IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 12, Issue 10 Ser. I (October. 2019), PP 49-53
www.iosrjournals.org

Immobilised of 4-(Dimethylamino)benzaldehyde (DABD) as an optical reflectance sensor for copper(II)

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Abstract: *Immobilisation of 4-(Dimethylamino)benzaldehyde (DABD) onto chitosan film was attempted in this research to develop an optical Cu(II) sensor. The measurements of wavelength were carried out at 736nm since it yielded the most significant difference in reflectance spectra before and after the reaction. At pH 3.0, the optimum response was obtained. In the concentration range of* 0.5×10^{-3} - 0.4×10^{-3} *M, the linear dynamic range of Cu(II) was found. From different probes (n = 7), the sensor response gives the value of relative standard deviation (R.S.D.) is 3.5 %. The results of the photostability were found to be good, with the R.S.D value of 1.06 %. Also, in this work, the effect of interfered ions at 1:1 molar ratio of Cu(II): foreign ion was studied.*
Keywords: *Immobilised 4-(Dimethylamino)benzaldehyde (DABD); chitosan; Optical fibre; Reflectance*

Date of Submission: 01-11-2019 Date of Acceptance: 16-11-2019

I. Introduction

The determination of heavy metals in the environment is of great interest because of their hazardous effects on the ecosystem, and human health depends on the dose and toxicity. Cu(II), like heavy metal, is, on the one hand, necessary for life, but the other side is very toxic for the organism, such as algae, fungi, and many bacteria and viruses (Mayr, Klimant, et al. 2002). Copper is suspected of causing liver damage in children. Drinking water can be a potential source of intake in heavy copper. Numerous analytical procedures have been proposed for the detection of Cu(II) (Mahendra, Gangaiya, et al. 2002). The use of immobilised reagents for the detection of copper rose rapidly today in the field of chemical sensing using the optical fibre sensor. The reagent usually is physically trapped by adsorption, attracted electrostatically or chemically bound to the reliable support. Many reagents immobilised on chitosan OptoSensors developing film type of flow cell, and probe type sensors have been described previously(Ahmad and Narayanaswamy 1994).

In this paper, the performance of the immobilised 4-(Dimethylamino)benzaldehyde (DABD) (Figure 1) on chitosan film as a reagent phase in the development of optical reflectance sensor for Cu(II) determination has been demonstrated. The 4-(Dimethylamino)benzaldehyde (DABD) forms a complex with Cu(II). According to the ligand field theory, when the copper (II) metal ion reacts with the ligand, the unshared of electron pairs are donated by oxygen atoms from the ligand to the vacant d subshell of metal ion to form coordinated covalent bonds (Cotton, Wilkinson, et al. 1999).

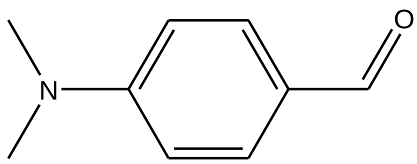

Figure 1: The structure of 4-(Dimethylamino)benzaldehyde (DABD) used in this study

Experimental section

In this study, the materials utilised are (a) chitosan, 4-(Dimethylamino)benzaldehyde, NaOH, and CH_3OH (b) Cu^{2+} (Sigma), (c) (Aldrich; Mw 1.86·105) and phosphate buffer (rest), (d) hydrochloric acid (HCl) 36% (e) ethanol 95% (Systerm) and (f) acetic acid (Ajax chemicals). All these chemicals are utilized without any purification.

Instrumentation and measurement procedure

In spectrophotometric studies, all absorption measurements are carried out by using UV–vis spectrophotometer, model Varian-Cary win UV 50. A glass slide coated with 4-(Dimethylamino)benzaldehyde

(DABD) is immobilised in a chitosan film submerged in more felt paper containing 4-(Dimethylamino)benzaldehyde (DABD) (0.003 M) phosphate buffer solution (pH 3) and Cu^{2+} (0.003 M). Absorption is recorded between 250 nm and 800 nm.

