



## Synthesis and Optical Study of Sensitive and Selective Detection of Fe(III) ions Based on Solvents



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### Abstract

This study accentuates the synthesis and characterization of vanillin azo dye conjugate based on naked-eye colored chemodosimeters. Vanillin azo dye conjugate exhibited high selectivity and sensitivity in absorbance for detection of Fe(III) ions in all solvents which can be observed simply by naked eye. Mostly the variation occurs in hypochromic shift of different metals with ligand but Fe(III) ions show hypsochromic in all solvents. It was found that the selectivity is more prominent in non-polar or less polar solvents like Chloroform, diethyl ether etc but less protruding in more polar solvents such as DMSO. The detection limit of the synthesized ligand with Fe(III) ions probe was shown by dilution method up to 0.39 ppm. The formation of complexes with azo dye was also affected by dielectric constant of the solvents

**Keywords:** Solvent polarity; Fe(III); Azo dye, Naked eye detection; Chemosensors.

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## Introduction

Transition elements have great significance due to their applications in environmental and biological processes. Iron, among transition metals, is the most ample trace element which plays a vital role in living cell systems of plants and animals [1, 2]. Several disorders are observed in the human body due to the excess or deficiency of iron. It is reported that its excess amount causes mental disorders and deficiency become the reason of anemia [3]. Iron is the main component of hemoglobin which is responsible to transport oxygen to the all parts of the body. It plays a vital role in proper functioning of the cells and the enzymatic systems of the body, particularly in the neural growth. It's quantity progressively increases in several cells and tissues and its excess amount accelerates the decay process of mitochondrial and broadly, imposes free radical destruction system to normal tissues [4, 5] Iron overloading is also the reason of many degenerative diseases, including heart attack, cancer and liver fibrosis.

Initially, the neural study indicated that increasing the level of iron was contemporary at the earliest inception of disease which point out that they had a potential to cause brain degeneration [6, 7]. In past, the detection and quantification of metals was done by inductively coupled plasma mass spectroscopy (ICPMS) and atomic absorption spectroscopy (AAS), which were costly and required complex instrumentation, tedious maintenance and highly trained personnel. These points generated problems for their effectively use in detection and imaging of  $\text{Fe}^{+3}$  in the samples of living things. Colored bio-imaging technique has provided a superficial and fewer cell destructive method which can be used safely and easily in the environmental and biological fields [8, 9]. So for the effective naked eye detection of  $\text{Fe}^{+3}$  ions chemosensors are required, especially for those which have the implementation in aqueous and non-aqueous solution due to their high sensitivity and selectivity. Due to the spectroscopic property of ligand complex such as large change in wavelength, nitroso and azo dyes present an ideal approach for the sensing of the  $\text{Fe}^{+3}$  ions [10, 11]. During the interaction of metal ions with dyes, bathochromic or hypsochromic shifts occur which

depend upon the structure of dye chromophore and metals. Numerous chemosensors have been synthesized for the detection of  $\text{Ag}^+$ ,  $\text{Hg}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Cr}^{+3}$ , and  $\text{Fe}^{+3}$  ions [12, 13].

The chelation of azo dye with different solvents due to its structural modifications is discussed. This dye acts as chromogenic and fluorogenic sensor for  $\text{Fe}^{+3}$  ions in different solvents. The quick analysis of  $\text{Fe}^{+3}$  ions, was done by developing color variation and simple test strip techniques which are required in useful application for rapid determination of environmental samples.

## Experimental

### 2.1 Apparatus, Reagents and Chemicals

Analytical grade vanillin, 2-aminophenol and solvents were purchased from Sigma Aldrich. The FT-IR was run on the single beam Nicolet IR 100 (Fourier-Transform); while the UV spectra of the samples were recorded in different solvents using UV-Visible spectrophotometer (V-730 JASCO). The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded in  $\text{DMSO-}d_6$  using Bruker Avance NMR spectrophotometer operating at 300 MHz. The elemental analysis (C, H, N, S) of the compounds was performed using Flash EA 1112 elemental analyzer.

