

CORROSION INHIBITION SCREENING OF BROMOSALEN AND BROMOSALEN-MN(II) COMPLEX BY A WEIGHT LOSS METHOD

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Abstract

Acid solutions such as hydrochloric acid and sulfuric acid are commonly being used as pickling or descaling agents playing a crucial role in the corrosion of mild steel. The excessive deterioration of mild steel during pickling can be controlled by adding an effective corrosion inhibitor in the pickling solution. Therefore, Schiff base ligand namely Bis(5-bromosalicylaldehyde) ethylenediamine (BromosalEn) derived from 5-bromosalicylaldehyde and ethylenediamine undergo further insertion with Mn(II) were synthesized, characterized and evaluated as corrosion inhibitor for mild steel in 1.0 M HCl solution using weight loss method. The main reasons for using Schiff bases and its complex as potential anticorrosive materials are that they are easily synthesized from comparatively inexpensive starting materials and are eco-friendly. The structure of BromosalEn behaves as a tetradentate ligand coordinate through azomethine nitrogen and phenolic oxygen, produces a tetrahedral geometry in Mn(II) complex (BromosalEn-Mn(II)). It has been found that BromosalEn-Mn(II) shows a greater corrosion inhibition efficiency than BromosalEn where at 0.1 M inhibitor concentration, the percentage of inhibitor efficiency of mild steel for BromosalEn-Mn(II) is at 97%. This is due to the larger size of BromosalEn-Mn(II) and greater stability of chelates besides having the heteroatoms like O, N and S together with the azomethine group. It can be concluded that as the concentration of studied inhibitors increases, the corrosion inhibition efficiency of the prepared compounds also increases. This study demonstrated that corrosion inhibitors for metals and alloys can preserve the quality and life of metals from corrosion. In this context, there is an important action to study the effective and easiest ways to produce a high quality of corrosion inhibitor that will reduce the problem of metal corrosion especially in the industry and is aiming to form various compounds for corrosion inhibitors.

Keywords: Schiff Base, Metal Complex, Tetradentate, Corrosion Inhibitor

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Introduction

The study of corrosion behavior in corrosive media has continued to attract substantial attention because of many important applications of the metals. Mild steel (MS) is the most versatile, least expensive and most widely used engineering material in various industries, severely attacked in acid solutions which are used during pickling, cleaning of industrial equipments and acidization of oil wells and much more (Zhang and Hua, 2009). So, in acidic media, the used of corrosion inhibitor is the most practical methods to protect the metal surface from acidic effect. The Schiff base derived compound has been previously reported as an effective corrosion inhibitor for steel, copper and aluminum in acidic media compared with corresponding amines and aldehydes (Solmaz, 2010).

Schiff bases are imines formed by the condensation reaction (elimination of water) of a primary amine and a carbonyl compound. Schiff base ligand is characterized by imines or azomethine group ($-C=N-$) that has been utilized for synthesizing metal complexes of transition metals (Adabiardakani *et al.*, 2012). According to Farag and Hegazy (2013), the high inhibitory performance of these compounds results from the substitution of different heteroatoms (e.g. N, O, Cl and Br) and π -electrons in their structure besides the presence of imine ($-C=N-$) functional group. These heteroatoms normally form a very thin and persistent adsorbed film that lead to decrease in the corrosion rate due to the slowing down of anodic, cathodic reaction or both. In another study, Schiff base-based cationic geminin surfactant was employed as corrosion inhibitor for carbon steel in HCl media. The results showed that, 97.75 % of corrosion inhibition efficiency at 5×10^{-3} M additive concentration. Schiff bases possess azomethine group that rich in lone pair electron to increase inhibition efficiency. In addition, hybridization of Schiff base and metal center will enhance the corrosion inhibition properties due to the effective electron delocalization and high stability of the complexes (Zakaria *et al.*, 2016). Even though a broad range of organic adsorption inhibitors presently applied in the corrosion domain, to the best of our knowledge, these organic inhibitors are expensive and difficult to be synthesized (Ahamad *et al.*, 2010) compared to BromosalEn and its Mn(II) complex. Moreover, studies about the effect of metal complexes as corrosion inhibitor for steel in acid solution appeared in the literature are extremely limited. The aim of the current work is to evaluate the efficiency of both compounds as a corrosion inhibitor using weight loss method. In this context, there is an important action to study the effective and easiest ways to produce a high quality of corrosion inhibitor that will reduce the problem of metal corrosion especially in the industry and is aiming to form various compounds for corrosion inhibitors. In addition, method of weight loss is suitable to check the various type of steels available in the market under accelerated corrosion atmosphere in the laboratory and this is the simplest and most convenient method than the all-other method. Thus, this paper provides a useful information on structure–inhibition activity relationship of Schiff base compounds on their performance as corrosion inhibitors of mild steel in acid media.

