DEVELOPMENT OF OPTICAL SENSOR MATERIAL FOR DETECTION OF CADMIUM USING ALIZARIN-RED S INDICATOR

Wan Elina Faradilla Wan Khalid[1*], Nurul Farahidora Binti Jaafar[1]

[1]*Faculty of Applied Sciences*
Universiti Teknologi Mara Negeri Sembilan, Kuala Pilah Campus, Pekan Parit Tinggi, 72000 Kuala Pilah

[*]*Corresponding author: wan_elina@uitm.edu.my*

Abstract

In this study, Alizarin Red S (ARS) reagent was used to detect cadmium (Cd^{2+}) in solution by using UV-Visible Spectrophotometer. Six parameters have been studied which are the effect of pH, effect of ARS concentration, photostability, linear range, reproducibility and interference study. ARS reagent form complex with Cd^{2+} and showed a maximum absorption at 424.50 nm in pH 6. Under optimized conditions, ARS reagent was able to detect the concentration of Cd^{2+} in the range of 0 – 5 ppm. The reproducibility study gives RSD values of 1.23% and 2.89% for the concentration of 1 ppm and 5 ppm, respectively. From this study, Fe^{3+} was found to interfere the most during the Cd^{2+} determination followed by Ni^{2+}, Hg^{+} and Cu^{2+}. The immobilization of the ARS reagent was conducted by using three immobilization matrix which is sol-gel, polyvinyl alcohol (PVA) and hybrid sol-gel/PVA. The finding suggested that the hybrid sol-gel/PVA can improve the leaching problem of the ARS reagent.

Keyword: Optical sensor; Cadmium; Alizarin Red-S; UV-Visible Spectrophotometer

Introduction

Heavy metals such as Hg^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+} and Cu^{2+} are the common environmental issue that can cause a threat to human health. Heavy metals which have the density of 4 g/cm^3 or 5 times larger than water (Buica et al., 2020; Ullah et al., 2018). Most of the heavy metals are toxic and can cause cancer, kidney failure and other fatal diseases even at lower concentration (Taneja et al., 2018; Zhang et al., 2020). Among different heavy metals, Cd^{2+} ion is considered highly toxic and generally will discharge from industrial waste and domestic wastewater. Hence, it is important to develop a method for Cd^{2+} ion detection, especially in water samples. A conventional method such as atomic absorption spectroscopy and inductively coupled plasma atomic emission spectroscopy have been used for Cd^{2+} ion detection. Although the conventional method offers accurate measurements and highly sensitive, these methods need trained personnel to handle the instruments and quite costly (Devadhasan & Kim, 2018; Gan et al., 2020). In this study, a spectrophotometric detection of Cd^{2+} was carried out using ARS indicator. Spectrophotometric analysis is a simple and rapid measurement method with high stability. ARS or sodium salt of 1,2-dihydroxyantraquinone-3-sulphonic acid (**Figure 1**) bears two hydroxyl groups in the positions 1 and 2 and a sulfo group in position 3 has been used to detect Cd^{2+} ion. Safavi et al., (2006) in their study has used ARS for determination of Cu^{2+}, Fe^{3+} and Al^{3+} ion simultaneously. The response was linear in the range of 140 and 4000 ng/mL with maximum absorbance at 505 nm. Supian et al., (2013) have fabricated Al^{3+} sensor based on ARS immobilize in the microsphere. In this study, ARS form reddish-orange complex with Al^{3+} in the range of 0.1–1.0 ppm with a response time of 35 s.

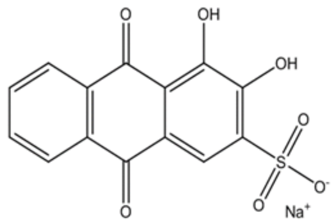

Figure 1 Structure of ARS

An immobilization study of ARS in the immobilization matrix has also been carried out to study the suitability of the ARS as a sensing material for Cd^{2+} determination. Usually, the immobilization of the chemical reagent has been carried out to develop an optical chemical sensor. The optical chemical sensor has attracted many researchers especially for heavy metal detection. Usually an optical chemical sensor is based on the interaction of the immobilized organic dye with an analyte and the measurements in the optical properties such as absorption, transmission and emission (Ullah et al., 2018). In this study, sol-gel, polyvinyl (alcohol) and hybrid sol-gel/PVA have been used to immobilize ARS indicator.

