A COMPARATIVE STUDY OF INHIBITIVE EFFECTS OF SOME NEW SCHIFF BASES ON COPPER CORROSION IN ACIDIC MEDIUM

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ABSTRACT

In this research two new Schiff bases N,N'-bis[(3,4-dihydroxy-5-nitrophenyl)methylidene]thiourea (BDHNPMTU) and 2-[(3,4-dihydroxy-5-nitrophenyl)methylidene]hydrazine-1-carbothioamide (DHNPMHC) were synthesized by condensation of 3,4-dihydroxcy-5-nitro-benzaldehyde with Thiourea and Thiosemicarbazide. The structures of Schiff bases were fully characterized by elemental analysis, FT-IR and UV–Vis methods. The inhibitive effects of two Schiff bases BDHNPMTU and DHNPMHC towards the corrosion on copper in 0.5M HCl were investigated using weight loss measurement technique. Surface morphology of metal surface in presence and absence of inhibitors were studied by scanning electron microscope (SEM). Results show that both BDHNPMTU and DHNPMHC are an effective inhibitor for copper corrosion in 0.5 M HCl solution. It was found that inhibition efficiency increases with increasing concentration of inhibitor. Adsorption of the inhibitor on the copper surface followed Langmuir adsorption isotherm. SEM study also support the inhibition of corrosion of copper. BDHNPMTU and DHNPMHC show maximum inhibition efficiency i.e. 96% and 95.83% at highest concentration of inhibitor (5×10^{-5}M). The order of inhibition efficiency of the two Schiff's bases for Cu metal are BDHNPMTU>DHNPMHC.

Keywords: BDHNPMTU, DHNPMHC, Corrosion, Copper, Weight loss measurement, SEM.

1. INTRODUCTION

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. The environment could be of any type such as atmosphere, water, seawater, acid, alkaline, steam, gases, soil and liquid metals etc. It is a natural process that converts a pure metal into a more chemically stable form such as oxide, hydroxide, or sulphide. Corrosion is one of the major causes of material failure and hence leads to a huge coast to our society. Corrosion has a huge economic and environmental impact on all facets of national infrastructure [1-6]. Copper is used as a conductor of heat and electricity, as a building material and as a constituent of various metal alloys, such as brass, bronze, gunmetal, German silver and thermocouples for temperature measurement. Due to the excellent mechanical properties and low cost, copper is extensively used as a constructional material in many industries [7, 8].Copper is resistant toward the influence of atmosphere and many chemicals, however, when exposed to the corrosive industrial environment,

it is easily corroded. Normally, acid solutions such as hydrochloric acid are widely used such as in acid pickling, industrial cleaning, oil well cleaning, etc. The use of inhibitor is one of the most practical methods for protection against corrosion to protect metal dissolution and acid consumption [9].

Organic compounds containing a heteroatom (N, O and S) in their structure act as good corrosion inhibitors. The corrosion inhibitor efficiency of organic inhibitor depends on the chemical structure and physiochemical properties of the compound like functional groups, electron density at the donor atom, p-orbital character, and the electronic structure of the molecule. They form a coordination bond with vacant d orbital of metal and form a protective layer on the surface of metal [10-16]. Most of organic inhibitors are expensive, toxic and have negative effect on the environment; these properties restrict its use to inhibit the metal corrosion. Thus it is important and necessary to develop low cost and environmentally safe corrosion inhibitors [17].

Schiff bases have important application in field of corrosion inhibition of metals and their alloys. It is based on the ease of synthesis from relatively inexpensive starting-materials and their eco-friendly or low toxic properties. Schiff bases have hetero atoms such as (P, S, N and O), and aromatic ring in their structure. Due to this property they form a protective layer. These molecules normally form very thin and persistent adsorbed films that lead to a decrease in the corrosion rate due to the slowing down of anodic, cathodic reaction or both. The efficiency of the inhibitor depends on the environment, in which it acts, the nature of the metal surface, and the structure of inhibitor itself [18-21].

Schiff bases of thiourea and thiosemicarbazide have been widely studied in past years due to their excellent corrosion inhibition efficiency for metals in acid media [22-31]. The Schiff bases of thiourea (BDHNPMTU) and thiosemicarbazide (DHNPMHC) are nontoxic, relatively cheap and easy to produce at high purity. These properties would justify the use of Schiff base of thiourea and thiosemicarbazideas corrosion inhibitor.

