Study of Antioxidant and Anticorrosion Activity of Some Microwave Synthesized Thiourea Derivative Ligands and Complexes

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Abstract

The great need to the antioxidants in our life and the increased demand of thiourea derivatives which exhibit great biological activity as anti-inflammatory, antimicrobial, antitumor, and also act as antioxidants and anticorrosive agents leads us to synthesize: N-(2-chlorophenyl)-N'-benzoyl thiourea (CBT) and N-(4-chloro phenyl)-N'-benzoyl thiourea (PCBT) by reflux method and then their metal complexes of CoII, NiII, CuII and ZnII were synthesized by microwave (green chemistry) in hope to get better activities. The structure of ligands and their complexes have been characterized by using elemental analysis, mass Spectroscopy, FT-Vis., ¹HNMR and ¹³CNMR. In this study the synthesized compounds were evaluated for their in vitro DPPH radical scavenging activity. They exerted varying degree of scavenging activity toward DPPH radical with IC₅₀ values between 84 and 250 µg/mL which is considered good and acceptable activity when compared with the activity of standard Ascorbic acid which give IC₅₀ = 14.4 µg/mL. Also the anticorrosion activity of the two synthesized ligands (CBT) and (PCBT) was evaluated on carbon steel coupons by using weight loss method.

Keywords: Antioxidant activity, DPPH radical scavenging, thiourea derivatives, transition metal complexes, Anticorrosion activity, weight loss method.

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INTRODUCTION

The reactive oxygen species, which include superoxide anions (O₂⁻), hydrogen peroxide (H₂O₂) and hydroxyl radicals (OH), and Lipid peroxidation, which involves a series of free radical mediated chain reactions processes, are associated with several types of biological damage. Sodium nitroprusside, a vasodilator drug induces oxidative brain injury, which is actually mediated by the hydroxyl radicals generated by iron element in sodium nitroprusside. Our defense system produces glutathione and other thiols which significantly reduce sodium nitroprusside and other reactive oxygen species. But for the neurodegenerative disorders, supplementation with external antioxidant agents is of need. Therefore much attention has been focused on the use of synthetic antioxidants to inhibit lipid peroxidation and to protect from damage due to free radicals[1]. Antioxidants play also an important role as corrosive inhibitor as they have the ability to inhibit oxidation process. There by leading to minimize oxygen which is considered one of the most corrosive agents removed by reductive inhibitors such as amines and hydrazines[2].

O₂ + N₂H₂ → 2 H₂O + N₂ In this example, hydrazine converts oxygen, a common corrosive agent, to water, which is generally benign. The problem of corrosion is common and occurs in various sectors, such as chemical industry, petrochemical, shipbuilding, construction, automotive, aviation, railway, maritime and others. The consequences of corrosion can result in economic loss, for example, the oxidation of residential pipes, vehicles and metal materials in general, but can also result in serious accidents, causing damage to both nature and man, for example, degradation in pipeline systems, bridge failures, and others[3, 4]. Coordination compounds possess high attention due to their structural variety, interesting physical & chemical properties and promising applications in many fields. Metal ions play an important role in the structure and function of many bio macromolecules and have important roles in the biological processes of metabolism as well as in pharmaceutical chemistry due to their chemical
properties. Compounds bearing carbonyl and thiocarbonyl groups are used as potential donor ligand for the preparation of complexes[5, 6]. Among these, thiourea and its derivatives are versatile ligands that coordinate to form stable compounds. They are able to coordinate with metal either as neutral or monoanion or dianion ligand[7]. These thiourea ligands and their metal complexes were reported to act as antioxidants, antimicrobial, antibacterial, antifungal, antimalarial, anti-tuberculosis, anticancer activities and anticorrosive agents. In view of the importance of thiourea and their derivatives it was important to synthesize N-substituted thiourea ligand and their complexes with transition metal elements because it was observed that this activity was enhanced by complexing with certain transition metal elements[7]. Complexes were synthesized using microwave-assisted irradiation. Microwave gives shorter reaction times, clean, high yields and low cost[7, 8]. A rapid, simple and inexpensive method to measure antioxidant activity is the use of the free radical, 2, 2-Diphenyl-1-picrylhydrazyl (DPPH) which is widely used to test the ability of compounds to act as free radical scavengers or hydrogen donors and to evaluate antioxidant activity[9]. The DPPH assay method is based on the reduction of DPPH, a stable free radical[10]. The free radical DPPH with an odd electron gives a maximum absorption at 517 nm (purple color). When Antioxidants react with DPPH, which is a stable free radical becomes paired off in the presence of a hydrogen donor (e.g., a free radical scavenging antioxidant) and is reduced to the DPPHH and as consequence the absorbance’s decreased from the DPPH[11] Radical to the DPPH-H form, results in decolorization (yellow color) with respect to the number of electrons captured[12]. More the decolorization more is the reducing ability. This test has been the most accepted model for evaluating the free radical scavenging activity of any new drug[13]. When a solution of DPPH is mixed with that of a substance that can donate a hydrogen atom, it rises to the reduced form (Diphenylpicrylhydrazine; non radical) with the loss of this violet color (although there would be expected to be a residual pale yellow color from the picryl group still present)[14].