### 2.2 General Procedure for Synthesis of vanillin based Azo Dye

First 1.09 g (0.01 mol) *o*-hydroxy aniline was dissolved in 20 mL of distilled water in a three necked round bottom flask. 5 mL of 30 % HCl was added into the reaction flask and cooled the flask from 0-5 °C by keeping the flask in an ice bath. In the reaction mixture 5 mL aqueous solution of sodium nitrite (0.76 g, 0.01 mol) was added with continuous stirring by keeping the temperature constant. The reaction mixture was stirred for 1.5 hours until the complete diazotization was evidenced by TLC. In another flask, vanillin 1.83 g (0.012 mol) was dissolved in 20 mL basic water solution pH = 8.5 with continuous stirring while keeping the temperature  $\leq 5$  °C. The Previously prepared diazonium salt was added slowly to vanillin solution by maintaining the pH  $\geq 8.0$ . The progress of reaction was monitored by TLC with 50:50 ethanol and *n*-hexane. Dye solution was

acidified to pH = 2 with dilute HCl solution to obtain the precipitates. The products was separated by filtration and recrystallized from methanol and chloroform (1:1) mixture.

Colour: Yellowish brown solid (77 %), M.P = 269 °C. FT-IR (KBr)  $\text{cm}^{-1}$ : 3364 (O-H), 2902 (OCH<sub>3</sub>, str), 1713 (C=O), 1595 (N=N), 1145 (C-O-C). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 MHz)  $\delta$  (ppm): 15.45 (OH, s, br) 15.05 (OH, s, br), 10.14 (CHO, s), 7.87 (1H, s), 7.75 (1H, m), 7.55 (1H, d, <sup>3</sup>J= 8.7 Hz), 7.30 (1H, d, <sup>3</sup>J= 9.6 Hz), 7.10 (1H, m), 6.90 (1H, s), 3.81 (3H, s). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 75 MHz)  $\delta$  (ppm): 190.2, 169.5, 163.2, 155.9, 149.0, 143.8, 130.3, 128.4, 122.2, 114.5, 108.2, 104.0, 56.8. C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>, Calculated: C, 61.76; H, 4.44; N, 10.29; Found: C, 61.56; H, 4.42; N, 10.34.

## Results and Discussion

### Synthesis of Vanillin based azo dye

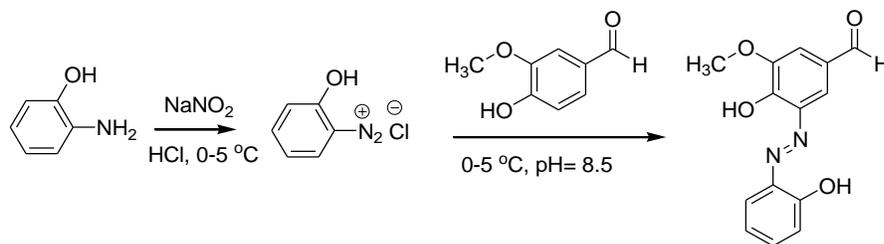
Synthesis of vanillin based azo dye was achieved in two steps which involved the diazotization and coupling to obtain the desired product. Diazonium salt of *o*-amino phenol was prepared separately according to the standard diazotization procedure. This dye was obtained by coupling of the synthesized diazonium salt with vanillin in basic medium at low temperature. The coupling was

done in alkaline aqueous solution to increase the nucleophilicity of vanillin (Scheme 1).

### Characterization of vanillin based azo dye

The synthesized vanillin based azo dye was characterized with the help of UV-Vis, FT-IR and NMR (<sup>1</sup>H, <sup>13</sup>C). These absorptions were due to the excitations of electrons in  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  orbitals which were the part of the conjugated framework of dye molecule. Different absorption maxima were present in dye spectra which may be attributed to the presence of distinct chromophores. This dye has the property of hydrogen bonding which is more prominent in different solvents. More polar solvents with high dielectric constant values prefer the intermolecular hydrogen bonding with dye (i.e. DMSO, acetonitrile) and less polar or non-polar (i.e. diethyl ether, chloroform etc.) solvents dye exhibit intramolecular, which is clearly indicated by the shifting in the value of  $\lambda_{\text{max}}$  as shown in Figure 1.

