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## ORIGINAL ARTICLE

# Highly selective and sensitive determination of copper ion by two novel optical sensors

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## KEYWORDS

Copper ion;  
Optical sensor;  
1,1'-2,2'-(1,2-Phenylene)bis(ethene-2,1-diyl)dinaphthalen-2-ol (L<sup>2</sup>);  
1,1'-4-Nitro-1,2-phenylene)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-lidene)dinaphthalen-2-ol (L<sup>1</sup>)

**Abstract** New optical sensors for the determination of copper ion by incorporation of 1,1'-(4-nitro-1,2-phenylene)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-lidene)dinaphthalen-2-ol(L<sup>1</sup>), 1,1'-2,2'-(1,2-phenylene)bis(ethene-2,1-diyl)dinaphthalen-2-ol (L<sup>2</sup>), dibutylphthalate (DBP) and sodium tetraphenylborate (Na-TPB) to the plasticized polyvinyl chloride matrices were prepared. The tendency of both ionophores (L<sup>2</sup> and L<sup>1</sup>) as chromoionophore was significantly enhanced by the addition of DBP to the membrane. The proposed sensors benefit from advantages such as high stability, reproducibility and relatively long lifetime, good selectivity for Cu<sup>2+</sup> ion determination over a large number of alkali, alkaline earth, transition and heavy metal ions. At optimum values of membrane compositions and experimental conditions, both sensors' response was linear over a concentration range of  $7.98 \times 10^{-6}$  to  $1.31 \times 10^{-4}$  mol L<sup>-1</sup> and  $1.99 \times 10^{-6}$  to  $5.12 \times 10^{-5}$  mol L<sup>-1</sup> for L<sup>2</sup> and L<sup>1</sup>, respectively. Sensor detection limit based on the definition that the concentration of the sample leads to a signal equal to the blank signal plus three times of its standard deviation was found to be  $3.99 \times 10^{-7}$  and  $5.88 \times 10^{-7}$  mol L<sup>-1</sup> for L<sup>2</sup> and L<sup>1</sup>, respectively. The response time of the optodes (defined as the time required reaching the 90% of the peak signal) was found to be 5–8 min for L<sup>2</sup> and 20–25 min for L<sup>1</sup> based sensor. The proposed optical sensors were applied successfully for the determination of Cu<sup>2+</sup> ion content in water samples.

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## 1. Introduction

Although copper (ions) is essential for living organisms, at high levels it has high toxicity to some organisms (Fleming and Trevors, 1989; Morrison and Berthon, 1995). It has high toxicity to bacteria at higher concentrations and restricts the self-purification ability of rivers and seas and reduces the ability of biological reprocessing systems in water (the critical limit being 1 mg/kg) (Forstner and Wittman, 1979). Copper (II)

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ions emerged to different ecosystems from various industrial effluents such as waste waters of electro-plating plants and water supply systems due to corrosion of copper pipes. Determination of copper assumes importance in view of its widespread occurrence in environmental samples. Although large concentrations of copper can be tolerated by human, its excessive dosage and long term exposure may cause irritation of the nose, mouth and eyes. It causes headache and stomach problems, while its maximum tolerable level is  $2.0 \text{ mg L}^{-1}$  in drinking water (Ibaoglu et al., 2004; Citak and Tuzen, 2010; Tuzen et al., 2008; Kazi et al., 2010; Afridi et al., 2009; Soyлак et al., 1997; Narin et al., 2001; Soyлак, 2004). Its excessive intake manifests in certain diseases in humans such as Menke's syndrome and Wilson's disease. Thus, the determination of copper is important in view of its utility as well as toxicity.

Optical chemical sensors or optodes have become an important area of research. Optical sensors are compact and ideally are miniaturizable, while at the same time they are free of electrical interference and are based on simple photometric measurements. Many optical chemical sensors utilize color complexing (Madden et al., 1996; Cov et al., 1998; Oehme et al., 1998) or redox reagent (Newcombe et al., 1994, 2000) loaded polymeric membrane. These membranes suffer from limitation such as leakage of the reagent into aqueous solutions. The ideal and simple loading technique to produce a highly stable structure of molecules is its direct immobilization on the surface of membrane (Ensafi and Kazemzadeh, 1999, 2002) or increasing the lipophilicity of the corresponding reagent (Sands et al., 2002). During the past two decades, considerable attention devoted to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors (Snell and Metzler, 1968; Djebbar et al., 1997). This may be attributed to their stability, biological activity and potential applications in many fields such as oxidation catalysis and electrochemistry. Schiff's bases are characterized by their capacity to completely bind metal ions to form a chelate. To our knowledge, no such studies have been done on copper complexes of these polydentate Schiff base ligands. In this work, highly selective and sensitive optical sensors for  $\text{Cu}^{2+}$  were investigated and applied successfully for the analysis of real samples. The proposed sensors have following advantages: (1) Highly selective and sensitive for  $\text{Cu}^{2+}$  ion; (2) Operation in the visible range in the wide pH range; (3) Simple preparation of ionophores with high yield in short time; (4) Wide dynamic working range; (5) Applicability in various matrices with low  $\text{Cu}^{2+}$  ion concentrations; (6) Low RSD and high recoveries and low detection limit comparable with expensive instruments such as flame atomic absorption spectrometry.

