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DERGİSİ

Sakarya University Journal of Science
SAUJS

ISSN 1301-4048 | e-ISSN 2147-835X | Period Bimonthly | Founded: 1997 | Publisher Sakarya University |
http://www.saujs.sakarya.edu.tr/

Title: Investigation of The Effects of Diaminopyridine and o-Vanillin Derivative Schiff Base Complexes of Mn(II), Mn(III), Co(II) and Zn(II) Metals on The Oxidative Bleaching Performance of H_2O_2

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Recieved: 2021-06-06 18:30:00

Accepted: 2021-06-28 21:51:16

Article Type: Research Article

Volume: 25
Issue: 4
Month: August
Year: 2021
Pages: 984-994

How to cite
Murat TUNA, Tuğba UĞUR; (2021), Investigation of The Effects of Diaminopyridine and o-Vanillin Derivative Schiff Base Complexes of Mn(II), Mn(III), Co(II) and Zn(II) Metals on The Oxidative Bleaching Performance of H_2O_2. Sakarya University Journal of Science, 25(4), 984-994, DOI: 10.16984/saufenbilder.948657 Access link
http://www.saujs.sakarya.edu.tr/en/pub/issue/64755/948657

Sakarya University Journal of Science 25(4), 984-994, 2021

Investigation of The Effects of Diaminopyridine and o-Vanillin Derivative Schiff Base Complexes of Mn(II), Mn(III), Co(II) and Zn(II) Metals on The Oxidative Bleaching Performance of H_2O_2

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Abstract

Catalytic applications are widely used in industrial and individual applications today due to their many advantages, especially the energy and time they provide. For this purpose, many coordination compounds have been synthesized, and their catalytic performances have been investigated in recent years. In this study, the Schiff base ligand, (N,N'-bis(2-hydroxy-3-methoxyphenylmethylidene)-2,6-pyridinediamine, BHMP), was synthesized with 2,6-diaminopyridine with o-vanillin. Mn(II), Mn(III), Co(II), Zn(II) complexes were obtained with the synthesized ligand. Spectroscopic methods such as FT-IR, ^{1}H-NMR, UV-*vis*, Mass, and melting point determination methods were used for the structure elucidation of the synthesized compounds. The performances of the obtained complexes as bleach catalysts, which are an important application area of Schiff base complexes, were investigated. According to the bleaching measurement results, the highest catalytic effect on the bleaching performance of H_2O_2 in pH 10.5 buffer at 25 °C under homogeneous conditions was obtained with Co(II) complex. It was understood that this complex was followed by Mn(II), Mn(III), and Zn(II) complexes, respectively.

Keywords: Schiff base, o-vanillin, metal complexes, bleach catalyst

1. INTRODUCTION

The literature in which some metal complexes of Schiff bases are used as catalysts is expressed in thousands of publications in the last five years. These complex molecules are used as catalysts in many of these publications and have started to gain importance in industrial applications [1-6]. In addition to these application areas, these complexes have an important place in biological activities such as antibacterial, antifungal, and antitumor, analytical chemistry, paints, polymer industries, applications of vitamins and enzymes [7-12].

Mainly, manganese and iron Schiff base complexes used as oxidation catalysts have found a wide area of use in industrial and domestic laundry due to their catalytic effect, being harmless to the environment, and effective use on the bleaching potential of hydrogen peroxide. These complexes have played an important role in textile applications by preventing damage to the washed fabric while ensuring the bleaching of

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stains, especially at low temperatures [13-14]. With this advancing technology, besides the ability to wash at low temperatures in washing machines, methods that can bleach using less water and include short-term washing programs are being developed [15-16]. Bleaching or whitening is defined as the de-coloration reaction by degrading the molecules that give color as a dye or paint-like by oxidation reaction [15-18]. For the bleachers containing hydrogen peroxide, the effective use temperature was reduced from 90 °C to less than 40 °C by using 1-5% of these molecules as activators in a washing period [15-16]. Due to the use of activators, both time and energy savings have been achieved. With the efforts to develop transition metal complexes as activators to replace the metal salts - due to the difficulty of use in alkaline conditions and its adverse effects on the fabric - proposed in the 1980s, the catalysts compatible with laundry and dishwashing detergents have been developed for the last decade [19-20]. Metal ions in most metal-containing catalysts as coordination compounds have partially empty orbitals in the d orbitals. These somewhat empty orbitals can be used in the resulting oxidation mechanisms. The ions of transition elements, such as especially manganese, iron, cobalt, nickel, palladium, platinum, tungsten, silver, and copper, have frequently been used in different oxidation numbers in obtaining these catalysts [21-27].

