Research Article

Chemical Review and Letters
journal homepage: www.chemrevlett.com
ISSN (online): 2645-4947 (print) 2676-7279

Design selective Cu^{2+} chemo-sensor based on Bis-Azo dye for determination of Cu^{2+} in water samples

Homa Shafiekhani[1,*], Fatemeh Mostaghni[1], Nosrat Maddadi Mahani[1]

[1]*Department of Chemistry, Payame Noor University, P.O. Box 19395-3697 Tehran, Iran*

ARTICLE INFO

Article history:
Received 12 January 2024
Received in revised form 1 March 2024
Accepted 21 June 2024
Available online 2 July, 2024

Keywords:
Bis-azo dye
Colorimetric chemosensor
Copper
Spectrophotometric.

ABSTRACT

In this work, a new bis-azo dye (BAD) was synthesized and characterized by Fourier-transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy. This ligand was used for selective determination of Cu^{2+} at trace levels in the aqueous solution. In the presence of Cu^{2+}, the color change of ligand from red to orange pale (under visible light) was seen. Under optimized conditions, the limit of detection and quantification were found to be 0.13 and 0.44 µM, respectively. Dynamic range was found in the concentration range of 1.6 –17.5 µM with a correlation coefficient of 0.9964. This sensor was reversible and the response time was estimated nearly 6 minutes. The stoichiometric ratio between the chemosensor bis-azo dye–Cu^{2+} [BAD-Cu^{2+}] complex was determined to be 1:1 according Job's plot. The results showed that this sensor was successful in determining Cu^{2+} in tap and mineral water samples.

1. Introduction

In addition to diverse biological processes, metal ions play an essential role in countless chemical reactions. Among metal ions, copper is one of the most widely used metals due to its valuable properties and numerous applications in modern economics and daily life [1–3]. Copper (II), as a trace element, is essential for plant and human health [4–5]. However, excessive consumption can also be harmful to health [6–7]. Copper can accumulate in hair, bones, and inside some soft tissues such as the kidneys, liver, lungs, or brain [8-9]. Therefore, the determination of copper in both the environment and biological samples is critical to public health and the environment. Various methods have been used to determine copper.

Despite the existence of conventional techniques, such as different spectroscopy [10–12], stripping voltammetry [13–14], luminescent [15], inductively coupled plasma spectroscopy (ICP-MS) [16], and cloud point extraction (CPE) [17–18], it is vital to develop a simple, cheap, and highly selective method for measuring metal ions.

Recently, chemical sensors based on optical signal measurements are considered as the advanced techniques due to their simplicity, reasonable selectivity, improved sensitivity, low detection limit, and fieldwork applicability [19–23].

In the development of chemical sensors based on organic compounds, molecules containing multiple heteroatoms such as N, S and O are often preferred because of their ability to absorb different ions [24–26]. In recent years, azo dyes have studied for their easy synthesis, and the wide variety. Azo compounds are characterized by the presence of the azo moiety (–N=N–) in their structure that is attached to two alkyl or aryl groups. The properties of these compounds are determined by the number of (–N=N–) groups, and the type of groups attached to them. These compounds are widely used in different applied fields, such as medicines, ink jet printing [27–29], fuel cells [30], sensitized solar cell dyes [31], foods additives [32–34], liquid crystal industry [35–38] etc.

In the present paper, we report the construction of a sensor to determine low levels of copper using a bis-azo dye as the sensing reagent. Bis-azo dye was synthesized by

* Corresponding author; e-mail: shafiee@pnu.ac.ir
https://doi.org/10.22034/crl.2024.435316.1279

bis-diazotization of the corresponding diamine (1, 4–phenylendiamine) and there after the coupling reaction (in a 1:2 molar ratio) of the resulting bis–diazonium salt with salicylaldehyde.