Materials and Methods

UV-Vis spectrophotometer with 1 cm matched cuvette was used to record or measure all the absorption spectrum and absorbance value in the wavelength range of 200 - 700 nm.

Absorption spectra of ARS reagent, Cd^{2+} and complex ARS-Cd^{2+}

The spectrum of ARS reagents, Cd^{2+} and complex ARS-Cd^{2+} were recorded using UV-Vis spectrophotometer in the wavelength range of 200-700 nm.

Effect of pH

For the determination of optimum pH, ARS was reacted with 5 ppm Cd^{2+} solution in the buffer solution pH 2 until pH 12.

Dynamic Range

For dynamic range determination, Cd^{2+} solution with the concentration range between 0 – 5 ppm was reacted with ARS solution.

Reproducibility Study

Reproducibility study was conducted to determine whether this method will give the same results for the determination of Cd^{2+}. Two different concentration of Cd^{2+} were used in this study, 1 ppm and 5 ppm. The reaction between ARS and 1 ppm Cd^{2+} was carried out in pH 6 and the same procedure was repeated for 10 times. The same steps also were carried out for 5 ppm Cd^{2+}.

Interference Study

Interference study was conducted to determine whether or not the presence of other ions can interfere with the current determination of Cd^{2+}. In this study, several kinds of cation and anions have been chosen to determine the level of interference to the analysis. Anions which have been chosen for this study is Cl^-, Br^-, NO_3^- and SO_4^{2-} while cation comprised of Cu^{2+}, Fe^{3+}, Hg^+ and Ni^{2+}. Mole ratios of Cd^{2+} to ions used were 1:1 and 1:10.

Preparation of Polyvinyl Alcohol (PVA)

About 10% (w/v) PVA was prepared by weighing 10 g of PVA powder in the beaker. Then 100 mL of deionized water was added into the same beaker. PVA solution was stirred on a hot plate until all the PVA was dissolved and homogeneous. PVA solution was then transferred into a bottle and kept overnight before used.

Preparation of Sol-gel

The sol-gel solution was prepared by mixing 30 mL of tetraethyl orthosilicate (TEOS), 30 mL of deionized water, 0.5 mL of 0.1 M HCl and 31 mL of ethanol in a 200 mL beaker. The sol-gel solution was stirred for 2 hours by using magnetic stirrer until homogenous (Wan Khalid et al., 2014). Then, the sol-gel solution was transferred into a bottle and it was kept overnight in the freezer before used.

Immobilization of ARS in sol-gel, PVA and Hybrid sol-gel/PVA

For the sol-gel film, ARS reagent was mixed with the 2 mL of sol-gel in the 25 mL beaker. For the PVA solution, ARS reagent was mixed with the 2 mL of PVA solution and for the hybrid sol-gel/PVA solution, the ARS reagent was mixed with 2 mL of PVA and 2 mL of sol-gel. Then the solution in the three different beakers was stirred for about 1 hour. After the solution was homogenized, 20 μL of each solution was drop coated into three different transparency film and was left to dry for 1 day.

Leaching test between PVA and hybrid sol-gel/PVA

For this study, the mass of ARS was fixed at 0.2 g with the volume ratio of the sol-gel and PVA 1:1. Sol-gel/PVA hybrid film was immersed in the deionized water in a cuvette every 2 minutes for 14 minutes. Then, the same method was repeated for PVA film. All the observation was recorded.

Results and Discussion

Absorption Spectra between ARS Reagent and Cd^{2+}

Figure 2 shows the absorption spectrum of the ARS reagent and complex ARS-Cd^{2+}. A complex will form color when the reagents have a chromophore group (Holzbecher et al., 1976). ARS, which is orange red, will produce a yellow complex when it reacted with Cd^{2+}. All the measurements and absorbance value were made at wavelength 424 nm. **Figure 3** shows the expected chemical structure of the ARS-Cd^{2+} complex.