In this study, the Schiff base ligand, N,N'-bis(2-hydroxy-3-methoxyphenylmethylidene)-2,6-pyridinediamine, BHMP), was synthesized with 2,6-diaminopyridine with o-vanillin. Mn(II), Mn(III), Co(II), Zn(II) complexes were obtained with the synthesized ligand. Spectroscopic methods such as FT-IR, ^{1}H-NMR, ^{13}C-NMR, UV-*vis*, Mass, AAS, and melting point determination methods were used for the structure elucidation of the synthesized compounds. The performances of the obtained complexes as bleach catalysts, an important application area of Schiff base complexes, were investigated.

2. EXPERIMENTAL STUDIES

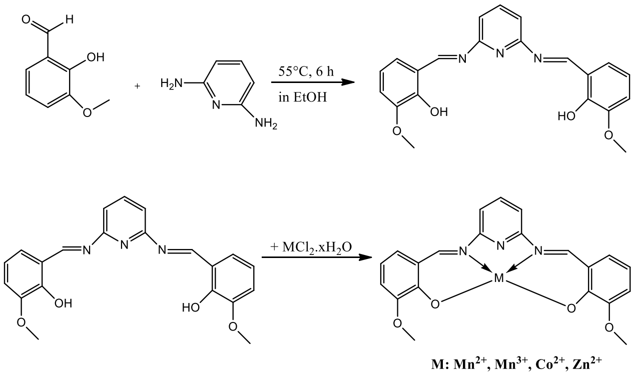
2.1. Materials and Devices

The materials used in this study were obtained from companies such as Merck, Fluka, and Aldrich. During chemical experiments; 2,6-Diaminopyridine, o-vanillin, Ethanol (EtOH), Methanol (MeOH), Dichloromethane (DCM), Acetone, Sodium carbonate (Na_2CO_3), Sodium bicarbonate ($NaHCO_3$), Dimethylformamide (DMF), Tetrahydrofuran (THF), Hexane, Nitric acid (HNO_3), Hydrochloric acid (HCI), Chloroform ($CHCl_3$), Deuterochloroform ($CDCl_3$), Hexadeutero-dimethyl sulfoxide (d_6-DMSO), Manganese(II) chloride hexahydrate ($MnCl_2.6H_2O$), Cobalt(II) chloride hexahydrate ($CoCl_2.6H_2O$), Zinc chloride ($ZnCl_2$), Sodium hydroxide (NaOH), Oxygen (O_2), Silica gel, Morine, Hydrogen peroxide (H_2O_2) and purified water are used.

For spectroscopic characterization of synthesized substances; Infrared Spectrometer ((Perkin Elmer Spectrum Two (PerkinElmer UATR Two diamond ATR)), ^{1}H-NMR Spectrometer, (Varian Mercury Plus 300 MHz Spectrometer), Bruker Microflex LT MALDI-TOF-MS Spectrometer (Gebze Technical University), UV-*vis* Spectrophotometer (Hitachi UV-2900 Spectrophotometer) and Melting Point Tester (Stuart SMP-10) were used.

2.2. Synthesis Studies

According to the literature data, the synthesis of the Schiff base ligand was carried out first [28-30]. Complexes were synthesized after it was understood that the structural characterization data of the obtained ligand molecule were compatible with the literature data. The synthesis plan is given in Scheme 1.



Scheme 1 The synthesis plan of Schiff base complexes

2.2.1. Synthesis of BHMP as a ligand

The Schiff base ligand, N,N’-bis(2-hydroxy-3-methoxyphenylmethylidene)-2,6-pyridinediamine, was prepared according to the references [28-30].

2.2.2. Synthesis of metal complexes

2.2.2.1. Synthesis of the Schiff base Manganese(II) complex

0.5 mmol (0.189 g) Schiff base ligand was dissolved in 20 mL THF. The temperature was fixed at 55 °C, and 0.5 mmol (0.063 g) $MnCl_2$ was added dropwise. The reaction mixture was cooled to room temperature after three hours, and the solvent was removed by a rotary evaporator. Afterward, chloroform washing, the solid product was obtained by centrifugation and kept waiting in a vacuum oven overnight. Yield: 0.127 g (58.79%), m.p. > 300 °C. FT-IR (PIKE MIRacleTM ATR) ν_{max}, cm^{-1}: 3063 (Ar, C–H), 2975 (aliph., C–H), 1630 (C=N), 1549 (C=C), 1442 (C–N), 1065 (C–O). MALDI-TOF-MS, (m/z): Calculated: 430.34; found: 430.11 $[M^+]$.

