

# Synthesis and characterization of novel copper(II) and zinc(II) complexes for improved leather dyeing performance using N-phenyl gamma-acid oximes

Muhammad Sajid Ali<sup>1\*</sup>, Samra Barkaat<sup>1</sup>, Muhammad Zuber<sup>1</sup>, Ghulam Hussain<sup>2</sup>, Fatima Noor<sup>1</sup>, Noor Asif<sup>1</sup>, Umm e Kalsoom<sup>1</sup>

<sup>1</sup>Department of Chemistry, Riphah International University Faisalabad, Pakistan

<sup>2</sup>SRC (Pvt.) Ltd. Formerly Shafi Reso-chem, Lahore, Pakistan

**Corresponding Author:** Department of Chemistry, Riphah International University Faisalabad, Pakistan

**Abstract:** This study focused on the synthesis, of metal complexes prepared from N-Phenyl Gamma Acid (NPGA) as potential antimicrobial agents. In the method, NPGA is nitrosated with NaNO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> to give an oxime (confirmed by color change on addition of FeSO<sub>4</sub>). The complexes were then slightly metallized using Cu<sup>2+</sup> and Zn<sup>2+</sup>, followed by FTIR and UV-visible spectroscopy. The results showed that the new material has distinct spectral features for Cu-(II) and Zn (II)- complexes, which confirms the formation of these two metal-complexes. Finally, the prepared metal complexes were investigated their ability to dye natural leather. Where the Cu-complex gave deeper hue development than corresponding un-metallized dye, while Zn-complex showed balance color properties. A study has demonstrated metal complexes deepen intensity and permanence of the dye, with far superior results than covalent attachment (Zn-complex is more effective).

**Keywords:** Metal complex, oxime synthesis, nitrosation, leather dyeing, FTIR spectroscopy

## I INTRODUCTION

Dyeing is considered one of the most critical processes in the leather industry as it is the stage where the visual aesthetics and marketability of the product are enhanced [1, 2]. Fostering vibrant and long-lasting colours on leather has been a long-term goal that necessitates various explorations in dyeing agents and techniques [3, 4]. Metal complex dyes, particularly those involving transition metals such as copper and zinc [5], have proven incredibly effective due to improved fastness properties such as washing, light, and heat resistance [6]. N-Phenyl Gamma Acid is a versatile ligand known to form oximes readily [7, 0]. It can coordinate with metal ions to form metal complexes with distinct absorption and fastness properties, making them viable for the dyeing industry [9, 10]. Previous research has shown that introducing metal ions into the internal structures of organic dyes can dramatically alter their colour, solubility, and coordination properties [11-13]. However, there is a need for more research regarding the metallization of NPGA [14] and its oximes due to the lack of detail available in the literature, particularly with copper and zinc [15]. Even more importantly, the direct effects of these oxime complexes on the dyeing performance, including colour fastness [16, 17],

penetration, and perspiration fastness, are yet to be thoroughly studied [10, 19]. Hence, the current study is designed to meet these objectives.

Therefore, the study aims to synthesize and characterize copper(II) and zinc(II) complexes of N-Phenyl Gamma-Acid oximes to address the gap. The synthesis path includes nitrosation of NPGA to oxide, followed by metallization to produce the copper(II) and zinc(II) complexes. The synthesized complexes are characterized using optical methods such as UV-visible absorption spectroscopy and Fourier-transform infrared spectroscopy to establish their structural and optical properties. The performance of the complexes as dyes is further tested on leather substrates; thereafter, their colour fastness, penetration, and perspiration fastness are evaluated. It is observed from the findings that both copper(II) and zinc(II) complexes present different absorption spectra and optical properties and better performance as a dye compared to unmetallized NPGA, as shown in Figure 11. The copper(II) complex presented an absorption maximum at 360 nm with an olive-brown colour, while the zinc(II) metal complex absorbed light maximally at 360 nm due to the unbound and coordinated N-H free atoms at the metal complex. Both complexes dissolved fully in water, implying solubility in water-based dyeing systems. The FTIR revealed that the copper and zinc ions coordinated with the ligands, forming the complexes. The dyed leather samples demonstrated colour fastness with better light-fastness and water resistance properties. These findings imply that the metallized dyes could replace the standard dyes in the leather dyeing industries. The metallized complex colours are stable and have higher fastness to prevail longer compared to the standard dyes. The knowledge generated by this research study can enhance other fields, such as textiles, to make dye types that exhibit fastness to light and water. Therefore, this study bridges the known gap and promotes the application of coordination chemistry in the dyeing industry.