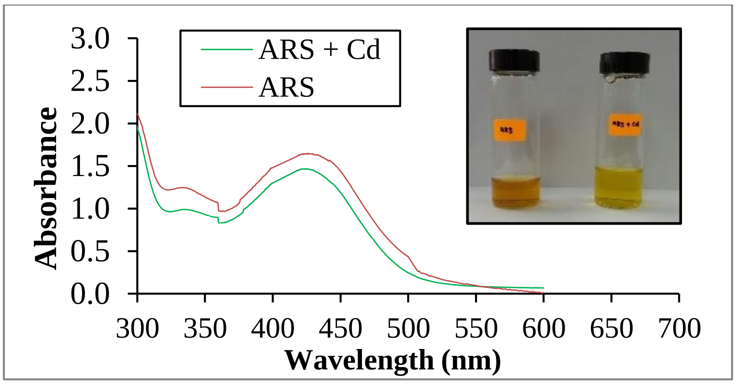

Figure 2 Absorption spectrum of ARS reagent and complex ARS-Cd^{2+} with ARS concentration of 3.71×10^{-4} M and Cd^{2+} at 5 ppm (Inset: Colour of ARS reagent and complex ARS-Cd^{2+})

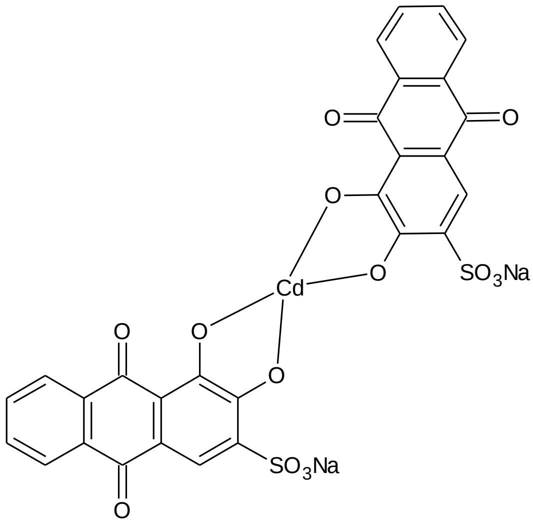

Figure 3 Expected chemical structure of the Cd^{2+}-ARS complex

pH study

Study of pH was carried out to determine the optimum pH for the complete reaction between ARS and Cd^{2+}. The complete reaction between ARS and Cd^{2+} occurred at pH 6.

Dynamic Range

In this study, the concentration of ARS reagent was fixed at 3.71 x 10^{-4} M while the Cd^{2+} used were within 0 - 5 ppm. Based on **Figure 4**, it shows that the absorbance increased as the concentration of Cd^{2+} increased and the response was linear in the concentration range of 0 – 5 ppm. Ullah & Haque (2011) has reported almost the same trend in the concentration of 0.1 – 40 µg mL^{-1}.

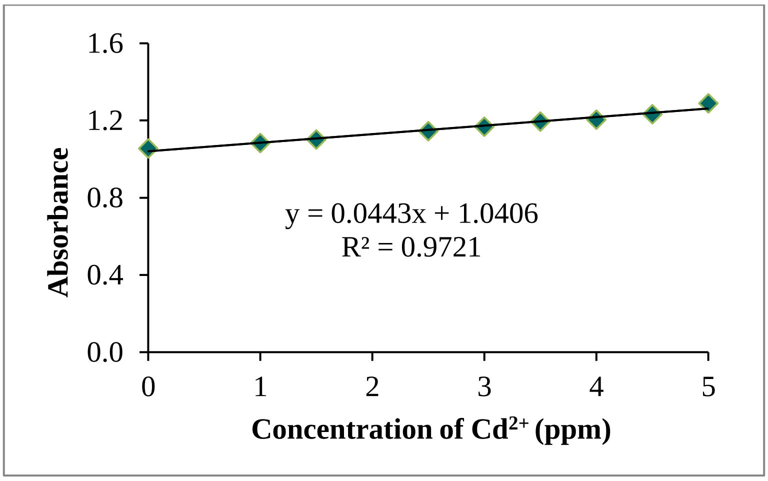

Figure 4 Plot of absorbance versus Cd^{2+} concentration in the range of 0 - 5 ppm with ARS concentration of 3.71 x 10^{-4} M and pH 6 at wavelength 424.50 nm

Reproducibility Study

This study will determine whether these methods could give a similar result for each time an analysis was carried out. Two different concentration of Cd^{2+} solutions were used (1 ppm and

5 ppm) and the measurements were repeated 10 times for each concentration of Cd^{2+} (**Figure 5**). The RSD value for reproducibility study was found to be 1.23% for 1 ppm and 2.89% for 5 ppm. Small RSD value indicates that the complex produces a similar absorbance and capable to provide the same response for every measurement. Based on the RSD value, it indicates the good reproducibility of the reaction between ARS and Cd^{2+}.