2.2.2.2. Synthesis of the Schiff base Manganese(III) complex

1 mmol (0.378 g) Schiff base ligand was dissolved in 20 mL ethanol. 1 mmol (0.126 g) $MnCl_2$ solution in 20 ml ethanol was added. After starting the reaction at room temperature for 10-15 minutes, a solution of 0.002 mol (0.08 g) NaOH in a small amount of pure water was added to the mixture. The reaction mixture was continued the stirring at 80 °C for 2 hours. Then, O_2 gas was passed into the reaction medium with the help of a pump, and the reaction was continued for three hours. The resulting mixture was filtered, and the crude product was washed with hot ethanol. The precipitate was left to dry in the vacuum oven overnight. Yield: 0.31 g (71.59%), m.p. > 300 °C. FT-IR (PIKE MIRacleTM ATR) ν_{max}, cm^{-1}: 3079 (Ar, C–H), 2935 (aliph., C–H), 1605 (C=N), 1549 (C=C), 1436 (C–N), 1065 (C–O). MALDI-TOF-MS, (m/z): Calculated: 430.34; found: 429.98 $[M^+]$.

2.2.2.3. Synthesis of the Schiff base Cobalt(II) complex

0.5 mmol (0.189 g) of Schiff base ligand was dissolved in 40 mL of methanol. After the temperature was fixed at 55 °C, a 0.5 mmol (0.065 g) $CoCl_2$ solution in 10 mL of methanol was added dropwise. After the reaction was continued for three hours, vacuum distillation was carried out, and after washing with chloroform, filtration was carried out to obtain a solid product. The precipitate was left in a vacuum oven overnight. Yield: 0.152g (69.72%), m.p. > 300 °C. FT-IR (PIKE MIRacleTM ATR) ν_{max}, cm^{-1}: 3060 (Ar, C–H), 2935 (aliph., C–H), 1630 (C=N), 1477 (C=C), 1436 (C–N), 1062 (C–O). MALDI-TOF-MS, (m/z): Calculated: 434.31; found: 466.09 $[M^+ + CH_3OH + 2]$.

2.2.2.4. Synthesis of the Schiff base Zinc(II) complex

0.5 mmol (0.189 g) Schiff base ligand was dissolved in 50 mL ethanol. After the temperature was fixed at 55 °C, a solution of 0.5 mmol (0.068 g) $ZnCl_2$ metal salt in 10 mL of ethanol was added dropwise. After the reaction was continued for three hours, vacuum distillation was carried out, and after washing with chloroform, filtration was carried out to obtain a solid product. The precipitate was left in a vacuum oven overnight. Yield: 0.121 g (54.75%), m.p. > 300 °C. FT-IR (PIKE MIRacleTM ATR) ν_{max}, cm^{-1}: 3050 (Ar, C–H), 2972 (aliph., C–H), 1599 (C=N), 1480 (C=C), 1436 (C–N), 1068 (C–O). MALDI-TOF-

MS, (m/z): Calculated: 439.05; found: 531.21 $[M^+ + 2C_2H_5OH]$.

2.3. Measuring the Effects of Molecules on Bleaching Performance

Bleaching activities for Morin dye of synthesized Schiff base metal complexes as oxidative bleach catalyst were tested to determine using UV-*vis* Spectroscopy. Morin is a dye in which the bleaching effects of the substances whose oxidative catalyst effect can be examined can be seen easily. Hydrogen peroxide (H_2O_2) was used as a bleacher in the kinetic analysis. The bleaching effect of hydrogen peroxide; is based on its decomposition, mainly depending on the pH value and hydrogen and perhydroxyl ion (HOO^-). This perhydroxyl ion then reacts with a hydrogen peroxide molecule to form the superoxide radical anion. Since hydrogen peroxide is a stable compound under acidic conditions, the perhydroxyl ion formation starts with the addition of alkali necessary for the initiation of decomposition. Perhydroxyl ion ($HO_2\bullet$) behaves like weak dibasic acid in an aqueous solution, and degradation continues [31]. The bleaching rate and the changes in absorbance versus time obtained as a result of the process that proceeds in this direction were graphed and it was investigated whether the complexes showed catalytic effects. It was provided to monitor the spectral changes and determine the bleaching rate of the dye as a percentage.