## II METHODOLOGY

### A. Oxime synthesis (Nitrosation)

N-Phenyl Gamma Acid (NPGA) 35.0 g (0.1 mol) and water 200

mL in a 1000-mL beaker (+50% NaOH, 10 mL). And to the mixture, 7.3 g (0.135 mol) of NaNO<sub>2</sub> and 200 g ice were added. The beaker was jacketed and maintained at near 0°C, and a solution of H<sub>2</sub>SO<sub>4</sub> (25% in water), 50 mL, added from above as to dropwise. After 1 hour complete nitrosation. Further addition of 5g, sulphamic acid to this removed excess nitrous acid and the product oxime so obtained was isolated. Successful nitrosation was confirmed by the formation of a bright color upon addition with FeSO<sub>4</sub>. The nitrosated product (450 mL) was divided in 3 equal portions for metallization [20].

### B. Metalization

After nitrosation, the whole oxime solution was divided into six parts; its pH was maintained at 6.5 to 7.0. For metal complex production metal complex [21, 22], 150g of this solution divided was then weighed into a 250 mL beaker; being the 250 mL of this beaker. A 25 mL solution of 0.1 moles of Cu and Zn salt solution was then made up and added to the oxime solution beaker. The Mixture in the beaker was heated on a burner for 55 minutes at 55 to 65 °C, then it was swirled with a glass rod; thereafter, it was cooled to room temperature. Its pH did not fluctuate from 6.5 to 7.0. The method of investigation was paper chromatography; the paper chromatography sensor told us that we were producing the metal. An unmetallized oxime (UMO) was used as standard.

### C. Isolation

Separation of the metal complexes by salting out at different salt concentrations [23]. Separated about 13% of the copper and zinc with around 6% comparison to total acid-based oxime solution.

### D. Characterization

Synthesized complexes were characterized by using absorption spectroscopy (UV-visible) and Fourier-transform infrared spectroscopy (FTIR) for the structure determination as well of their composition.

FTIR spectra of the Un-Metallized Oxime (UMO) showed to have stretching bands for NH, H<sub>2</sub>O, OH stretching's; C=O stretching and oximes C=N stretching as signals of organic functional groups. The λ<sub>max</sub> at 390 nm was recorded.

FT-IR spectra from Cu complex showed typical absorption bands of i.e., NH, H<sub>2</sub>O, OH stretching C=O stretches; oxime group vibrations (-N = O); CH=C stretch (1606 cm<sup>-1</sup>), N=N (Nitroso) groups; NO symmetrical and asymmetrical stretching, etc. morphology for this compound close at 360 nm. FTIR spectra of the Zn complex also showed absorption bands at wavelengths corroborated with NH, H<sub>2</sub>O and OH stretching, C=O stretching can be seen as well as oxime C=N, C=C stretching, N=N Stretching NO stretch etc. functional group λ<sub>max</sub> recorded give 360 nm.

## III RESULTS AND DISCUSSION

### E. Nitrosation Conformation

First step study was the nitrosation of N-phenyl Gamma acid through the in situ generation of nitrous acid. During the oxime synthesis, three different conformers were observed. The color of the resulting oxime changed from dark to brown with a λ<sub>max</sub> of

300 nm indicative of the formation of oxime compounds. Oxime is a pigmented compound that absorbs violet light. The FeSO<sub>4</sub> test verified the presence of oximes and provided us with an intense white (sometimes green) coloration. In the dry oxime's Fourier-transform infrared spectroscopy analysis, it can be seen that some absorption bands increased and shifted towards red, particularly at 1606 cm<sup>-1</sup>, revealing the H-bonding in the oxime nitroso derivative.