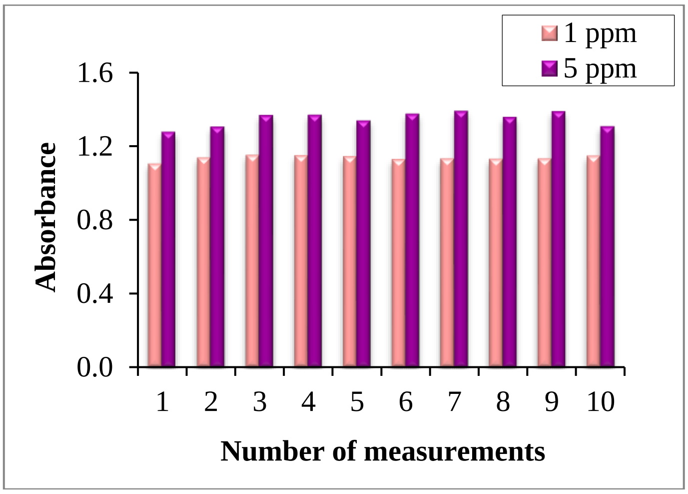

Figure 5 Reproducibility study of the ARS-Cd^{2+} complex with 1 ppm and 5 ppm Cd^{2+}

Interference study

Interference study was conducted to determine whether the presence of other ions would interfere with the determination of Cd^{2+}. The effect of foreign ions on the absorbance of the ARS-Cd^{2+} complex is summarised in **Table 1**. Positive interference normally occurred when the cations react with the reagent. Then, the reaction will produce more intense coloured species and resulting in a higher reading in absorbance. The negative interference produces a result from the reaction of the anions with the analyte being determined and lead to the decrease in the absorbance (Supian et al., 2013). From this study, Fe^{3+} was found to interfere the most during the Cd^{2+} determination followed by Ni^{2+}, Hg^{+} and Cu^{2+}. The interference from Cu^{2+} and Fe^{3+} was predictable in this study because ARS can also form complex with both cations (Safavi et al., 2006; Supian et al., 2013). As mentioned in the study by Safavi et al., (2006), anion Br^{-} did not show any interference to the analysis.

Table 1 Relative error during the determination of Cd^{2+} in the presence of cations and anions

Ions	Mole ratio (Cd^{2+}: Interference ion)	Relative error (%)
Cu^{2+}	1:1	23.48
	1:10	26.91
Fe^{3+}	1:1	21.94
	1:10	46.36
Hg^{+}	1:1	27.16
	1:10	29.56
Ni^{2+}	1:1	27.51
	1:10	30.16
Br^{-}	1:1	0.86
	1:10	-1.12
Cl^{-}	1:1	-3.60

	1:10	-38.13
NO_3^-	1:1	-12.08
	1:10	-35.99
SO_4^{2-}	1:1	-2.83
	1:10	-33.50

Note: Interference (%) = ((*x*-*y*)/*y*) x 100, where *x* is the absorbance value for mixed solution of Cd^{2+} and foreign ions, *y* is the absorbance value for Cd^{2+} solution only.

Immobilization of ARS in sol-gel, PVA and hybrid sol-gel/PVA

Immobilization of a chemical reagent into the immobilization matrix is one of the essential methods in the fabrication of the optical sensor. In this study, ARS reagent was immobilized in three types of immobilization matrix namely sol-gel, PVA and hybrid sol-gel/PVA by using drop coat method. Sol-gel has been widely used for sensor development during the past decade. However, the main problem of the sol-gel film is leaching of reagent from the sol-gel film and cracking on the film. Therefore, efforts have been made to resolve these problems. Mohammad et al., (2014) has used hybrid sol–gel/butyl acrylate to immobilize the 3-methyl-2-benzothiazolinone hydrazine (MBTH) dye. **Figure 6** shows the observation when the sol-gel was drop coat on the transparency film. After the sol-gel film was left for one day, the cracking on the sol-gel film can be seen while hybrid sol-gel/PVA shows no cracking

