Performance of cellulose-diethylenetriamine as binding layer in the diffusive gradients in thin films method for measurement of Cu in environmental waters

Khairuddin¹, A W Wahab², Buchari³, I Raya²

¹Department of Chemistry, Faculty of Mathematics and Natural Science, Tadulako University, Palu
²Department of Chemistry, Faculty of Mathematics and Natural Science, Hasanuddin University, Makassar
³Department of Chemistry, Faculty of Mathematics and Natural Science, Bandung Institute of Technology, Bandung

E-mail: heru_jns@yahoo.co.id

Abstract. Palu Bay and Poboya River, Central Sulawesi, Indonesia, was an environmental waters near site to the location of traditional gold mining and residential areas. This research aimed to apply of cellulose-diethylenetriamine material as a binding layer on the diffusive gradients in thin films method to evaluate the distribution copper labile species release into Palu Bay and Poboya River. On this method, influence of ionic strength, pH, initial concentration, gel thickness were evaluated. The results showed that the concentrations of copper labile metal measured by DGT method could be significantly different, indicating that the labile fractions of copper metals were adsorbed well on the functional group of the binding agents. By choosing cellulose-diethylenetriamine as binding layer, the proposed approach was successfully employed measurements in the aquatic system.

1. Introduction
Copper (Cu) ion dispersion from industrial waste into the aquatic environment is an important pollutant concern due to potential bond in biota and toxicological effects [1]. Copper is one of the most toxic and causing to human health and the aquatic environment, even at low concentrations. It has been well reported that the accumulation of copper in the human body causes pancreas, brain, and heart disease. The permissible copper limit is 2.5 mg / L in water [2]. To overcome the problem pollution by copper in water, various methods have been applied to determination copper from water, especially in environmental waters [3].

The diffusive gradient in thin films (DGT) is a technique that is capable of monitoring contamination of copper ions by the species's labile kinetic diffusion transport to estimate contaminant concentrations [4]. Thin film diffusive gradient (DGT) techniques have been applied to measurements of trace metal ions [5, 6], radionuclides [6], arsenic [7, 8] and phosphorus [4] in environmental waters. This method is a technique for passive sampling, especially metals in environmental water, easy to use, versatile and has interesting features such as preconcentration and direct measurement on the spot.

The diffusive gradient in thin films method, developed by Davison and Zhang [6] for in situ determination of concentration of labile species in aquatic systems. In a DGT unit, there are three layer:
a binding layer followed by a hydrogel layer as diffusive layer and lastly a membrane filter usually 0.45 µm that related the aquatic systems (figure 1). Dissolved metal ion, which are smaller than the pore size of the membrane, diffuse through diffusive layer `gels (thickness ∆g and surface area A) and are chelated by cellulose-diethylenetriamine as a binding layer. After exposure for a time in a environmental waters, the amount of Cu labile species absorbed by the cellulose-diethylenetriamine and the mass M of Cu attached was calculated.

![Figure 1. DGT unit and gel layers assembly.](image)

When DGT unit is contact in solution or environmental waters, the flux of Cu labile species pass through diffusive layer gel followed by the diffusion of Fick’s first law:

\[ J = D \frac{dC}{dx} \]  

where \( J \) is the flux of mass of labile species per unit time and area, \( D \) is the diffusion coefficient and \( \frac{dC}{dx} \) is the concentration gradient in the diffusive gel. Diffusion coefficient of Cu (II) metal with polyacrylamide diffusion gel at a temperature of 30°C is 7.10 x 10^-6 cm².s⁻¹. Cu labile species that pass through the diffusive layer gel are rapidly bounded in the cellulose-diethylenetriamine gel.