## 2. Experimental

### 2.1. Material and reagents

All reagents from Merck (Dermasdat, Germany) were of analytical reagent grade and used as purchased without further purification, except for vacuum drying. For membrane preparation, high molecular weight polyvinyl Chloride (PVC), dibutyl phthalate (DBP) and freshly distilled tetrahydrofuran (THF) were used. Sodium tetraphenylborate ( $\text{NaTPB}$ ) was used as an additive (in the membranes) and as the ionic strength stabilizer in the spectrophotometric solution

studies. The metal ions tested were of their nitrate salt. Doubly distilled and deionized water was used throughout. A stock solution of  $10^{-3} \text{ M}$  copper (II) solution was prepared by weighing  $0.012 \text{ g}$  of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Fluka) and adjusting the volume to  $50 \text{ mL}$ . Working standard solutions of lower concentrations were prepared by suitable dilutions of the stock solution with water. Buffer solutions were prepared from boric acid/citric acid/phosphoric acid ( $0.04 \text{ mol L}^{-1}$ ) and the pH adjustments were made by the addition of sodium hydroxide solutions ( $1.0 \text{ mol L}^{-1}$ ).

### 2.2. Instrumentation

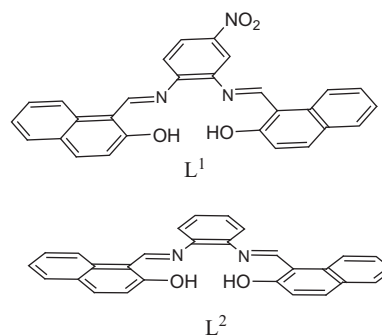
The UV-VIS absorbance spectra were recorded on a Jasco (V-530) spectrophotometer (Made in Japan) with  $1.0 \text{ cm}$  glass cell was used. A Jenway model 692 (Metrohm) (Made in England) pH meter was used to measure pH. All experiments were operated at room temperature,  $25 \pm 1 \text{ }^\circ\text{C}$ .

### 2.3. Preparation of 1,1'-2,2'-(1,2-phenylene)bis(ethene-2,1-diyl)dinaphthalen-2-ol ( $L^2$ ) and 1,1'-(4-nitro-1,2-phenylene)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-lidene)dinaphthalen-2-ol( $L^1$ )

The ligand,  $L^2$  was prepared according to our previous publication (Ghaedi et al., 2012). The ligand  $L^1$  was also synthesized by a procedure similar to  $L^2$  by condensation of 4-nitro-1,2-phenylenediamine and 2-hydroxy-1-naphthaldehyde in absolute EtOH under reflux for 4–5 h. Elemental analysis, %  $\text{C}_{28}\text{H}_{19}\text{N}_3\text{O}_4$ : C, 72.88; H, 4.15; N, 9.11; found: C, 71.9; H, 4.3; N, 9.7. IR(KBr,  $\text{cm}^{-1}$ ): 3300–3500(bs, vOH), 3058(w, CH– Aromatic), 2850(w,  $\text{CH}_{\text{imine}}$ ), 1633(vs  $\text{C}=\text{N}$  (asym)), 1602(s,  $\text{C}=\text{N}$  (sym)), 1580(m,  $\text{C}=\text{C}$ ), 1485(s,  $\text{NO}_2$  (asym)), 1314(m,  $\text{NO}_2$  (sym)), 1175(m, C–N), 1091(m,  $\text{C}-\text{O}$ ), 820(m), 744(s), 735(s), 674(m), 657(w), 461(w), 408(w). The structure of the ligands are illustrated in Scheme 1.

### 2.4. Preparation of the membrane optodes

Na-TPB was used as an additive in the membranes and as the ionic strength stabilizer in the spectrophotometric solution studies. The nitrate salts of all metal ions were used to prepare desired solution. Doubly distilled and deionized water was used throughout.



**Scheme 1** The structure of the ligands.

The optode membranes were prepared by mixing 60.0 mg plasticizer (DBP), 30.0 mg PVC, 1.5 mg of L<sup>2</sup> and 4.0 mg Na-TPB dissolved for L<sup>2</sup>-optode and for L<sup>1</sup>-optode, membrane was prepared by mixing 60 mg plasticizer (DBP), 30 mg PVC, 0.8 mg of L<sup>1</sup> and 5 mg Na-TPB. The membrane components were dissolved in exactly 2.0 ml THF. A 200.0  $\mu$ l of the THF cocktail was pipette and transferred on the glass plate. Prior to coating, all glass plates were cleaned with pure THF and HNO<sub>3</sub> to remove organic impurities and dust. After 2 min spinning (using a spin-on device) with a rotation frequency of 600 rpm, the membrane was allowed to dry in air for a few minutes. The optimal membrane had a thickness of approximately 5–7  $\mu$ m. In all studies, the reference membrane had the same composition as the proposed membranes except the ligand was absent.

### 2.5. Procedure

The optical sensor membrane was placed into the spectrophotometer cell filled with 2.5 mL of acetate buffer (pH 3.0 and 4.0 for L<sup>2</sup> and L<sup>1</sup>, respectively). After the addition of known amount of Cu<sup>2+</sup> ion solution the absorption spectrum against a reference blank membrane was recorded over the wavelength range of 340–700 nm at 1 nm interval.

