Digest Journal of Nanomaterials and Biostructures Vol. 17, No. 3, July - September 2022, p. 913 - 920

Visible light photocatalytic dye degradation activity of Fe^{3+}, Co^{2+}, Mn^{2+} and Zn^{2+}mononuclear complexes derived from O-vanillin bidentate schiffbase ligands

A. Jaan[a], W. Iqbal[b], B. Shahzad[c], Y. Iqbal[d,e], M. U. Rehman[c], I. Haider[f], M. T. Javid[g], U. Anwar[c,*]
[a]*Institute of Chemical Sciences, Bahauddin Zakariya University, Multan, 60800, Pakistan*
[b] *Department of Chemistry and Chemical Technologies, University of Calabria, 87036 Rende, Cosenza, Italy*
[c]*Soochow Institute for Energy and Materials Innovations, College of Energy, Soochow University, Suzhou 215006, China*
[d]*Department of Chemistry, Government College University Faisalabad-38000, Pakistan*
[e]*Department of Chemistry, University of Sialkot-51040, Pakistan*
[f]*Materials Modeling Laboratory, Department of Physics, Hazara University, Mansehra, Pakistan*
[g]*Department of Chemistry, Rawalpindi Women University Rawalpindi, 46300, Pakistan*

O-Vanillin derived schiff base ligands were synthesized with 1,3-diaminapropane and oxamidei.e L_1 and L_2. These schiff base ligands were then used to synthesize mononuclear schiff base metal complexes by treating them with Fe^{3+}, Co^{2+},$Mn^{2+}$and Zn^{2+} metal salts, giving L_1Fe, L_1Co, L_1Zn and L_2Co, L_2Mn metal complexes. L_1 and L_2ligandsand L_1Fe, L_1Co, L_1Zn and L_2Co, L_2Mn metal complexes were characterized by FT-IR, UV-vis and PXRD. The synthesized metal complexes were used against rhodamine blue (RB) dye for their comparative study of degradation properties. Among the synthesized complexes L_1Co showed maximum degradation of RB after 70 min of interval of about 56.835% whereas, the degradation property shown by L_1Zn, L_1Fe, L_2Co and L_2Mn is 42.446%, 32.733%, 20.863% and 13.309% respectively. The order of degradation of RB by all the metal complexes is as follows; $L_1Co > L_1Zn > L_1Fe > L_2Co > L_2Mn$.

(Received April 15, 2022; Accepted August 15, 2022)

Keywords: Schiff base ligands, Metal complexes, Dye degradation

1. Introduction

There is an extensive use of schiff base metal complexes in various fields like catalyst, antimicrobial, supramolecular chemistry, antioxidants anticancer and electrochemistry, DNA binding, electrocatalysts and photocatalysts.[1-14]. In recent years, due to rapidly developing population and uncontrollable industrial development, the environmental pollution exhibiting organic pollutants has reached to very serious level. Including them, organic dyes are very essential and hence extensively used in cosmetics, textiles, plastics, paper and pharmaceutical industries. Instead, organic dyes are also characteristic type of organic pollutants, initiating the serious water, air and soil contamination, giving rise to catastrophic environmental hazards and health problems. [15-20]. For that reason, for the safety of environment and for human health the recognition and careful adsorption of organic dyes has become very crucial need of the era.[21, 22]. Co(II), Ni(II) and Cu(II) complexes of (2E)-2-[(2E)-3-phenylprop-2-en-1-ylidene]hydrazinecarbothioamidewere recently reported showing the degradation property against MB in the absence of H_2O_2[23] Lately, Schiff base metal complexes have been extensively studied for their good photocatalytic degradation of the organic dyes[24, 25].