The interface concentration of Cu labile species in the cellulose-diethylenetriamine can be admitted to be near zero provided the binding layer has not reached saturated point. If consider \( dC \) can be be equal to the concentration for the Cu labile species in the solution or environmental water (dC = C). The total thickness of the diffusive layer gel (dx) is the sum of the thickness, the diffusive layer gel and membrane filter \( \Delta g \). Eq. (1) can rearranged to be simplified:

\[ C = \frac{J \Delta g}{D} \]  

The flux of mass of Cu can be take placed as \( J = M/At \), where \( M \) is the mass of Cu labile species accumulated in the cellulose-diethylenetriamine gel, \( A \) is the surface area of the diffusive gel and \( t \) is deployment time to the aquatic system. So Eq. (2) could be:

\[ C_{DGT} = \frac{M \Delta g}{D A t} \]  

Cu on the cellulose-diethylenetriamine were eluted in 2 mL of 1M HNO₃. The Cu concentrations in the eluted HNO₃ acid (\( C_{elu} \)) were determinated and the Cu mass flux accumulated were calculated using Eq. (4):

\[ M = \frac{C_{elu}(V_{gel}+V_{acid})}{f_e} \]  

where \( V_{gel} \) is volume of cellulose-diethylenetriamine binding layer gel, \( V_{acid} \) is volume of added acid and \( f_e \) is the efficiency of elution.

Alternative materials have been proposed and developed as binding agents for the DGT technique. As biosynthesized cellulose, cellulose from nata de coco is an cellulose produced by bacteria of genus *Acetobacter Xylinum*. The structure of cellulose from nata de coco is similar to plant cellulose that is
unbranched polymer glucopyranose. So that, the fibrous structure of nata de coco cellulose is different from of cellulose plant. The cellulose from nata de coco has been reported in the previous literature applied as adsorbent of metal ions in water and waste water [9, 10] but the adsorption capacity is relatively deficient therefore, it is necessary to modify cellulose from nata de coco with a better structure in the interest of increase the capture capacity. To work up the metal labile species uptake of cellulose, it was chemically modified by diethylenetriamine in the functional groups.

2. Material and Method

2.1. Material

DGT units from DGT Research Ltd. (UK). The polyacrylamide gel were prepared using acrylamide (Sigma Aldrich, Germany), ammonium persulfate (Sigma-Aldrich, Germany), tetramethyl ethylenediamine (Sigma Aldrich, Germany). To characterization of functional group using FTIR and determination of Cu concentration using Inductively Coupled Plasma-Mass Spectrometre (ICP-MS).

2.2. Preparation of cellulose-diethylenetriamine

The preparation of cellulose from nata de coco started by addition 15% alkaline solution at a room temperature for one hour, followed by wash it with water. The cellulose (1 g) was take placed with a magnetic stirring in a round-bottom flask equipped magnetic bar. After that, a mixture of 8% alkaline solution (100 mL) and epichlorohydrin (3 mL) was added. The reaction was observed at 20°C for 10 hours while stirring. The product was washed until pH 7.0 was reached with deionized water and anhydrous ethanol, and finally dried at 60°C. The cellulose product (1 g) was mixed with 1 g of diethylenetriamine and 100 mL of deionized water, and added sodium bicarbonate as a catalyst (10 g/L) under stirring at 50°C for 2 hours. The product was washed until pH 7 with deionized water and ethanol, and then dried at 60°C. Finally, white cellulosic powder was formed [11].

2.3. Polyacrylamide diffusive gels preparation

Production of polyacrylamide gels followed by Jennifer Morford et al procedure used [12]. Polymerization was started by adding 7 µL of 10% ammonium persulfate and 2.5 µL of tetramethyl ethylenediamine (TEMED) per millilitre of gel solution. The gels formed was cast between two plates of glass and maintained for 10 min. Then, the gels were hydrated in deionized water for 24 h to allow gels to obtain a stable thickness. The discs gels were cut and stored in 0.01M NaNO₃.

2.4. Cellulose-diethylenetriamine gels preparation

Treatment of Cellulose-Diethylenetriamine gels were prepared from a diffusive gel solution of the same composition. Amount 0.2 g (100 mesh) of cellulose - diethylenetriamine were added per millilitre of the gel solution. The polymerization rate was terminated by adding 6 µL of ammonium persulfate and 2µL of TEMED per millilitre of the pre-gel solution to allow settling of the cellulose-diethylenetriamine binding layer gel. After hydration, the discs gels were cut and stored in deionized water.

2.5. DGT assembly

Gels were assembly on the top of the piston of DGT unit. The binding layer gel was covered by diffusive gel and a cellulose nitrate 0.45 µm pore size as membrane filter. Pressed tightly the front cap DGT unit was.