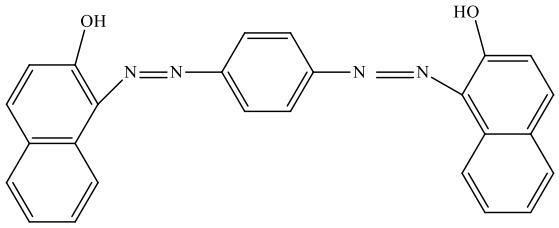
2. Experimental

Materials and instruments

All chemicals were analytical grade (>99.5%) and purchased from B.D.H, Fluka and Merck Companies Switzerland and Germany. Metal cationic samples (Ag^{+}, Ca^{2+}, Na^{+}, K^{+}, Li^{+} , Cr^{3+}, Ni^{2+}, Mn^{2+}, Mg^{2+}, Zn^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+}, Al^{3+}) were prepared with nitrate, acetate, chloride and sulfate salts. The working Cu (II) solutions were obtained by dissolving 25 mg $CuSO_4.5H_2O$ in deionized water that, final concentration was 1×10^{-2} M. A stock solution of BAD at concentration (5×10^{-3} M) was prepared by dissolving (20.9 mg) of BAD in 10 ml of DMF. Shimadzu UV-1601 PC (Shimadzu, Kyoto, Japan) UV-VIS spectrophotometer was used to absorption spectra and all measurements were recorded at 340–700 nm. pH Meter Model 713 Metrohm (Switzerland) equipped with combined glass calomel electrode was used to measure the pH of the solutions. ^{1}HNMR spectra were recorded at 400 MHz by Bruker Avance spectrometer (USA). Infrared spectra were recorded using a Frontier IR spectrometer (Nicolet iS 10, USA). A Hamilton microliter syringe (10, 50 µL) was used for the titration experiment.

Synthesis of BAD

The chromoionophore BAD were prepared by linking phenylendiamine to beta naphthol through diazo–coupling reactions. 1, 4–phenylenediamine (1.08 g, 10 mmol) was added to a 10 mL solution of 1 M sulfuric acid while stirring and placed in an ice bath. Then the solution of sodium nitrite 1 M (10 mL) was added dropwise so that the temperature was maintained at 0–5º C. A solution of beta naphthol (2.88 g, 20 mmol) in 30 ml of 10% NaOH was slowly added to the prepared diazonium salt solution for 30 minutes with vigorous stirring. The resulting solution was stirred for 20 min in an ice bath and then allowed to reach room temperature. Finally, the reaction mixture was acidified with sulfuric acid. The reddish–brown precipitate was filtered, washed several times with cold water, and purified by recrystallization from DMF/H_2O. The structure of the employed dye molecule is shown in Figure 1.
IR (KBr) ν=3373, 16280, 1199, 1158, 1093, 994, 961 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ=6.74-6. 92 (m, 4H), 6.95-7. 05 (t, *J* = 7.4 Hz, 2H), 7.12-7. 19 (t, *J* = 7.5 Hz, 2H), 7.39-7.46 (d, *J* = 11.1 Hz, 2H), 7.44-7.55 (m, 6H), 9.49 (s, 2H) ppm.



Scheme 1. Chemical structure of BAD.

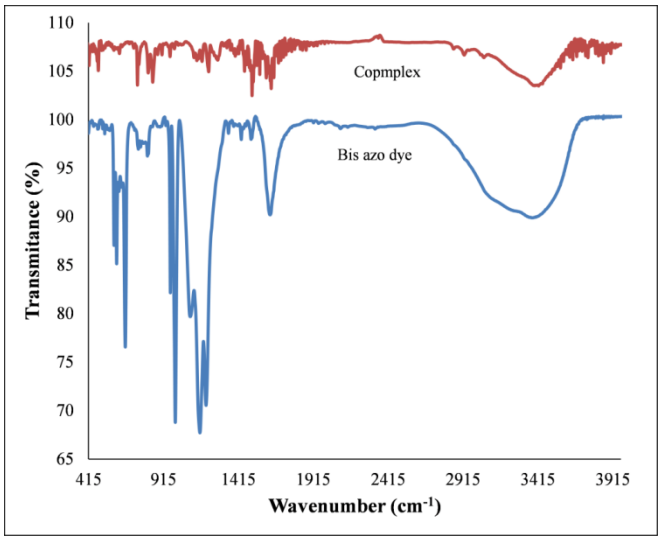
Spectrophotometric titration of BAD with Cu^{2+}

In this research, BAD was used as a colorimetric indicator for Cu^{2+} detection and determination. In order to complexation studies, BAD solution (2.5 mL) was transferred to the 1 cm quartz cuvette and the UV-Vis spectrum was recorded at wavelengths of 340–700 nm. An initial 2.5 ml solution of BAD (5.0×10^{-5} M) was continually titrated with various concentrations of Cu^{2+} and monitored with a spectrophotometer.

3. Result and discussion

FTIR spectra & binding mode

Using the infrared spectrum, helpful information can be obtained about the functional groups involved in the formation of the complex. FTIR spectrum of BAD indicated the stretching vibration of υ (OH) group at 3462 cm^{-1}. This peak was absent in the complex, which indicated deprotonation and coordination of oxygen atom with metal ion. Bathochromic displacement of the characteristic azo bridge vibration band (N = N) at 1500 cm^{-1} to a lower frequency of 1456 cm^{-1} along with splitting indicates the bonding of this group with the metal ion. The appearance of two new bands in the 419 and 480 cm^{-1} was assigned as υ (M–N) and δ (M–O) stretching and bending bands [39]. Therefore, it can be concluded that the synthesized compound acts as a bidentate ligand and binds to the metal ion through phenolic oxygen and nitrogen of azo group.