Methodology

Chemicals

Acetone, methanol, 5-bromosalicylaldehyde, ethylenediamine, manganese(II) chloride tetrahydrate and hydrochloric acid, HCl (37%) were obtained from R&M Chemicals.

Instruments

The characterization techniques used in this study are elemental analysis (CHN), molar conductivity, melting point, Infrared Radiation spectroscopy (FTIR-ATR) and UV-visible spectroscopies. Table 1.1 show the lists of instruments used for characterization of the synthesized ligand and complex.

Table 1. Instrument and model of the instrument that were used

| Instrument | Analysis |
|---|--|
| Elemental Analysis (CHN) model Flash EA110 | Determination of elemental composition in the synthesized ligand and complex |
| FTIR Spectroscopy ATR-FTIR Spectrometer spectrum 100 Perkin Elmer | Used to analyze the functional group present in both synthesized ligand and complex. |
| Melting Point model SMP10 Stuart | Melting point determination |
| Molar conductivity Model SI Analytics GmbH | Determining the efficiency of a given electrolyte in conducting electricity in a solution |
| UV-Visible spectroscopy T80+ UV/Vis Spectrometer | To determine analyte concentrations or the chemical conversion of a component in solution. |

Preparation of BromosalEn (L)

The ligand was synthesized based on a slight modification of method from Jamil *et al.* (2018). The acidity of 25 mL methanolic solution of 5-bromosalicylaldehyde (9.95 mmol, 2.00 g) was adjusted with a few drops of 0.5 M H₂SO₄ until pH of 5-6. The catalyzed solution was reacted with 25 mL methanolic solution of ethylenediamine (4.98 mmol, 0.33 mL) in 2:1 (aldehyde:amine) molar ratio in a round bottom flask. The reaction solution was refluxed with continuous stirring for 4-5 hours at 50 °C. The precipitates obtained were filtered and washed several times with cold methanol to obtain pure Schiff base and were left to dry. Figure 1 shows the synthesis pathway for BromosalEn.

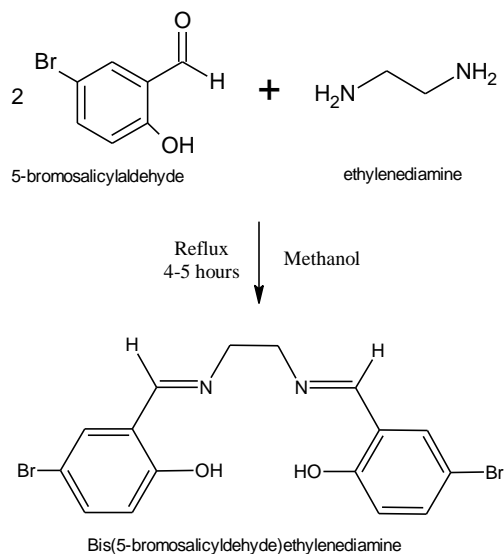


Figure 1. Synthesis pathway for BromosalEn

Synthesis of BromosalEn-Mn(II) (MnL)

A 0.469 mmol solution of Bis(5-bromosalicylaldehyde)ethylenediamine ligand was dissolved in 20 mL hot methanol at 40 °C, was added slowly the 20 mL methanolic solution of manganese(II) chloride tetrahydrate (0.09 g, 0.469 mmol) in 1:1 (Mn:L) molar ratio in a round bottom flask. The reaction mixture was mixed with continuous stirring at 50 °C for 4-5 hours and was allowed to stand overnight at room temperature.

The precipitated formed were filtered, washed with cold methanol, dried and recrystallized from methanol. A dark brown precipitate was obtained. Figure 2 shows the synthesis pathway for BromosalEn-Mn(II) complex (Pui and Mahy, 2007).