2.6. DGT performance tests

To test the validity of DGT measurement for Cu labile species some analysis were carried out.

2.6.1. Time-dependence experiments. The DGT probe were filled with cellulose-diethylenetriamine gel and polyacrylamide diffusive gels covered by membrane filter. The assembly of DGT probe was floated for different time periods in a stirred solution 250 µg/L, 3, 6, 9, and 12 h. At each sampling time, DGT
units were taken from the solution, cellulose - diethylenetriamine gel were eluted with HNO₃ and the concentration of Cu ions measured with ICP-MS and then calculated as C_{DGT} in all these pieces.

2.6.2. Effect of concentration. The influence of the concentration variation is done by floated of DGT units in a stirred solution for different Cu²⁺ concentration of 400, 600, 800, and 1000 µg/L in a glass beaker. After a certain time DGT units removed and washed with demineralized water and cellulose - diethylenetriamine gels eluted in 2 mL of 1 M HNO₃ acid solution for 24 hours and diluted to 10 mL.

2.6.3. Effect of pH. Effect of pH is the important parameter for the experiments. The various of pH values were done between 2 – 8. The evaluation of the effect of pH on Cu ions uptake was carried out by maintaining a Cu concentration of 100 µg/L and an ionic strength of 0.01 mol/L NaNO₃. After a certain time DGT units removed and washed with demineralized water and cellulose - diethylenetriamine gels eluted in 2 mL of 1 M HNO₃ solution for 24 hours and diluted to 10 mL.

2.6.4. Effect of Gels Thickness. Polyacrylamide diffusion gel with three variations of 0.42 mm, 0.78 mm and 1.20 mm thickness was used to determine the effect of the diffusion layer thickness on the adsorption of Cu ions by the binder layer. The DGT sampler loaded with a cellulose - diethylenetriamine gels, diffusion layer and membrane filter was applied in a 500 µg / L Cu²⁺ solution with a deployment time of 12 hours and a temperature of 30°C. The cellulose - diethylenetriamine is separated and eluted with 2 mL HNO₃ 1M for 24 hours. The concentration of Cu²⁺ is measured by ICP-MS.

2.6.5. Effect of Ionic Strenth. Effect of ionic strength as NaNO₃ concentration was done with spike of Cu²⁺ 250 µg / L solution in NaNO₃ solution with concentration variation (0.001M, 0.01M, 0.1M and 1M). The diffusion layer tested in this DGT method is polyacrylamide gel. The position of the DGT sampler is arranged to be located at the top of the solution by binding the DGT sampler with the rope. The effect of ionic strength was tested on each solution with 12 hours contact time and 30°C solution temperature. After deployment was completed, the cellulose - diethylenetriamine gel was separated and then eluted with 2mL 1M HNO₃ for 24 hours and Cu metal concentration measured by ICP-MS.

2.7. Applications in Environmental Water
Seawater and river water sampled with a combined method (composite samples) in which a mixture of instantaneous samples taken from seawaters Palu Bay and Poboya River location. Water samples filtered with filter paper and then 800 mL take placed in glass beaker 1000 mL. The DGT units was floated and rinsed with distilled water after retrieval then measured by ICP-MS.

3. Results and Discussion

3.1. Characterization of Cellulose-Diethylenetriamine
Modification of cellulose structure process occurs through etherification reactions between C6 glucose carbon atoms from cellulose. Modification of cellulose functional groups begins with reacting cellulose of nata de coco with NaOH to form sodium cellulose. This product is then reacted with epichlorohydrin to produce a reactive epoxy group to facilitate further reaction with diethylenetriamine. Hydroxyl groups of cellulose of nata de coco reacted with epichlorohydrin to produce an epoxy derivative.