Scheme 2. IR spectra of free BAD and [BAD- Cu^{2+}] complex.

Spectrophotometry studies

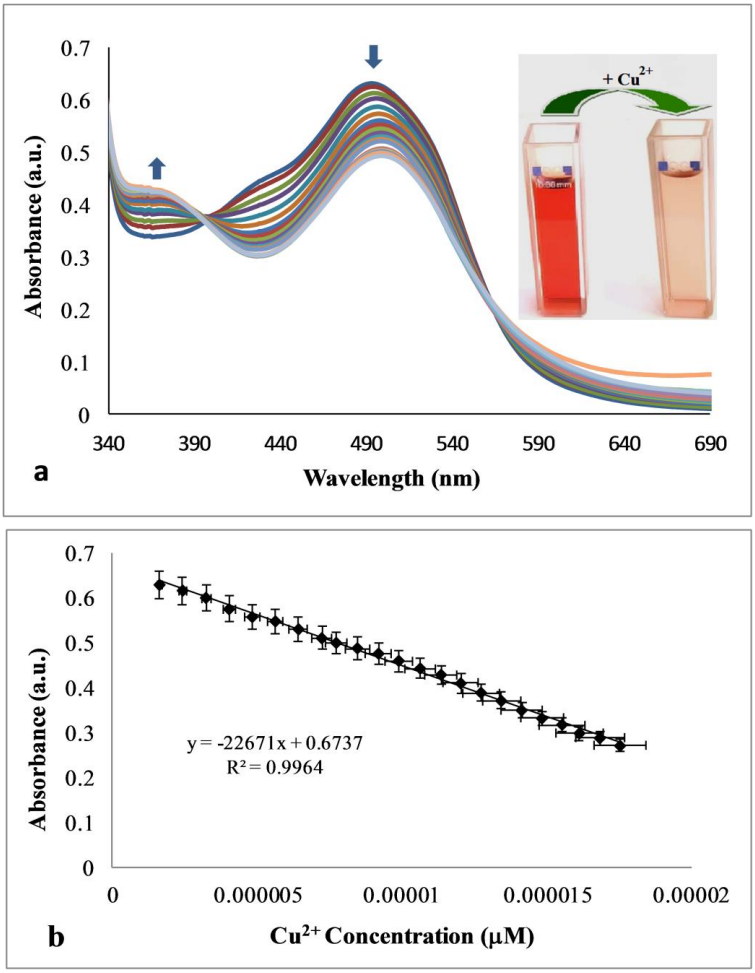
The selectivity and sensitivity of the sensor against various metal ions are the significant factors in evaluating its practical applications. Here, the UV-Vis titration method has used to determine selectivity and sensitivity. The aqueous solutions (2.0×10^{-4} M) of all metal ions were utilized for complexation studies. Among all cations and anions, including Ag^{+}, Ca^{2+}, Na^{+}, K^{+}, Li^{+} , Cr^{3+}, Ni^{2+}, Mn^{2+}, Mg^{2+}, Zn^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+}, Al^{3+}, NO_3^{-}, NO_2^{-}, SO_4^{2-}, OAC^{-} , Cl^{-}, I^{-}, PO_4^{3-}, HPO_4^{2-}, MoO_4^{2-}, just Cu^{2+} was showed binding properties with BAD in DMF solution. The absorption spectra of the BAD ligand solution were recorded at wavelengths of 340–700 nm. An initial 2.5 ml solution of BAD (5.0×10^{-5} M) was continually titrated with various concentrations of Cu^{2+} and monitored with a spectrophotometer. Upon addition of copper ion (1.6-17.5 µM) the maximum absorbance at 493 nm gradually decreased in intensity and a new absorption peak appeared at 425 nm with the change of the color of the solution from red to pale orange. At the same time, two isobestic points were observed at about 393 nm and 567 nm during the titration, indicating the formation of a stable complex between the BAD and Cu^{2+} (Figure 3a). In the concentration range of 1.6-17.5 µM, the UV-Vis absorption had a linear relationship with Cu^{2+} ion concentration. The regression equation was $y = -22671x + 0.6737$ with a correlation coefficient of 0.9964 (figure 3b). Based on the titration and linear relationship, the detection limit ($\frac{3Sb}{slope}$) and the quantification limit ($\frac{10sb}{slope}$) [40] were calculated to be 0.13 and 0.44 µM respectively.

The stoichiometric determination of the bond between the chemical sensor and the copper cation has been studied by performing the Jobs plot and mole ratio experiments [41]. Job's plot and mole ratio for the titration data support forming a 1:1 complex (Figures 4, 5).