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[*] Corresponding author: 20197240003@stu.suda.edu.cn

https://doi.org/10.15251/DJNB.2022.173.913

In this study, we have planned and synthesized *N,N'*- Bis (O-vanillinidene)propylenediamine (O-VPDH_2)and *N,N'*- Bis (O-vanillinidene)ethanediamide (O-VEDH_2) Schiff base ligands namely L_1 and L_2 respectively and employed them for the synthesis of $[C_{18}H_{22}FeN_2O_4]H_2O$ (1), $[C_{18}H_{22}CoN_2O_4]H_2O$ (2), $[C_{18}H_{22}ZnN_2O_4]H_2O$ (3) mononuclear schiff base complexes namely, L_1Fe, L_1Co and L_1Zn and $[C_{18}H_{14}CoN_2O_6]H_2O$ (4), $[C_{18}H_{14}MnN_2O_6]H_2O$ (5) mononuclear schiff base complexes namely L_2Mn, L_2Co respectively. The main aim of current work is to synthesize transition metal complexes through synthesized schiff base ligands and focusing the study of their comparative dye degradation applications mainly degradation of rhodamine blue dye. The schiff base ligands were characterized by FT-IR, UV visible and Powder XRD. The catalytic degradation of rhodamine blue was investigated by UV-visible spectra using five synthetic schiff base metal Complexes. Complexes L_1Fe, L_1Co, L_1Zn and L_2Co, L_2Mn showed photocatalytic dye degradation activity when used as photocatalyst against rhodamine blue dye. The highest degradation activity was shown by the L_1Co. The order of degradation by the complexes is as follows L_1Co> L_1Zn> L_1Fe> L_2Co> L_2Mn.

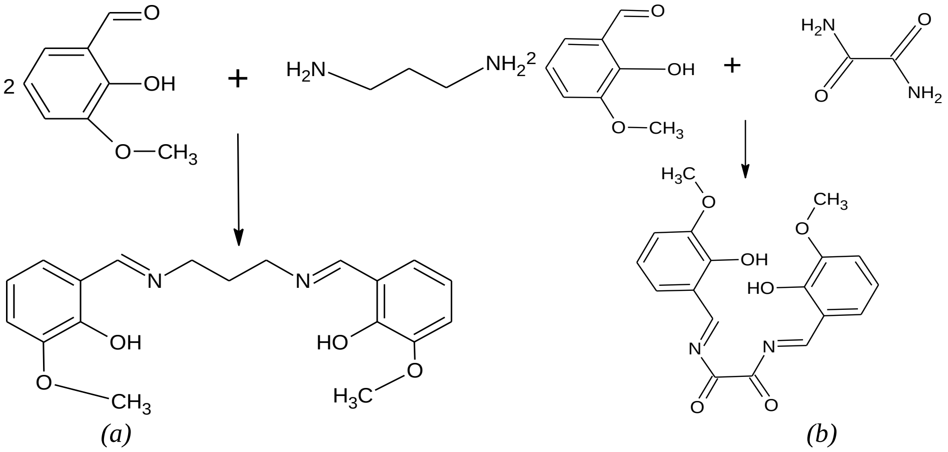
2. Experimental

2.1. Chemicals and apparatus

Commercially available reagent grade chemicals and solvents were used without any purification.Infrared spectra were documented as KBr discs on a FT-IR JASCO-680 spectrophotometer in the range of 4000-500 cm^{-1}. UV-1800, Shimadzu UV spectrophotometer was used to record UV spectra in the range of 200-800 nm. PXRD analysis was performed on XRD Philips X'PERT MPD model, under light acceleration of 40kV/35mA, on the slope 2h, 5-80.

