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Determination of Cu(II) in environmental water samples using polymer inclusion membrane-TAC optode in a continuous flow system

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Abstract

A polymer inclusion membrane was developed for the selective determination of copper (II) in river water system. It is composed of 42% di(2-ethylhexyl) phosphoric acid (D2EHPA) as the carrier, 8% dioctyl phthalate (DOP) as the plasticizer, 49% poly(vinyl chloride) PVC as the base polymer and 1% 2-(2-thiazolyazo)-p-cresol (TAC) as the chromophore. The system works by extracting the copper from the water sample forming copper-D2EHPA which then carries the metal along the PIM to form the green copper-TAC complex. The PIM-TAC was incorporated in a continuous flow system. The quantification was done using a circuit with a light emitting diode (LED) and a light dependent resistor (LDR) connected to a voltmeter. Voltage readouts on a computer were obtained for the results. Running the system under optimal conditions provided a limit of detection (LOD) of 0.10mg L^{-1} and a limit of quantitation (LOQ) of 0.35mg L^{-1}. The optimized CF-PIM-TAC system was used to determine the concentration of Cu(II) in water samples near mining sites.

Key words: polymer inclusion membrane, copper, 2-(2-thiazolyazo)-p-cresol, environmental, sensor

Introduction

Copper is used for different purposes and is released in the environment from different sources. When copper reaches high concentration in the environment, it can cause health risks to human beings and other organisms. [1, 2]. In the Philippines, monitoring of copper levels in water systems has been a part of the environmental programs. The Department of Environmental and Natural Resources (DENR) has set the maximum allowable limit of Cu(II) in fresh water surface to 0.02 mg L^{-1} [3].

Recent studies have developed optical sensors for metal extraction and detection. Optical sensors are known for their selectivity and inexpensive production [4, 5]. Polymer inclusion membrane is one of the technologies integrated in optical sensors that are used for the determination of copper concentration. It is made up of a base polymer, plasticizer and a carrier [6]. A chromophore is incorporated to improve its sensitivity to the metal of interest [7]. In this study, the PIM is composed of poly(vinyl chloride)(PVC) as the base polymer, dioctyl phthalate (DOP) as the plasticizer, di(2-ethylhexyl) phosphoric acid (D2EHPA) as the extractant and 2-(2-thiazolyl)-p-cresol (TAC) as the chromophore. This paper reports on the development and optimization of the PIM-TAC optode incorporated in the continuous flow system for the determination of Cu(II) in water systems near mining sites.

Experimental Details

The PIMs were optimized by dissolving different amounts of the base polymer (PVC), extractant (D2EHPA), plasticizer (DOP) and chromophore (TAC) with a total mass of 0.7g in 7.5 mL THF. At optimum condition, extraction and quantification of Cu(II) was done with a continuous flow (CF) system (Fig. 1). Interferences of the metal ions found in water samples were also studied. This system was then applied to water samples from the midstream of a river near a mining site.

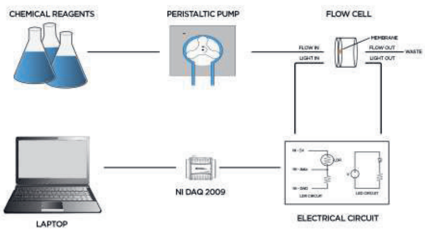

Fig. 1. Schematic diagram of the CF system

Results and discussion

The Cu(II)-TAC stoichiometry was determined using Job's method and mole ratio method which showed results of 1:1 ratio. The same results were observed by Rerkpalin, where she was able to postulate the structure of the complex (Fig 2) based on the IR spectra of TAC and Cu-TAC [8].

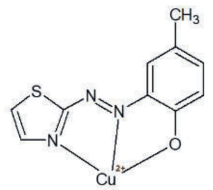

Fig 2. *Postulated structure of Cu(II)-TAC complex (generated using ChemSketch)*

After confirming the complexation of Cu(II) with TAC, the composition of the PIM was optimized. The LED wavelength, source phase acidity, membrane stability, flow rate, stop-time, and concentration of retrieving HCl solution were also taken into account for the optimization of CF-PIM-TAC system.