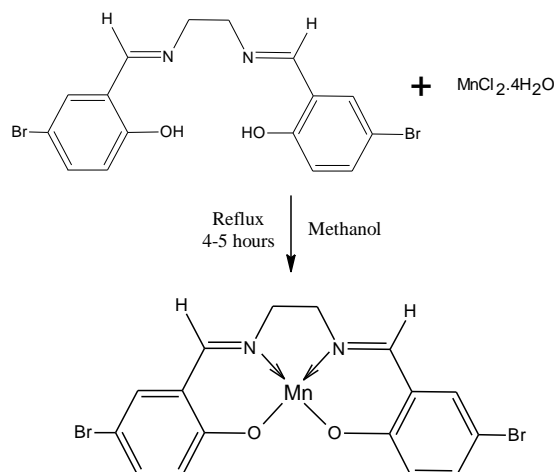


Figure 2. Synthesis pathway for BromosalEn-Mn(II)

Preparation of corrosion inhibitors and immersion test

Different concentrations of BromosalEn and BromosalEn-Mn(II) were prepared as a corrosion inhibitors solution for immersion test by using a serial dilution method from a stock solution of 0.1 M. The stock solution of 0.1 M was prepared by dissolving 0.8522 g of BromosalEn with 1 M HCl and 0.958 g of BromosalEn-Mn(II) with 1 M HCl into a 20 mL volumetric flask, respectively. A 0.01 M and 0.001 M concentration of studied inhibitors were prepared by serial dilution from 0.1 M stock solution in a 20 mL volumetric flask.

The mild steel specimens used for immersion test have coupon dimensions of 2 cm x 3.5 cm. The coupons were abraded with sand papers, washed with distilled water, cleaned with acetone and finally were dried at room temperature. For each test, 0.1 M, 0.01 M and 0.001 M inhibitors concentration of the Schiff base and its metal complex were used for immersion of the coupons.

The coupons were immersed in 15 mL of the studied inhibitors at 40 °C for an immersion period of 24 hours. The coupons were washed with distilled water, cleaned and dried at room temperature. The specimens were finally weighed on an analytical balance, and the differences in weights at each interval were noted (Al-Amiery *et al.*, 2021).

Results and Discussion

Characterisation of BromosalEn and BromosalEn-Mn(II)

Elemental analysis

A Schiff base ligands derived from 5-bromosalicylaldehyde and ethylenediamine was synthesized in 2:1 molar ratio was then undergo insertion of Mn(II) as central atom to produced complex compound.

The analytical data for BromosalEn and BromosalEn-Mn(II) were listed in Table 2. The data shows that the percentage of carbon, hydrogen and nitrogen obtained were in reasonable agreement with the theoretical

ones. The BromosalEn and BromosalEn-Mn(II) are colored-solid and air-stable. The molar conductance of BromosalEn-Mn(II) was measured in ethanol using 1×10^{-3} M solutions at room temperature and the conductance value obtained is $2.3 \mu\text{S}/\text{cm}$ suggest that the complex are non-electrolyte in nature (Shafaatian *et al.*, 2016).

Table 2. The analytical data for BromosalEn and BromosalEn-Mn(II)

| Schiff base | Molecular weight (g/mol) | Colour | Yield (%) | Elemental analysis found (calculated) (%) | | |
|-------------------|--------------------------|--------|-----------|---|-------------|-------------|
| | | | | C | H | N |
| BromosalEn | 426.10 | Yellow | 75.0 | 44.19 (45.10) | 3.67 (3.31) | 6.59 (6.57) |
| BromosalEn-Mn(II) | 479.02 | Brown | 72.5 | 35.58 (40.12) | 2.98 (2.52) | 5.31 (5.85) |

Infrared spectroscopy

In the absence of X-ray crystallography technique that is more advanced in elucidating the structure of the compounds, IR spectroscopy has been chosen in order to study the functional group presence and thus assigned the mode of bonding of ligands to the metal center, respectively. The main stretching frequencies of the IR spectra of BromosalEn and BromosalEn-Mn(II) complex was tabulated in Table 3 while Figure 3 and 4 shows the IR spectrum of BromosalEn and BromosalEn-Mn(II) respectively.