2.2. Synthesis of Schiff Base Ligands [(O-VPDH_2(L_1)and O-VEDH2(L2)]

The O-vanillin base Schiff base ligands [(O-VPDH_2 (L_1)and O-VEDH2(L2)]were synthesized by mixing of the stirred methanolic solution of O-Vanillin (0.5g) for1,3-diaminopropane (0.3g) and oxamide (0.24g) i.e., 2:1 each and these two solutions were stirred constantly for 15 min at room temperature resulting in the formation of yellow precipitates. The precipitates of the two mentioned ligands were filtered,washed and dried finally. Ultimately, appropriate yellow precipitates were formed by slow evaporation of methanol during 5 days. The yield of schiff base ligands is 80% (0.486g). Solubility: acetonitrile, dimethyl sulfoxide, dimethylforfamide (DMF).Selected IR data in cm^{-1} for L_1 3120 (s), 1600 (m), 1650 (b), 1150(m) and for L_2 3012 (s), 1655 (m), 1699 (b), 1279(m). [s= strong, m= medium, b= broad] (for detailed discussion of IR spectra of Ligands, see Fig. 3.1 and 3.2). Scheme 1 presents the synthesis of Schiff base ligands [(O-VPDH_2 (L_1)and O-VEDH_2(L_2)].

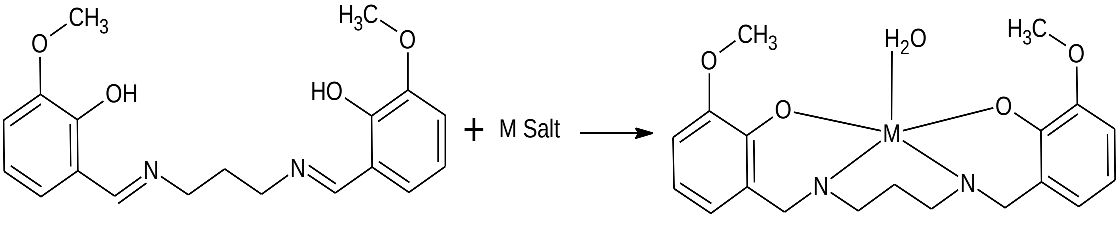


Scheme 1. a.N,N'- Bis (O-vanillinidene)propylenediamine (O-VPDH_2)(L_1)b.N,N'- Bis (O-vanillinidene)ethanediamide (O-VEDH_2)(L_2).

2.3.Synthesis of mononuclear Schiff Base Complexes of L_1 $[C_{18}H_{22}FeN_2O_4]H_2O$

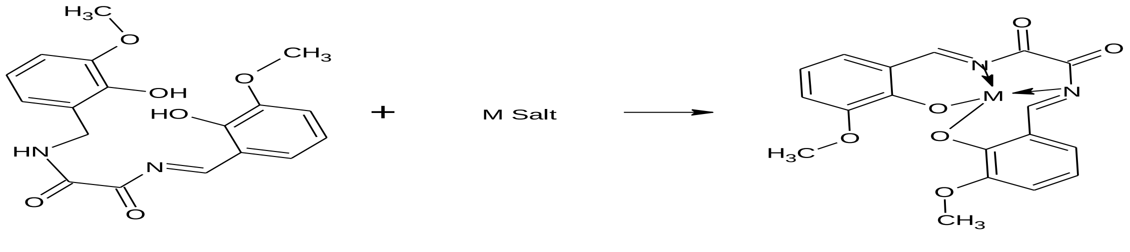
(L_1Fe), $[C_{18}H_{22}CoN_2O_4]H_2O$ (L_1Co), $[C_{18}H_{22}ZnN_2O_4]H_2O$ $(L_1Zn)$and L_2 $[C_{18}H_{14}CoN_2O_6]H_2O$ (L_2Co), $[C_{18}H_{14}MnN_2O_6]H_2O$ (L_2Mn)