In order to carry out the analysis, 10 mg of the synthesized products were taken and completed with 10 mL of DMF. $NaHCO_3$ / Na_2CO_3 (pH: 10.5) was used and the buffer solution was prepared and placed in a quartz cuvette. Pure water was added to the reaction vessel on the heater and its temperature was kept at 25 °C. A magnetic stirrer was placed in the reaction vessel to ensure continuous mixing. After removing the baseline of the device, the initial absorbance of the Morine in the buffer solution was measured before the catalyst and hydrogen peroxide were added. Then 900 μL of Morine (in two parts), the calculated amount of catalyst for each complex and 480 μL H_2O_2 were added respectively. A peristaltic pump was used to transfer the reaction solution to the quartz cuvette in the UV-vis Spectrophotometer. In the spectrophotometer, 11 spectral values were recorded at 5-minute intervals with the kinetic-scanning program. The obtained values were converted into graphics for kinetic interpretation.

Morine bleaching was then followed as reductions in 411 nm absorbance, and the percentage of bleaching was calculated using the following equation depending on the change in absorbance values obtained [32].

$$Bleaching\ (\%) = \frac{(A_0 - A_t)}{A_0} x100$$

in the formula, A_0 = absorbance at zero time; A_t = absorbance at specific time.

3. RESULTS AND DISCUSSIONS

3.1. Structural Characterization

Common spectroscopic methods such as FT-IR, ^{1}H-NMR, UV-*vis*, and MS were used for the characterization of the synthesized compounds, and the results confirmed the expected results for the structures.

In the structural characterization of the synthesized BHMP ligand and its some metal complexes, FT-IR, ^{1}H-NMR, and MS methods were primarily used. In this context, since the ligand molecule was synthesized before, FT-IR, NMR, and mass analysis were carried out to compare with the literature data. It was seen that the data obtained from the measured spectra are in complete agreement with the literature data.

It has been observed that the wavenumber values of the peaks of OH, aromatic C=C, C=N, O-CH_3 functional groups seen in the FT-IR spectra are compatible with the literature data. In addition, NMR spectroscopy was used to characterize the ligand molecule, and the shifts in the NMR spectra obtained supported the FT-IR data and were observed to be compatible with the literature. Structural characterization of the ligand molecule was completed by mass spectroscopy, and it was observed that $[M^+]$ = 379.47 m/z peaks in the mass spectra (Fig. 3). In addition, the peaks seen in 395.30 m/z and 411.56 m/z in the mass spectra were interpreted as belonging to [$H_2L+H_2O^+$] and [$H_2L+2H_2O^+$] molecules, respectively. This situation is also supported by the spring peak seen at 3484 cm^{-1} in the FT-IR spectra, and this situation arising from the structural properties of the synthesized Schiff base ligand has also been demonstrated in the literature data (Fig. 2) [28].

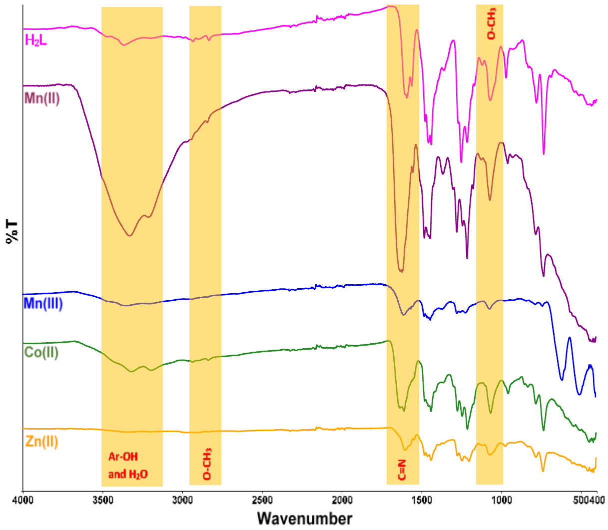


Figure 1 FT-IR spectra of synthesized ligands and complexes

The most basic functional group sought in the FTIR analysis of Schiff base ligands and their complexes is the peak of the C = N group seen in the range of approximately 1600-1700 cm^{-1}. While the peak in the FTIR spectrum of the ligand was observed at 1602 cm^{-1}, in the FTIR spectra of the metal complexes of the ligand, this peak was observed in the range of 1599-1630 cm^{-1} and the shift was interpreted that was due to metal-ligand bonding. On the other hand, a similar situation has been observed in the ligand molecule, which belongs to the C = N bond in pyridine, and the C = N stretching peak seen at 1561 cm^{-1} is in the range of 1542-1558 cm^{-1}. The decrease in the % transmittance values of these peaks was interpreted as the N atom coordinated with the metal atoms (Fig. 1) [28, 33, 34].