Optimum condition in synthesis of cellulose-diethylenetriamine previously has been reported by Hassan, El-Wakil, and Sefain (2001). Elemental analysis of the product give value in Nitrogen is 13.12%. The results conclusion that the morphology of cellulose can be influenced by the amination. Furthermore, microfibrils from nata de coco cellulose are much thinner than plant cellulose’s fibers, therefore hydroxyl groups of of nata de coco cellulose can be functionalized. Gregorio et al (2005) reported that if increased of the epoxy group to the amine group will cause the increase of amine content and reaction temperature.
3.2. FT-IR spectroscopy

Figure 2 showed for the cellulose of nata de coco spectrum, peaks of 3379 cm\(^{-1}\) mark of O-H stretching, 2733 cm\(^{-1}\) to 2889 cm\(^{-1}\) mark of C-H stretching, 1163 cm\(^{-1}\) mark of C=O-C stretching and 1029 cm\(^{-1}\) to 1058 cm\(^{-1}\) mark of C-O stretching. Other fingerprint regions for cellulose are peaks around 1300 cm\(^{-1}\) mark of C=H bending and around 1400 cm\(^{-1}\) mark of CH\(_2\) bending.

![FTIR spectrum](image)

**Figure 2.** FTIR spectrum (a) cellulose of nata de coco (b) sodium-cellulose (c) cellulose- epichlorohydrin. (d) cellulose-diethylentriamine (e) Cu-cellulose-diethylentriamine.

3.3. Effect of deployment time

Adsortion of Cu labile species by cellulose-diethylentriamine hypothesized to occur with the following steps. Uptake Cu takes places depends on functional groups of the cellulose-diethylentriamine charge as. If there are Cu– amine and hydroxyl complexes of the same charge, limited flux mass transport will occur across the surface of cellulose-diethylentriamine. The variety of rate mechanisms may be involved depending on the Cu labile species under consideration, binding form and the hydrodynamic situation.

Figure 3 shows that as the contact time increases, the mass of Cu ions bound by cellulose -diethylentriamine using polyacrylamide diffusion gel increases linearly until 12 hours of deployment time. The use of 12 hours deployment time is then used in testing the Cu (II) metal concentration determination on other method performance parameters.

3.4. Effect of pH

Testing the pH effect on binding layer cellulose -diethylentriamine ability of Cu ion was carried out with a variety of pH to obtain maximum absorption of Cu ions concentration. The degree of acidity (pH) of ion Cu ions solution was varied at pH 2-8, deployment time of 12 hours, and temperature of 30°C. The effect of pH on the binding layer is related to the association process and dissociation of several functional groups such as amines, and hydroxyl groups present in the binding layer. Protonation of the active side will increase or decrease throughout the binding process of metal ions due to changes in pH. The test results showed that ionic strength with 0.01M NaNO\(_3\) concentration showed the average value of maximum Cu (II) concentration by using polyacrylamide diffusion layer which was 163.74 μg /L.
Figure 3. Effect of deployment time on Cu ions concentration which is bound to cellulose-diethylentriamine gel.

Figure 4. The effect of pH on Cu concentrations in the cellulose-diethylentriamine binder layer.

Figure 4 showed that the effect of initial pH on Cu concentrations on at the range values of 2–8. When the initial pH was adjusted to 2, a less of Cu labile was bounded by the cellulose–diethylentriamine gel. This is caused by the proton of amine and hydroxyl functional group was very difficult to dissociate or protonation with the functional groups in the cellulose-diethylentriamine. However, the uptake efficiency of Cu labile ions increases remarkably as the pH increasing from 2 to
4, and the maximum capacity of Cu ions uptake occurs at pH 4. This might happen the protonation of the amino groups in acidic conditions. But when the pH value is above 4, the uptake capacity declined. The reason may be described that the very unstable complex between Cu ions and the N atom also OH atom when pH > 2.

3.5. Effect of Cu ion concentration
The studied of cellulose-diethylenetriamine complexes uptake capacities binding layer were determined by vary of Cu concentration (uptake from single metal ions-solutions) at constant pH and temperature degree. The cellulose-diethylenetriamine binding layer has active groups -OH and -NH$_2$ so that they can be used as chelating Cu ions through the interaction of chelate formation, electrostatic interactions, or ion exchange. Bonding between the active group binding layer and metal ions through two donor atoms produces a cyclic complex. Meanwhile, the electrostatic force arising from the attraction between the ions opposite the charge will produce ionic bonds.