### F. FTIR Analysis

Spectra of the oxime, unmetallized (UMO), and metal complexes (MO) were recorded by FTIR analysis. FTIR data (Peak-height) have been presented graphically in fig to show characteristic spectra of compounds analyzed.

#### N-Phenyl Gamma Acid

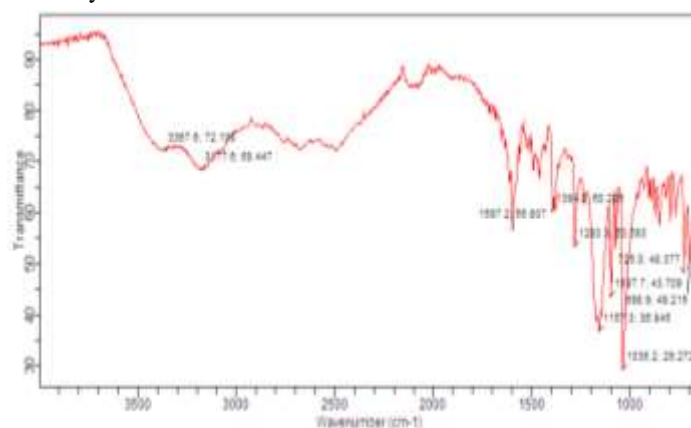


Fig. 1. FTIR spectrum of N-Phenyl Gamma Acid

FTIR spectra with N-Phenyl Gamma Acid showed in Figure 1 prominent hydrogen bonding absorption bands in the region 3000 to 3500 cm<sup>-1</sup> due H<sub>2</sub>O, OH and NH at values of maximum absorbance (3367 cm<sup>-1</sup> or 3177 cm<sup>-1</sup>). Between 1500 and 2000 cm<sup>-1</sup> bands, the absorption peaks for C=C, N=N also differ; here there is a narrow band peak at 1597 cm<sup>-1</sup>, as well as one due to O-N=O. The bands which appeared between 1000 cm<sup>-1</sup> and 1500 cm<sup>-1</sup> are due to N-nitroso, S=O, C=N and C=O with the highest peak at ~1394 cm<sup>-1</sup>. Fingerprint region (600-1200 cm<sup>-1</sup>) in both Cu and Li-Cu regions showed the metal complex chemicals due to peaks at 1157, 1007, and 1036 cm<sup>-1</sup>. CH bonding and aromatic compounds were well established with single, strong absorption bands at 030 cm<sup>-1</sup> (para) to give the signature for N-Phenyl Gamma

## Un-Metallize Oxime (UMO)

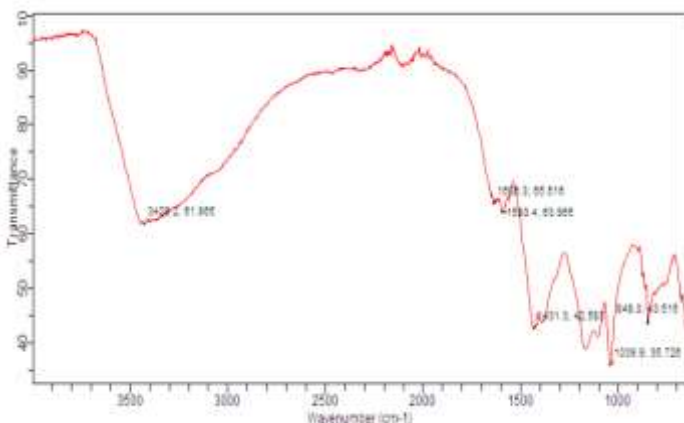


Fig. 2. FTIR spectra of un-metallize oxime (UMO)