When the sample was run in methanol, four peaks were obtained at 220, 280, 315 and 410 nm with the highest intensity of absorbance at 220 nm and the lowest at 315 nm. Similarly, the sample was run in other solvents and the peak appeared at different position are summarized in Table 1. The highest bathochromic shifts were observed in acetic acid and chloroform revealing the smallest band gap [14].



Scheme 1: Synthesis of Vanillin based azo dye.

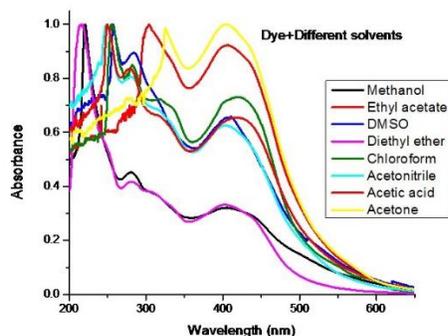


Figure 1: UV-Vis. Spectra of vanillin based azo dye in different solvents.

Table 1: UV-Vis. Spectra of vanillin based azo dye in different solvents

Sr. No.	Solvents	$\epsilon_r$	$\lambda_1$ (nm)	$\lambda_2$ (nm)	$\lambda_3$ (nm)	$\lambda_4$ (nm)
1	Methanol	32.61	220	280	315	410
2	Ethyl acetate	6.02	286	305	407	-
3	Dimethyl sulfoxide	46.68	255	285	409	-
4	Diethyl ether	4.30	220	281	311	405
5	Chloroform	4.71	257	281	320	424
6	Acetonitrile	35.69	248	279	317	405
7	Acetic acid	6.20	250	277	318	424
8	Acetone	21.00	274	326	405	-

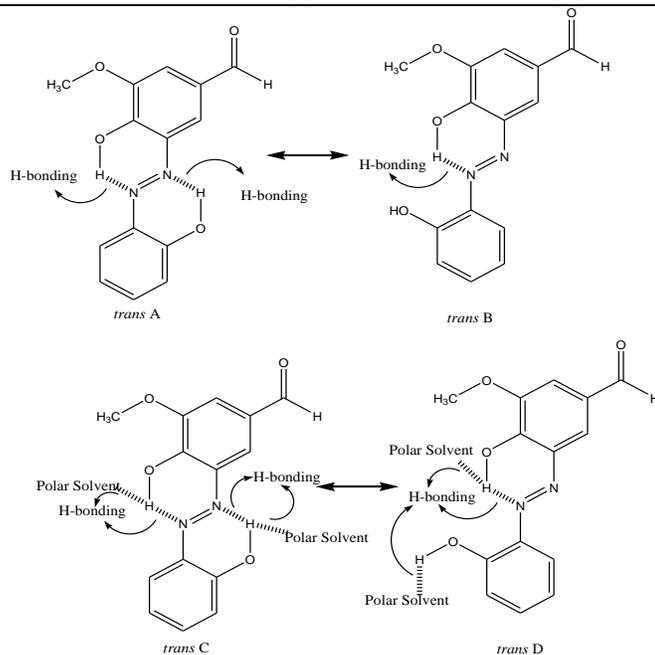


Figure 2: Hydrogen bonding at different place into the dye or with solvents

Mostly the given solvents make hydrogen bonding with dye and some dipole-dipole interactions that causes the change in electronic clouds and ultimately shifting in the  $\lambda_{\max}$ . The most probable

structure of compounds in polar or nonpolar solvent is shown in Figure 2 [15]. The *trans A* form is more stable than *trans B* because in this structure H-bonding is formed in two six

membered rings but in *trans* B only one ring [14, 16-18].

FT-IR spectra of the dye provided the evidence for the presence of different functional groups within the dye molecule. The hydroxyl groups produced broad range absorption at  $3364\text{ cm}^{-1}$  due to extended hydrogen bonding in the dye. The aldehyde and azo groups in the dye molecule were indicated from their peaks at  $1713$  and  $1572\text{ cm}^{-1}$  respectively. The presence of the peak at  $2902\text{ cm}^{-1}$  is due to C-H stretching vibrations of methoxy group. Furthermore, a strong absorption peak appeared at  $1145\text{ cm}^{-1}$  revealed the presence of C-O-C group.