The aim of the present study is to compare the anticorrosive properties of Schiff bases of thiourea (BDHNPMTU) and thiosemicarbazide (DHNPMHC) on copper corrosion in 0.5 N HCl.

2. MATERIAL AND METHODS

All the reagents used in this study were of analytical grade. 3,4-dihydroxcy-5-nitro-benzaldehyde, thiourea and glacial acetic acid were of obtained from (SLR, India). Thiosemicarbazide, ethyl alcohol and hydrochloric acid were directly procured from Molychem India Limited. The BDHNPMTU and DHNPMHC were synthesized and characterized on the basis of reported various past research studies [32-37].

2.1. Synthesis of BDHNPMTU

The N,N'-bis[(3,4-dihydroxy-5-nitrophenyl)methylidene]thiourea (BDHNPMTU) was synthesized from 3,4-dihydroxcy-5-nitro-benzaldehyde and thiourea in equal molar ratio in ethanol (20ml) in presence of glacial acetic acid (2ml). The content was refluxed for about 4-5 hours at 70°C with water condenser. On cooling the contents the dark brown coloured solid (M.P.110°C) separated out. The method of synthesis is summarized in Fig.1.

2.2. Synthesis of DHNPMHC

The Schiff base 2-[(3,4-dihydroxy-5-nitrophenyl) methylidene]hydrazine-1-carbothioamide (DHNPMHC was synthesized from 3,4-dihydroxcy-5-nitrobenzaldehyde (2gm) and thiosemicarbazide (2gm) in ethanol (20ml) in presence of glacial acetic acid (2ml). The content was refluxed in round bottom flask fitted with water condenser for about 6-7 hours at 70°C. On cooling the contents the shining yellow colored solid (M.P.175-180°C) separated out. The yield of (DHNPMHC) is 3.35gm (81.25%). The method of synthesis is summarized in Fig.2.
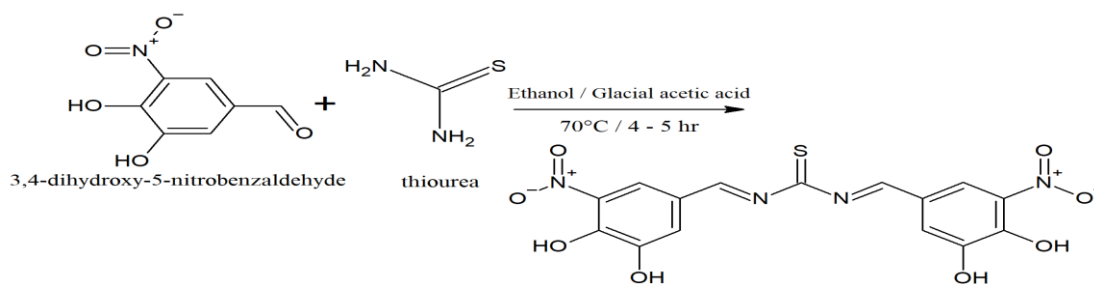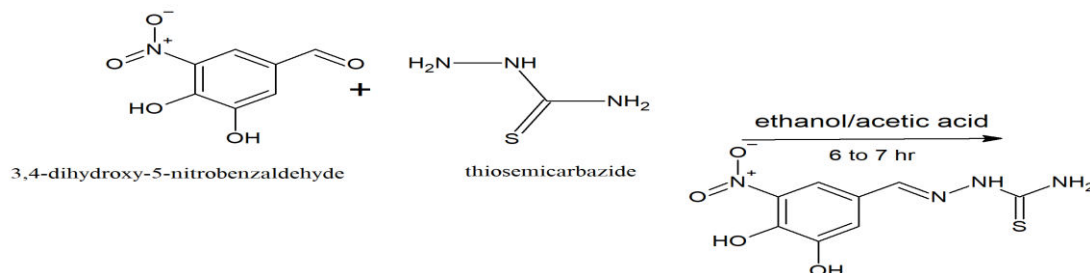

Fig. 1: Synthetic scheme of BDHNPMTU

Fig. 2: Synthetic scheme of DHNPMHC

2.3. Characterization of BDHNPMTU

The structure of compound was characterized by elemental analysis, IR and electronic studies. The elemental study of compounds shows the presence of C (44.34%), H (2.48%), N (13.79%), O (31.50%), S (7.89%) in BDHNPMTU and C (37.42%), H (3.08%), N (21.79%), O (24.88%), S (12.42%) in DHNPMHC. Absence of a υ(C=O) band of aldehyde and presence of υ(C=N) band of azomethine group occurred at 1690-1640 and 1695-1650cm^{-1} in the IR spectra of BDHNPMTU and DHNPMHC respectively confirmed the synthesis of BDHNPMTU and DHNPMHC. In the electronic spectrum of BDHNPMTU and DHNPMHC, n- π^* absorption peak of azomethine group were observed at 310.5, 320.5, 341.5, 354, 370 nm and 352, 366.5, 390, 391, 416, nm respectively.