In Figure 2 showed the UMO FTIR spectra had broad absorption between 3000 and 3500  $\text{cm}^{-1}$ , with a peak at 3429  $\text{cm}^{-1}$ , indicating hydrogen bonding  $\text{H}_2\text{O}$ , OH, NH. Unsaturated carbon atoms CO stretched between 1715 and 1695  $\text{cm}^{-1}$ , and an absorbance peak of 1606  $\text{cm}^{-1}$  was obtained. Other broad narrow bands at 1500 and 2000  $\text{cm}^{-1}$  showed C = C, N = N, C-nitroso stretching. The peaks were 1593  $\text{cm}^{-1}$  NO and C-nitroso, 1493  $\text{cm}^{-1}$  and 1039  $\text{cm}^{-1}$  CO, N-nitroso,  $\text{SO}_2$ , C = N, phenolic OH, NO. Metal complex molecules were observed in the fingerprint area 600-1200  $\text{cm}^{-1}$ , with a strong absorbance at 030  $\text{cm}^{-1}$  para and 750  $\text{cm}^{-1}$  ortho, indicating aromatic CH bonding.

## Cu Complex

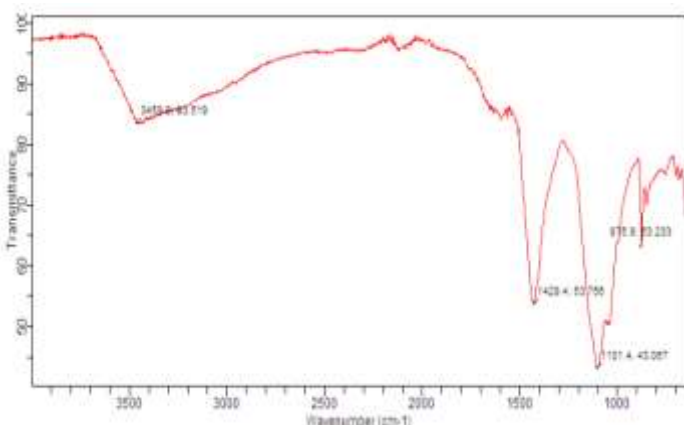


Fig. 3. FTIR spectra of Copper complex

FTIR spectra of the Cu-complex revealed an important  $\text{H}_2\text{O}$ , OH and NH stretching in range 3000 – 3500  $\text{cm}^{-1}$  with a peak at this location (3459  $\text{cm}^{-1}$ ). This band from 1000 to 1500  $\text{cm}^{-1}$  (at peak at overlying: 1429  $\text{cm}^{-1}$ , N-nitroso stretching) was proposed for unsaturated carbon atoms (as N-nitroso, sulfoxide, C=O; oxime C=N; phenolic OH). The hydrocarbon moieties because of the C-O at 1101  $\text{cm}^{-1}$  and C=C bonds a tall power speak to around 075 cm for Hydrogen bonding spreading; it demonstrates that plant removed ligands are organized among high orders. The presence of bands at 030  $\text{cm}^{-1}$  (para) and 750  $\text{cm}^{-1}$  (ortho), indicative

aromatic CH bonds was consistent with that the Cu(II)-oxime complex.