## 3. Results and discussion

### 3.1. Spectral characteristic

Fig. 1 shows the absorption spectra of bulk solution and respective membrane incorporated spectra which obtained after equilibrium buffer solution (pH 3.0 and 4.0 for L<sup>2</sup> and L<sup>1</sup>, respectively) following the addition of different increments of Cu<sup>2+</sup> ion solution. Following the addition of Cu<sup>2+</sup> ion, strong complexation and interaction between Cu<sup>2+</sup> ions and both carriers occur that leads to a significant change. The absorbance maximum wavelengths of the membrane based L<sup>2</sup> and L<sup>1</sup> are located at 457 and 381 nm for L<sup>2</sup> and at 460 and 389 nm for L<sup>1</sup>. Bathochromic shifts ranging from 10 to 30 nm were observed when compared to respective aqueous solutions. That may be attributed to change in structural conformation of the incorporated ligand in membrane that is more planar than that of its solution analog [Jones and Porter, 1988]. As can be seen from Fig. 1, the decrease in the absorption at 457 and 381 nm for L<sup>2</sup> and an increase at 460 nm and a decrease at 389 nm for L<sup>1</sup> are more pronounced in the membrane with an increase in the Cu<sup>2+</sup> ion concentration. The wavelengths of 381 nm for L<sup>2</sup> and 389 nm for L<sup>1</sup> were selected for further studies because of higher selectivity and sensitivity at these wavelengths (Safavi and Bagheri, 2005).

### 3.2. Influence of amount of ligand on the response of the proposed optodes

The influences of ligand amount in the range of 0.5–2.5 mg at fixed concentration of Cu<sup>2+</sup> ( $1.31 \times 10^{-4}$  mol L<sup>-1</sup>) for L<sup>2</sup> and 0.5–1.5 mg at fixed concentration of Cu<sup>2+</sup> ( $5.12 \times 10^{-5}$  mol L<sup>-1</sup>) for L<sup>1</sup> are investigated and respective results are present in Fig. 2a. In the absence of ligand due to low complexation, the low sensitivity is achieved. By the addition of L<sup>2</sup> up

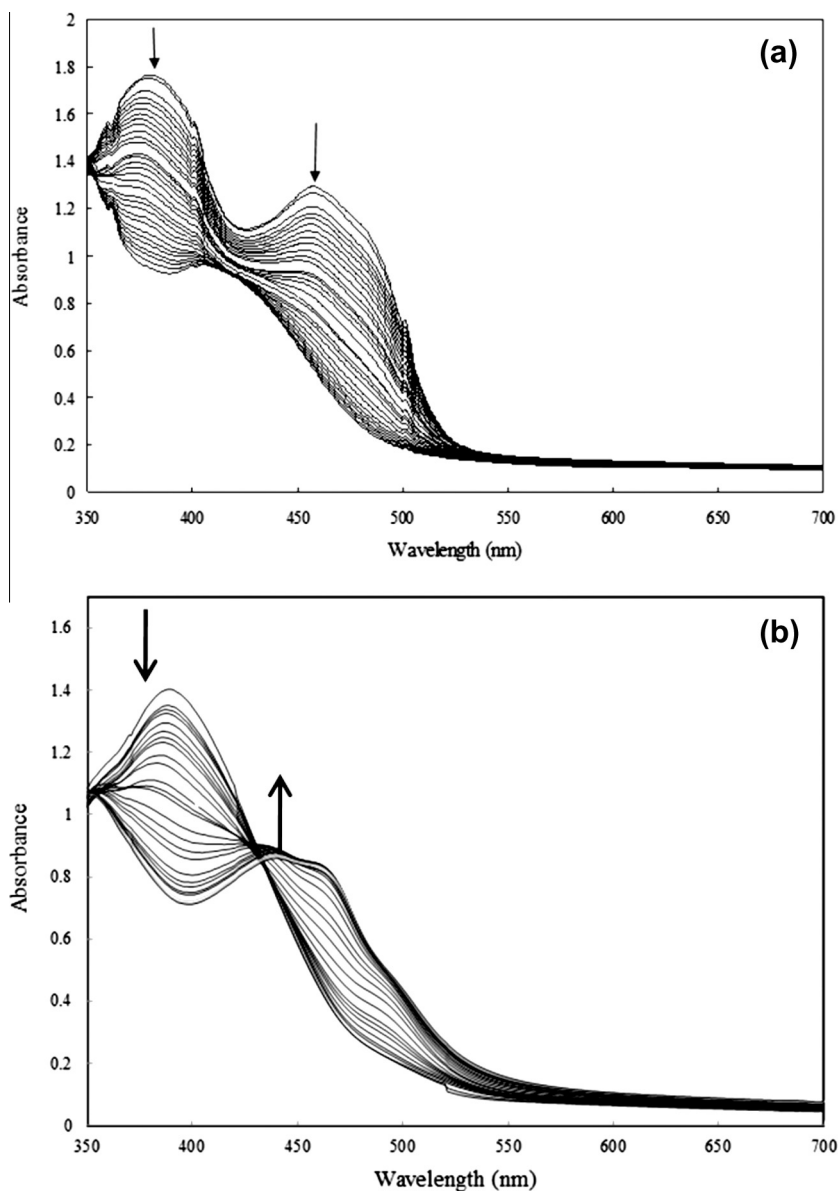
to 1.5 mg the amount of Cu<sup>2+</sup> ion migrates to the membrane significantly increased and the amount of complex significantly increased. Further addition of L<sup>2</sup> did not have a significant effect on the response and sensitivity of this optode and upon addition of L<sup>1</sup> up to 0.8 mg the amount of Cu<sup>2+</sup> ion migrates to the membrane significantly increased and the amount of complex significantly increased (Fig 2b). Therefore, 1.5 mg of L<sup>2</sup> and 0.8 mg of L<sup>1</sup> are recommended for subsequent works.