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  study of dye confirmed the synthesis of targeted compound. There were broad peaks in  $^1\text{H-NMR}$  at  $15.47$  and  $15.05$  ppm due to presence OH groups in the azo part and vanillin coupler respectively. These peaks were highly deshielded due to the hydrogen bonding with polar DMSO solvent which snatched mostly electronic cloud from the hydrogen of OH group. A characteristic singlet was appeared at  $10.14$  due to the aldehydic proton. Two singlets appeared at  $7.87$  and  $6.90$  ppm due to the protons present at *ortho* position to the aldehyde group in vanillin. One characteristic singlet of methoxy protons appeared at  $3.81$  ppm.  $^{13}\text{C-NMR}$  of dye showed signal at  $190.2$  ppm due to CHO group of vanillin aromatic nucleus. The peaks at  $169.5$  and  $163.2$  ppm were due to the OH group containing carbons of vanillin and diazonium salts. These carbon atoms were also deshielded due to hydrogen bonding. All other carbons of vanillin base azo dyes showed signals at their respective regions. A peak at  $56.8$  ppm was attributed to methoxy carbons of the vanillin [19, 20]. The NMR spectra of the dye are shown in Figures 3 & 4.

#### Applications of vanillin based azo dye

The dye has hydroxyl groups at *ortho* to azo linkage at both sides of the molecule which have the ability to act as a ligand. So this dye was tested for detection of different metal ions such as  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Hg}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{Pb}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Cr}^{+3}$  and  $\text{Ni}^{+2}$  in their non-aqueous solutions. Solvents which used for detection of different metals were acetone, acetic acid, acetonitrile, methanol, ethyl acetate,

diethyl ether, chloroform and DMSO. The color change was clearly observed by naked eye which is shown in Figure 5.

The dye showed valuable interactions with these metal ions that were also affected by changing the solvents which were studied with the help of UV visible spectrophotometer. All metal ions on interaction with dye exhibited bathochromic or hypsochromic shifts, but the maximum changes were seen for  $\text{Fe}^{+3}$  ions in the absorption of visible light and in color of the complex from the original dye as evident in Figure 6.

In graph A, first of all  $10\text{ ppm}$  solution was prepared using acetic acid as solvent in  $250\text{ mL}$  beaker. In the UV visible spectra, four peaks were observed at  $250$ ,  $277$ ,  $318$  and  $424\text{ nm}$ . The strongest intensity of absorbance was at  $250\text{ nm}$ , intermediate at  $277$  and  $424\text{ nm}$  and the lowest at  $318\text{ nm}$ . When  $10\text{ ppm}$  solution of dye and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  ( $1:1$ ) were recorded then the four peaks were appeared at almost same wavelength but their absorbance intensity at  $421\text{ nm}$  lower than the dye. Similar behaviour was seen with other metal ions but the largest difference was attained in  $\text{Fe}^{+3}$  ion solution. In its solution, three peaks were obtained at  $248$ ,  $313$  and  $360\text{ nm}$ . The absorbance at  $313$  and  $360\text{ nm}$  were almost of equal intensity but it was higher at  $248\text{ nm}$ . Similarly, the other UV visible spectra were recorded by changing the solvents and same behavior was observed.  $\text{Fe}^{+3}$  ions showed blue shift in all solvents but other metal ions exhibits red shift because it has highest oxidation state as compared to others and hence it snatched more electronic clouds from the ligand in which the donor atoms are O and N. The UV visible spectra proved that the difference of energy level between the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) were the largest when the complex formation occurred between ligand and  $\text{Fe}^{+3}$  ions. All the graphs given in the Figure 6 indicate that the solvents have an important role for selective detection of different types of metals. This factor is mainly depending upon the solubility of ligands and metals. Mostly the variation occurs in hypochromic shift of different metals with ligand but  $\text{Fe}^{+3}$  ions show hypsochromic in all solvents.

From the graph A-H, it was indicated that the selectivity was more prominent in non-polar or less polar solvents (chloroform, diethyl ether etc.) but was less evident in more polar solvents such as DMSO. When the spectra were run in DMSO, each metal exhibits its own characteristic peaks and was difficult to differentiate for selective detection of any metal ion.