2.4. Experimental

For the mass loss study, rectangular copper specimens of size 3.0cm x 2.0cm x 0.1 cm with a small hole of about 0.02 cm. diameter near the upper edge were employed. All the chemicals employed were of analytical grade and the corresponding solutions were prepared in double distilled water. Test solutions with given concentration of the inhibitor in the acid was prepared by properly diluting the bulk solution of the both inhibitors (0.01N). To prepare stock solution of DHNPMHC, small amount of DMSO was added for solubility reasons. Concentrations of inhibitors (BDHNPMTU and DHNPMHC) in various test solution ranged from 1.0% to 5.0%.

Each specimen was suspended by a V- shaped glass hook made by capillary glass tube and immersed in a glass beaker containing 50 ml of test solution at room temperature. After the exposure of sufficient time, the test specimen was taken out, cleaned under running water and dried in oven, after drying, specimens were weighted. The variation in mass loss was followed at an interval for 4 hours to 72 hours in 0.5 N HCl as shown in the tables 1 and 2.

The percentage corrosion inhibition efficiency was calculated as

$$\eta \% = 100 \, (\Delta M_U - \Delta M_i) / \Delta M_U$$

Where, ΔM_U: Mass loss of metal in uninhibited solution, ΔM_i: Mass loss of metal in inhibited solution

The degree of Surface coverage (Θ) of metal specimen by inhibitor was calculated as:

$$\Theta = (\Delta M_U - \Delta M_i)/\Delta M_U$$

The corrosion rates can be calculated by the following equation:

Corrosion rate (mm/yr) = (Mass loss x 87.6)/DAT

Where, D: density of copper, A: surface area of metal specimen, T: time exposure

Table 1: Concentration of inhibitor (COI), mass loss (ΔM), inhibition efficiency (η), surface coverage (ϴ) and corrosion rate (mm/yr) for copper metal in presence of BDHNPMTU at different time interval

CO I(%)	4 hours				24 hours				48 hours				72 hours			
	ΔM (mg)	η (%)	ϴ	CR (mm /yr)	ΔM (mg)	η (%)	ϴ	CR (mm /yr)	ΔM (mg)	η (%)	ϴ	CR (mm /yr)	ΔM (mg)	η (%)	ϴ	CR (mm /yr)
blank	0.09	...	...	0.391	0.15	...	...	0.10	0.25	...	...	0.08	1.5	...	...	0.349
1	0.036	62	0.62	0.146	0.059	62	0.62	0.039	0.09	61	0.61	0.03	0.52	65.7	0.65	0.119
2	0.025	73	0.73	0.101	0.045	71	0.71	0.030	0.07	71	0.71	0.03	0.34	77.4	0.77	0.078
3	0.012	87	0.87	0.048	0.025	84	0.84	0.016	0.04	83	0.83	0.01	0.19	87.5	0.87	0.043
5	0.003	96	0.90	0.012	0.009	94	0.94	0.006	0.01	93	0.93	0.003	0.11	92.8	0.92	0.025

Table 2: Concentration of inhibitor (COI), mass loss (ΔM), inhibition efficiency (η), surface coverage (ϴ) and corrosion rate (mm/yr) for copper metal in presence of DHNPMHC at different time interval

CO I(%)	4 hours				24 hours				48 hours				72 hours			
	ΔM (mg)	η (%)	ϴ	CR (mm /yr)	ΔM (mg)	η (%)	ϴ	CR (mm /yr)	ΔM (mg)	η (%)	ϴ	CR (mm /yr)	ΔM (mg)	η (%)	ϴ	CR (mm /yr)
blank	0.09	...	...	0.39	0.15	...	...	0.10	0.25	...	...	0.08	1.5	...	...	0.339
1	0.02	72.9	0.72	0.10	0.057	63	0.63	0.03	0.10	61	0.61	0.033	0.48	68	0.68	0.108
2	0.009	90.6	0.90	0.03	0.038	75	0.75	0.02	0.05	80	0.80	0.016	0.38	74.6	0.74	0.085
3	0.006	93.7	0.93	0.02	0.022	85	0.85	0.01	0.03	85	0.85	0.012	0.16	89.3	0.89	0.036
5	0.004	95.8	0.95	0.01	0.009	94	0.94	0.006	0.01	93	0.93	0.005	0.11	92.6	0.92	0.024