### 3.3. Effect of membrane compositions

It is well known that the sensitivity and selectivity obtained for a given ionophore (ligand) depend significantly on the membrane composition and the nature of solvent mediator and additives [Oehme et al., 1998]. Thus, the influence of the nature of plasticizer, amount of ionophore and NaTPB as lipophilic additive (anionic site) on the response behavior of the proposed optical sensor was investigated. As shown in Fig. 3, an increase in amount of Na-TPB up to 4.0 mg for L<sup>2</sup> and 5.0 mg for L<sup>1</sup> leads to an improvement in response of the proposed optodes and further addition of Na-TPB did not significant effect on its response. Therefore, 4.0 mg of Na-TPB for L<sup>2</sup> and 5.0 mg for L<sup>1</sup> are recommended for subsequent works. Addition of plasticizer (solvent mediator) compatible with PVC as a common polymer is required to have a homogenous organic phase. In this work, DBP, DES and DMS were applied as potential plasticizers with different polarities. Addition of DMS to membrane causes improper physical properties. Membranes based on the other two plasticizers have similar property and sensitivity, while the addition of DBP leads to better characteristic and signal properties of the proposed optical sensor. The absorbance measurements for the optode membrane with different types of plasticizer were made in  $1.31 \times 10^{-4}$  mol L<sup>-1</sup> and  $5.12 \times 10^{-5}$  mol L<sup>-1</sup> of copper for L<sup>2</sup> and L<sup>1</sup>, respectively, against a reference membrane and results are shown in Table 1.

### 3.4. Effect of pH on the sensor response

View glance to the structure of both ionophores shows the presence of hydroxyl group and nitrogen atoms as more reactive atom for binding metal ions with high pH dependency of their complexation tendency. Therefore, the response of the optodes based on incorporation of these two new ionophores significantly affected by the pH of buffer. The effect of pH on the optode response (extent of complexation) in the pH range of 2–6 in the buffer and non-buffer solutions was studied and results are shown in Fig 4. As can be seen in Fig. 4, a maximum value in the sensor response was obtained at pH 3 and 4 for L<sup>2</sup> and L<sup>1</sup>, respectively. This pH was selected for further studies. At lower pH probably due to protonation of reactive sites and competition of proton with metal ions the sensitivity significantly decreased. At higher pH due to hydrolysis of Cu<sup>2+</sup> ion to Cu(OH)<sup>+</sup> and Cu(OH)<sub>2</sub> and/or probably due to deprotonation of carriers and formation of charged species in membrane and their possible bleeding from membrane to aqueous solution, the sensitivity is decreased. On the other hand, at high pH probably due to appearance of negative charge of ionophores, their bleeding to bulk solution significantly increased and leads to a decrease in response and sensitivities of both optodes.



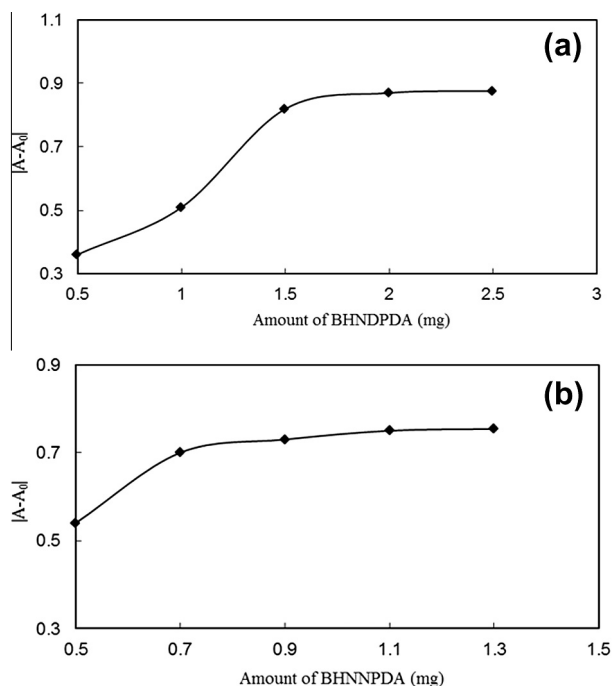
**Figure 1** Absorbance spectra of the proposed optical sensor in the presence of the varying concentrations of  $\text{Cu}^{2+}$  ion.; (a)  $\text{L}^2$  (The copper concentrations are from  $7.98 \times 10^{-6}$  to  $1.31 \times 10^{-4}$  mol  $\text{L}^{-1}$  in an acetate buffer solution of pH 3; (b)  $\text{L}^1$  (The copper concentrations are from  $1.99 \times 10^{-6}$  to  $5.12 \times 10^{-5}$  mol  $\text{L}^{-1}$  in an acetate buffer solution of pH 3.