## Zn Complex

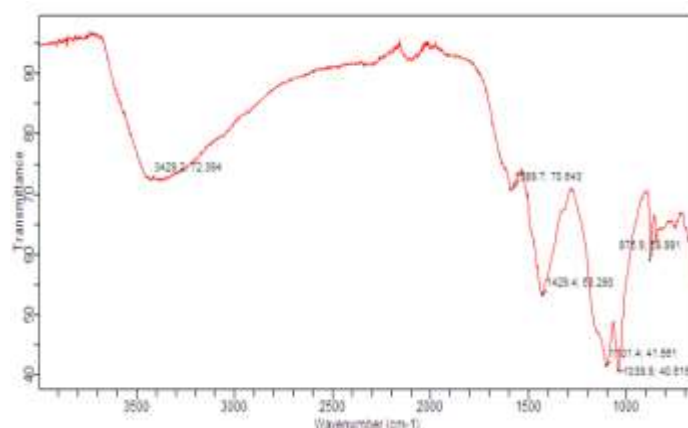


Fig. 4. FTIR spectra of Zn complex

Zn-complex FTIR spectra indicated hydrogen bonding with a significant absorption band between 3000 and 3500  $\text{cm}^{-1}$ , peaking at 3429  $\text{cm}^{-1}$ . Unsaturated carbon atoms showed peaks in the narrow band between 1500 and 2000  $\text{cm}^{-1}$ : C=O and oxime C=N (1690-1620  $\text{cm}^{-1}$ ), C=C (1600-1625  $\text{cm}^{-1}$ ), N=N (1630-1575  $\text{cm}^{-1}$ ), and C-nitroso (1600-1500  $\text{cm}^{-1}$ ). A peak at 1509  $\text{cm}^{-1}$  supported N=N and C-nitroso stretching. Another band (1000-1500  $\text{cm}^{-1}$ ) included peaks at 1429  $\text{cm}^{-1}$  (N-nitroso stretching), 1101  $\text{cm}^{-1}$  (C-O stretching), and 1039  $\text{cm}^{-1}$  (S=O sulfoxide stretching). The fingerprint area (600-1200  $\text{cm}^{-1}$ ) indicated metal complex compounds, with C=C bonds peaking at 075  $\text{cm}^{-1}$ . Aromatic CH bonds peaked at 030  $\text{cm}^{-1}$  (para) and 750  $\text{cm}^{-1}$  (ortho). FTIR spectra confirmed the successful synthesis of the Zn-oxime complex (Enders et al., 2021).

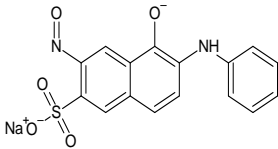
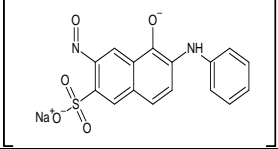
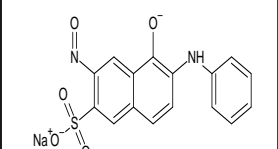
### G. Physical Properties of Metal Complexes

Preparation of oxime using N-Phenyl Gamma Acid was made in two color forms. These colors were Copper and Zinc complexes with a none metallized dye in the case of the first one. Details of physical features are given in Table 1 shows the data concerning the three oxime complexes. The first one is unmetallized oxime; its molecular formula is  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_5\text{SNa}$ . The UMO is dark brown, its  $\lambda_{\text{max}} = 390$  has an absorbance of 1.75, and the complex is water-soluble. The copper complex

$C_{10}H_{10}CuN_2O_5SNa$  other metallized complex is olive brown with  $\lambda_{max} = 360$ , which is due to the metallization, and an absorbance of 1.65 – of course, the complex remains water-soluble. The third complex, the zinc one with the molecular formula  $C_{10}H_{10}ZnN_2O_5SNa$ , is black brown and has  $\lambda_{max} = 360$  and an

absorbance of 1.3. The metallized versions of water solubility of the complexes do not change. Thus, the metal complex differences are the altered color and absorption. The first two parameters indicate a change in metallization, and the absorbance reduces compared to UMO.

**Table 1.** Physical properties of complexes


Sr.No	Oxime/Complexes	Structure	Molecular Formula	Colour	$\lambda_{max}$ Absorbance	Solubility
101	UMO		$C_{10}H_{10}N_2O_5SNa$	Dark Brown	390/1.75	Water
103	Copper		$C_{10}H_{10}CuN_2O_5SNa$	Olive Brown	360/1.65	Water
104	Zinc		$C_{10}H_{10}ZnN_2O_5SNa$	Black Brown	360/1.3	Water

#### H. Leather Application

All the polyamides, like nylon, leather, wool or acrylic can be dyed by acidic metal complexes with  $SO_3H$  group. The substrate used in this investigation was leather. Leather was treated with compounds of different concentrations and the magnitude of color shade development. Dyeing was carried out in a drum machine. Two concentrations, 2 % and 5% of two colours; these were formulated and allowed to dry off. Colors were Pantone matched.