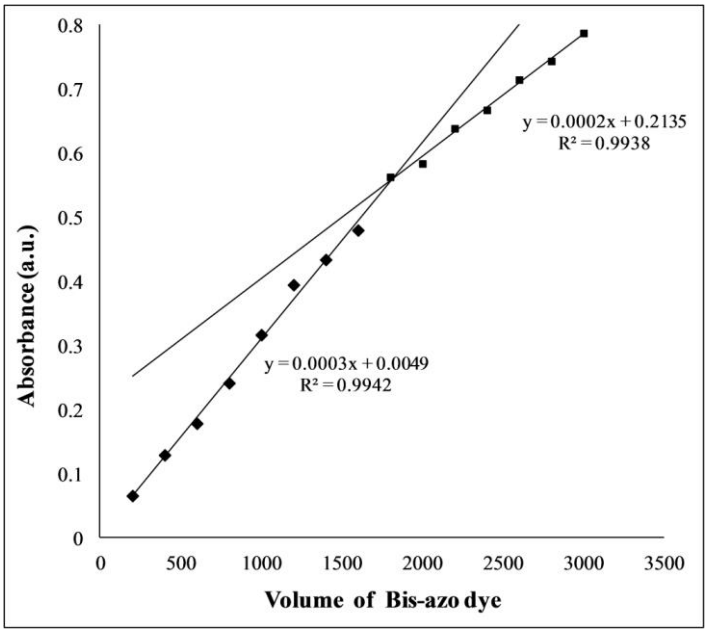
Effect of pH on sensor response

To investigate the effect of pH of aqueous solutions on the absorption of the [BAD– Cu^{2+}] complex, we made solutions with different pH. The absorbance measurements were done in the pH range 2.0–11.0 adjusted using KHP and HCl (2.2-3.8), KHP and NaOH (4.0-6.2), sodium tetraborate and HCl (7.7-9.2), sodium tetraborate and NaOH (9.2-11), buffer solutions [42]. According to the obtained results (Figure 6), the absorption efficiency of complex enhanced at pH =9.0.

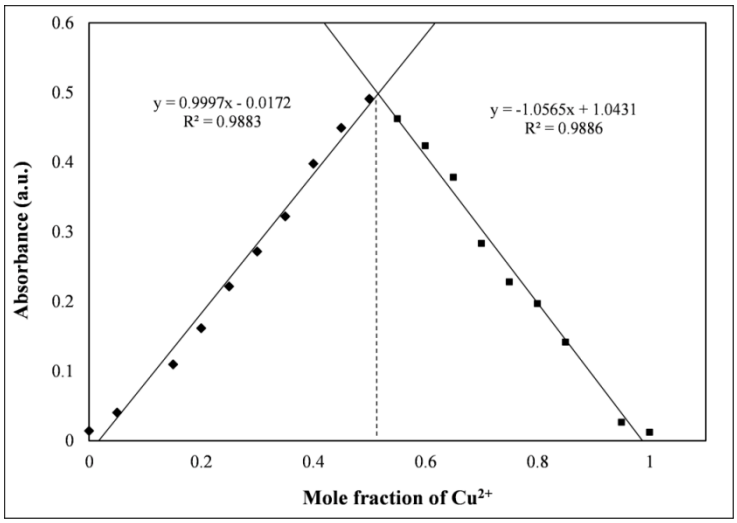
In the acidic medium, the decrease in absorbance intensity was attributed to the hydroxyl-attached proton in the BAD. In addition, the low absorbance values obtained at high pH (pH> 9) indicate that the Cu^{2+} ion may be hydrolyzed as hydroxide and may not form a complex with the bis- azo chemosensor [43]. Therefore pH= 9.0 was selected for further studies while an orange pale complex [BAD– Cu^{2+}] was formed.



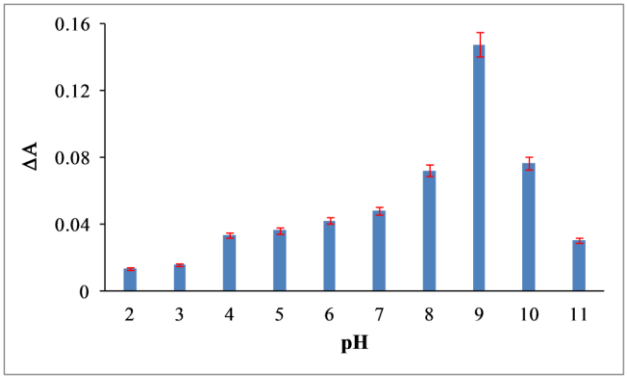
Scheme 3. (a) The UV–Vis spectra of chemosensor BAD (50.0 µ mol L^{-1}) upon addition of Cu^{2+} ion (1.6 -17.5 µM) in DMF, (b) Calibration plot of the absorbance vs concentration of Cu^{2+}.