### 3.5. Dynamic range

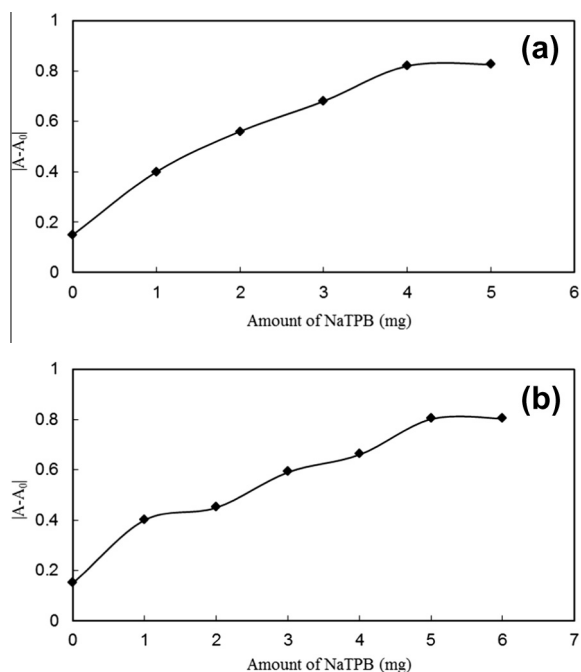
Fig. 5 (calibration curve) shows the absorption signals of the optode film to the various concentrations of  $\text{Cu}^{2+}$  ions. The signal is based on the absorbance (difference between the absorbance of membrane containing  $\text{L}^2$  and  $\text{L}^1$  in the absence and presence  $\text{Cu}^{2+}$  ions). As can be seen, the calibration curve is linear over concentration range of  $7.98 \times 10^{-6}$  to  $1.31 \times 10^{-4}$  mol  $\text{L}^{-1}$  and  $1.99 \times 10^{-6}$  to  $5.12 \times 10^{-5}$  mol  $\text{L}^{-1}$  for  $\text{L}^2$  and  $\text{L}^1$ , respectively. The optical sensor detection limit based on well-known definition (the concentration of the analytes makes possible to obtain a signal equal to the blank signal plus three times of its standard deviation) was found to be  $3.99 \times 10^{-7}$  and  $5.88 \times 10^{-7}$  mol  $\text{L}^{-1}$  for  $\text{L}^2$  and  $\text{L}^1$ , respectively.

### 3.6. Response time

The response time of the proposed optodes significantly displays the required time for the analyte diffusion from the bulk of the solution into the membrane interface followed by association of ionophore. Fig. 6 depicts a typical response of the optodes versus time for  $8.55 \times 10^{-6}$  M and  $3.84 \times 10^{-5}$  mol  $\text{L}^{-1}$  of  $\text{Cu}^{2+}$  ions for  $\text{L}^2$  and  $\text{L}^1$ , respectively. The dynamic response time of the optodes (defined as the time required reaching 90% of the final equilibrium signal) that was found to be 5–8 min for  $\text{L}^2$  and 20–25 min for  $\text{L}^1$  in solution with different concentrations of  $\text{Cu}^{2+}$  ion was monitored as a function of time. Response time is affected by different factors including:  $\text{Cu}^{2+}$  ion concentration that controls its diffusion into the membrane as well as the ionophore loading



**Figure 2** Effect of amount of ligand on the response of the proposed optodes, (a)  $L^2$  (at present  $1.31 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$ ); (b)  $L^1$  (at present  $5.12 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$ ).

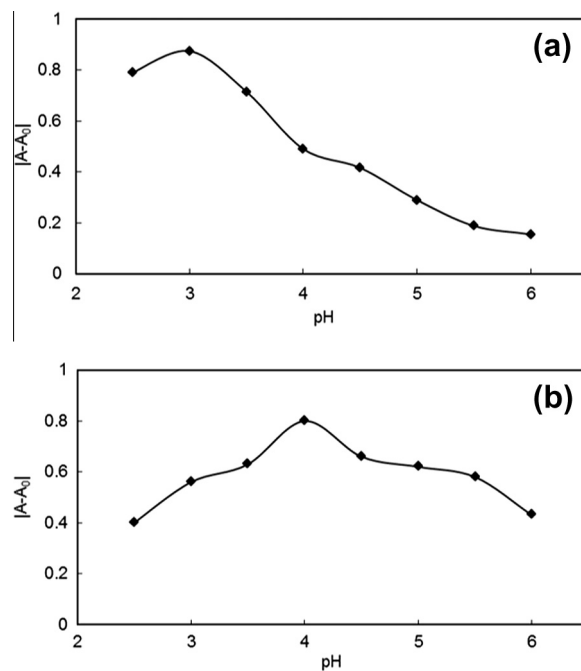


**Figure 3** Effect of amount of Na-TPB on the response of the proposed optodes, (a)  $L^2$  (at present  $1.31 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$ ); (b)  $L^1$  (at present  $5.12 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$ ).

technique (Absalan et al., 2004) and membranes' thickness. The observed difference can be related to the difference in the ionophore structure. The presence of the nitro group in the structure of  $L^1$  ionophore significantly diminishes its ability

**Table 1** Effect of plasticizers on the response characteristic of the proposed optodes.

Plasticizers	$L^2$ ( $\Delta A$ )	$L^1$ ( $\Delta A$ )
DBP	0.74	0.76
DMS	0.66	0.35
DES	0.69	0.46



**Figure 4** Effect of pH on the response of the proposed optodes, (a)  $L^2$  (at present  $1.31 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$ ); (b)  $L^1$  (at present  $5.12 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$ ).

for complexation of more reactive atom in Irvin Williams's series. This group by inductive and resonance effect decreases the electron density and its complexation tendency. It seems that ionophore without this nitro group is softer than the nitro containing compound and has higher ability for binding boarder line soft copper ions.