Peaks for phenolic hydroxyl groups, one of the most specific functional groups for the synthesized ligand molecule, were observed in the range of 3463-3194 cm^{-1} as expected, while the % transmittance changes seen in the FTIR spectra of the relevant metal complexes were interpreted as due to the hydroxyl group coordinated with the metal atoms. However, bound water in molecules in the synthesized complex molecules can be seen in FTIR spectra and mass spectra (Fig. 1) [28, 33, 34].

Another functional group-specific for the synthesized ligand molecule is the methoxy group. The O-C peak, one of the two critical peaks of this group, was observed in the range of 1062-1065 cm^{-1}. The other significant peak is the aliphatic C-H peak of the CH_3 group, and this peak was observed at approximately 2850 cm^{-1} in accordance with the literature data (Fig. 1) [35].

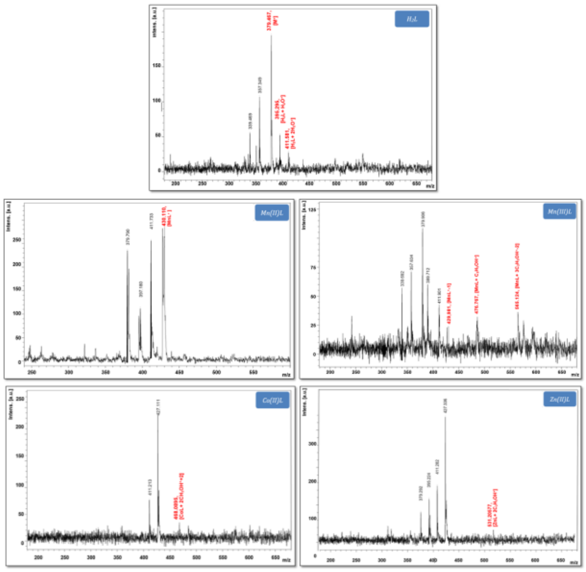


Figure 2 MS spectra of synthesized ligands and complexes

Mass spectra of synthesized Schiff base ligand and its metal complexes were taken in MALDI-TOF spectrometer and the presence of DMSO solvent. In the mass spectra, molecular ion peaks were observed at 379.467 and 430.110 m/z values for the ligand molecule and Mn(II) complex, respectively. On the other hand, for the Mn(III) complex, instead of the molecular ion peak, the peak ([MnL]$^+$-1) was observed at 429.981 m/z in the mass spectrum. In the mass spectra of the Co(II) and Zn(II) complexes; molecular ion peaks were not observed, and it was concluded that these complexes interacted with solvent molecules and, as a result, peaks with values of 468.0895 and 531.20577 m/z, respectively, were the peaks of $[CoL+2CH_3OH+2]^+$ and $[ZnL+C_2H_5OH]^+$ molecules (Fig. 2) [36,37].

^{1}H-NMR spectra of the ligand molecule were taken in the presence of DMSO solvent. In the proton NMR spectrum were obtained signals, in consistent with the literature, 2.48 (6H), 3.82 (6H), 6.89 (2H), 7.08 (2H), 7.21 (2H), 7.41 (2H), 8.28 (H), 9.31 (2H), and 10.25 (2H) ppm, respectively [28].

As can be seen from Fig. 3, the Schiff base attached to the benzene ring showed a broad and strong absorption peak at 434 nm due to the n-p* transition with the unbounded electron pair electrons located on the nitrogen atom in the C=N group. In addition, a second peak was observed at 374 nm belonging to the ligand molecule and was thought to originate from the methoxy group attached to the benzene ring. Because the said peak was observed exactly in the complex molecules and it did not undergo any change, which strengthened this prediction. The peak Mn(II) Co(II) complexes of the azomethine group observed at a wavelength of 434 nm showed a blue shift at the wavelengths of 408 nm and 406 nm, respectively. It was observed that the said shift shifted more specifically at 382 nm in the Mn(III) complex.