Construction of sensor

In these studies, sensor construction is done using one type of chitosan. Chitosan powder, which is mixed with a 0.1% (v/v) HCl solution, is stirred for 2 hours. Chitosan solution (0.2%, w/v) is made by dissolving 2 g of chitosan powder in 100 ml of HCL (0.1%, v/v). The viscous chitosan solution is stirred overnight at room temperature. Standard Cu^{2+} solution of 7×10^{-3} M is made by melting 0.032 g of Cu^{2+} in 25 ml deionised water. 4-(Dimethylamino)benzaldehyde (DABD) standard stock solution of 7×10^{-3} M is prepared by melting 0.043 g in 25 ml of deionised water. Another chitosan solution (2%, w/v) is made by dissolving 2 g of chitosan powder in 100 ml of hydrochloric acid (0.1%, v/v). The viscous chitosan solution is stirred overnight at room temperature. A homogeneous stock solution of 4-(Dimethylamino)benzaldehyde (DABD)/ chitosan mixture is made by mixing 2.5 ml of a 2% (w/v) chitosan solution and 1.5 ml of 4-(Dimethylamino)benzaldehyde (DABD) solution in an eppendorf tube. The mixture is stirred slowly for 45 minutes. The stock solution is freshly prepared before the fabrication of the optical film. The formulation will be changed accordingly to the experimental parameters being examined. In the beginning, 4 ml and 0.5 ml pH 3 of the stock 4-(Dimethylamino)benzaldehyde (DABD)/chitosan mixture is pipetted into a filter paper and smeared gently over an area. This solution is then dried at room temperature. The immobilised 4-(Dimethylamino)benzaldehyde (DABD) should be kept at 4 °C when not being used (Zhu, Zhu, et al. 2002).

II. Results and Discussion

In this study, several experiments are carried out to optimise sensor response. In order to evaluate the ability of the sensor based on the detection limit, optimal conditions, dynamic range, and stability, Cu^{2+} has been used as a substrate.

The UV–vis spectrum of 4-(Dimethylamino)benzaldehyde (DABD), Cu^{2+}, and (DABD) with Cu^{2+} (complex) showed three bands at 0.0005nm, 0.0140nm, and 0.0636nm, respectively. These bands are assigned to π-π*, n-π*, and *d-d* transitions. At 3×10^{-3} M, the Uv–vis spectra of the complex, as shown in Figure 2, displays similar absorption spectra of the ligand that are shifted to higher wavelengths. Findings show an increase or appearance of the peak due to d-d transition that is verified by the carbonyl group and appearance of the new peak (Sundari, Ahmad, et al. 2006).