Scheme 4. Mole ratio plot for [BAD– Cu^{2+}] complex



Scheme 5. Jobs plot suggesting stoichiometry among chemosensor [BAD– Cu^{2+}] =1:1.



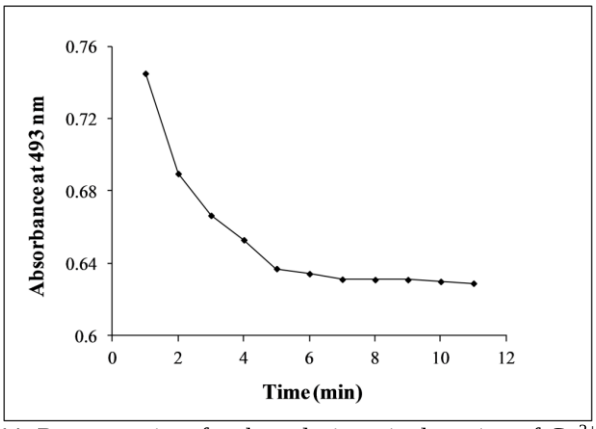
Scheme 6. Effect of pH on the absorbance intensity at maximum absorption wavelength of [BAD– Cu^{2+}] at 493 nm, upon addition of Cu^{2+} ion (1×10^{-5} M).

Performance of the probe

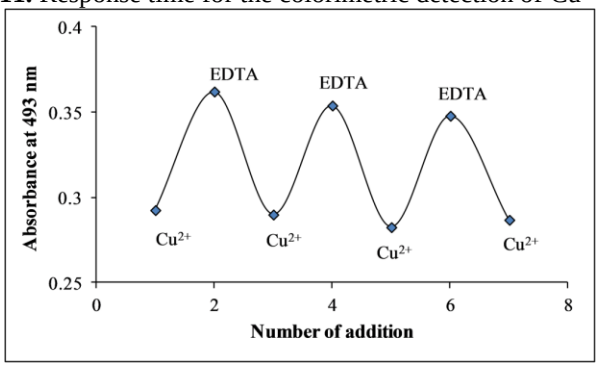
The parameters such as, response time and reversibility were studied duo to evaluate the practical performance of the probe, using absorption spectrum. Figure 7 show the effect of time on the progress of the [BAD– Cu^{2+}] complex. Although a steady-state response happened after 6 min, the approximate response time of the chemosensor was investigated at intervals of 0–11 minutes. This short response time could provide a new real-time method for determining copper. The reversibility experiments were tested by using Na_2EDTA as the chelating agent. After the addition of Na_2EDTA to the solution of [BAD– Cu^{2+}] complex, the absorbance band at 493 nm increased gradually because of its greater binding affinity of EDTA for Cu^{2+} ions than BAD. Upon addition of Cu^{2+} again to the above solution, the absorbance at 493 nm was recovered to the initial intensity. The absorbance changes at 493 nm were almost reversible even after several cycles with the sequentially alternative addition of Cu^{2+} and Na_2EDTA (Figure 8). Such reversibility could be significant for the fabrication of sensing devices for Cu^{2+} recognition.

Application for real samples

The colorimetric chemosensor BAD was used to determine Cu^{2+} ions in both tap water from Department of Chemistry, Payame Noor University, Shiraz, Iran, and mineral water from local markets. Before analysis, 400 ml of tap water was filtered through a filter paper of pore size 0.45 µm. Then, 8 ml concentrated nitric acid, and 3 ml 30% hydrogen peroxide was added and boiled for 20 minutes, until their volume reached one-tenth of the original volume. The resulting solution was cooled, and adjusted to pH 9, diluted to 100 ml with distilled water in a calibrated flask and used to determine copper in water samples. The results were shown in Table 1. These results indicated that BAD is an effective sensor for Cu^{2+}ions in both tap water and mineral water samples.



Scheme 11. Response time for the colorimetric detection of Cu^{2+} ion ((1× 10^{-5} M).



Scheme 7. Reversibility cycle by UV-Vis experiment BAD after the sequential addition of Cu^{2+} ion(1× 10^{-5} M) and EDTA at pH=9.0.

Table 1. Determination of Cu^{2+} ion in water samples by the proposed method (n=4).

Sample	Added (Cu^{2+}), µmol L^{-1}	Found (Cu^{2+}), µmol L^{-1}	Recovery(±SD) %	%RSD
	-	1.6	-	
Tap water	4.0	3.7	92 ± 1.93	2.09
	12.0	11.5	96 ± 1.24	1.29
	16.0	16.5	103 ± 1.04	1.01
	-	1.8		
Mineral water	4.0	3.9	97 ± 1.83	1.88
	12.0	11.9	99 ± 1.20	1.21
	16.0	17.0	106 ± 2.37	2.23

Average of four replicates

Table 2. Comparison of various sensors for Cu^{2+} detection.

