Microscopic Analysis of Cu (II) ions using C-Cinnamal Calix[4] Resorcinarena Synthesized from Cinnamon Oil (Cinnamon burmanii)

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Abstract. This study discussed the effect of pH, contact times and concentrations on absorption of Cu (II) metal ions in the solution using C-Cinnamal Calix[4] Resorcinarena (CCCR). CCCR was synthesized through electrophilic substitution reaction of cinnamaldehyde isolated from cinnamon oil with resorcinol in an acidic atmosphere at 77 °C for 2 hours. Isolation of cinnamaldehyde from cinnamon oil produced 8.324 grams of cinnamaldehyde with a yield of 27.72% of 30 grams of cinnamon oil. The Absorption of Cu (II) metal ions in the solution by (CCCR) synthesized was carried out in a batch system with variation, i.e. pH 2, 3, 4, and 5, contact time variations, i.e. 5, 15, 30, 60, 120, 150, 180 minutes and different concentrations which are i.e. 10, 20, 40, 60, 80, 100 mg / L. The optimum condition for the absorption of Cu (II) metal ions by CCCR was in pH 4 with 90 minutes of the contact time, and 80 ppm showing absorption capacity of 0.896 mg / g.

1. Introduction
Pollution is a condition that has changed from its original form to a worse condition. This may result from the entry of pollutants. Heavy metal ions are one of the pollutants, usually derived from an industrial waste. Heavy metal is a solid or liquid body having a density of 5 grams / mL [1]. The existing heavy metal ions are essential and non essential, some heavy metal ions are very important and required by the body because they are used in metabolism, such as zinc ions (Zn), copper (Cu), iron (Fe), cobalt (Co) and etc. Some heavy metal ions are non essential and even toxic to living things Heavy metals that are toxic include copper (Cu).

Copper (Cu) is a useful and important element for metabolism. Cu can cause unpleasant taste in water. Heavy metals like copper also serve as metalloenzymes in the human body, such as the ascorbic oxidase enzyme, cytochrome C oxidase, polyphenol oxidase, amino oxidase required for the oxidative enzyme system [2, 3].

Several methods used to detect copper have been developed. The method directly uses instruments such as: GF-AAS (Graphite Furnace Atomic Absorption Spectroscopy) [4], ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) [5], XRF (X-ray Fluorescence) or Energy Dispersive The Spectrometer (EDS) [6], has been able to detect the presence of copper, but it faced the constraints in the availability of instrumentation, cost of analysis and maintenance which is quite expensive. The technique that can provide a solution to the limitations of instrument in determining...
copper metal at very low concentrations is the preconcentration technique. This technique can be biosorption (absorption of metals using biological substances such as algae) and adsorption (using activated substances such as activation of coconut fiber media with alkaline).

A technique that can provide solutions to the limitations of instrument tools in the determination of copper, plumbum and cadmium metals at very low concentrations is preconcentration technique, such as the biosorption method and the absorption method. Other preconcentration methods that can be used to measure the content of Cu metals in very small concentrations is solid phase extraction. Solid phase extraction is one of the concentration techniques through the sorption (adsorption-desorption) process which is still being developed. This technique has advantages when compared with other techniques, mainly because the cost is small and the adsorbent material can be reused (reusable). In this technique, the adsorbent is generally a material that has an active side on the surface and has a large touch surface area.

In the previous study, many types of solid phase extraction using resins and ligands as supportive polymer materials can be used for the analysis of Cu ions which have their respective disadvantages and advantages, such as the use of a modified polynynyl diphenylene benzene with alpha-nitroso -beta-naphthol [7], the use of Cu (II) -Impirited polymers [8], the use of Ca-alginate microcapsule resin [2], but the weakness of supporting polymer materials are the expensive cost of purchasing materials and the materials used are difficult to find.

To overcome those problems, the researchers wanted to use natural materials as supporting polymer materials for the retention of Cu ions. One of the natural materials that can be used is cinnamon oil obtained from cinnamon plants. The content of this cinnamon oil is sinamaldehyde. The reaction between sinamaldehyde and resorcinol can produce C-Cinnamal Calix [4] Resorsinarene (CCCR).

One type of calixarene is calixarena derivative or calix [4] resorsinarene. Calix [4] resorsinarene is synthesized from resorcinol or its derivatives and various types of aldehydes, both aliphatic and aromatic aldehydes. The calix structure [4] resorcinene will be different for each aldehyde, therefore research on calixarena is very broad [9]. One of them is the reaction between cinnamaldehyde and resorcinol which can produce C-cinnamal calix [4] Resorsinarene. CCCR has twelve benzene residues, eight hydroxyl groups, and four alkenyl groups (double bonds). The existence of a free electron pair in a hydroxyl group, as well as the presence of electrons in aromatic residues and double bonds are expected to have a special activity on heavy metal cations.

Calixarena macromolecular compounds have great potential to be developed as adsorbents. Calixarena) is a cyclic oligomeric compound composed of aromatic units connected by a methylene bridge. One type of calixarena is calix [4] resorsinarene. Calix [4] resorcinarene has a unique geometry shaped like a basket and hollow with an active group in it which allows this compound to be used as a host molecule (host) for other molecules (guest), both in the form of anions, cations, and neutral compounds [10].

Sinamaldehyde is a sinamat derivative which is the main component of cinnamon oil cinnamaldehyde has an aldehyde group so when reacted with resorcinol it has the potential to produce C-cinnamal calix[4] resorcinarene (CCCR) which is a calyx due to the calix derivative [4] resorsinarene.