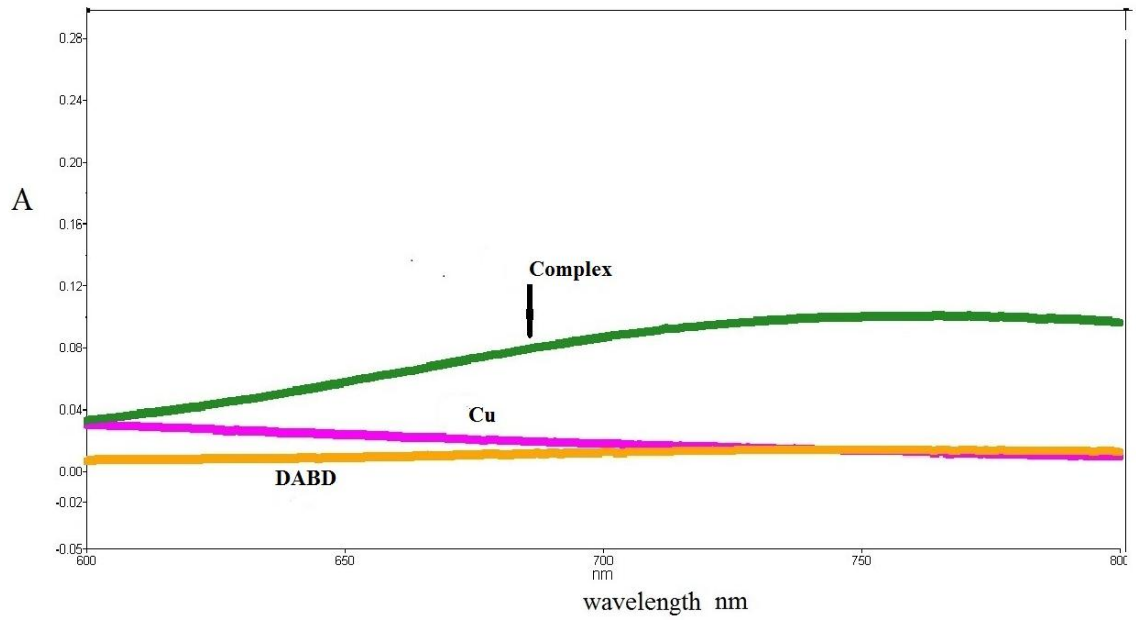

Figure 2: UV–vis absorption spectra of the solution (DABD), $Cu^{2+,}$ and Complex at 3×10^{-3}M.

The influence of pH is also examined using different pH values in 3×10^{-3}M phosphate buffer, as in Figure 3. Besides, pH is an essential factor throughout extraction and storage due to its correlation with shelf life and stability of the product (Zhu, Zhu, et al. 2002). Hence, the mean pH of immobilisation 4-(Dimethylamino)benzaldehyde (DABD), a reagent with Cu^{2+} analyte, is pH 3.0.

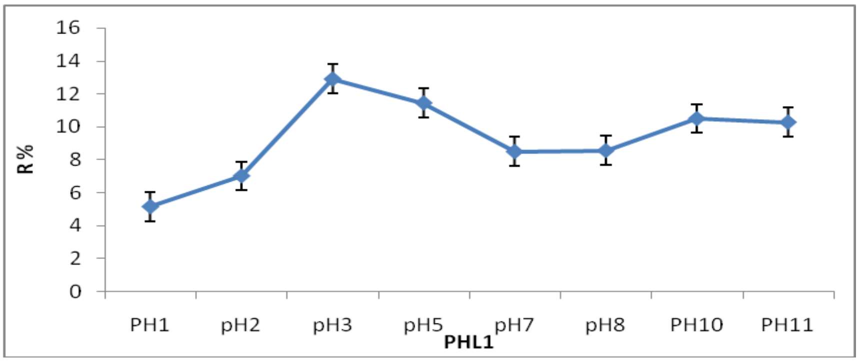

Figure 3: The Effect of working pH on the absorbance of (DABD) upon reaction with (3 × 10-3) Cu^{2+} solution.

Different amount of (DABD) is used to identify the influence of loading on sensor response. Figure 4 displays the optimum (DABD) loading that is seen at a concentration of 0.007 M. Therefore, 0.007 M is utilized for further immobilisation processes.

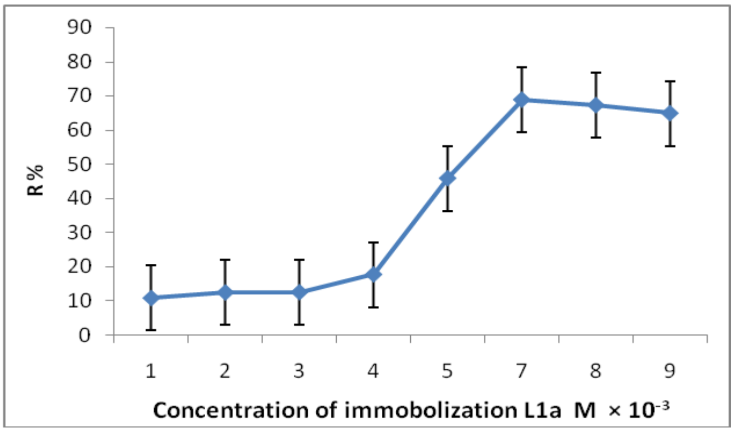

Figure 4: The effect of (DABD) concentration on the response of the method when the Cu^{2+} concentration used was at 3×10^{-3} M with a buffer solution of pH 3.0.

Figure 5 displays the response curve of the sensor towards Cu^{2+} in the concentration range of 0.005 to 0.5 M. Initially, the reflectance signal increases radically as the increase of the Cu^{2+} concentration. As the Cu^{2+} concentration gets high, the response will slowly level off and will get saturated at 0.4 M Cu^{2+}. A higher Cu^{2+} concentration will allow more reaction between the sensor and the analyte molecules which are present in the next phase. Hence, a higher signal is noticeable. The reflectance signal will eventually plateau since nearly all immobilisation sites are entirely full of analyte molecules. The figure below illustrates the calibration curve obtained under optimised circumstances. The relative reflectance has a linear correlation (R^2 = 0.948) with Cu^{+2} concentration in the concentration range of 0.4 M.