These metal ions study of vanillin azo dye enable them to be used as sequestrates for metal ions in their solutions in different solvents [22, 23]. In order to determine the number of water molecules, volumetric method was carried out which

provides the evidence for the involvement of water molecules during metal ion chelation.

UV visible data showed that the shifting in  $\lambda_{\max}$  was affected by changing solvent due to intermolecular, intramolecular and H-bonding forces responsible for changes in structure. Their effect was clear from spectra (Figure 7) in which equimolar solution of ligand and  $\text{Fe}^{+3}$  metal ions were present indicating the clear-cut shifting in  $\lambda_{\max}$ .

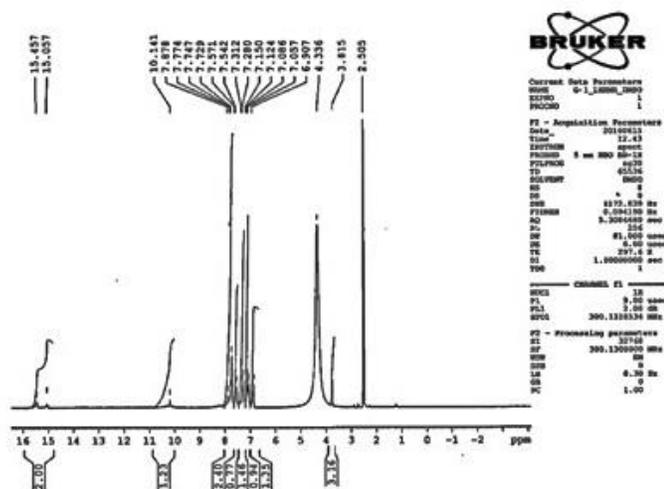


