Inhibition of Iron Corrosion using Schiff base Cu(II) Complex in Saline and Acidic Medium

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1 Introduction

Corrosion is an inevitable phenomenon and a naturally occurring process where it can be defined as the deterioration of a metal surface through chemical or electrochemical interaction with its surrounding environment. Iron is one of the cheapest and strongest metal. Iron is utilized in many different applications including industrial pipelines, structural components and kitchen appliances. Iron corrodes severely when exposed to aggressive environments. When iron is exposed to oxygen in the presence of water, iron oxide ($Fe_2O_3 \cdot xH_2O$) is formed. Iron corrosion is accelerated by saline and acidic conditions because they enhance and allow electron transfer.

Metals lose their usable properties due to corrosion, which has a significant effect on financial costs, environmental issues, and public safety. In 2011, Hansson reported, due to the steel pipe corrosion 23,000 persons lost their lives in an Indian chemical plant disaster in 1984.[1] Numerous corrosion related cases with significant effects on human life have been reported in the literature. Therefore, Strategies for preventing corrosion may lead to significant global savings. One technique for preventing iron from corrosion is the use of synthetic inhibitors. Schiff base complexes are part of those synthesized inhibitors. Electronegative nitrogen and oxygen atoms improve the inhibitor adsorption on an iron surface, which facilitates efficient corrosion prevention.

In this study, self-assembled layer is used as coatings that prevent corrosion, which is a film deposition technique, to transfer a complex onto a solid substrate. Corrosive substances cannot pass through the self-assembled layer because it has dense and stable structure which acts as an insulating barrier.[2] A self-assembled layer is a layer of surfactant molecules that spontaneously forms on a substrate. Inhibitor molecules absorb onto an iron substrate.[3] The advantages of this technique over other techniques are ease of formation, cost effectiveness and chemical stability.

2 Materials/ Methodology

2.1 Synthesis of the Schiff base Cu(II) Complex

Salicylaldehyde and 4-chloroaniline were taken into a beaker and mixed thoroughly. The mixture was exposed to microwave radiation for three mins at 160 W power. The reaction mixture was kept in the ice bath, after completion of the reaction. The yellow solid obtained was filtered using Buchner funnel and recrystallized from ethanol.

Synthesized Schiff base ligand was transferred into a beaker and dissolved in hot ethanol. Then copper(II) chloride was also dissolved in ethanol and transferred into the same beaker containing solution of Schiff base ligand and mixed thoroughly. Schiff base ligand:metal ratio is 2:1. The mixture was exposed to microwave radiation for three mins at 160 W. The solid obtained was filtered and recrystallized from ethanol.[4]

2.2 Preparation of the Self-assembled Layer

Schiff base Cu(II) complex was dissolved in absolute ethanol. The iron substrate was polished using sandpaper. After polishing, the iron substrate was washed with absolute ethanol and distilled water, then dried. Iron plates (1 cm × 4 cm) were immersed in Schiff base Cu(II) complex solution. The immersion time was 3 hours. Immersed iron plates kept in a desiccator to dry. In this study, 99.99% pure iron plates were used.[5]

2.3 Qualitative Corrosion Analysis

For ferroxyl staining, Agar was dissolved in boiling water. Once Agar is completely dissolved, 0.1 M $K_3[Fe^{III}(CN)_6]$, Phenolphthalein and 3% NaCl were added into the Agar medium. Iron plate was placed in the petri dish and agar was poured and set aside for a day to observe color changes. Same experiment was carried out for 0.01 M H_2SO_4, instead of 3% NaCl. Same procedure was followed without Phenolphthalein in both 0.01 M H_2SO_4 and 3% NaCl separately.[6]

Iron substrates were immersed in 0.01 M H_2SO_4 and 0.1 M NaCl solutions for 5 days separately to get images with a SEM.

3 Results and Discussion

3.1 Characterization of the Schiff base Cu(II) Complex

Fourier Transform Infrared (FTIR) Spectroscopy and CHN Analysis was done for the characterization of Schiff base Cu(II) complex. The FTIR spectra showed C=N stretching vibration at 1616 cm^{-1} reigon.[7] The appearance of two new bands at 590 cm^{-1} and 448 cm^{-1} in the spectra can be attributed to the Cu-O and Cu-N stretching vibrations respectively.[8]

A strong correlation between the experimental and theoretical values was revealed by CHN analysis. The CHN analysis supported the proposed structure.
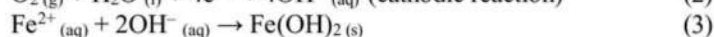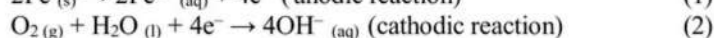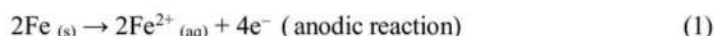
3.2 Contact Angle Measurement

Surface wettability is significant to coating because it tells whether a surface is hydrophobic or hydrophilic, depending on the molecules on the surface. Monitoring surface wettability was done using contact angle measurement. Sessile drop method was used for that. Schiff base Cu(II) complex coated iron plate showed contact angle of 93.30° when compared to the bare iron substrate at 72.34° confirms enhancement of surface hydrophobicity.