**Table 2.** Shade card of un-dyed leather, un-metallized dye, Cu-Complex & Zn-Complex

Leather pieces were impregnated with 1 mL solutions of unmetallized (2%) Oxime(UMO), Copper and Zinc metallized respectively. These pieces were then retrieved for additional color index matching after 24 hours of drying. At the second phase, a piece of leather and 5% UMO solution (3.0 mL) were accommodated in a plastic box containing 50 ml in water.

Shade Card of N-Phenyl Gamma-Acid Oxime and Its Metal Complexes			
	Name	2% Shade	5% Shade
101	Un dyed Leather		
102	Un-metalized dye		
103	Cu-Complex		
104	Zn-Complex		

### I. Penton Matching System

Table 3 below compares the PMS shades of N-Phenyl-Gamma-Acid Oxime and its metal complexes at 2% and 5% concentrations. At either concentration, the un-metalized dye gives off similar shades where PMS 1555 shifts the shade of 1655 to a darker PMS 1545. Cu-complex gives off shades PMS 1265 which is darker than PMS 1545 and PMS 1555 at 2% and 5% respectively. For Zn-complex, the shade from PMS 1555 at 2% is shifted to PMS 1615 at 5%. This suggests that metal complexes greatly influence the intensity and hue of shades, especially at 5% concentration.

**Table 3.** Comparison of Pantone Matching System (PMS) shades for N-Phenyl-Gamma-Acid Oxime and its metal complexes

Dye #	Name	PMS # of 2% Shade	PMS # of 5% Shade
102	Un-metalized dye	1555	1545

103	Cu- Complex	1265	1545
104	Zn- Complex	1555	1615

### J. Light Fastness

Once the leather dyes are applied, the lightfastness of the product was measured based on color. The following properties were evaluated: lightness, penetrability, and perspiration. Values varied between 1, meaning "weak," to 5, meaning "best". Only dark dyes are resistant to leach, while light-colored dyes and complex metal dyes are more resistant because metal absorbs UV light and converts it to heat. The test was performed covering half of the leather piece and exposing sunlight to the other half. The color did not manifest any visible sign, which means that the dyes applied showed overall high fastness.

**Table 4.** Physical properties of shade card

Dye #	2% Shades			5% Shades		
	Light	Penetration	Perspiration	Light	Penetration	Perspiration
101	Std.	Std.	Std.	Std.	Std.	Std.
102	2-3	4-5	1-2	2-3	4-5	1-2
103	2-3	4-5	2-3	2-3	4-5	2-3
104	3-4	4-5	3-4	4-5	4-5	3-4

Physical parameters of dyes in 2% and 5% concentrations are presented in Table 4. They include lightfastness, penetration, and perspiration resistance. Dye 101 shows average performance in all cases, which is expected since it is made of undyed Lather. Dye 102 has moderate lightfastness and high penetration but very low perspiration resistance. Dye 103, another Cu-complex, has similar penetration and slightly better perspiration. However, Dye 104 is the best in these parameters exhibiting very good lightfastness and high penetration and the best perspiration resistance, especially in 5% concentration. Thus, it can be expected that the performance of dyes will generally improve while using metal complexes, with the Zn-complex being the most well-balanced.