Figure 3:  $^1\text{H}$  NMR of dye

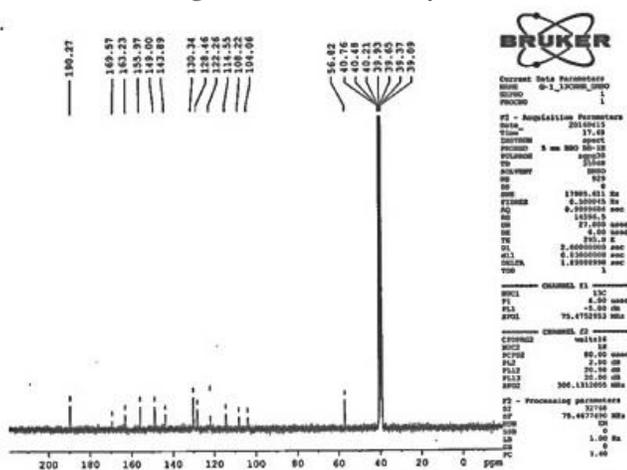


Figure 4:  $^{13}\text{C}$  NMR of dye



Figure 5: Naked-eye detection simply by variation in color in diethyl ether

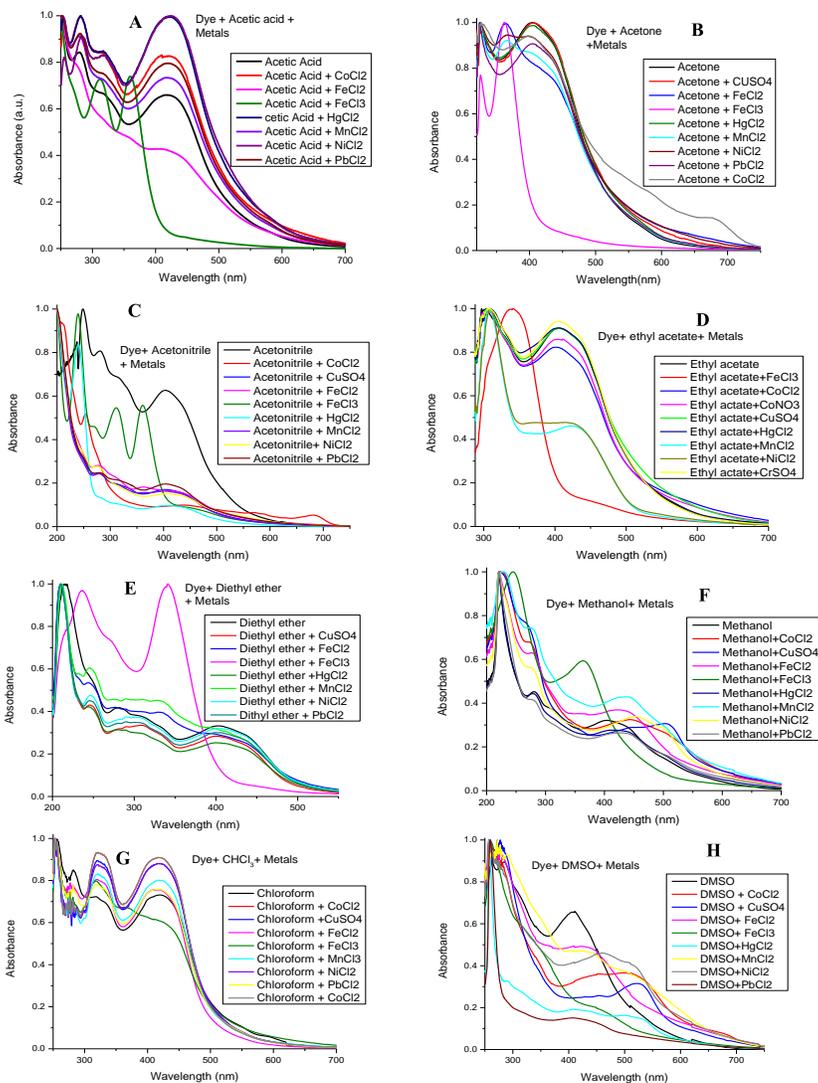


Figure 6: UV-Vis. Spectra of azo dyes with different metals (1:1 molar ratio) in different solvents in 10 ppm.

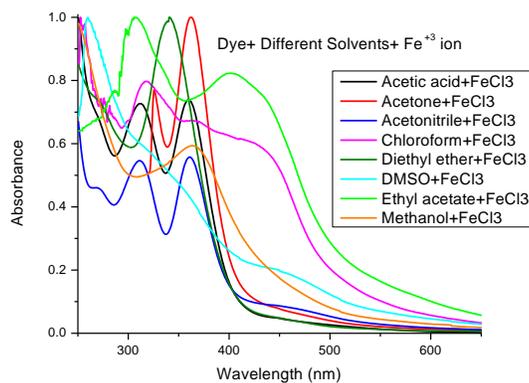


Figure 7: UV-Vis. Spectra of dye with metal Fe(III) ions in different solvents

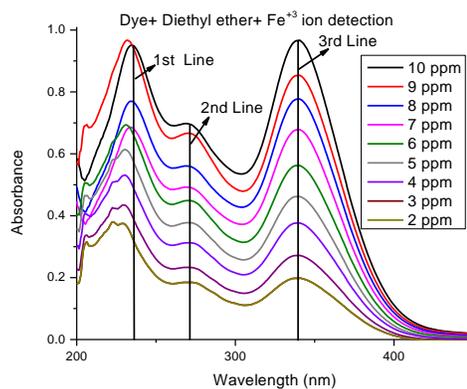


Figure 8: Detection limit of  $\text{Fe}^{+3}$  with dye in diethyl ether

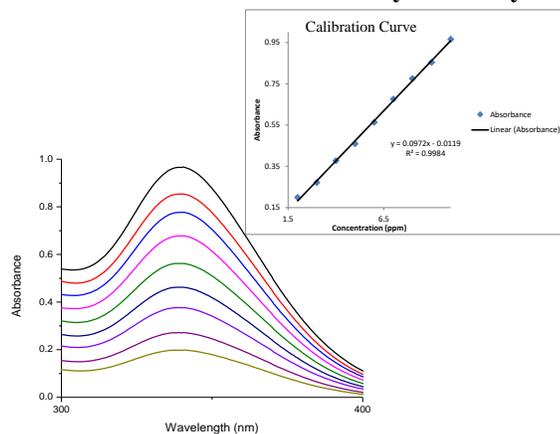


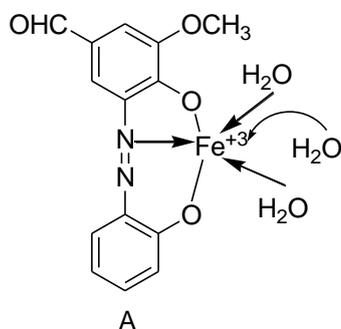
Figure 9: Spectra of calibration curve of  $\text{Fe}^{+3}$  with dye in diethyl ether