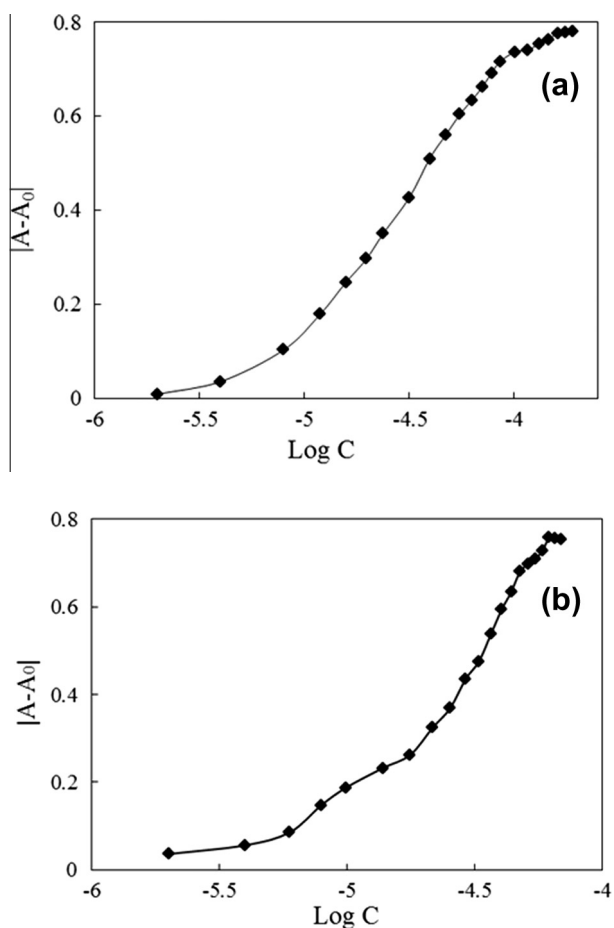
### 3.7. Life time

The life time of the optode film was determined by adding buffer solution (pH 3 and 4) in cuvette including film. The signal was recorded at wavelength of 381 and 389 nm for  $L^2$  and  $L^1$ , respectively over a period of time (about 8 h). No significant loss of the carriers occurs during this time. Via exposure of radiation to membrane a stable signal (without divergence) versus time was achieved that may be attributed to the fixed composition of membrane (absence of significant carrier bleeding from membrane to the bulk aqueous solution). No drift in signal was occurred. However, prepared membranes were kept under water when not in use to prevent them from drying out.

### 3.8. Sensor selectivity

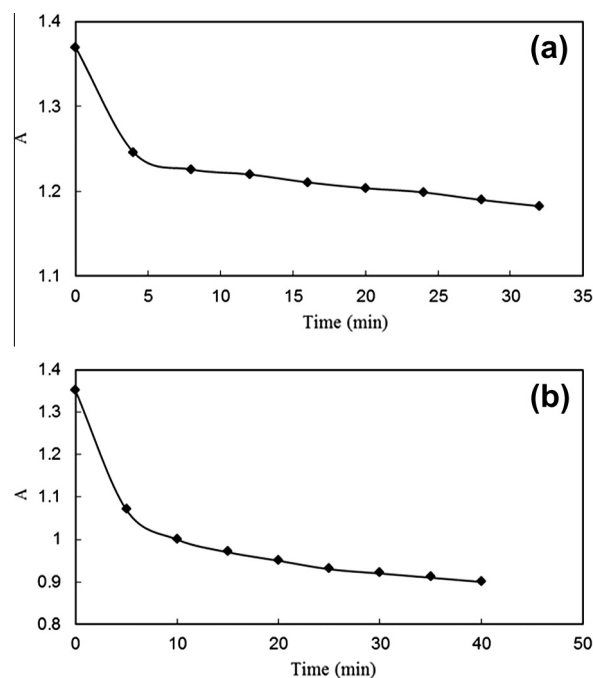
One of the most important performance of each sensor that limits its utility for real sample analysis is the selective





**Figure 5** Calibration plot of  $\Delta A$  against  $\log [Cu^{2+}]$ ; (a)  $L^2$ , (b)  $L^1$ .

coefficient of the proposed sensor. The interference of different inorganic cations on the response of the proposed optical sensor was examined using  $10.0 \times 10^{-6} \text{ mol L}^{-1}$  solution of  $Cu^{2+}$  ion in the presence of different concentrations of the interfering cations in acetate buffer of pH 3.0 and 4.0 for  $L^2$  and  $L^1$ , respectively. The tolerance ratio was defined as the ratio of the concentration of interfering ion to the  $Cu^{2+}$  ion concentration that causes a relative error of 5%. The resulting tolerance ratio ( $[M^{n+}]/[Cu^{2+}]$ ) for the various interfering ions ( $M^{n+}$ ) summarized in Table 2 shows that the  $Cu^{2+}$  ion content with high accuracy can be determined selectively using the proposed optical sensors in the presence of excess amounts of the investigated potential interferences. This moderate selectivity shows the applicability of the proposed sensors for evaluation and monitoring the copper content in different real samples with complicated matrices in the presence of excess of several other coexisting cationic species. The Schiff base ligands of  $L^2$  and  $L^1$  were chosen based on their structures by changing the amine part in order to study their influence on the metal coordination sphere. The differences among these values of selectivity coefficient are probably due to the change in the nature of ligands effecting on coordination of them to metal ion. In our view, an electron withdrawing substituent can affect its potential for complexation to copper ion. In fact, the presence of the nitro-group in the  $L^1$  may lead to diminish its complexation ability and decrease selectivity and tolerance



**Figure 6** Response time of the proposed optodes; (a)  $L^2$  (at present  $8.55 \times 10^{-6} \text{ mol L}^{-1} Cu^{2+}$ ), (b)  $L^1$  (at present  $3.84 \times 10^{-5} \text{ mol L}^{-1} Cu^{2+}$ ).

limit of the proposed sensor. Increasing the charge density and amount of resonance, increases the tendency of new Schiff base for complexation of  $Cu^{2+}$  ion as more reactive atoms in Irving Williams's series.