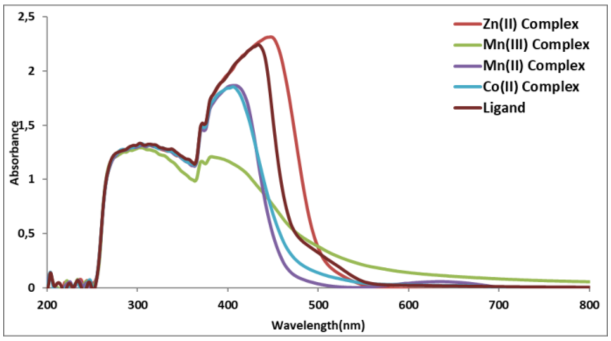


Figure 3 UV-*vis* spectra of synthesized ligands and complexes

On the other hand, in the Zn(II) complex, the azomethine peak in question is red-shifted and observed at a wavelength of 450 nm. The red shift was observed in Zn(II) complexes with fully occupied d orbitals, where the d orbitals in metal atoms depend on the presence of electrons, while the most prominent blue shift was observed in the Mn(III) complex with the poorest d orbital electrons. The weak peaks observed in the spectra of the ligands and their complexes in the range of about 270-360 nm are attributed to the p–π conjugation and n–π* transition between the lone pair electrons of the phenolic hydroxyl oxygen atom and the benzene ring, and the π-π* transition of the large conjugated bond in the benzene ring [28,38].

3.2. Bleaching Performances of The Complexes

Bleaching processes have been one of the main processes in today's industrial applications, especially in textiles, in all sectors where there is a need to eliminate the adverse effects of chromophores. For these processes, hydrogen peroxide, etc., bleaching agents are used. These agents act through a mechanism that provides the degradation of chromophore molecules with an oxidative effect. However, the improvement of the conditions of use has been the subject of research for a long time since the effects of these agents are shown depending on the need for a long time and high temperature. For this purpose, tetraacetylethynediamine (TAED) and nonanoxybenzene were synthesized as the first bleaching agent activator and started to be used in laundry detergents. In this way, it is ensured that the oxidation agents, which are effective above 60 °C, show the same performance below 40 °C. According to these results, the energy savings achieved have drawn attention to the importance of bleach activators. It has been tried as a complex molecular bleaching catalyst synthesized with many transition metal complexes. The main goal in these studies is to provide oxidation of chromophore groups in a shorter time and at low temperatures (preferably at room temperature) [39].

It is seen that very different complexes have been synthesized, especially in activator researches on hydrogen peroxide activators. However, when these studies are examined, it is seen that phthalocyanine complexes and Schiff base complexes show remarkable results [40,41]. For these reasons, in this study, the bleaching performance of the complexes obtained with the synthesized ligand molecule was investigated against Morin dye. Morin dye was chosen here because of the polyphenolic chromophore properties of flavonoids as model markers for wine stains. In order to determine the decomposition rate of Morin dye at 25 °C, the complexes were prepared with carbonate buffer, and pH value of 10.5 was followed over the absorption values of Morin dye at 411 nm under homogeneous catalysis conditions with hydrogen peroxide. The measurements were made by measuring absorption every five minutes for 50 minutes.

The obtained spectral results are given graphically in Fig. 4. In the figure, it is seen that all complex molecules have an effect on the bleaching rate of hydrogen peroxide and a positive effect on the decomposition rate of Morin. However, the said effect did not occur at the same rate in the complex molecules, and it was observed that the Zn(II) complex, especially with the d^{10} electron structure, showed a relatively lower catalytic effect (Fig. 4.-IV). Similarly, it has been determined that the Mn(III) complex also functions as a lower activator compared to other complexes. It has been interpreted that the reason for this is that the catalytic effect is weakened, contrary to what is expected, with the effect of electrons coming from the helper ions bound into the molecular structure and the ligands to the empty d orbitals on the Mn(III) atom (Fig. 4.-II). Co(II) and Mn(II) complexes showed an effective catalytic effect in the degradation of Morin dye and it was observed that it caused an effective degradation in the first 5 minutes (Fig 4.-I and III). When the % bleaching performance of all complexes is examined, it is seen that the Co(II) and Mn(II) complexes reach a degradation rate of over 75% within the first 10 minutes.