#### IV CONCLUSION

In this work, synthesizing and characterizing metal complexes of N-Phenyl Gamma Acid (NPGA) proficiently carried out via nitrosation followed by metallization with copper along and as well zinc ions was noted. This was found to produce an oxime in the nitrosation process and this confirmed by a characteristic  $\text{FeSO}_4$  color reaction. For the metal complexes extracted, structural analysis was carried out using FTIR and UV-visible spectroscopy and unique spectral characteristics consistent with a complex formation was observed. Both Cu(II) and Zn(II)-complexes showed better dyeing properties especially a satisfactory colorant (deep, bright colors for copper complex; balanced overall hue in the case of Zinc). Results from the cowhide trials indicated that metalized dyes are especially better than un-metallized oxime in respect to intensity and fastness, with zinc complex giving the best performance. Findings include efforts to improve metal complex formulations for improved dye properties and the use of new metal ions for a different array of colors. Later perspectives should also concern scaling-up of these processes for industrial use and assessing the resulting environmental consequences from each metal complex. This

could potentially have great consequences for textile dyeing technologies and industrial uses in general: less energy use, fewer toxins diffusing into the environment.

#### ACKNOWLEDGEMENT

We are thankful to Riphah International University, Faisalabad for providing the resources and support. The author thanks the faculty and staff for their help, guidance, and expertise required to perform this research. The support which the university administration gives is very important to us.

#### AUTHORS

**First Author** – Muhammad Sajid Ali, M.Phil., Department of Chemistry, Riphah International University Faisalabad, Pakistan.

**Second Author** – Samra Barkaat, Ph.D., Department of Chemistry, Riphah International University Faisalabad, Pakistan.

**Third Author** – Muhammad Zuber, Ph.D., Department of Chemistry, Riphah International University Faisalabad, Pakistan.

**Fourth Author** – Ghulam Hussain, <sup>2</sup>SRC (Pvt.) Ltd. Formerly Shafi Reso-chem, Lahore, Pakistan.

**Fifth Author** – Fatima Noor, M.Phil., Department of Chemistry, Riphah International University Faisalabad, Pakistan.

**Sixth Author** – Noor Asif, M.Phil., Department of Chemistry, Riphah International University Faisalabad, Pakistan.

**Seventh Author** – Umm e Kalsoom, M.Phil., Department of Chemistry, Riphah International University Faisalabad, Pakistan.