2.5. Surface Morphological Studies

The surface morphology of the copper surface after its immersion in the acidic medium in the absence and in the presence of the BDHNPMTU and DHNPMHC (at 5% concentrations) were carried out by scanning electron microscope (SEM) at 25.0kv and 10μm resolution.

2.6. Adsorption Isotherms

The corrosion inhibitors act by adsorbing over the metallic surface. An adsorption isotherm is the mathematical expression, which relates the bulk concentration of adsorbing species to its surface concentration at constant temperature. An adsorption isotherm gives the relationship between the coverage of an interface with an adsorbed species and the concentration of the species in solution. Most of the organic inhibitors obey Langmuir adsorption isotherm. An inhibitor is found to obey Langmuir if a log $\theta/(1-\theta)$ v/s log C gives a linear plot.

3. RESULT AND DISCUSSION

The results of weight loss technique show that both Schiff bases BDHNPMTU and DHNPMHC inhibit the corrosion rate of copper in acidic medium (0.5N HCl). Corrosion rate values decrease as the concentration of inhibitor increases. Inhibition efficiency increases with increasing concentration of Schiff bases Fig.5. DHNPMHC have shown a decrease in its inhibition performance by rising exposure time or immersion time. BDHNPMTU and DHNPMHC show maximum inhibition efficiency i.e. 96% and 95.8% at 5% (5 X 10^{-4}M) inhibitor concentration (4 hr immersion time). The plot log $\theta/(1-\theta)$ v/s log C gives a straight line for both inhibitors Fig.6. Hence, adsorption of both inhibitors on copper surface obey Langmuir isotherm. The SEM images of a fresh copper, copper after immersion in 0.5N hydrochloric acid and with inhibitors for a period of 4 hour are shown in Fig.7 a-d. It also revealed that the metal surface was smooth and free from depressions in the case of copper immersed in 0.5 N hydrochloric acid containing BDHNPMTU and DHNPMHC, whereas the surface is damaged in the case of copper immersed in 0.5N hydrochloric acid without inhibitors. The order of efficiency of Schiff bases are BDHNPMTU >DHNPMHC.
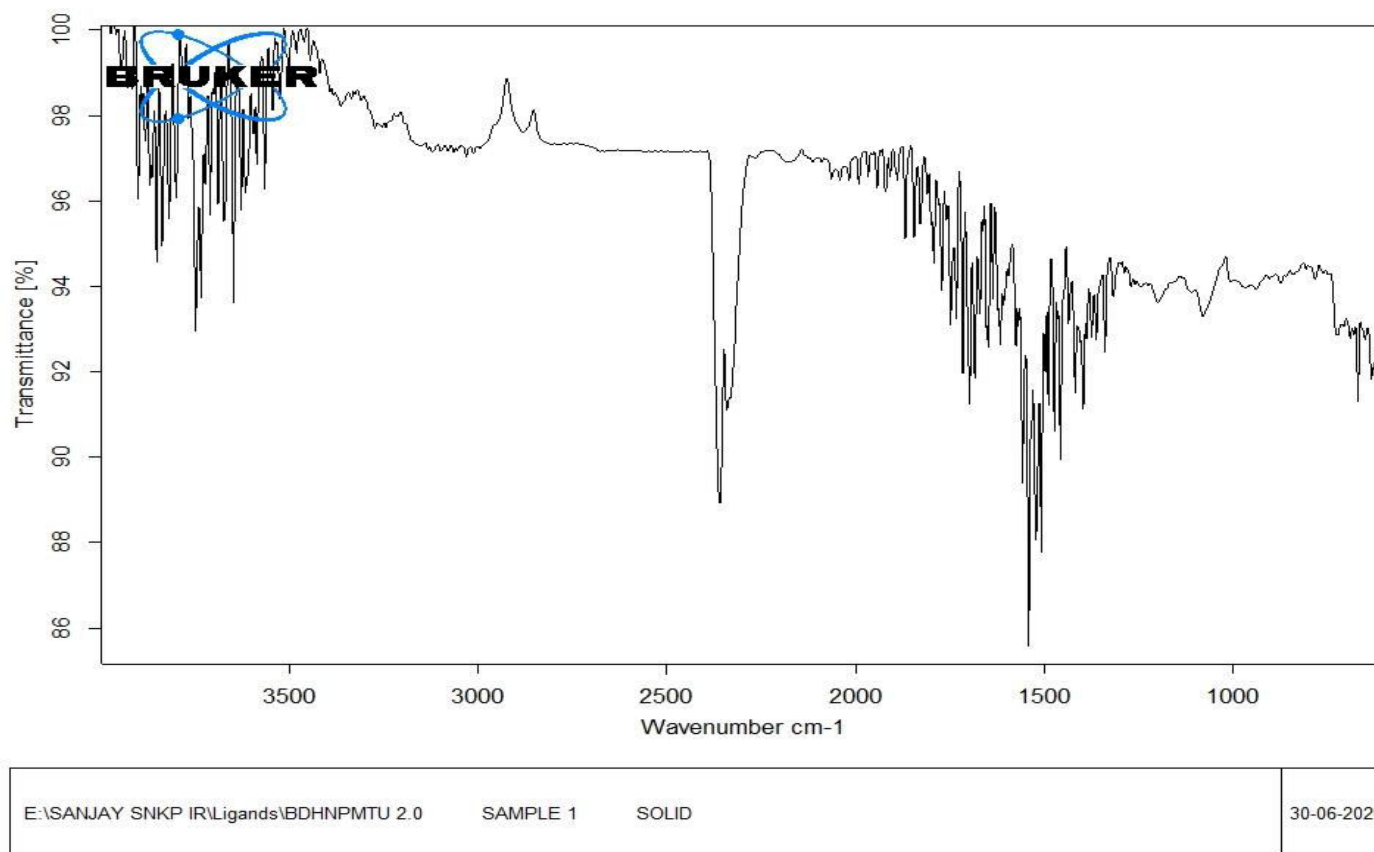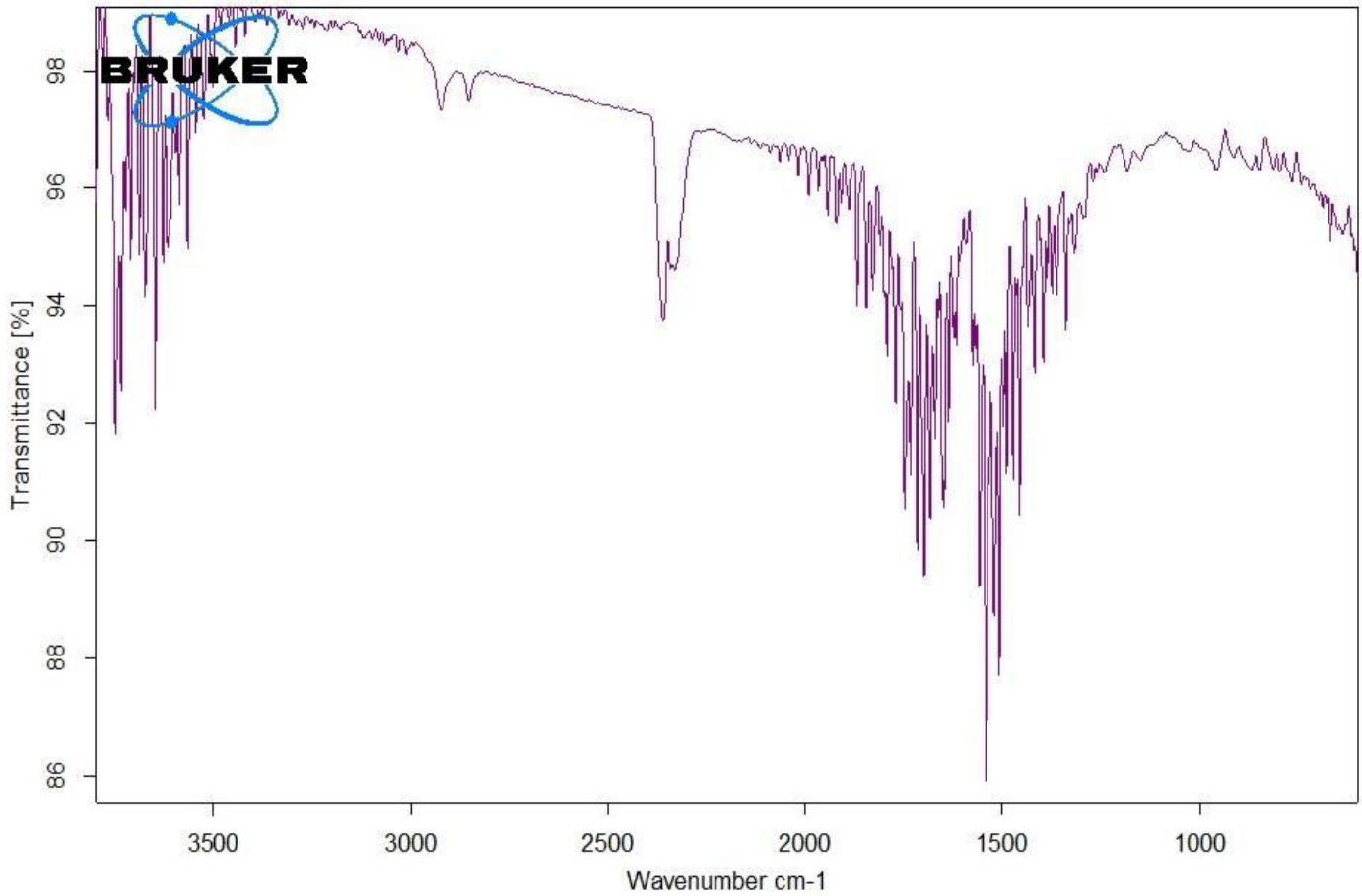

