) and Ni(II). When the adsorption has
reached equilibrium, the adsorption power of nanomagnetite-CMKC would be decreases, so the ability to adsorb metal ions will also decrease. It is possible when nanomagnetite-CMKC reaches the saturated state caused the adsorbent to erode and the attached metal ions could be separate from the active adsorbent group. Therefore, when the metal ion and adsorbent are contacted at the optimum contact time, the adsorbent will gradually lose its absorption.

| Metal | pH | Cu(II) (ppm) | Co(II) (ppm) |
|-------|----|--------------|--------------|
|       | 3  | 5.53         | 43.31        |
|       | 5  | 5.53         | 43.31        |
|       | 7  | 5.53         | 43.31        |
| C_{initial} |   |              |              |
| C_{remain}   |   |              |              |
| C_{desorption} | |              |              |

| Metal | pH | Ni(II) (ppm) | Cr(III) (ppm) |
|-------|----|--------------|---------------|
|       | 3  | 27.1         | 18.76         |
|       | 5  | 27.10        | 18.76         |
|       | 7  | 27.1         | 18.76         |
| C_{initial} |   |              |              |
| C_{remain}   |   |              |              |
| C_{desorption} | |              |              |

Table 1. The Effect of pH on Metal Ion Adsorptions by CMKC-Coated-Nanomagnetite.

The effectivity determination of preconcentration procedures was carried out by using the optimum condition, which is at pH 7 and 40 minutes for Cu(II) and Cr(III), while Ni(II) and Co(II) at pH 7 and 60 minutes. Table 3 presented data of adsorption capacity and percentage of metal ion removal, meanwhile the data for desorption capacity and concentration increasing are presented in Table 4. According to the data, the adsorption capacity of nanomagnetite-CMKC around 2.76 – 21.50 mg/g. Adsorption capacity is defined to the amount of metal ion that attached to per gram of nanomagnetite-CMKC. Percentage of metal ion removal showed that nanomagnetite-CMKC has high result which is above 99% for all of metal ions.

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Based on Table 4, desorption capacity is defined the amount of metal ion that desorbed or unattached from nanomagnetite-CMKC. Metal ions released by addition of 20 mL of HNO₃. HNO₃ was chosen as desorption solution because it produces a lot of H⁺ ion that could deprotonated carboxyl groups of the adsorbent that bind with metal ions. In contrast with adsorption capacity, the result of
The desorption capacity was slightly different, in which the highest desorption capacity was shown by Cr(III) ion (12.50 mg/g) and the lowest percentage was shown by Cu(II) ion (3.71 mg/g).

The different between initial concentration and desorption concentration was used to determine the increasing of sample concentration as presented in Table 7. The highest value was shown by increasing concentration was Cr(III) ion, because Cr(III) ion has the biggest atomic radius that made them easier to be un-attached from the nanomagnetite than other metal ions.

Table 3. The effectivity of metal ion adsorption at the optimum condition for each metal ions.

| Metal Ion | pH 7 and 40 minutes | pH 7 and 60 minutes |
|-----------|---------------------|---------------------|
|            | $C_{\text{initial}}$ (ppm) | $C_{\text{remain}}$ (ppm) | Adsorption Capacity (mg/g) | $\%$ Metal Ion Removal | $C_{\text{initial}}$ (ppm) | $C_{\text{remain}}$ (ppm) | Adsorption Capacity (mg/g) | $\%$ Metal Ion Removal |
| Cu(II)     | 5.53                | 0.0019              | 2.76                  | 99.97                  | 27.1                | 0.00837              | 13.55                  | 99.97                  |
| Cr(III)    | 18.755              | 0.0391              | 9.36                  | 99.80                  | 43.31              | 0.32                | 21.50                  | 99.26                  |

Table 4. The effectivity of metal ion desorption at the optimum condition for each metal ions

| Metal Ion | pH 7 and 40 minutes | pH 7 and 60 minutes |
|-----------|---------------------|---------------------|
|            | $C_{\text{initial}}$ (ppm) | $C_{\text{desorption}}$ (ppm) | Desorption Capacity (mg/g) | Increasing Concentration | $C_{\text{initial}}$ (ppm) | $C_{\text{desorption}}$ (ppm) | Desorption Capacity (mg/g) | Increasing Concentration |
| Cu(II)     | 5.53                | 18.57               | 3.71                  | 3.36                  | 27.1                | 35.2                | 7.04                  | 1.30                  |
| Cr(III)    | 13.9                | 62.5                | 12.50                 | 4.50                  | 43.31              | 104.56              | 10.46                 | 2.41                  |

4. Conclusion

Nanomagnetite Fe$_3$O$_4$ were synthesized by co-precipitation method and coated with carboxymethyl kappa-carrageenan. These materials used for preconcentration method in a water artificially contaminated by metal ions, such as Cu(II), Co(II), Ni(II), and Cr(III). Nanomagnetite has mean particle size of 31 nm and 51 nm for nanomagnetite coated by CMKC. Saturation magnetization of nanomagnetite was 56 emu/g meanwhile for nanomagnetite coated by CMKC was 23.5 emu/g. The most optimum condition to adsorb metal ions was pH 7 in 40 minutes for Cu(II) and Cr(III) ions, while pH 7 in 60 minutes for Ni(II) and Co(II). The highest adsorption capacity of nanomagnetite-CMKC is Co(II) ion (21.50 mg/g) and the lowest is Cu(II) ion (2.76 mg/g), meanwhile for the highest desorption capacity is Cr(III) ion (12.50 mg/g) and the lowest is Cu(II) ion (3.71 mg/g). This preconcentration procedure effectively remove metal ions at trace level and the preliminary study on this research could be developed in further research.

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