**Correspondence Author** – Muhammad Sajid Ali,

## REFERENCES

- [1] S. Dave, J. Das, B. Varshney, and V. Sharma, "Dyes and pigments: Interventions and how safe and sustainable are colors of life!!!," in *Trends and Contemporary Technologies for Photocatalytic Degradation of Dyes*: Springer, 2022, pp. 1-20.
- [2] N. R. J. Hynes *et al.*, "Modern enabling techniques and adsorbents based dye removal with sustainability concerns in textile industrial sector-A comprehensive review," *Journal of cleaner production*, vol. 272, p. 122636, 2020.
- [3] A. Thakur and A. Kumar, "Polyphenols for Dyes Application," *Science and Engineering of Polyphenols: Fundamentals and Industrial Scale Applications*, pp. 157-210, 2024.
- [4] V. Rognoli, B. Petreca, B. Pollini, and C. Saito, "Materials biography as a tool for designers' exploration of bio-based and bio-fabricated materials for the sustainable fashion industry," *Sustainability: Science, Practice and Policy*, vol. 10, no. 1, pp. 749-772, 2022.
- [5] A. Ramdass, V. Sathish, E. Babu, M. Velayudham, P. Thanasekaran, and S. Rajagopal, "Recent developments on optical and electrochemical sensing of copper (II) ion based on transition metal complexes," *Coordination Chemistry Reviews*, vol. 343, pp. 270-307, 2017.
- [6] A. C. Silva, A. J. Silvestre, C. S. Freire, and C. Vilela, "Modification of textiles for functional applications," in *Fundamentals of natural fibres and textiles*: Elsevier, 2021, pp. 303-365.
- [7] A. Porcheddu and G. Giacomelli, "Synthesis of oximes and hydroxamic acids," *The Chemistry of Hydroxylamines, Oximes and Hydroxamic Acids*, vol. 1, pp. 163-231, 2009.
- [8] J. Fotie *et al.*, "The fundamental role of oxime and oxime ether moieties in improving the physicochemical and anticancer properties of structurally diverse scaffolds," *International Journal of Molecular Sciences*, vol. 24, no. 23, p. 16054, 2023.
- [9] S. Velusamy, A. Roy, S. Sundaram, and T. Kumar Mallick, "A review on heavy metal ions and containing dyes removal through graphene oxide-based adsorption strategies for textile wastewater treatment," *The Chemical Record*, vol. 21, no. 7, pp. 1570-1610, 2021.
- [10] T. A. Khattab, M. S. Abdelrahman, and M. Rehan, "Textile dyeing industry: environmental impacts and remediation," *Environmental Science and Pollution Research*, vol. 27, no. 4, pp. 3003-3010, 2020.
- [11] M. S. Khan, M. Khalid, and M. Shahid, "What triggers dye adsorption by metal organic frameworks? The current perspectives," *Materials Advances*, vol. 1, no. 6, pp. 1575-1601, 2020.
- [12] Y. Jiao, Y. Zuo, H. Yang, X. Gao, and C. Duan, "Photoresponse within dye-incorporated metal-organic architectures," *Coordination Chemistry Reviews*, vol. 430, p. 213640, 2021.
- [13] Z. Liu, W. He, and Z. Guo, "Metal coordination in photoluminescent sensing," *Chemical Society Reviews*, vol. 42, no. 4, pp. 1560-1600, 2013.
- [14] I. Ciofi *et al.*, "RC benefits of advanced metallization options," *IEEE transactions on electron devices*, vol. 66, no. 5, pp. 2339-2345, 2019.
- [15] D. S. Bolotin, N. A. Bokach, M. Y. Demakova, and V. Y. Kukushkin, "Metal-involving synthesis and reactions of oximes," *Chemical Reviews*, vol. 117, no. 21, pp. 13039-13122, 2017.
- [16] G. Hussain *et al.*, "Synthesis and characterization of chromium (III), iron (II), copper (II) complexes of 4-amino-1-(p-sulphophenyl)-3-methyl-5-pyrazolone based acid dyes and their applications on leather," *Dyes and Pigments*, vol. 130, pp. 90-90, 2016.
- [17] N. Ibrahim, D. Ibrahim, B. Eid, W. El-Zairy, and T. Tawfik, "Upgrading the functional properties of reactive dyed cotton knits," *The Journal of The Textile Institute*, vol. 100, no. 9, pp. 1634-1642, 2017.
- [18] O. Avinc, D. Phillips, and M. Wilding, "Influence of different finishing conditions on the wet fastness of selected disperse dyes on polylactic acid fabrics," *Coloration Technology*, vol. 125, no. 5, pp. 200-295, 2009.
- [19] M. A. Hannan, P. Haque, S. F. Kabir, and M. M. Rahman, "Scope of sustainable pretreatment of cotton knit fabric avoiding major chemicals," *Journal of natural fibers*, 2020.
- [20] J. Brand, T. Huhn, U. Groth, and J. C. Jochims, "Nitrosation of Sugar Oximes: Preparation of 2-Glycosyl-1-hydroxydiazene-2-oxides," *Chemistry—A European Journal*, vol. 12, no. 2, pp. 499-509, 2006.
- [21] O. Ajani, B. A. Kasali, and K. Abdulahi, "Synthesis and characterization of Cu and Fe (1: 2) metal complexes based on their substituted pyridones acid dyes and their application on wool fabrics," *Journal of Chemistry Letters*, vol. 3, no. 4, pp. 101-100, 2022.
- [22] N. Abbas, "Nitrosopyrazolone Metal Complexes, Synthesis, Characterization and Biological Studies," *Sch Int J Chem Mater Sci*, vol. 4, no. 6, pp. 112-126, 2021.
- [23] R. R. Romero-González and R. Verpoorte, "Salting-out gradients in centrifugal partition chromatography for the isolation of chlorogenic acids from green coffee beans," *Journal of Chromatography A*, vol. 1216, no. 19, pp.