Detection limit	Dynamic range	Detection medium	Ref.
6.08 µmol L^{-1}	(1-100) µmol L^{-1}	9:1 DMSO/ H_2O	44

2.03 μmol L^{-1}	(10-100) μmol L^{-1}	8:2 MeCN/H_2O	45
6.82 μmol L^{-1}	(0-40) μmol L^{-1}	DMSO	46
1.01 μmol L^{-1}	1.66-25 μmol L^{-1}	1:1 isopropanol/ H_2O	47
0.13 μmol L^{-1}	(1.6- 17.6) μmol L^{-1}	DMF	This work

Some of the Cu^{2+} ions sensors with various detection methods are presented in Table 2.

3. Conclusion

In this study, we have synthesized and characterized the bis-azo dye (BAD) that can be used to detection of Cu^{2+} ion in an aqueous solution. A spectrophotometric study showed that BAD had a good selectivity and sensitivity for Cu^{2+} ion. The detection can be monitored by the significant color changes from red to orange pale in DMF media under visible light. The detection limits for Cu^{2+} were found to be 0.13 μM, that much lower than in previous research. This comparison has shown in table 2. The probe and Cu^{2+} ion were found to react at a ratio of 1:1 [BAD– Cu^{2+}] complex by Job's method. The advantages of this method are simplicity, convenience, accuracy, high selectivity and reproducibility.

References

[1] C. Cerqua, V. Morbidoni, MA.Desbats, M. Dorimo, C. Frasson, S. Sacconi, MC. Baldion, G. Sartori, G. Basso, L. Salviati, E. Trevisson. COX16 is required for assembly of cytochrome c oxidase in human cells and is involved in copper delivery to COX_2, *Biochim Biophys Acta*.,1859(4) (2018**)** 244–252.

[2] S. Pietrzyk, B. Tora, Trends in global copper mining – a review. *IOP Conf Ser Mater Sci Eng.,* 427 (2018) 26-29.

[3] A. Potysz, ED. van Hullebusch, J. Kierczak, M. Grybos PNL.Lens, G. Guibaud. Copper metallurgical slags – current knowledge and fate: a review. *Crit Rev Environ Sci Technol* ., 45 (22) (2015) 2424–2488.

[4] J. Wang, RS.Li, HZ. Zhang, N. Wang, Z. Zhang, CZ. Huang, Highly fluorescent carbon dots as selective and visual probes for sensing copper ions in living cells via an electron transfer process. *Biosens Bioelectron.,* 97 (2017) 57–163.

[5] M. Kaur, SK. Mehta, SK. Kansal, Amine- functionalized titanium metal-organic framework (NH_2-MIL-125 (Ti)): a novel fluorescent sensor for the highly selective sensing of copper ions. *Mater Chem Phys., 254* (2020) 123539.

[6] KT. Aspli, TP. Flaten, PM. Roos, T. Holmøy, JH. Skogholt, J. Aaseth, Iron and copper in progressive demyelination – New lessons from Skogholt's disease. *J Trace Elem Med Biol.,* 31 (2015) 183–187.

[7] B. Witt, D. Schaumlöffel, T. Schwerdtle, Subcellular localization of copper—cellular bioimaging with focus on neurological disorders. *Int J Mol Sci.,* 21(7) (2020) 2341.

[8] R. Prego, A. Cobelo-Garcia, Twentieth century overview of heavy metals in the Galician Rias (NW Iberian Peninsula). *Environ Poll.* 121 (2003) 425–452.

[9] H. Xiong, B. Wang, W. Wen, X. Zhang, S. Wang, Fluorometric determination of copper (II) by using 3-aminophenylboronic acid-functionalized CdTe quantum dot probes. *Microchim Acta., 186* (2019) 392

[10] R. Bandi, R. Dadigala, BR. Gangapuram, FK. Sabir, M. Alle, SH. Lee, V. Guttena, N-Doped carbon dots with pH-sensitive emission, and their application to simultaneous fluorometric determination of iron(III) and copper(II). Microchim Acta., 187 (2020) 30.

[11] PV. Racheva, NP. Milcheva, F.Genc, KB. Gavazov, A centrifuge-less cloud point extraction-spectrophotometric determination of copper (II) using 6-hexyl-4-(2-thiazolylazo) resorcinol. Spectrochim Acta Part A: Mol Biomol Spectros., 262 (2021) 120106.

[12] X. Zuo, J. Xu, F. Jiang, X. Duan, LH. Guo, Y.Changcun, Y.Yu, Utilization of AuNPs dotted S-doped carbon nanoflakes as electrochemical sensing platform for simultaneous determination of Cu (II) and Hg (II). J Electroanal Chem.,794 (2017) 71–77.