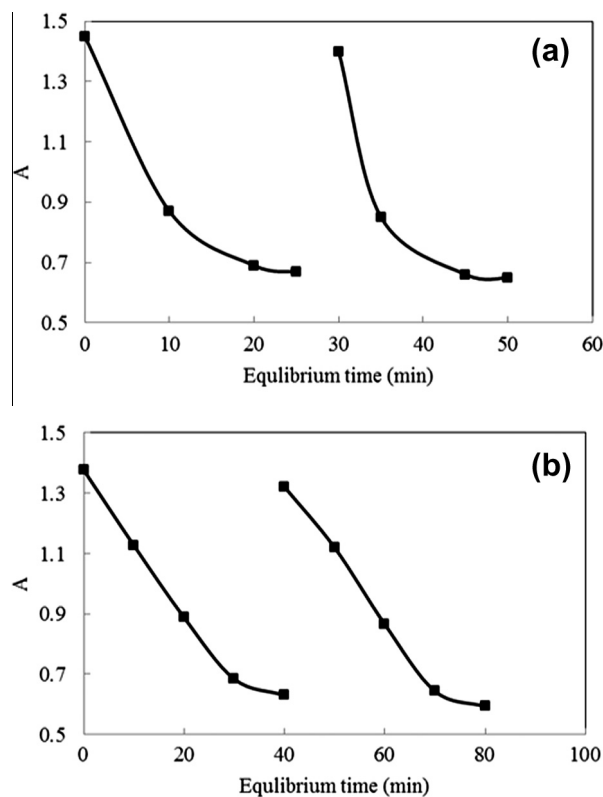
### 3.9. Repeatability and regeneration

The repeatability of the membrane response at 381 nm for  $L^2$  and 389 nm for  $L^1$  using a single membrane was tested by performing various replicate measurements for  $1.314 \times 10^{-4}$  and  $5.12 \times 10^{-5} \text{ M}$  of  $Cu^{2+}$  ion solution for  $L^2$  and  $L^1$ , respectively. The relative standard deviation (RSD) for these determinations was found to be less than 2%.

The regeneration of the membrane response was tested by multiple usages of each sensor for  $Cu^{2+}$  ion determination in test solutions of  $1.31 \times 10^{-4} \text{ mol L}^{-1}$  and  $5.12 \times 10^{-5}$  for  $L^2$  and  $L^1$ , respectively. After each absorbance reading, the membrane was regenerated by  $0.1 \text{ mol L}^{-1}$  EDTA solution, rinsed with deionized water and soaked in acetate buffer solution (pH 3.0 and 4.0 for  $L^2$  and  $L^1$ , respectively) for a few minutes. As shown (Fig. 7), good regeneration was obtained for the signal at  $Cu^{2+}$  ion concentration of  $1.31 \times 10^{-4} \text{ mol L}^{-1}$  and  $5.12 \times 10^{-5}$  for  $L^2$  and  $L^1$ , respectively. The corresponding R.S.D. value was found to be  $\pm 2.6\%$ . The short-term stability of the optodes was studied by their absorbance difference measurements in contact with  $1.31 \times 10^{-4}$  and  $5.12 \times 10^{-5} \text{ mol L}^{-1}$  of  $Cu^{2+}$  ion solution at pH 3.0 and 4.0 for  $L^2$  and  $L^1$ , respectively over a period of 5 h. From the absorbance intensity taken every 10 min ( $n = 30$ ), it was found that the response is almost complete with only 2.7% increase in absorbance after 5 h monitoring. The lifetime of the membrane was tested over a period of 3 months during which four prepared membranes were stored in 5% (v/v) ethanol at 4 °C. The mean absorbance differences of the membranes were found to be 0.062

**Table 2** Tolerance limit of foreign ions in the determination of  $1.0 \times 10^{-5}$  mol L<sup>-1</sup> Cu<sup>2+</sup> ions.

L <sup>2</sup>		L <sup>1</sup>	
Species	Tolerance ratio (TR)	Species	Tolerance ratio (TR)
IO <sub>4</sub> <sup>-</sup> , SCN <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , Mn <sup>2+</sup> , ClO <sub>3</sub> <sup>-</sup> , Bi <sup>3+</sup> , Cr <sup>3+</sup> , Fe <sup>3+</sup> , Ca <sup>2+</sup> , Cd <sup>2+</sup> , Co <sup>2+</sup> , Hg <sup>2+</sup> , Zn <sup>2+</sup> , Pb <sup>2+</sup>	1000	IO <sub>4</sub> <sup>-</sup> , SCN <sup>-</sup> , K <sup>+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , Mn <sup>2+</sup> , Bi <sup>3+</sup> , Cr <sup>2+</sup> , Pb <sup>2+</sup> , Fe <sup>3+</sup> , Ca <sup>2+</sup> , Al <sup>3+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Hg <sup>2+</sup> , Zn <sup>2+</sup> , Cd <sup>2+</sup> , La <sup>3+</sup> , SO <sub>4</sub> <sup>2-</sup>	1000
	500		1000

**Figure 7** Regeneration of the optode signal, (a). L<sup>2</sup> (at present  $1.31 \times 10^{-4}$  mol L<sup>-1</sup> Cu<sup>2+</sup> ion). (b). L<sup>1</sup> (at present  $5.12 \times 10^{-5}$  mol L<sup>-1</sup> Cu<sup>2+</sup> ion).