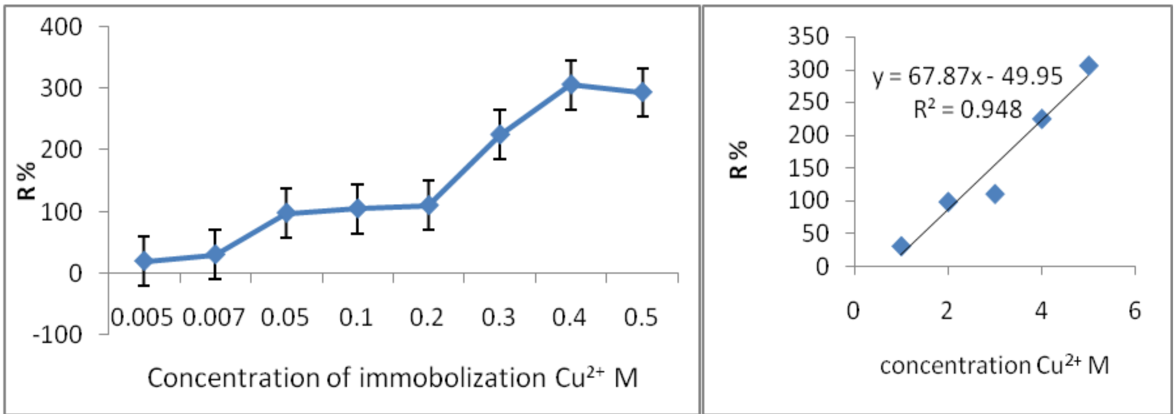

Figure 5: The response curve of the method at different concentrations of Cu^{2+}. Inset is the linear dynamic range of the Cu^{2+} solution.

The reproducibility of the immobilised 4-(Dimethylamino)benzaldehyde (DABD), that iscarried out at a Cu^{2+} concentration of 3×10^{-3} M is good with a calculated RSD value of 3.55% (Figure 6). The sensor demonstrates excellent stability for about six hours with a calculated RSD value of 1.069% (Figure 7). An interference from several ions during Cu(II) determination was also examined in this work. Table 1 summarises the degree of interference measured for several foreign ions at 1:1 molar ratio of Cu(II): foreign ion. The tolerance ratio of each foreign ion was taken as the most considerable amount yielding an error below ±5% (Yusof and Ahmad 2002). From Table 1, Al(III), Fe(II), Co(II), Ni(II), and F^- exhibited error values lower than 5%, and therefore these ions did not interfere during Cu(II) detection. The advantage of employing (DABD) based sensor over the conventional methods for Cu(II) determination lies in the ease of its detection, fewer chemicals used, and less time-consuming.

Table 1: The degree of interference at 1:1 molar ratio of Cu(II): foreign ion

Ion	Relative error, % (reagent solution)
Co^{2+}	-68.25
Ni^{2+}	-102.44
Fe^{2+}	-9.24
F^-	-8.21