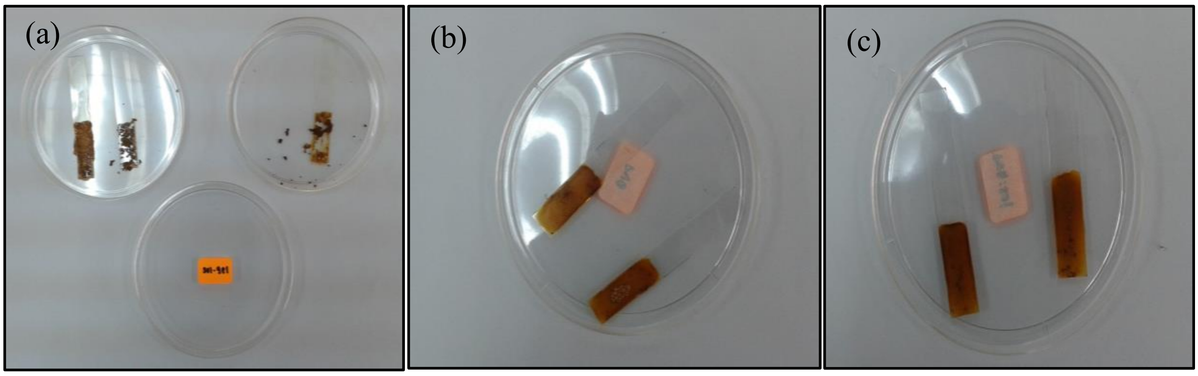

Figure 6 ARS reagent immobilized in (a) sol-gel (b) PVA (c) Hybrid sol-gel/PVA

Study of ARS Leaching from the Film

Leaching test was conducted to verify whether or not sol-gel/PVA hybrid film with volume ratio 1:1 could overcome the leaching tendency of the pure PVA film. Optical sensor development that involves immobilization of chemical reagent into the suitable matrix or polymers usually has a leaching problem. Chemical reagent is likely to leach out from the immobilization matrix when immersed in the sample solution that make the lifetime of the sensor decrease. Leaching of the reagent from the sol-gel matrix was the main problem to develop a longer lifetime optical sensor. Mohammad et al., (2014) also stated that the main problem of the sol-gel film is leaching and cracking on the film. From the observation, PVA film was easily leached out to the solution (**Figure 7**) while the sol-gel/PVA hybrid film (**Figure 8**) has less leaching as compared to the pure PVA film. This happened because the highly hydrophilic PVA must be crosslinked either chemically or physically to make it insoluble and could assist in retaining the ARS reagent in the matrix (Mohd Zain et al., 2011).

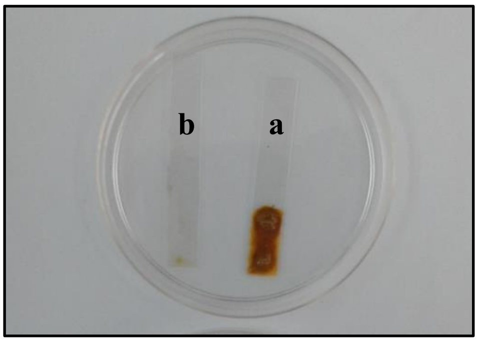

Figure 7 The PVA film (a) before and (b) after the leaching test

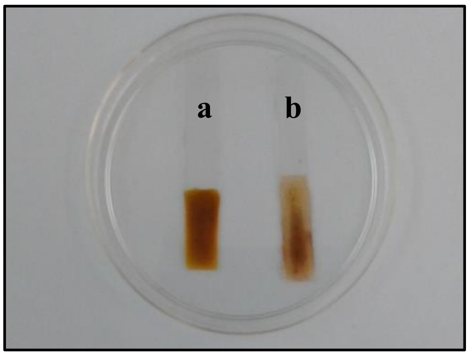

Figure 8 The hybrid sol-gel/PVA film (a) before and (b) after the leaching test

Conclusion

As a conclusion, a simple, rapid, and cheap detection method for Cd^{2+} has been developed by using ARS. It was found that reaction between ARS reagent and Cd^{2+} give a maximum absorption at 424.50 nm. ARS reagent produces a yellow complex when reacting with Cd^{2+} at pH 6 with a linear range of 0 – 5 ppm. Other than that, this study also provides a low RSD value for photostability and reproducibility study. The RSD value for photostability is 1.77% while the RSD value for reproducibility study for 1 ppm and 5 ppm was found to be 1.23% and 2.89%, respectively.