3.3 Qualitative Corrosion Analysis

The effect of coatings on iron corrosion was investigated by covering approximately one-half of the iron plate with Schiff base Cu(II) complex to provide qualitative information on corrosion.

Corrosion consists of oxidation and reduction reactions. Main steps of the iron corrosion can be written as follows.

$$2Fe_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + 4e^- \text{ (anodic reaction)} \tag{1}$$
$$O_{2(g)} + H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)} \text{ (cathodic reaction)} \tag{2}$$
$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)} \tag{3}$$
$$Fe(OH)_{2(aq)} + O_{2(g)} \rightarrow Fe_2O_3 \cdot xH_2O_{(s)} \tag{4}$$

Ferroxyl staining is used to determine the effect of acidic and saline media, on 99.99 % pure iron surfaces coated with Schiff base Cu(II) complex.

The agar forms a semisolid gel upon cooling, that encases the substrate. To identify the corrosion processes taking place in the anode and cathode, indicators are used. The anode and cathode locations in the corrosion process were determined using $K_3[Fe^{III}(CN)_6]$ and the acid-base indicator phenolphthalein. Phenolphthalein turns to pink color in the presence of OH^- ion. $K_3[Fe^{III}(CN)_6]$ react with Fe^{2+} ions and form a prussian blue complex which represents the anode. Half of the length of iron substrates used in the experiments were covered with Schiff base Cu(II) complex, while the other half remained bare. The iron substrates are exposed to both saline and acidic media for one week to take observations. Experiments without phenolphthalein were also conducted to confirm the iron degradation process. The coated region in both experiments did not exhibit any blue coloration with Fe^{2+} generation, suggesting that the self-assembled layer act as a barrier to prevent corrosion in both saline and acidic environments. Because iron (II) generation is inhibited, rust formation is prevented.[6]

The morphological information of the iron surface, surface damage, and rust formation were obtained by SEM images. In acidic medium, the unprotected blank iron substrate exhibited rough, corroded, and irregular surfaces. While corrosion was inhibited well in the coated iron substrate with Schiff base Cu(II) complex. In saline medium, unprotected blank iron substrates showed a rougher and corroded surface when compared to the coated iron substrate with Schiff base Cu(II) complex. The Schiff base Cu(II) complex coated iron plates are smooth.[6]
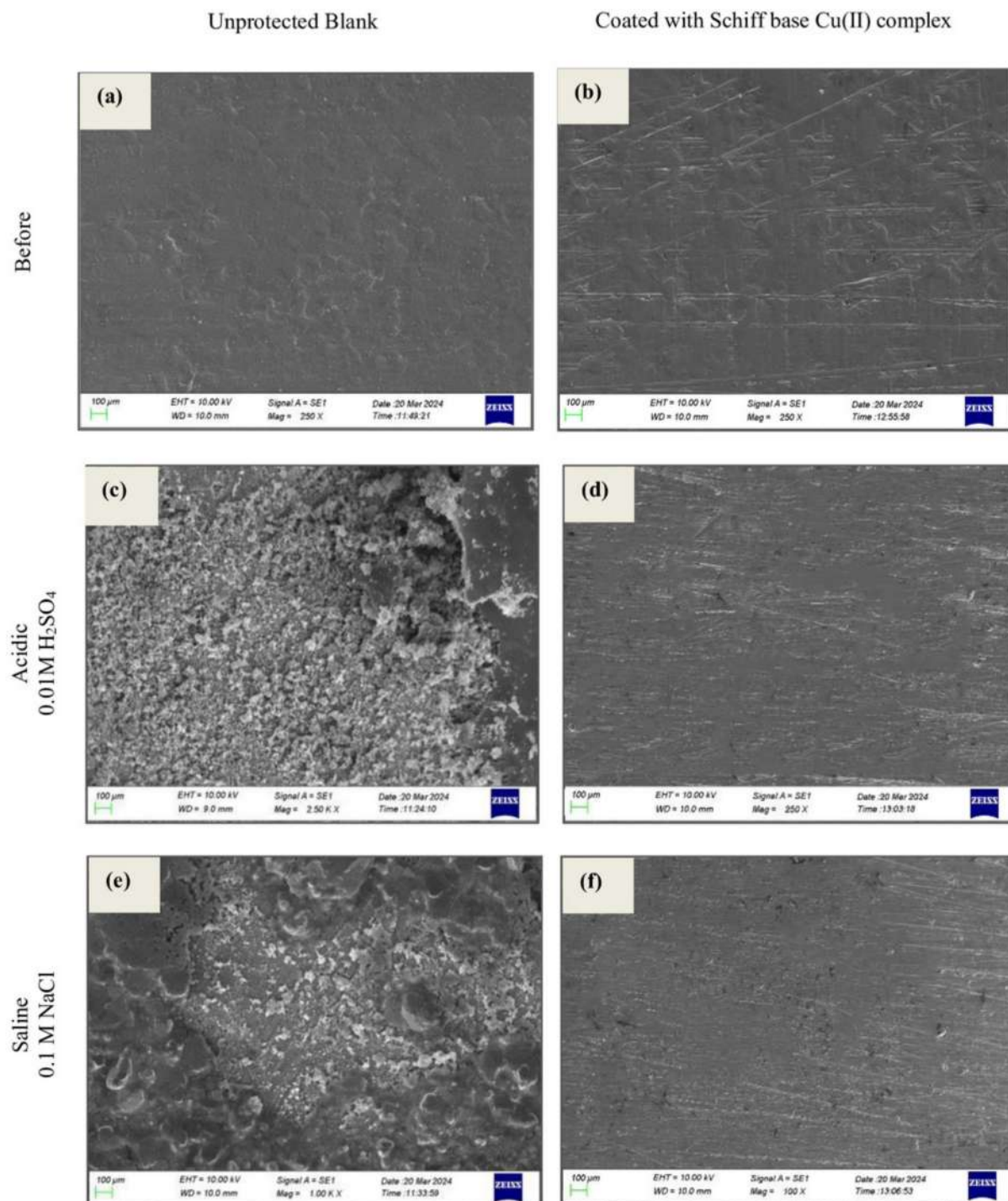
Fig. 1. SEM images for the unprotected blank iron substrate on (a), (c), (e) and Schiff base Cu(II) complex coated iron substrate on (b), (d), (f) in acidic and saline media.