Although the maximum effect was reached in the 15th minute for both complexes, it is seen that the Co(II) complex has a faster catalytic effect than the Mn(II) complex (Fig. 4.-V). When the final bleaching performances obtained as a result of the application were examined, it was observed that the highest performance as of 50 minutes belonged to the Co(II) complex with 87.44%. This is followed by Mn(II) with 85.23%, Mn(III) with 71.95% and Zn(II) with 53.98%, respectively.

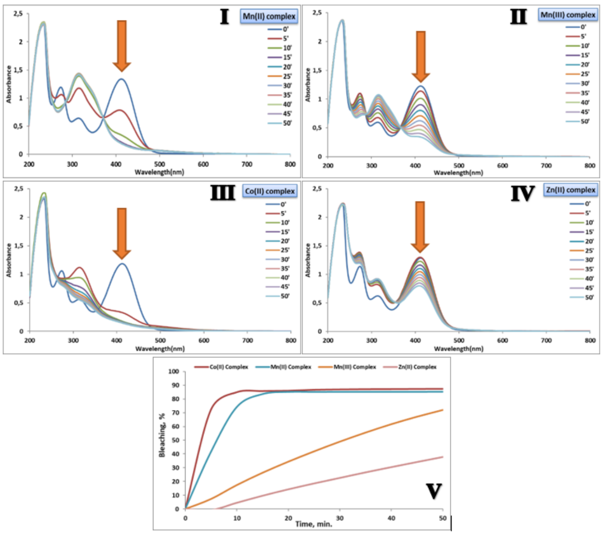


Figure 4 UV-*vis* spectral changes of Morin dye for bleaching experiments; (**I**) Mn(II) complex, (**II**) Mn(III) complex, (**III**) Co(II) complex, (**IV**) Zn(II) complex, and (**V**) under homogeneous conditions % bleaching performance

Table 2 The effects of complexes used as activators on % bleaching performance

Activator (Catalyst) complex	**% Bleaching**	
	25. min	**50. min**
Mn(II)	85.09	85.23
Mn(III)	41.87	71.95
Co(II)	86.76	87.44
Zn(II)	18.57	37.84

In addition, it was observed that the same performance values had the same order at 25 minutes of the measurements (Table 2). When the literature data is examined, the % bleaching performance remained at the level of 3.2% in 20 minutes and 5.26% in 45 minutes when the catalyst is not used (only H_2O_2 is used) under the same conditions, revealing the catalytic effects of the synthesized complexes. On the other hand, when the commercially used TAED molecule is compared with the bleaching performance in the literature, similar results are seen. The bleaching applications with TAED show a performance of 19.21% in 20 minutes and 42.68% in 45 minutes [39].

4. CONCLUSION

According to the results obtained from this study; the synthesis of transition metal complexes with the catalytic activity that can be considered effective in homogeneous conditions was carried out, and it was observed that especially Co(II) and Mn(II) complexes caused the bleaching performance of H_2O_2 to be realized at a very high rate in a concise time. In addition, according to other results obtained during the study; It is understood that it does not show the expected catalytic effect due to the occupied d orbitals in the Zn(II) complex and the side groups coordinated to the cavities in the Mn(III) complex.

One of the most important results obtained here is that the catalytic properties of Schiff base complexes are greatly affected by the interaction between ligand molecules and metal atoms. It was observed that especially the side groups coordinated with the molecule greatly affected this effect. According to all the activation results obtained, Co(II) complex was the catalyst with the highest activation. It has been clearly seen that the results obtained from this application show a highly effective catalytic effect when compared with commercially used TAED and only H_2O_2; thus, it will save both time and energy due to the application temperature.

Acknowledgments

We would like to thank Prof. Dr. Salih Zeki YILDIZ, one of the faculty members of Sakarya University Faculty of Arts and Sciences, Department of Chemistry, for sharing information in the realization of this study. In addition, we would like to thank the referees and editors for their support to the quality of the publication during the publication phase of the study.

Funding

"We did not receive any financial support for the research, authorship, or publication of this work." statement should be written. On the other hand, Tuğba Uğur worked with 100/2000 YÖK doctoral scholarships in this study.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

Authors' Contribution

Tuğba Uğur contributed to the design of the experiments and conducted experiments; Murat TUNA designed the experiments, analyzed and interpreted the data, revised the article. All authors discussed the results and contributed to the final manuscript.

The Declaration of Ethics Committee Approval

The authors declare that this document does not require an ethics committee approval or any special permission

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical, and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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