The band gap energy was calculated simply using the equation (1) [21].

$$E_g = hv = 1242/\text{wavelength} \quad (1)$$

The solution was diluted to calculate the detection limit of metal ions and their spectra was shown in Figure 8. The 1<sup>st</sup> vertical line showed hypsochromic effect by dilution along with absorbance intensity but in 2<sup>nd</sup> and 3<sup>rd</sup> vertical lines only intensity of absorbance decreases. The values of Limit of Detection (LOD) and Limit of Quantitation (LOQ) were 0.39 ppm and 1.17 ppm respectively which calculated by the calibration curve (Figure 9).

The most probable structure of the complex is shown in Figure 10. The -OH and azo groups donate the electron pair to the central metal ion.



**Figure 10: Most probable metal ion interaction mechanism**

The color variation of complex with respect to dye was monitored by simple test strip which is in Figure 11



**Figure 11: Test strip for rapid monitoring the chelation.**

### Conclusions:

Chemodosimeter based on azo dye conjugate was synthesized. Azo dye conjugate exhibited selectivity and sensitivity toward  $\text{Fe}^{3+}$  ions in all organic solution with hypsochromic shifts in their absorbance. From the graph A-H, it was indicated that the selectivity was more prominent in non-polar or less polar solvents (chloroform, diethyl ether etc.) but not in more polar solvents such as DMSO due to

solubility effect of metal salts and dye. The significant changes in the color could be used for naked-eye detection of  $\text{Fe}^{3+}$  ions in some environmental regions with a detection limit up to 0.39 ppm.

### Conflicts of interest

There are no conflicts to declare.

### References

- [1] G. Sivaraman, V. Sathiyaraja, D. Chellappa, Turn-on fluorogenic and chromogenic detection of Fe (III) and its application in living cell imaging, *Journal of luminescence* 145 (2014) 480-485.
- [2] K. Jomova, M. Valko, Advances in metal-induced oxidative stress and human disease, *Toxicology* 283(2-3) (2011) 65-87.
- [3] Y.W. Choi, G.J. Park, Y.J. Na, H.Y. Jo, S.A. Lee, G.R. You, C. Kim, A single schiff base molecule for recognizing multiple metal ions: a fluorescence sensor for Zn (II) and Al (III) and colorimetric sensor for Fe (II) and Fe (III), *Sensors and Actuators B: Chemical* 194 (2014) 343-352.
- [4] S.-R. Liu, S.-P. Wu, New water-soluble highly selective fluorescent chemosensor for Fe (III) ions and its application to living cell imaging, *Sensors and Actuators B: Chemical* 171 (2012) 1110-1116.
- [5] U.E. Schaible, S.H. Kaufmann, Iron and microbial infection, *Nature Reviews Microbiology* 2(12) (2004) 946-953.
- [6] J. Wang, Y. Li, N.G. Patel, G. Zhang, D. Zhou, Y. Pang, A single molecular probe for multi-analyte ( $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ ) detection in aqueous medium and its biological application, *Chemical Communications* 50(82) (2014) 12258-12261.
- [7] X. Fang, S. Zhang, G. Zhao, W. Zhang, J. Xu, A. Ren, C. Wu, W. Yang, The solvent-dependent binding modes of a rhodamine-azacrown based fluorescent probe for  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ , *Dyes and Pigments* 101 (2014) 58-66.
- [8] A. Chatterjee, M. Santra, N. Won, S. Kim, J.K. Kim, S.B. Kim, K.H. Ahn, Selective fluorogenic and chromogenic probe for detection of silver ions and silver nanoparticles in aqueous media, *Journal of the American Chemical Society* 131(6) (2009) 2040-2041.