[13] M. Samadi Kazemi, MR. Jamali, V. Yazdan, Application of a synthetic ligand in rapidly synergistic cloud point method for separation and preconcentration trace amounts of copper of water samples. Sep Sci plus., 4 (2021) 370-376.

[14] F. Ahour, M. Taheri, Anodic stripping voltammetric determination of copper (II) ions at a graphene quantum dot-modified pencil graphite electrode. J Iran Chem Soc., 15 (2018)15:343–350.

[15] S. Yang, W. Jiang, Y. Tang, L. Xu, B. Gao, H. Xu, Sensitive fluorescent assay for copper(II) determination in aqueous solution using quercetin–cyclodextrin inclusion. RSC Adv., 8 (2018) 37828-37834.

[16] T. King, R. Sheridan. Determination of 27 elements in animal feed by inductively coupled plasma-mass spectrometry. J AOAC Int., 102 (2) (2019) 434–444.

[17] S. Mandal, S. Lahiri, A review on extraction, preconcentration and speciation of metal ions by sustainable cloud point extraction, Microchem J., 175 (2022) 107150.

[18] V. Petya, NP. Racheva Milcheva, F. Genc, KB. Gavazov, A centrifuge-less cloud point extraction-spectrophotometric determination of copper (II) using 6-hexyl-4-(2-thiazolylazo) resorcinol. *Spectrochim Acta* Part A: *Mole Biomol Spect.,* 262 (2021)120106.

[19] N. Alizade, S. Pirsa, A. Mani-Varnosfaderani, MB. Alizadeh, Design and Fabrication of Open-Tubular Array Gas Sensors Based on Conducting Polypyrrole Modified With Crown Ethers for Simultaneous Determination of Alkylamines. IEEE Sensors 15 (2015) 4130-4136.

[20] JP. Vareda, AJM. Valente, L. Durães. Ligands as copper and nickel ionophores: Applications and implications on wastewater treatment. *Advanc Colloid Interfac Sci., 289* (2021) 102364.

[21] S. Alizadeh, S. Pirsa, S. Amiri, S. Amiri, Development of a colorimetric sensor based on nanofiber cellulose film modified with ninhydrin to measure the formalin index of fruit juice. J Biol Macromol., 253 (2023) 127035.

[22] G. Huang, X. Luo, X. He, Y. Han, H. Zhao, W. Tang, T. Yue, Z. Li, Dual-emission carbon dots based ratiometric fluorescent sensor with opposite response for detecting copper (II). Dyes Pigm., 196 (2021) 109803.

[23] F Khakpour, S Pirsa, S Amiri, Modified Starch/CrO/Lycopene/Gum Arabic Nanocomposite Film: Preparation, Investigation of Physicochemical Properties and Ability to Use as Nitrite Kit *J Polym Environ.*, 31 (2023) 1-19.

[24] YS. Kochergin, SM. Beladi-Mousavi, B. Khezri, P. Lyu, MJ. Bojdys, M. Pumera, Organic photoelectrode engineering: accelerating photocurrent generation via donor–acceptor interactions and surface-assisted synthetic approach. *J Mater Chem* A., 9 (11) (2021) 7162-7171.

[25] C. Zhang, G. Pan, Y. He, Conjugated microporous organic polymer as fluorescent chemosensor for detection of Fe^{3+} and Fe^{2+} ions with high selectivity and sensitivity. *Talanta.*, 236 (2022) 122872.

[26] R.I. Alsantali, Q.A. Raja, A.Y.A. Alzahrani, A. Sadiq, N. Naeem, E.U. Mughal, M. M. Al-Rooqi, N. El Guesmi, Z. Moussa, S.A. Ahmed, Miscellaneous azo dyes: A comprehensive review on recent advancements in biological and industrial applications, Dyes Pigm. 199 (2022), 110050.

[27] C. Gao, T. Xing, X. Hou, G. Chen, Preparation of disperse inks for direct inkjet printing of non-pretreated polyester fabrics. *RSC Adv.*, 9 (2019) 19791-19799.

[28] S. Lykidou, E. Karanikas, I. sagalias, N. Nikplaidis, E. Tsatsaroni, Synthesis, characterization and ultrafiltration of reactive dyes. Application by exhaustion and/or ink-jet printing. Fibers Polym., 18 (2017) 1697–1707.

[29] A.A. Ali, M.M. Elsawy, S.S. Salem, A.A. El-Henawy, H. Abd El-Wahab, Preparation and evaluation of antimicrobial thiadiazol azo disperse dyes as colored materials in digital transfer printing ink for printing onto polyester fabric. Pigment Resin Technol., 52 (2023) 19-32.