Acknowledgement

The authors would like to thank Universiti Teknologi MARA Negeri Sembilan for the services and facilities to carry out the work.

Conflict of interests

Author declares no conflict of interest.

References

Buica, G. O., Stoian, A. B., Manole, C., Demetrescu, I., & Pirvu, C. (2020). Zr/ZrO_2 nanotube electrode for detection of heavy metal ions. *Electrochemistry Communications*, *110*, 2–7.

Devadhasan, J. P., & Kim, J. (2018). A chemically functionalized paper-based microfluidicplatform for multiplex heavy metal detection. *Sensors & Actuators: B. Chemical*, *273*, 18–24. https://doi.org/10.1016/j.snb.2018.06.005

Gan, Y., Liang, T., Hu, Q., Zhong, L., Wang, X., Wan, H., & Wang, P. (2020). In-situ detection of cadmium with aptamer functionalized gold nanoparticles based on smartphone-based colorimetric system. *Talanta*, *208*. https://doi.org/10.1016/j.talanta.2019.120231

Holzbecher, Z., Divis, L., Kral, M., Sucha, L., & Vlacil, F. (1976). *Handbook of organic reagents in inorganic analysis*. Ellis Horwood Limited.

Mohammad, R., Ahmad, M., & Heng, L. Y. (2014). Chilli hotness determination based on optical capsaicin biosensor using stacked immobilisation technique. *Sensors and Actuators B: Chemical*, *190*, 593–600. https://doi.org/10.1016/j.snb.2013.09.023

Mohd Zain, N. A., Suhaimi, M. S., & Idris, A. (2011). Development and modification of PVA-alginate as a suitable immobilization matrix. *Process Biochemistry*, *46*, 2122–2129. https://doi.org/10.1016/j.procbio.2011.08.010

Safavi, A., Abdollahi, H., & Mirzajani, R. (2006). Simultaneous spectrophotometric determination of Fe(III), Al(III) and Cu(II) by partial least-squares calibration method. *Spectrochimica Acta Part A*, *63*, 196–199. https://doi.org/10.1016/j.saa.2005.05.004

Supian, S. M., Ling, T. L., Heng, L. Y., & Chong, K. F. (2013). Quantitative determination of Al(III) ion by using Alizarin Red S including its microspheres optical sensing material. *Analytical Methods*, *5*, 2602–2609. https://doi.org/10.1039/C3AY40238J

Taneja, P., Manjuladevi, V., Gupta, K. K., & Gupta, R. K. (2018). Detection of cadmium ion in aqueous medium by simultaneous measurement of piezoelectric and electrochemical responses. *Sensors and Actuators B: Chemical*, *268*, 144–149. https://doi.org/10.1016/j.snb.2018.04.091

Ullah, M. R., & Haque, M. E. (2011). Spectrophotometric Determination of Toxic Elements (Cadmium) in Aqueous Media. *Journal of Chemical Engineering*, *25*(1), 1–12. doi:10.3329/JCE.V25I0.7233

Ullah, N., Mansha, M., Khan, I., & Qurashi, A. (2018). Nanomaterial-based optical chemical sensors for the detection of heavy metals in water: Recent advances and challenges. *Trends in Analytical Chemistry*, *100*, 155–166. https://doi.org/10.1016/j.trac.2018.01.002

Wan Khalid, W. E. F., Ahmad, M., & Heng, L. Y. (2014). Characterization of a simple optical chemical sensor for Cu(II) detection based on immobilization of lipophilized nitroso-r reagent in sol-gel matrix. *Chiang Mai Journal of Science*, *41*(2), 383–394.

Zhang, M., Zhu, G., Li, T., Lou, X., & Zhu, L. (2020). A dual-channel optical fiber sensor based on surface plasmon resonance for heavy metal ions detection in contaminated water. *Optics Communications*, *462*, 124750. https://doi.org/10.1016/j.optcom.2019.124750