Calculated amounts of metal salts of Fe^{3+}, Co^{2+} and Zn^{2+}were dissolved in 10 mL of methanol each, followed by the dropwise addition of O-VPDH$_2$ (L_1)and (separately soluble in methanol) and stirred for another 2 hr until clear solutions obtained. Final solutions were filtered and dried giving rise to black, pink, and white precipitates respectively. Yield: 37% approximately (0.18g, 0.15g and 0.19g) as new mononuclear schiff base complexesof $L_1[C_{18}H_{22}FeN_2O_4]H_2O$, $[C_{18}H_{22}CoN_2O_4]H_2O$, $[C_{18}H_{22}ZnN_2O_4]H_2O$, namely L_1Fe,L_1Co and L_1Zn respectively.Selected IR data in cm^{-1} for complex L_1Fe is 3150 (b), 1625 (m), 1700 (m), 1235 (m), 420(m), 550 (s), for complex L_1Co is 3179 (b), 1665 (m), 1750 (m), 1125 (m), 599 (m), 600 (s) and for complex L_1Zn is 3310 (b) , 1650 (m), 1699 (m), 1175 (m), 610 (m) and 540 (s) respectively. [s= strong, m= medium, b= broad] (for detailed discussion of IR spectra of Ligand L_1, see figure 3.1, 3.2). Scheme 2 presents mononuclear Schiff Base Complexes of $L_1[C_{18}H_{22}FeN_2O_4]H_2O$, $[C_{18}H_{22}CoN_2O_4]H_2O$, $[C_{18}H_{22}ZnN_2O_4]H_2O$, ($L_1Fe$,$L_1Co$ and L_1Zn).



Scheme 2. Metal complexes of L_1($M = Fe^{+3}, Co^{+2}, Zn^{+2}$).

Similar method was followed for the synthesis of metal complexes of Schiff base ligand L_2(O-VEDH$_2$) by taking metal salts of Co^{2+} and Mn^{2+}. Yield 30% approximately (0.1, 0.13 respectively) as new mononuclear schiff base complexes ofL_2 $[C_{18}H_{14}CoN_2O_6]H_2O$, $[C_{18}H_{14}MnN_2O_6]H_2O$ namely, L_2Co and L_2Mn respectively. Selected IR data in cm^{-1} for complex L_2Co is 3045 (b), 1660 (m), 1610 (m), 1125 (m), 500 (m), 650 (s) and for complex L_2Mn is 3225 (b), 1655 (m), 1700 (m), 1210 (m), 445 (m), 656 (s) respectively. [s= strong, m= medium, b= broad] (for detailed discussion of IR spectra of Ligand L_2, see figure 3.4, 3.5). Scheme 3 presents mononuclear Schiff Base Complexes of L_2 $[C_{18}H_{14}CoN_2O_6]$ H_2O (L_2Co), $[C_{18}H_{14}MnN_2O_6]$ H_2O (L_2Mn).



Scheme 3. Metal complexes of L_2($M = Co^{+2}, Mn^{2+}$).

2.4. Photocatalytic Dye Degradation Experiments

Photocatalytic dyedegradation activities of the synthesized complexes were assessed by degradation of the aqueous rhodamine blue (RB) as the model pollutant under a complete setup of photoreactor, exhibiting a hotplate system having tungsten filament bulb of 5000 watt. The dye solution was firstly taken in dark to guarantee the establishment of adsorption-desorption equilibrium between the photocatalyst and the rhodamine blue dye. Magnetic stirring of the solution was done in the dark for 2 hr. After that it was wide-opened to tungsten filament bulb light with continuous magnetic stirring for 70 minutes. At definite time intervals, particular amount of the solution was withdrawn and separation of photocatalysts was done by centrifugation, after that, changes in the concentration of RB were observed using UV-visible spectrophotometer. The process was repeated for every schiff base metal complex as the photocatalyst.