Calix [4] resorcinarene compounds have been used for a variety of purposes, including additives in capillary electrophoresis, liquid membranes, solvent extraction, chemical sensors, and stationary phases of high performance liquid chromatography (HPLC) columns. However, the use of calix [4] resorcinarene as a solid phase extractor from heavy metal cations is still very limited [10].

Based on the above, a further study was carried out, namely utilizing the synthesized CCCR compound [11] as an absorber of Cu (II) metal ions. This study is expected to provide benefits to overcome the limitations of materials and instruments, and methods and ligands which is good for Cu metal ions.

The purpose of this study was to effect of pH retention, effect of optimum contact time and determination of the retention capacity of Cu on CCCR.
2. Experimental Section

2.1. Material and Equipments
The equipments used in this research are reflux set, buchner funnel, FTIR (Jasco 460 plus Spectroscopy), rotary evaporator (Heidolph Laborota 4000), Desiccator, Ultraviolet Spectroscopic Agilent 8453 UV-Vis. A flame atomic absorption spectrometer AA1009M013 with Hitachi lead hollow-cathode for Atomic Absorption measurement. For pH measurement, a Hitachi-Horiba Model M-5 glass electrode pH meter was used.

The materials are NaOH (merck), HNO3 (merck), resorcinol (merck), cinnamaldehyde, HCl 5%, ethanol (merck), diethyl ether (merck), NaHSO3 (merck), Ether (merck), Na2SO4 (merck), Sweetwood Oil (PT STS), Cu(NO3)2.

2.2. Research Procedures [9, 10]

2.2.1. Determination of pH retention of Cu.
A total of 10 ml of Cu (II) 10 mgL-1 metal solutions were prepared with variations of pH 2,3,4 and 5. The solution was then fed into a beaker containing 0.06 g CCCR. The mixture is stirred at room temperature. The resulting filtrate was measured using AAS.

2.2.2. Effect of optimum contact time of Cu on CCCR.
As much as 20 ml of Cu (II) metal solutions were prepared in concentrations of 20 mgL-1 at the optimum pH. The solution is then contacted into CCCR with a contact time variation of 5, 10, 30, 60, 120, 150, and 180 min. The mixture is stirred at room temperature. The resulting filtrate was measured using AAS.

2.2.3 Determination of the retention capacity of Cu on CCCR.
A total of 20 ml of Cu solutions at optimum pH were prepared with certain concentration variations. The solution is then fed into a beaker containing 0.06 g CCCR. The mixture is stirred at room temperature. The resulting filtrate was measured using AAS.

3. Results And Discussion

3.1. The Effect of pH and contact time
The parameters that determine the adsorbent's ability to absorb metals on the solid-liquid surface are pH and contact time. The pH measurements are performed simultaneously with the contact time. The measurement contact time is carried out in order to know how long it takes for Cu metal ions to be well-preserved in the resin, and there is possible chemical bonds between the adsorbent and the adsorbate at the variation of pH. This is related to the protonation or deprotonation of the active side surfaces of the adsorbent. Measurements of the pH effect on adsorption of Cu (II) metal ions to CCCR were carried out at pH 2-5 and contact time variations were used 5 minutes to 90 minutes show in Figure 1.
Figure 1. Effect of pH and contact time on Cu (II) extraction on CCCR.

Figure 1 showed that CCCR can form chelates with Cu (II) metal ions at pH 4 with a contact time of 90 minutes and absorption capacity of 0.664 mg / g. At pH 2-3 the amount of H+ in solution is larger, so it is supposed to be competition H+ with copper metal ion to bind with between the functional group. H+ Ion blocks Cu to the surface of the functional group, so that the uptake at pH becomes low [12]. At pH 4 there is a competition of complex formation reactions between chelate compounds with hydroxide ions. At pH 5 there is a decrease in the amount of H+ ions, whereas OH- in the solution increases, so it is expected that there is a competition between OH- and the functional groups in bonding to form Cu (OH)2 deposits, resulting in fewer Cu (II) metal ions which are fixed by CCCR [13] Seen in Figure 1 the contact time of 5-90 minutes indicates that the extraction capacity with the increase of interaction time, and at a pH of 4 to 90 minutes indicates extraction is very high, so it is assumed that in 90 minutes Cu (II) metal ions can be well retained in the resin and the extraction achieves an equilibrium between the extracted metal ions and the free ions present in the solution.

3.2. The effect of concentration

The effect of Cu (II) concentration on CCCR sorption was done at optimum pH (4), with contact time 90 minutes. The Cu (II) metal ion retention capacity of CCCR is shown in Figure 2.

Figure 2. Effect of metal concentration on Cu (II) extraction with CCCR.
Figure 2 showed the effect of metal concentration on Cu (II) extraction on CCCR, the number of Cu (II) extracted increases with the increasing of metal concentration and reaches a maximum absorption value of 0.896 mg / g at a concentration of 80 ppm.

According to Etika [11], the increase in the concentration of the solution will increase the uptake of metal ions until there is a constant uptake at concentration increase, this occurs on the CCCR surface when no more empty space can be filled by positively charged ions, so the number of positive metal ions is no longer proportional to the active groups present on the surface, it can also be said on the surface has been saturated.

4. Conclusion
Based on the results of experiment on analysis of Cu (II) ions using C-Cinnamal Calix[4]Resorsinarena from Cinnamon Oil, the conclusion is the effectiveness of CCCR as a ligand in the retention of Cu (II) ions occurs at pH 4 with a contact time of 90 minutes with retention capacity of 0.896 mg / g at a concentration of 80 ppm.

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