( $\pm 0.0026$ ) and  $0.063 (\pm 0.0024)$ , before and after this period, respectively.

### 3.10. Analytical applications

To test the practical application of the proposed optical sensors, their applications for direct determination of Cu<sup>2+</sup> ions in three samples including the dental amalgam, shaft water, and fountain water were carried out. The water samples collected were firstly acidized with HNO<sub>3</sub> and then filtered through a packed filter to remove oils and other organic impurities. Under the optimal conditions for the proposed optodes, the real samples were analyzed by a standard addition calibration method. As shown in Table 3, the results have good agreement with data obtained by FAAS. In addition, the proposed Cu<sup>2+</sup> optical sensor was found to work well under laboratory conditions for its accurate evaluation and its application as an indicator device for the titration of Cu<sup>2+</sup> ion solution with EDTA.

## 4. Conclusion

The Cu<sup>2+</sup> membrane sensor that is prepared on the basis of L<sup>2</sup> and L<sup>1</sup> in this work shows very good selectivity for Cu<sup>2+</sup> over other common metal ions. The membrane shows a high sensitivity and low detection limit that is sufficient for direct determination of the analyte in natural water samples. Preparation of the membrane is easy and the establishment of a covalent bond between L<sup>2</sup> and L<sup>1</sup> and the membrane results in a long

**Table 3** Recovery results for copper spiked in water samples.

Water samples	Concentration <sup>A</sup> (mol L <sup>-1</sup> )	Added (mol L <sup>-1</sup> )	Found <sup>B</sup> (mol L <sup>-1</sup> )	RSD (%)	Recovery (%)
<i>a: L<sup>2</sup></i>					
Beshar river	$1.7 \times 10^{-6}$	$6.5 \times 10^{-6}$	$8.5 \times 10^{-6}$	4.8	104.0
Mishi fountain	$1.4 \times 10^{-6}$	$7.1 \times 10^{-6}$	$8.4 \times 10^{-6}$	4.5	97.0
Abesard fountain	$1.2 \times 10^{-6}$	$7.2 \times 10^{-6}$	$8.5 \times 10^{-6}$	4.3	102.0
<i>b: L<sup>1</sup></i>					
Beshar river	$1.7 \times 10^{-6}$	$6.0 \times 10^{-6}$	$7.5 \times 10^{-6}$	4.9	97.0
Mishi fountain	$1.4 \times 10^{-6}$	$6.2 \times 10^{-6}$	$7.4 \times 10^{-6}$	5.0	96.0
Abesard fountain	$1.2 \times 10^{-6}$	$6.6 \times 10^{-6}$	$7.7 \times 10^{-6}$	4.7	99.0

<sup>A</sup> Measured value by FAAS.<sup>B</sup> Measured value by Optodes.**Table 4** Comparative data from some recent studies.

System	pH	Detection limit (mol L <sup>-1</sup> )	Linear range (mol L <sup>-1</sup> )	Refs.
1-hydrpxy-2-(prop-2'-enyl)-4-(prop-2'-enyloxy)-9,10-anthraquinone	5.5		$1 \times 10^{-2}$ to $1 \times 10^{-6}$	Shamsipur et al. (2006)
Dithizone on a triacetylcellulose	1.9	$2.0 \times 10^{-6}$	$8 \times 10^{-8}$ to $1.6 \times 10^{-5}$	Safavi and Bagheri (2005)
<i>N,N'</i> -(4,4'-ethylene biphenyl)bis (3-methoxy salicylidine imine)	4.0	$8.0 \times 10^{-9}$	$1 \times 10^{-9}$ – $3.2 \times 10^{-5}$	Arvand and Lashkari (2013)
1-hydroxy-3,4-dimethyl-9 <i>H</i> -thioxanthen-9-one			$1.6 \times 10^{-7}$ to $1.3 \times 10^{-2}$	Yari and Afshari (2006)
<i>N,N'</i> -bis(salicylidene)-1,2-phenylenediamine	5.5	$4.7 \times 10^{-8}$	$5.0 \times 10^{-8}$ to $6.3 \times 10^{-4}$	Gholivand et al. (2005)
1,1'-2,2'-(1,2-phenylene)bis(ethene-2,1-diyl)dinaphthalen-2-ol (L <sup>2</sup> ) or 1,1'-(4-nitro-1,2-phenylene)bis (azan-1-yl-1-ylidene)bis(methan-1-yl-1-lidene) dinaphthalen-2-ol (L <sup>1</sup> )	3.0	$3.9 \times 10^{-7}$ and $5.8 \times 10^{-7}$	$7.98 \times 10^{-6}$ to $1.31 \times 10^{-4}$ and $1.99 \times 10^{-6}$ to $5.12 \times 10^{-5}$	Present work

lifetime and short response time optodes with no evidence of the dye leaching. The membrane may be easily regenerated by an EDTA solution and have the possibility of multiple usages for environmental monitoring of Cu<sup>2+</sup> ions. The comparison of the results found in the present study and some recent studies using optodes of Cu<sup>2+</sup> [Shamsipur et al., 2006; Safavi and Bagheri, 2005; Arvand and Lashkari, 2013; Yari and Afshari, 2006; Gholivand et al., 2005] is given in Table 4.

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