- [9] L. Zecca, M.B. Youdim, P. Riederer, J.R. Connor, R.R. Crichton, Iron, brain ageing and neurodegenerative disorders, *Nature Reviews Neuroscience* 5(11) (2004) 863-873.
- [10] T. Ito, C. Goto, K. Noguchi, Lanthanoid ion-selective solvent polymeric membrane electrode based on 1-phenyl-3-methyl-4-octadecanoyl-5-pyrazolone, *Analytica chimica acta* 443(1) (2001) 41-51.
- [11] Y.-W. Duan, H.-Y. Tang, Y. Guo, Z.-K. Song, M.-J. Peng, Y. Yan, The synthesis and study of the fluorescent probe for sensing  $\text{Cu}^{2+}$  based on a novel coumarin Schiff-base, *Chinese Chemical Letters* 25(7) (2014) 1082-1086.
- [12] Y. Zhang, Y.-G. Gao, Y.-D. Shi, L.-Q. Tan, J.S. Yue, Z.-L. Lu, [12] aneN3-based BODIPY as a selective and sensitive off-on sensor for the sequential recognition of  $\text{Cu}^{2+}$  ions and ADP, *Chinese Chemical Letters* 26(7) (2015) 894-898.
- [13] N. Narayanaswamy, T. Govindaraju, Aldazine-based colorimetric sensors for  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ , *Sensors and Actuators B: Chemical* 161(1) (2012) 304-310.
- [14] A. Saeed, P.A. Channar, G. Shabir, F.A. Larik, Green synthesis, characterization and electrochemical behavior of new thiazole based coumarinyl scaffolds, *Journal of fluorescence* 26(3) (2016) 1067-1076.
- [15] D. Li, C. Li, Y. Liu, Effects of solvent polarity and hydrogen bonding on coumarin 500, *Journal of Molecular Liquids* 218 (2016) 670-675.
- [16] J.L. Cook, C.A. Hunter, C.M. Low, A. Perez-Velasco, J.G. Vinter, Solvent effects on hydrogen bonding, *Angewandte Chemie International Edition* 46(20) (2007) 3706-3709.
- [17] O.K. Abou-Zied, Steady-state and time-resolved spectroscopy of 2, 2'-bipyridine-3, 3'-diol in solvents and cyclodextrins: Polarity and nanoconfinement effects on tautomerization, *The Journal of Physical Chemistry B* 114(2) (2010) 1069-1076.
- [18] G. Shabir, M. Arif, A. Saeed, G. Hussain, Synthesis and Optical Study of Sensitive and Selective Calix [4] Based  $\text{Cu}^{2+}$  Ion Detection Probes, *Russian Journal of General Chemistry* 89(4) (2019) 813-818.
- [19] H.Y. Lee, X. Song, H. Park, M.-H. Baik, D. Lee, Torsionally Responsive C 3-Symmetric Azo Dyes: Azo-Hydrazone Tautomerism, Conformational Switching, and Application for Chemical Sensing, *Journal of the American Chemical Society* 132(34) (2010) 12133-12144.
- [20] Y. Zhu, I. Heim, B. Tieke, Red Emitting Diphenylpyrrolopyrrole (DPP)-Based Polymers Prepared by Stille and Heck Coupling, *Macromolecular Chemistry and Physics* 207(23) (2006) 2206-2214.
- [21] N. Kabay, E. Erdem, R. Kılınçarslan, E.Y. Sarı, Synthesis and characterization of some o, o'-dihydroxyazo dyes and their metal complexes, *Transition Metal Chemistry* 32(8) (2007) 1068-1072.
- [22] B.B. Mahapatra, R.R. Mishra, A.K. Sarangi, Synthesis, characterisation, XRD, molecular modelling and potential antibacterial studies of Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Hg (II) complexes with bidentate azo dye ligand, *Journal of Saudi Chemical Society* 20(6) (2016) 635-643.
- [23] A. El-Bindary, G. Mohamed, A. El-Sonbati, M. Diab, W. Hassan, S.M. Morgan, A. Elkholy, Geometrical structure, potentiometric, molecular docking and thermodynamic studies of azo dye ligand and its metal complexes, *Journal of Molecular Liquids* 218 (2016) 138-149.