3.Results and discussion

3.1. IR- Characteristics

FT-IR spectra of the synthesized ligands L_1 and L_2 showed their broad peak of –OH at 3012 cm^{-1} and 3120 cm^{-1}.The appearance of new peak at 1600 cm^{-1} and 1655 cm^{-1} confirm the formation of schiff base ligands L_1 and L_2 respectively, as this peak was absent in the IR spectra of the reactants. Similarly, peaks at 1150 $cm^{-1}$and 1279 cm^{-1} showed the C-N peak for both ligands L_1 and L_2. FT-IR spectra of both ligands are shown in Fig. 1 and Fig. 2 respectively. Likewise, there is disappearance of –OH peak in the FTIR spectra of the respective metal complexes of ligands L_1 and L_2 showing the metal complex formation, with the schiff base bond C=N shifted towards lower frequency. Metal complexes, L_1Fe, L_1Co, L_1Zn and L_2Co and L_2Mn in comparison with free schiff base ligands L_1 and L_2 representing the synchronization of schiff base bond to metal atom. Whereas, the other peaks i.e, O-C, N-C also appeared in metal complexes L_1Fe, L_1Co, L_1Zn and L_2Co and L_2Mn at 1100 cm^{-1} also appearance of new peaks from 700-550 cm^{-1} indicates the bonding between M-O And M-N atoms. The FTIR spectra ofschiff base ligands L_1 and L_2 and their metal complexes L_1Fe, L_1Co, L_1Zn and L_2Co and L_2Mn respectively are shown in Fig.3.1 andFig.3.2 respectively.

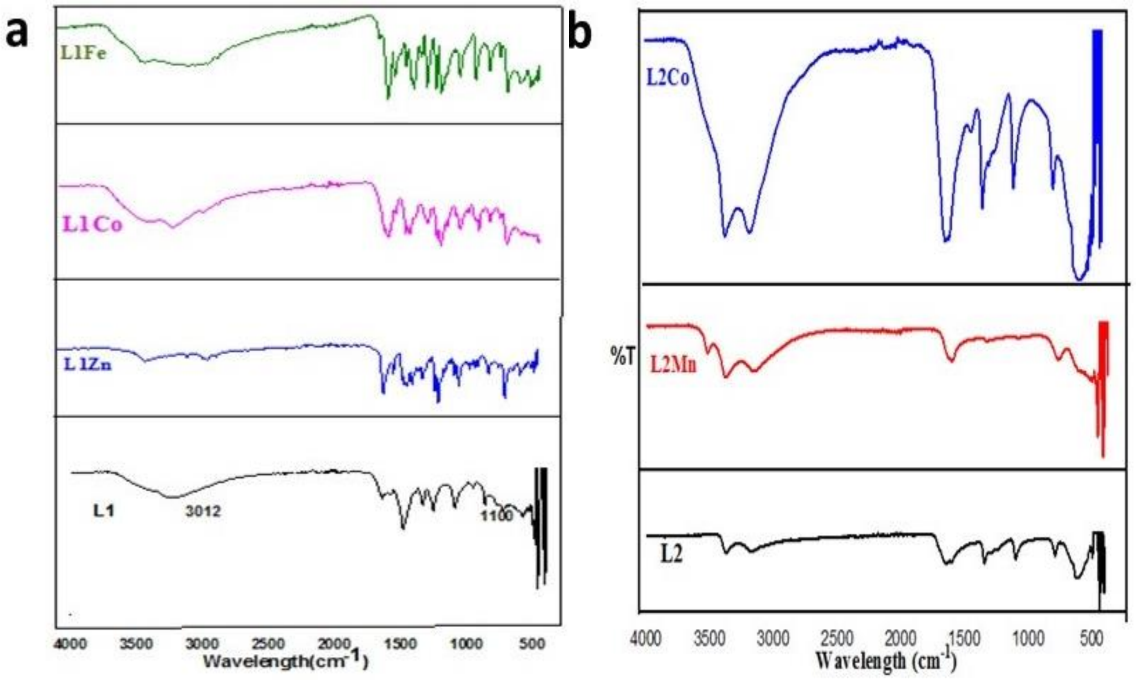


Fig. 1. a) (FT-IR spectra of schiff base ligand $L_1$with its metal complexes L_1Fe, L_1Co, L_1Zn)b)(FT-IR spectra of schiff base ligand L_2 with its metal complexes, L_2Co, L_2Mn).