Table 3. IR data of BromosalEn and BromosalEn-Mn(II)

| Compound | Wavenumbers (cm^{-1}) | | | | | |
|-------------------|----------------------------------|---------------|---------------|---------------|---------------|---------------|
| | ν O-H (b) | ν C-H (m) | ν C=N (s) | ν C=C (m) | ν M-N (w) | ν M-O (w) |
| BromosalEn | 3357 | 1567 | 1476 | 1631 | - | - |
| BromosalEn-Mn(II) | - | 1526 | 1452 | 1629 | 691 | 659 |

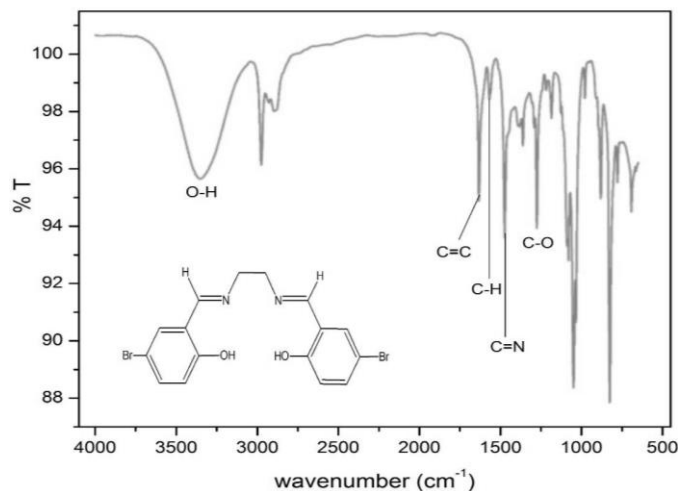


Figure 3. IR spectrum of BromosalEn

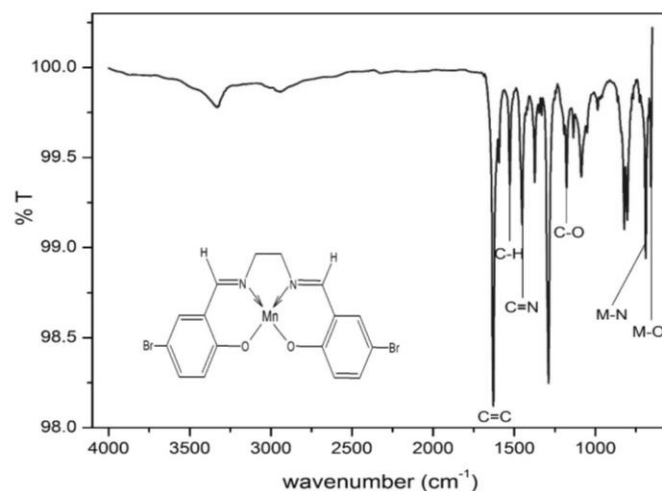


Figure 4. IR spectrum of BromosalEn-Mn(II)

The IR spectra of the free ligand and its metal complex exhibit various bands in 500 – 4000 cm^{-1} region. The BromosalEn and BromosalEn-Mn(II) shows a medium $\nu(\text{C-H})$ bands in the range of 1519 – 1567 cm^{-1} , strong $\nu(\text{C=N})$ bands in the range of 1452 – 1476 cm^{-1} and medium $\nu(\text{C=C})$ bands in range of 1629 – 1637 cm^{-1} . After complexation of BromosalEn with Mn metal center occurs, each of the vibration bands were decreased in intensity and shifted to higher region in their IR spectra and thus shifted to the lower wavenumber and some peaks were disappeared in the spectra of the BromosalEn-Mn(II) (Kursunlu *et al.*, 2013). This were displayed by the disappearance of the OH bands of the BromosalEn-Mn(II) as in Figure 1.3. Research done by Gondia and Sharma (2018) found that the disappearance of OH bands in BromosalEn-Mn(II) was due to the coordination of the phenolic oxygen of the ligand to the metal center. Upon comparison with BromosalEn, the stretching frequency of $\nu(\text{C=N})$ in BromosalEn-Mn(II) are found to be shifted to the lower frequency at 1452 cm^{-1} compared to the free ligand indicates that the azomethine nitrogen participate in the coordination to the metal center that involve in the reduction of the double bond character of the C=N character. Meanwhile, the $\nu(\text{C-O})$ vibration frequency also shifted to lower wavenumber in the complex compared to ligand. The shifting of the wavenumber to the lower region indicates the involvement of the phenolic group in the complex formation as pointed by Shafaatian *et al.* (2016). The new bands appeared at 691 cm^{-1} are tentatively assigned to $\nu(\text{M-N})$ while $\nu(\text{M-O})$ bands were found at of 659 cm^{-1} which provides strong evidence for the involvement of nitrogen and oxygen in coordination with metal center.