Fig. 3: IR spectrum of BDHNPMTU

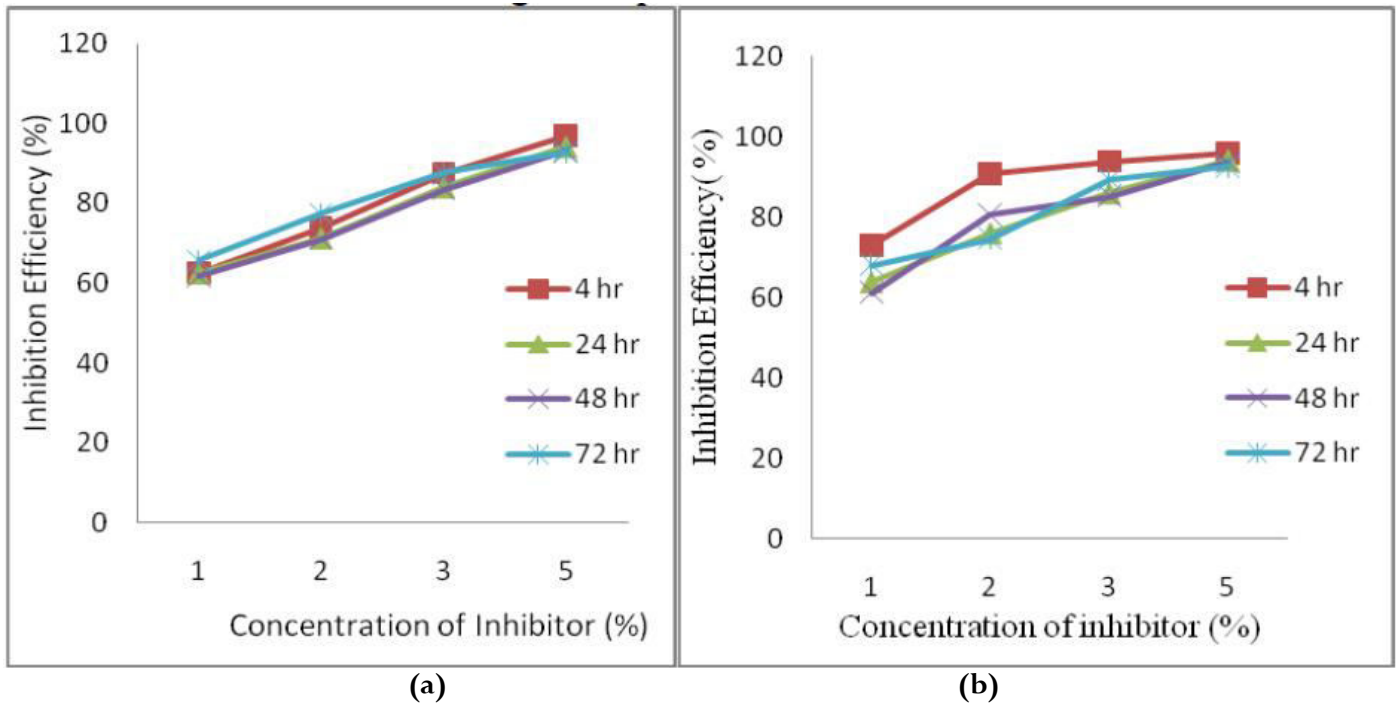**Fig. 4: IR spectrum of DHNPMHC**

Fig. 5: The graph inhibition efficiency v/s concentration of inhibitor (%) at different time interval for copper in 0.5 M HCl (a) In presence of BDHNPMTU (b) In presence of DHNPMHC
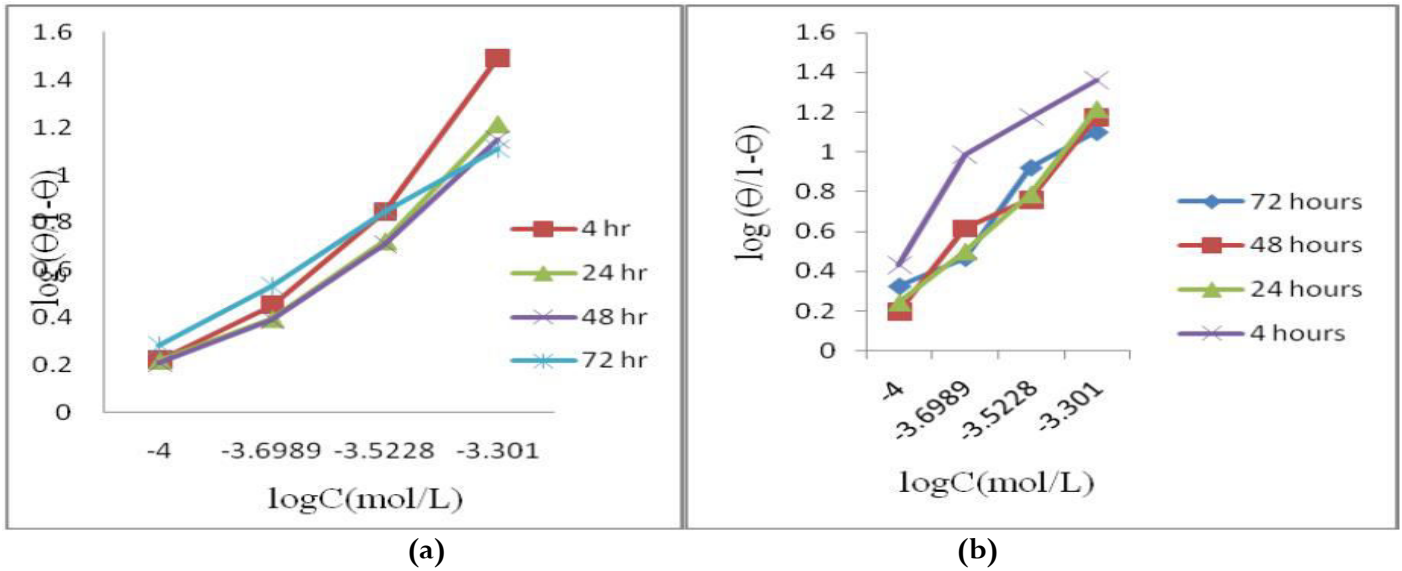
Fig. 6: Langmuir adsorption isotherm plot for copper in 0.5 N HCl with Schiff base (a) BDHNPMTU (b) DHNPMHC
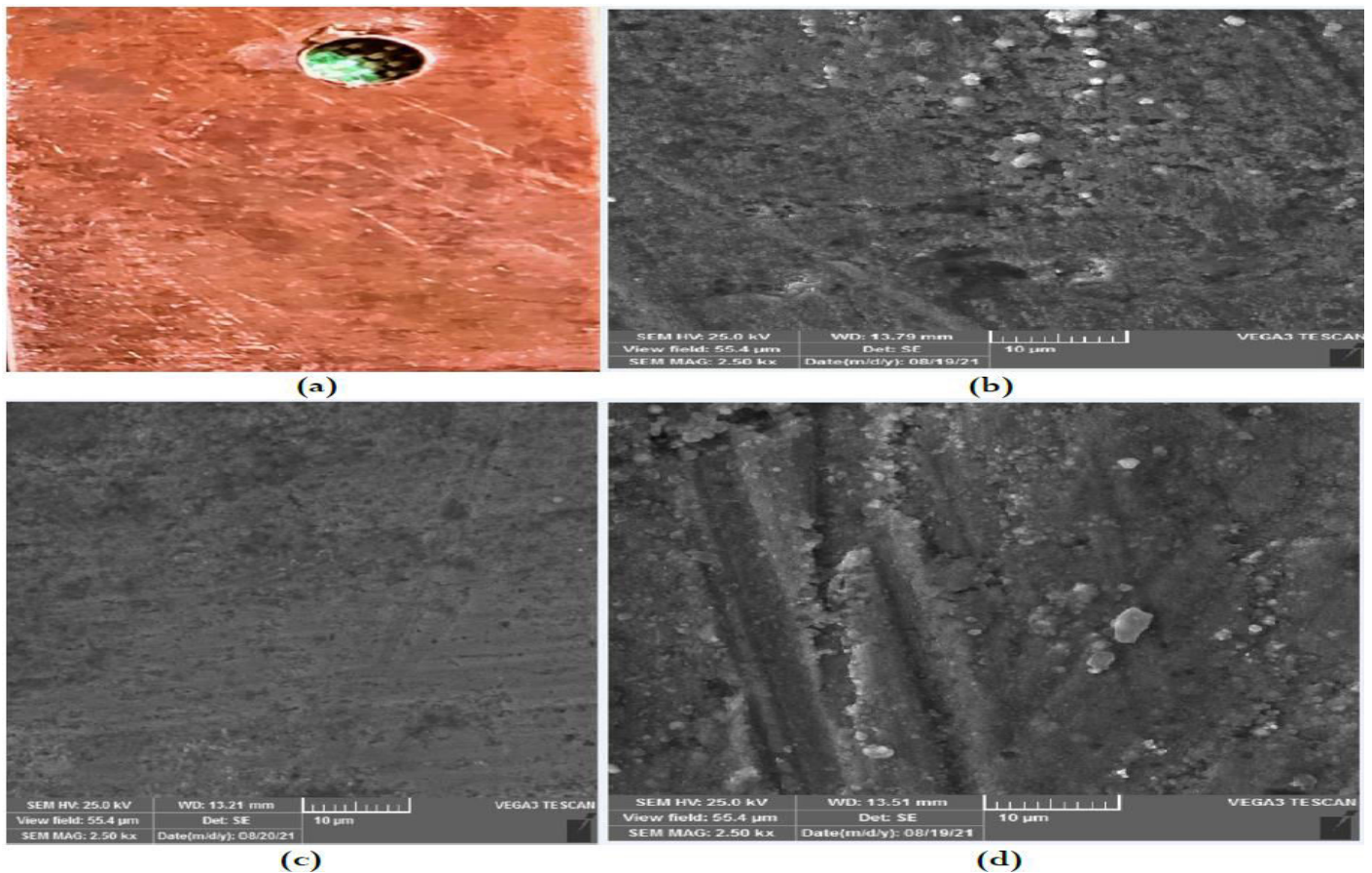

Fig. 7: (a) Fresh Copper. SEM Image for 4 hour time duration (b) Cu + 0.5 N HCl (c) Cu + 0.5 N HCl+5% BDHNPMTU (d) Cu + 0.5 N HCl + 5% DHNPMHC

4. CONCLUSION

The efficiency of synthesized Schiff bases BDHNPMTU and DHNPMHC as corrosion inhibition for copper in acidic media have been studied. Results obtained from weight loss technique indicate that both Schiff bases act as efficient inhibitor for copper corrosion in acidic

media. The graph between inhibition efficiency and concentration shows that the inhibition efficiency increases with concentration of inhibitor. Adsorption of both the inhibitors on copper surface obey Langmuir isotherm. SEM study also support the inhibition of copper corrosion in acidic medium. All results shows that the Schiff base BDHNPMTU is more efficient inhibitor than DHNPMHC for copper corrosion in acidic medium. This work may contribute towards the research of copper corrosion inhibitors for copper metal and its alloys.

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