3.2. UV-visible study

The UV-visible spectra of the synthesized schiff bases indicated absorptions at 350nm for L_1 and L_2. This absorption peak indicates that there is n→π* shifting of the azomethine group in the schiff base ligands L_1 and L_2. These absorption peaks usually show the π→π* transitions for the aromatic ring (C=C) and n→π* transitions for the schiff base imine –C=NH, respectively in ligands L_1 and L_2. The presence of double bond in the schiff base ligandsL_1 and L_2 is indicated by the π→π* transitions and formation of imine group having hetero atom nitrogen coordination with the alkene carbon atom is revealed by the n→π* transitions. Addition of metal salts like Fe^{3+}, Co^{2+}, Zn^{2+} and Mn^{2+} with the schiff base ligands L_1 and L_2 resulted with the color change and peak pattern altered for both ligands due to formation of chelates and shifting of wavelength from ~350 nm to ~650 nm. Coordination of metals like Fe^{3+}, Co^{2+}, Zn^{2+} and $Mn^{2+}$with the ligandsL_1 and L_2 resulted shifting of λ_{max} from lower to higher wavelength. i.e red shift. This is due to charge transfer transition (CTT) i.e N lone pair shifing towards metal. The red shift order of schiff base metal complexes for L_1 is Fe^{3+}>, $Zn^{2+,}$> Co^{2+} and for L_2 is Co^{2+},> Mn^{2+} respectively[26]. Fig. 3 and 4.

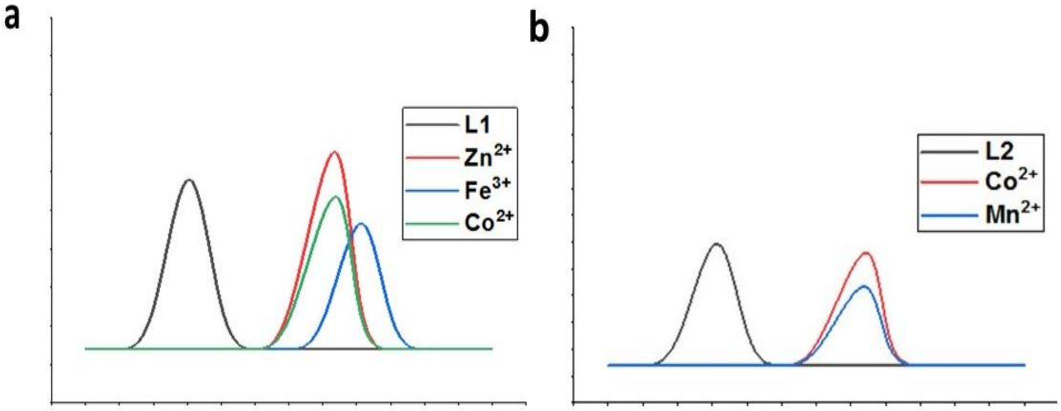


Fig. 3. a) (UV-vis spectra of schiff base ligand L_1 with its metal complexes L_1Fe, L_1Co, L_1Zn). b) (UV-vis spectra of schiff base ligand L_2 with its metal complexes, L_2Co, L_2Mn).

3.3.X-ray diffraction spectroscopy

Schiff base ligands L_1 and L_2 showed their XRD patterns at 2θ = 10.1° and 11.3° respectively. Fig 4.showing the schiff base imine. XRD patterns clearly reveals the formation of schiff base ligands L_1 and L_2. XRD values are recorded from 2θ= 0-80° for L_1 and L_2 and their metal complexesL_1Fe, L_1Co, L_1Zn and L_2Co and L_2Mn. During powder X-ray diffraction analysis, L_1Zn complex showed the sharp peak, while no peaks were observed for the rest of the complexes of L_1 and L_2, demonstrating their amorphous nature. Broadening of the crystalline diffraction peak in the ZnL_1 complex indicated higher crystallinity. Indication of the crystalline nature of the complexes was done by the comparison of the diffractograms of the ligand and complexes. By literature, this might be because of the incorporation of water molecule inside the coordination sphere[27]. Instead, single crystal X-ray crystallography is the more accurate way of knowledge regarding the structure of the complex. However, obtaining of suitable crystals in proper symmetric form has rendered this method unsuitable for such study.Fig.5 and 6.for PXRD of L_1 with its metal complexes and and L_2 with its metal complexes respectively.