UV-Vis Spectroscopy

The UV-Vis spectra of BromosalEn and BromosalEn-Mn(II) were shown in Figure 5 was recorded at room temperature by using methanol as a solvent. The maximum absorption, λ_{max} peak was observed in both of the spectrums of BromosalEn and BromosalEn-Mn(II) at 250.50 nm, respectively. This suggests the existence of $n-\sigma^*$ transition of saturated compounds that contain nitrogen atom with a lone pair of electrons. The peak at range 271-329 nm may be attributed to $\pi-\pi^*$ transition that was pointed as benzene ring. Meanwhile the other peak at range 361.50-414.50 nm were pointed as $n-\pi^*$, for the electron localized on the C=N chromophore.

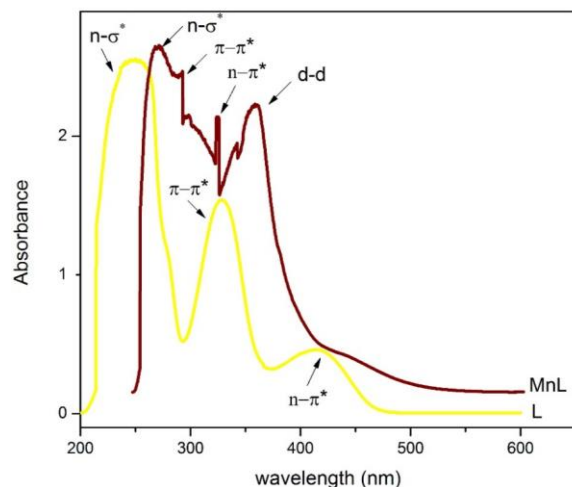


Figure 5. UV-Vis spectrum of BromosalEn and BromosalEn-Mn (II)

The λ_{\max} was slightly shifted to the longer wavelength in the complex compared to the free ligand. This is due to the enlargement of the conjugate structure which showed the coordination of the metal ion with the ligand. For BromosalEn-Mn(II), the low energy peak appeared at 435 nm were assigned to the d-d transition in complex. The UV-Vis data for BromosalEn and BromosalEn-Mn(II) were recorded in Table 4.

Table 4. The UV-Vis data for BromosalEn and BromosalEn-Mn (II)

| Schiff base | λ_{\max} (nm) | Assignments |
|-------------------|-----------------------|-----------------|
| BromosalEn | 250.50 | n- σ^* |
| | 329.00 | π - π^* |
| | 414.50 | n- π^* |
| BromosalEn-Mn(II) | 250.50 | n- σ^* |
| | 295.50 | π - π^* |
| | 361.50 | n- π^* |
| | 435.00 | d-d |

Corrosion inhibition study

The effect of inhibitor concentration on mild steel were studied by using weight loss (WL) measurements of mild steel (MS) in 1 M HCl for 24 hours in the absence and presence of studied inhibitors at 40 °C. The values of weight loss (WL) and inhibition efficiency of mild steel (%IE_{MS}) at different concentrations of the studied inhibitors were summarized in Table 4.

The values of inhibition efficiency, % IE_{MS} was calculated by using equations below.

$$\%IE = \frac{(WL_a - WL_b)}{S} \times 100\% \quad (1.1)$$

$$\% IE_{WL} = IE_{WL} \times 100 \quad (1.2)$$

$$\% IE_{MS} = 100 - \% IE_{WL} \quad (1.3)$$

where WL_a and WL_b are the corrosion rates before and after immersion in the studied inhibitors, respectively.

Figure 6 shows the effect of various concentration of inhibitors on mild steel after 24 hours immersion time. It has been found that BromosalEn and BromosalEn-Mn(II) inhibits the corrosion of MS at all studied inhibitor concentrations. When the studied inhibitor concentration increased, the WL will decrease and % IE_{ms} will increased. This is due to the presence of π electron on the benzene ring and lone pair of electrons of the nitrogen atoms which provide stronger interaction with the metal surface as it coordinates with the active sites of the MS (Abdallah, 2002). Furthermore, Kumar and Mohana (2014) states that the lone pair on nitrogen atoms, facilitates the adsorption of inhibitor molecules on the MS surface and hence inhibits the corrosion process. The interaction between the mild steel and heteroatoms like O, N and S showed an important role in the anticorrosion activity caused by the free electron pairs. Electron rich azomethine (C=N) group present in different transition metal complexes are one of the good corrosion inhibitors. The molecules can be absorbed on the steel surface by forming a strong covalent bond between the lone pair electrons of N atoms in structure and vacant d-orbitals in the steel (Liang *et al.*, 2019).