![Figure 5](image)

**Figure 5.** Effect of initial concentration on Cu ions concentration attached to cellulose-diethylenetriamine binding layer.

Figure 5 shows the uptake of Cu in the cellulose-diethylenetriamine binding layer increased with the contact time, reaching a constant within 600 – 1000 µg/L.

3.6. Effect of gels thickness
An aspect that also influences the diffusion process of the analyte to be uptake in the binding layer gel is the thick of diffusive gel [7]. The thickness of the diffusive layer gel will determine the inorganic and organic labile metals that are bound to the binding layer. The thicker the membrane, the slower the diffusion speed. In addition, metal ions or complex analytes diffuse through the diffusion gel will pass if the size of the metal ion is smaller than the effective pore size and crosslinking of the diffusion layer polymer [5]. The test results showed that 0.78 mm thick the polyacrylamide gel diffusion layer resulted in Cu concentrations higher than Cu ions concentration with 0.42 mm diffusion gel thickness and 1.20 mm. The addition of diffusion gel thickness (0.78mm) and membrane filter thickness (0.13mm) becomes the constant diffusion gel thickness ($\Delta g = 0.091cm$) which will be used in the calculation of Cu metal.
concentration in the DGT method using cellulose-diethylentriamine with a diffusion layer of polyacrylamide gel.

![Graph](image)

**Figure 6.** Effect of gel thickness on Cu concentration attached to cellulose-diethylentriamine binding layer.

### 3.7. Effect of ionic strength

The effect of ionic strength is important because of the strength the ion from environmental waters is so low that it can affect the activity of the analyte to be bound to the binding layer (Wagner, 2004). In this study, ionic strength is expressed as NaNO$_3$ concentration and is used as a buffer of the binding strength of the cellulose-diethylentriamine in uptake Cu labile species can be optimized. In general, the performance of DGT applications in solutions with low ionic strength ($I < 2 \times 10^{-4}$M) is thought to interfere with Cu diffusion to the gel layer so that it also affects the value of the Cu diffusion coefficient of the analyte (Torre et al. In Wagner, 2004).

![Graph](image)

**Figure 7.** Effect of ionic strength as NaNO$_3$ concentration on Cu concentration in the cellulose-diethylentriamine gel layer.
3.8. Applications in sea water

The sampling location is located around Palu Bay. The source of copper metal pollutants is thought to come from domestic waste, settlements, and traditional mining around Palu City. All sampling locations show that copper content can be measured by the DGT method.

![Figure 8](image1.png)

**Figure 8.** Concentrations of Cu in Palu Bay Sea Water attached to cellulose-diethylenetriamine gel with polyacrylamide gel diffusion layer.

The greatest Cu level was found at location 3 (TP PA 3). In this location there are four drainage channels for small river water drainage and drainage water to Palu Bay water location and include surface water from the Poboya River location.

![Figure 9](image2.png)

**Figure 9.** Concentrations of Cu in Poboya River attached to cellulose-diethylenetriamine gel with polyacrylamide gel diffusion layer.
3.9. Applications in Poboya River

The DGT method was then tested using surface water, which is the water of the Poboya River that surrounds many traditional gold miners. The measurement results of Cu at two location points when compared to the water quality standard, the concentration of Cu metal is still below the threshold value that is allowed to be used to irrigate plants, but is relatively unsafe to use as drinking water.

4. Conclusion

The method of diffusion gradient in thin films using cellulose-diethylentriamine binding layer and a polyacrylamide gel diffusion layer may be used to uptake Cu labile in environmental waters. The performance test of cellulose-diethylentriamine binding layer with polyacrylamide showed that the Cu (II) concentration increased linearly until 12 hours, the initial concentration of the solution up to 1000 μg / L, the maximum concentration of Cu 0.78 mm diffusion gel, pH 4, and ionic strength with 0.01M NaNO3 at 30°C. The recovery of copper reached 92% with polyacrylamide diffusive gel. The application on the sea water samples of Palu Bay produced the concentration of copper metal of 12.72-90.19 μg/L. The application on the water samples of Poboya River produced copper concentration of 39.92-48.52 μg/L.

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