[30] EO. Moradi Rufchahi, A. Ghanadzadeh Gilani. Aryl and heteroaryl azo dyes derived from 6, 8-dichloro-4-hydroxyquinolin-2 (1 h) -one: Synthesis, characterisation, solvatochromism and spectroscopic properties. *Color Technol.,*135 (2019) 391–406

[31] S. Abu-Melha, Synthesis of novel biologically active thiazole dyes and their applications. Pigm Resin Technol, 48 (2019:375-382.

[32] S. Al Reza, M. Hasan, M. Kamruzzaman, I. Hossain, A. Zubair, L. Bari, Z. Abedin, A. Reza, KK. Bin-Ferdaus, KF. Haque, K. Islam, MU. Ahmed, K. Hossain, Study of a common azo food dye in mice model: Toxicity reports and its relation to carcinogenicity. *Food Sci Nutr.*, 7 (2019) 667–677

[33] Leulescu M, Palarie I, Moanta A, Cioatera N, Popescu M, Morîntale E, Varut MC, Rotaru P. Red-brown HT Physical, thermal and biophysical properties of the food azo dye. *J Therm Anal Calorim.*, 136 (2019) 1249–1268

[34] Leulescu M, Iacobescu G, Bojan M, Rotaru P. Ponceau 4R azoic red dye Thermal behavior, optical anisotropy and terahertz spectroscopy study. *J Therm Anal Calorim.*, 138 (2019) 2091–2101.

[35] N.A. Razali, Z. Jamain, Liquid Crystals Investigation Behavior on Azo-Based Compounds: A Review. Polymers, 13 (2021) 3462.

[36] A. Rotaru, A. Moanta, C. Constantinescu, M. Dumitru, HO. Manolea, A. Andrei, M. Dinescu. Thermokinetic study of CODA azoic liquid crystal and thin films deposition by matrix-assisted pulsed laser evaporation. *J Therm Anal Calorim.*, 128 (2017) 89–105.

[37] Y. Yue, Y. Norikane, R. Azumi, E. Koyama. Light-induced mechanical response in crosslinked liquid crystalline polymers with photoswitchable glass transition temperatures. *Nat Commun.*, 9 (2018) 3234.

[38] LK. Ong, ST. Ha, GY. Yeap, HC. Lin, Heterocyclic pyridine-based liquid crystals: Synthesis and mesomorphic properties. *Liq Cryst., 45* (2018) 1574–1584.

[39] A. Kakanejadifar, F. Esna-ashar, P. Hashem, A. Zabardast, Synthesis and characterization of an azo dibenzoic acid Schiff base and its Ni(II), Pb(II), Zn(II) and Cd(II) complexes. *Spectrochim Acta Part* A: *Molecul Biomol Spect., 106* (2013) 80-85.

[40] J. Tellinghuisen, Calibration: Detection, Quantification, and Confidence Limits Are (Almost) Exact When the Data Variance Function Is Known. Anal Chem., 91 (2019) 8715-8722.

[41] BD. Vanjare, PG. Mahajan, SK. Hong, KH. Lee, Discriminating chemosensor for detection of Fe^{3+} in aqueous media by fluorescence quenching methodology. *Bull korean Chem Soc.,* 39 (2018) 631-637.

[42] Handbook of analytical chemistry, Lurie J, Mir publisher, 1978, Moscow.

[43] D. Balasaheb, PG. Vanjare, HI. Mahajan Ryoo, NC. Dige, NG. Choi, Y. Han, SJ. Kim, CH. Kim, KH. Lee, Novel rhodamine based chemosensor for detection of Hg^{2+}: Nanomolar detection, real water sample analysis, and intracellular cell imaging. *Sens Actuators: B. Chemical., 330 (*2021)129308.

[44] E. Normay, R. Syuhada, H. Ismail, MN. Ahmad, MA.Yarmo, KHK. Bulat, Chemosensor development of Cu^{2+} recognition using 1,5-diphenylthiocarbazone: Optimization, COSMO-RS and DFT studies. *J Braz Chem Soc.*, 30 (2019) 1850–1859.

[45] A. Farhi, F. Firdaus, H. Saeed, A. Mujeeb, M. Shakir, M. Owais, A quinoline-based fluorescent probe for selective detection and real-time monitoring of copper ions-a

differential colorimetric approach. *Photochem Photobiol Sci.*, 18 (2019) 3008–3015.

[46] D. Yun, JB. Chae, C. Kim, A novel benzophenone-based colorimetric chemosensor for detecting Cu^{2+} and F^{-}. *J Chem Sci.*, 131 (2019) 10.

[47] MH. Mahnashi, AM. Mahmoud, SA. Alkahtani, R. Ali, MM. El-Wekil,. A novel imidazole derived colorimetric and fluorometric chemosensor for bifunctional detection of copper (II) and sulphide ions in environmental water samples. *Spectrochim Acta Part* A: *Molecul Biomol Spect*., 228 (2020) 117846.