From data tabulated in Table 5, it is very clear that at a high concentration of inhibitors in acidic solution, the corrosion rate will decrease compared to blank. It can be seen from the data that BromosalEn-Mn(II), shows a higher inhibition activity, compared to BromosalEn due to the larger size and greater stability of chelates besides having the heteroatoms like O, N and S together with the azomethine group (El-Sherif and Eldebss, 2011). The bulky BromosalEn-Mn(II) molecule could cover more than one active site. The inhibitive property of Schiff base metal complexes accounts for blanket preventing mild steel from coming in contact with acidic and the corrosive environment (Suraj *et al.*, 2012).

Table 5. Weight loss and corrosion inhibition efficiency (%IE) of mild steel from WL measurements containing various concentration of BromosalEn and BromosalEn-Mn(II)

| Inhibitor | Inhibitor concentration (M) | IE_{WL} (g) | % IE_{WL} (%) | % IE_{MS} (%) |
|-------------------|------------------------------------|---------------------------------|-----------------------------------|-----------------------------------|
| Blank | - | 0.126 | - | - |
| BromosalEn | 0.001 | 0.104 | 10.4 | 89.6 |
| | 0.01 | 0.079 | 7.9 | 92.1 |
| | 0.1 | 0.036 | 3.6 | 96.4 |
| BromosalEn-Mn(II) | 0.001 | 0.086 | 8.6 | 91.4 |
| | 0.01 | 0.068 | 6.8 | 93.2 |
| | 0.1 | 0.026 | 2.6 | 97.4 |

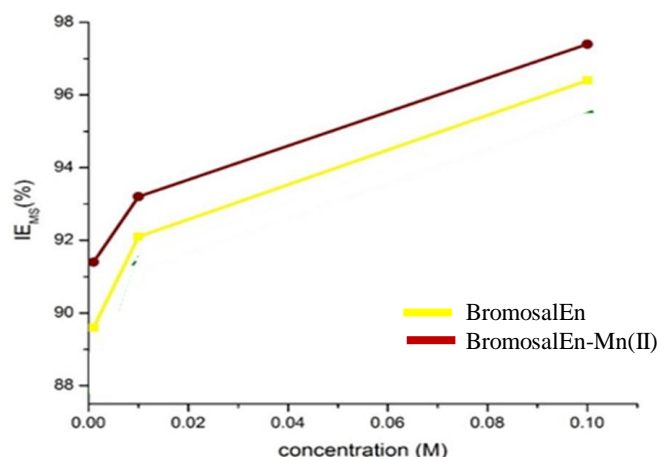


Figure 6. % IE_{MMS} at different concentration of the studied inhibitor, BromosalEn and BromosalEn-Mn(II)

Conclusion

In conclusion, mild steel corrosion inhibitors namely BromosalEn and BromosalEn-Mn(II) were synthesized and their structure was characterized by using spectroscopic techniques. The Mn(II) complex, BromosalEn-Mn(II) were found to be tetrahedral geometry as the synthesized ligand were coordinated to the metal center through the azomethine nitrogen (C=N) and phenolic oxygen. The IR data support the coordination between ligand and metal center through azomethine nitrogen, N and phenolic oxygen. Their abilities to inhibit mild steel corrosion in acidic media found that BromosalEn-Mn(II) shows high corrosion inhibition efficiency compared to BromosalEn. The higher inhibition activity performed by BromosalEn-Mn(II) was due to the presence of π electrons in aromatic systems and multiple bonds, azomethine group, electronegative atoms (O and N) as well as the larger size of inhibitor molecules structures and greater stability of chelates.

For further studies in synthesis and characterization of Schiff base ligand and its metal complex, it is recommended that ligand and metal complex can be synthesized in several conditions and suitable solvents. The characterization of the synthesized compound also can be improved by using magnetic susceptibility, mass spectroscopy and single X-Ray crystal analysis. For corrosion inhibition screening, it could be recommended that the efficiency of the studied inhibitors can also be studied in several methods through electrochemical test such as electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) measurements other than using the weight loss method.