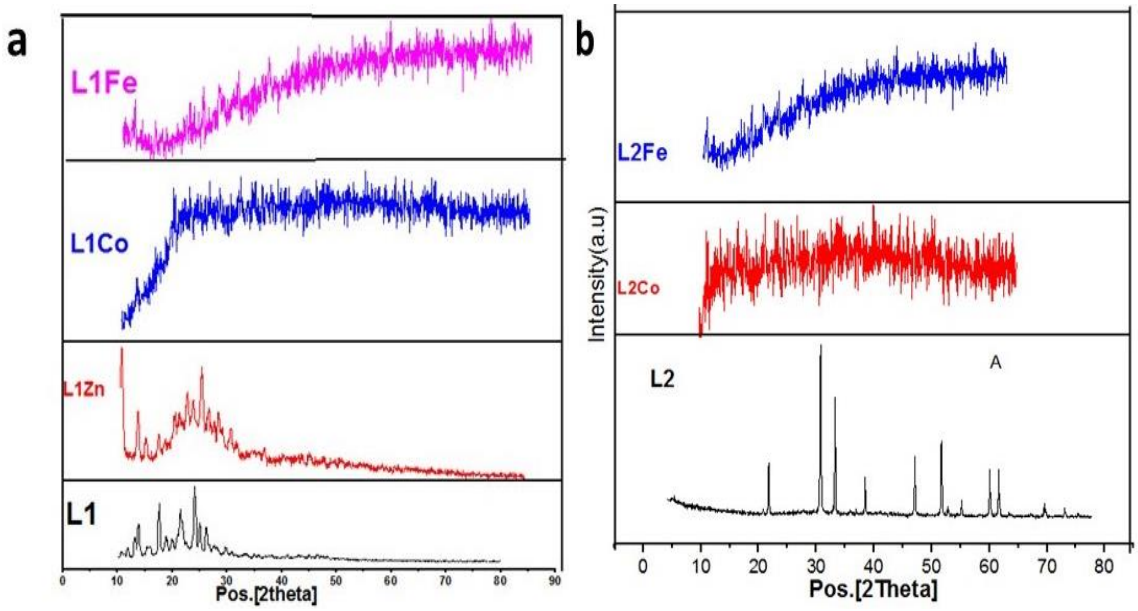


Fig. 5. a)(PXRD pattern of schiff base ligand $L_1$with its metal complexes L_1Fe, L_1Co, L_1Zn).b)(PXRD pattern of schiff base ligand L_2 with its metal complexes, L_2Co, L_2Mn).

3.4. Photocatalytic dye degradation of rhodamine blue (RB)

The degradation of organic dye rhodamine blue (RB) was evaluated through the synthesizedschiff base metal complexes. O-vanillin derived mononuclear schiff base metal complexes revealed the degradation property against the rhodamine blue dye[28-31]. ComplexesL$_1$Zn, L$_1$Fe, L$_1$Co, L$_2$Co and L$_2$Mn revealed their photocatalytic activity. The comparative study of the photocatalytic activity is shown in Fig. 7. The maximum degradation is shown by the L$_1$Co complex which degraded the RB dye maximum as compared to other complexes. Approximately 53.237% of the RB dye was degraded by the L$_1$Co complex after 10 min of interval and after 50 min interval the RB was further degraded to about 56.835%. whereas, the L$_1$Zn complex showed relatively lower order of photocatalytic activity approximately 31.655% by fading the color of the solution after 10 min, which were also very good results for RB dye degradation and after 70 min, dye degradation yield was increased to 42.4460%. The %age degradation activity shown by L$_1$Fe indicated that the dye was degraded upto 29.136% and activity increased upto 32.733% after 70 min interval of degradation. L$_2$Co complex showed its degradation activity as 20.863% after 10 min interval and after that upto 70 min no further degradation activity was shown by it. Lastly, L$_2$Mn complex showed degradation upto 10.072% and after 30 min about 13.309%. Fig.3.18So, photocatalytic activity was very effective and photocatalytic performance of various complexes can be written in the following order.L$_1$Co> L$_1$Zn> L$_1$Fe> L$_2$Co> L$_2$Mn.Fig.3.7.The degradation yield can be defined by the formula as follows