Conclusion

Metallic substrates, composed of 99.99% pure iron, were protected by the coating with Schiff base Cu(II) complex using self-assembled layer technique. Analysis of SEM images and ferroxyl staining confirmed, iron corrosion can be inhibited by coating of Schiff base Cu(II) complex in both acidic and saline medium.

Keywords: Corrosion inhibition, Schiff bases, Iron corrosion, Self-assembled

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References

(1) Hansson, C. M. The Impact of Corrosion on Society. Metall. Mater. Trans. A Phys. Metall. Mater. Sci. **2011**, 42 (10), 2952–2962.

(2) Zhou, Y.; Xu, S.; Guo, L.; Zhang, S.; Lu, H.; Gong, Y.; Gao, F. Evaluating Two New Schiff Bases Synthesized on the Inhibition of Corrosion of Copper in NaCl Solutions. RSC Adv. **2015**, 5 (19), 14804–14813.

(3) Shubha, H. N.; Venkatesha, T. V.; Vathsala, K.; Pavitra, M. K.; Punith Kumar, M. K. Preparation of Self Assembled Sodium Oleate Monolayer on Mild Steel and Its Corrosion Inhibition Behavior in Saline Water. ACS Appl. Mater. Interfaces **2013**, 5 (21), 10738–10744.

(4) Abubakar T; Haruna A; Isyaku S; Imam M. Microwave-Assisted Synthesis, Characterization and Antimicrobial Activity of Copper (Ii) Complex with Salicylaldehyde and P-Chloroaniline Schiff Base. Bayero J. Pure Appl. Sci. **2022**, 13 (1), 117–122.

(5) McArthur, S. L. Thin Films of Vanadium Oxide Grown on Vanadium Metal. Surf. Interface Anal. **2006**, 38 (c), 1380–1385.

(6) Gonawala, S.; Leopoldino, V. R.; Kpogo, K.; Verani, C. N. Langmuir-Blodgett Films of Salophen-Based Metallosurfactants as Surface Pretreatment Coatings for Corrosion Mitigation. Chem. Commun. **2016**, 52 (74), 11155–11158.

(7) Adesibikan, A. A.; Emmanuel, S. S. Synthesis and Characterization of Co (II) Complex with a Schiff Base Ligand Derived from Salicylaldehyde and 4-Chloroaniline. **2023**, 10 (2), 12–17.

(8) Baran, E. J. Structural Data and Vibrational Spectra of the Copper (II) Complex of L-Selenomethionine. Zeitschrift fur Naturforsch. - Sect. B J. Chem. Sci. **2005**, 60 (6), 663–666.