References

- Abdallah, M. (2002). Rhodanine azosulpha drugs as corrosion inhibitors for corrosion of 304 stainless steel in hydrochloric acid solution. *Corrosion Science*, 44(4), 717–728.
- Adabiardakani, A., Hakimi, M., & Kargar, H. (2012). Cinnamaldehyde schiff base derivatives: A short review. *World Applied Programming*, 2(11), 472–476.
- Ahamad I, Prasad R, Quraishi MA (2010). Thermodynamic, electrochemical and quantum chemical investigation of some Schiff bases as corrosion inhibitors for mild steel in hydrochloric acid solutions. *Corrosion Science*, Volume 52 (3), 933-942.

Al-Amiery A., Shaker L.M. and Betti N. (2021). Experimental studies on the inhibition performances of isatine Schiff base for the corrosion of mild steel in hydrochloric acid. *Materials Today: Proceedings*, available online on 9 December 2021. <https://doi.org/10.1016/j.matpr.2021.11.543>

Liang C., Liu Z., Linag Q., Han G, Han J., Zhang S., Feng X., (2019). Synthesis of 2-aminofluorene bis-Schiff base and corrosion inhibition performance for carbon steel in HCl. *Journal of Molecular Liquids*, 277, 330-340

El-Sherif, A. A., & Eldebss, T. M. A. (2011). Synthesis, spectral characterization, solution equilibria, in vitro antibacterial and cytotoxic activities of Cu(II), Ni(II), Mn(II), Co(II) and Zn(II) complexes with Schiff base derived from 5-bromosalicylaldehyde and 2-aminomethylthiophene. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 79(5), 1803–1814.

Farag A. A. and Hegazy M.A. (2013). Synergistic inhibition effect of potassium iodide and novel Schiff bases on X65 steel corrosion in 0.5 M H₂SO₄. *Corrosion Science*, 74, 168–177.

Gondia N.K. and Sharma S.K. (2018). Spectroscopic, characterization and photophysical properties of Schiff base metal complex. *Journal of Molecular Structure*, 1171 , 619-625.

Kursunlu, A. N., Guler, E., Sevgi, F., & Ozkalp, B. (2013). Synthesis, spectroscopic characterization and antimicrobial studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes with Schiff bases derived from 5-bromosalicylaldehyde. *Journal of Molecular Structure*, 1048, 476–481.

Kumar, C. B. P., & Mohana, K. N. (2014). Corrosion inhibition efficiency and adsorption characteristics of some Schiff bases at mild steel/hydrochloric acid interface. *Journal of the Taiwan Institute of Chemical Engineers*, 45(3), 1031–1042.

Pui, A., & Mahy, J.-P. (2007). Synthesis, characterization and catalytic activity of halo-methyl-bis(salicylaldehyde)ethylenediamine cobalt(II) complexes. *Polyhedron*, 26(13), 3143–3152.

Shafaatian, B., Mousavi, S. S., & Afshari, S. (2016). Synthesis, characterization, spectroscopic and theoretical studies of new zinc(II), copper(II) and nickel(II) complexes based on imine ligand containing 2-aminothiophenol moiety. *Journal of Molecular Structure*, 1123, 191-198.

Solmaz R. (2010). Investigation of the inhibition effect of 5-((E)-4-phenylbuta-1,3-dienylideneamino)- 1,3,4-thiadiazole-2-thiol Schiff base on mild steel corrosion in hydrochloric acid. *Corrosion Science*, 52, 3321–3330

Suraj B. Ade, M. N. Deshpande and D. G. Kolhatkar (2012). Corrosion a universal environmental Problem: a role of Schiff base metal complexes as inhibitors. *Journal of Chemical and Pharmaceutical Research*, 2012, 4(2):1033-1035.

Zakaria, K., Hamdy, A., Abbas, M. A., & Abo-Elenien, O. M. (2016). New organic compounds based on siloxane moiety as corrosion inhibitors for carbon steel in HCl solution: Weight loss, electrochemical and surface studies. *Journal of the Taiwan Institute of Chemical Engineers*, 65, 530-543.

Zhang Q.B. and Hua Y.X. (2009). Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid. *Electrochimica Acta*, 54, 1881–1887.