$$\text{Photodegradation yield (\%)} = (A_0 - A)/\ A_0 \times 100. \qquad (1)$$

whereas, A_0 is the absorbance value of the RB in the dark, i.e 2.78 and A is absorbance value after degradation. Fig. 3.8.

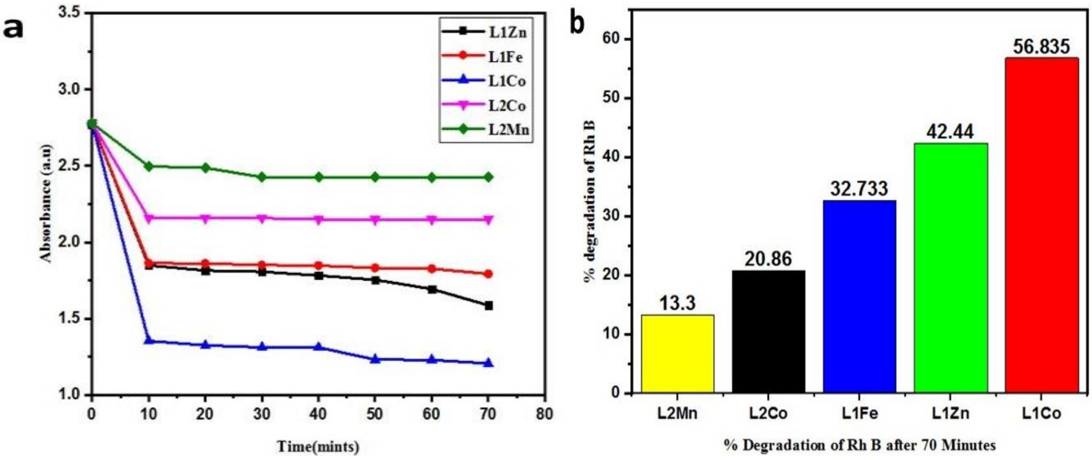


Fig. 7. a) Photocatalytic dye degradation comparative study of metal complexes. L_1Co> L_1Zn> L_1Fe> L_2Co> L_2Mn.b) %age RB degradation by complexes.

4. Conclusion

Five O-vanillin derived mononuclearschiff base metal complexes of L_1 and $L_2$by using metal salts of Fe^{3+}, Zn^{2+}, Co^{2+} and Mn^{2+} were synthesized. Schiff base ligands L_1 and L_2 were synthesized by reaction of O-vanillin with 1,3-diaminopropane and oxamide (namely L_1 and L_2 respectively). The synthesizedschiff base ligands L_1 and L_2 and their metal complexes L_1Zn, L_1Fe, L_1Co, L_2Co and L_2Mn have been analyzed by FT-IR spectra, UV-vis spectra and Powdered XRD. The synthesized metal complexes were used against rhodamine blue (RB) dye, showing their photocatalytic dye degradation activities. The maximum RB degradation was shown by the L_1Co complexi.e 56.835% whereas other four complexes L_1Zn, L_1Fe, L_2Co and L_2Mn revealed their photocatalytic activity relatively lower as compared to the L_1Co complex. The order of RB degradation was L_1Co> L_1Zn> L_1Fe> L_2Co> L_2Mn.

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