Table 1. Optimization of the PIM and CF system parameters.

Parameter	Optimal Value	Range
PIM components:		
D2EHPA (%, w/w)	42.0	
DOP (%, w/w)	8.0	6.0-10.0
PVC (%, w/w)	49.0	47.5-51.5
TAC (%, w/w)	1.0	0.5-1.0
Other parameters:		
pH of the source phase	3.5	1.0-14.0
HCl concentration (mol/L)	2.0	1.0-3.0
Flow rate (mL/min)	1.0	0.5-2.0
Stop-time (min)	5.0	3.0-10.0

In the interference studies conducted under optimum condition, negligible results were obtained from the common metal ions (i.e. Ca(II), Mg(II), Pb(II), Zn(II), Fe(III), Al(III), Cd(II), Ni(II), and Co(II)) found in water systems. Also, using the method in Harris [9] for the determination of LOD and LOQ, the system has an LOD of 0.10 mg L^{-1} and an LOQ of 0.35 mg L^{-1}.

The optimized system was then applied to the water samples from the midstream of a river that is located near a mining site in Benguet, Philippines. Results showed no statistically significant difference from that of the concentration using AAS (Table 2.)

Table 2. Determination of Cu(II) in river water samples using the optode CF method and AAS.

Sample Identification	C_{AAS} (SD) (n=3) (mg L^{-1})	C_{CF} (SD) (n=3) (mg L^{-1})
River water sample 1	0.518 (±0.009)	0.48 (±0.02)
River water sample 2	0.516 (±0.007)	0.44 (±0.07)

Conclusion

A CF-PIM-TAC was successfully developed for the on-line determination of Cu(II) in water systems. With the incorporation of TAC in PIM, Cu(II) was selectively extracted even in the presence of other metals. The results also showed that the Cu(II) in the river water sample exceeded the maximum allowable limit of 0.02 mg L^{-1} set by Philippine DENR for fresh water surfaces.

Author Disclosure

This article has been published in Sensors and Actuators B: Chemical (https://doi.org/10.1016/j.snb.2017.12.165) and all necessary permissions for conference presentations have been obtained.

References

[1] Agency for Toxic Substances and Disease Registry, (2004), ToxicologicalProfile for Copper. [ONLINE] [Last Accessed 19 September 2014]. Avaible at:https://www.atsdr.cdc.gov/toxprofiles/tp132.pdf.

[2] Environmental Aspects of Copper Production. [ONLINE] [Last Accessed 19September 2014] Available at: https://www.princeton.edu/~ota/disk2/1988/8808/880810.PDF.

[3] Philippine Department of Environmental and Natural Resources Administrative Order (DAO), No. 2016-08 [ONLINE] [Last Accessed 8 August 2017] Available at: http://server2.denr.gov.ph/uploads/rmdd/dao-2016-08. pdf.

[4] E. Pourbasheer, S. Morsali, A. Banaei, M.R.G. Aghabalazadeh, P. Norouzi,Design of a novel optical sensor for determination of trace amounts of copper by UV–vis spectrophotometry in the real samples, J. Ind. Eng. Chem. 26 (2015)370–374.

[5] H. Hisamoto, K. Suzuki, Ion-selective optodes: current developments andfuture prospects, Trends Anal. Chem. 18 (1999) 513–524.

[6] L.D. Nghiem, P. Mornane, I.D. Potter, J.M. Perera, R.W. Cattrall, S. Kolev,Extraction and transport of metal ions and small organic compounds usingpolymer inclusion membranes (PIMs), J. Membr. Sci. 281 (2006) 7–41.

[7] B.M. Jayawardane, Coo L. dlC, R.W. Cattrall, S.D. Kolev, The use of a polymerinclusion membrane in a paper-based sensor for the selective determinationof Cu(II), Anal. Chim. Acta 803 (2013) 106–112.

[8] W. Rerkpalin, Complex Formation of 2-(2'-Thiazolylazo)-p-cresol and ItsApplication as Chelating Reagent for Cadmium(II) and Copper(II) M.S. Thesis,Kasetsart University, 2003.

[9] Harris, D. (2010). *Quantitative Chemical Analysis (8th ed)*. New York: W. H. Freeman and Company.