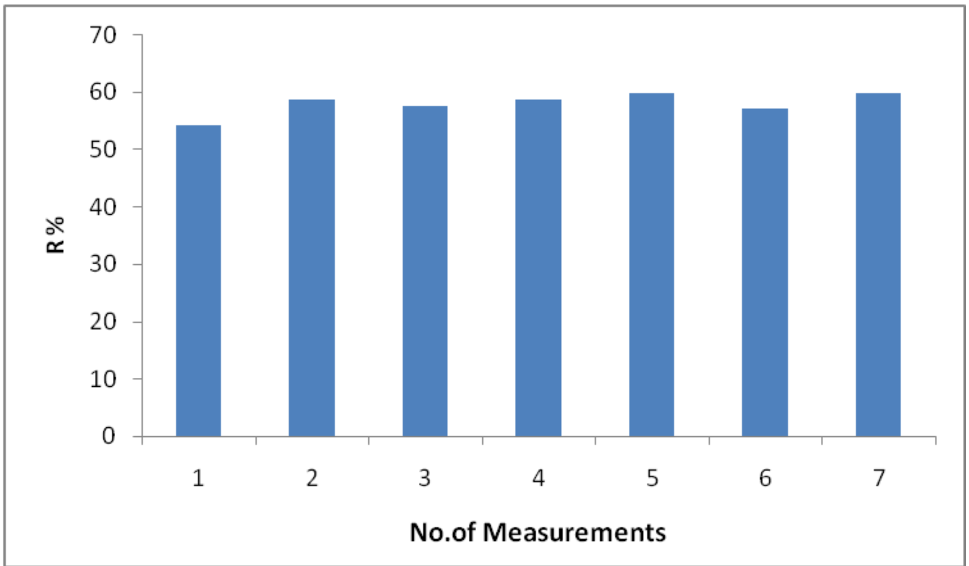

Figure 6: The reproducibility of the reagent (DABD) 3×10^{-3} M Cu^{2+} analyte forwards, in phosphate buffer (pH 3.0).

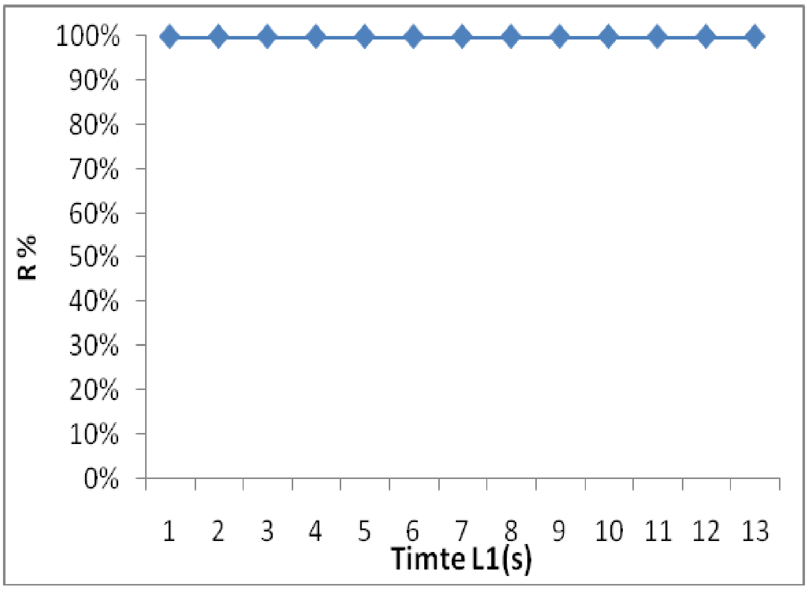

Figure 7: The photostability of (DABD) against time.

III. Conclusions

Usage of chitosan as a matrix for 4-(Dimethylamino)benzaldehyde (DABD) immobilisation in the development of an optical Cu^{2+} sensor has been examined in this study. After being exposed to the substrate for a day, the colour intensity of the adduct will increase proportionally with the increase of substrate concentration. The sensor has excellent sensitivity, photostability, and reproducibility features. The solution used for operation is maintained at pH 3, and the concentration of the reagent is 7×10^{-3} M. The reproducibility study shows a good RSD value of 3.55%. Photostability response with RSD of 1.069% is utilised to examine the process of photobleaching. 4-(Dimethylamino)benzaldehyde (DABD) is utilised as a solution and observed using Cu^{2+}. Al(III), Fe(II), Co(II), Ni(II), and F^- exhibited error values lower than 5%, and therefore these ions did not interfere during Cu(II) detection. The sensor which is developed has good potential in determining the quantity of Cu^{2+} in water.

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IOSR Journal of Applied Chemistry (IOSR-JAC) is UGC approved Journal with Sl. No. 4031, Journal no. 44190.

Rashd. M. El-Ferjani. " Immobilised of 4-(Dimethylamino)benzaldehyde (DABD) as an optical reflectance sensor for copper(II)." IOSR Journal of Applied Chemistry (IOSR-JAC) 12.10 (2019): 49-53.