**EXPERIMENTAL**

**Synthesis of ligands:**

The two Ligands were prepared by reflux method between 0.1 m of ammonium thiocyanate in acetone and 0.1 m of benzoyl chloride to form Benzoyl thiocyanate. Then Benzoyl thiocyanate refluxed with ortho chloro anilin and para chloro anilin to form: N-(2-chlorophenyl)-N'-benzoyl thiourea (CBT) and N-(4-chloro phenyl)-N'- benzyol thiourea (PCBT) respectively[19, 20].

**Synthesis of Metal Complexes**

The prepared ligand and the acetate salts of the metals: Co (CH₃COO)₂.4H₂O, Ni (CH₃COO)₂.4H₂O, Cu(CH₃COO)₂.H₂O and Zn (CH₃COO)₂.2H₂O were mixed in (1:1) ratio. Then irradiated in microwave for (3-5 min) to give the complexes with higher yields [19, 20]. Synthesis of N-(2-chlorophenyl)-N'-Benzyol thiourea (CBT), N-(4-chloro phenyl)-N'- benzyol thiourea (PCBT) and their metal complexes given in scheme 1 and 2.

**Scheme-1: Synthesis of N-(2-chlorophenyl)-N'-Benzyol thiourea (CBT) and its metal Complexes**
Evaluation of antioxidant activity by DPPH radical scavenging method:

Freshly prepared (0.004% w/v) methanol solution of 2, 2-diphenyl-1-picrylhydrazyl (DPPH) radical was prepared and stored at 10 °C in the dark. A DMSO solution of the test compound was prepared by dilution method[15]. The mixtures were then allowed to react in the dark for half an hour. Measurement of the mixture absorbance was achieved spectrophotometrically at 515 nm. Absorbance measurements were recorded immediately with a UV-visible spectrophotometer (UV-3101PC)[16]. The absorbance of the DPPH radical without antioxidant (control) and the reference compound ascorbic acid were also measured. All the determinations were performed in three replicates[17] and averaged. The percentage of the DPPH radical scavenging activity was calculated according to the equation: $\text{PI} = \left(\frac{\text{AC} - \text{AS}}{\text{AC}}\right) \times 100$.

Where: AC = Absorbance of the control [18] and AS = absorbance of the (sample + DPPH).

**Corrosion Inhibition studies:**

Corrosion inhibition behavior of the two synthesized ligands (CBT) and (PCBT) was evaluated on carbon steel coupons by using weight loss measurements as follows:

The surface of the carbon steel coupons was abraded successively by different grade of metallographic emery papers until the surface appears free from any scratches and other apparent defects, then degreased with hot acetone, washed with distilled water and finally dried at room temperature. Tests were conducted on carbon steel coupons of the following composition: (0.11% C, 0.45% Mn, 0.04% P, 0.05% S, 0.25% Si, and the remained is Fe). The concentrations of the prepared ligands were $0.5 \times 10^{-4}$ M, $0.75 \times 10^{-4}$ M, $2.5 \times 10^{-4}$ M, $5 \times 10^{-4}$ M, and $7.5 \times 10^{-4}$ M. All solutions were prepared using distilled water. The experiments were carried out using carbon steel coupons immersed in 1.0 M HCl solution in absence and presence of different concentrations of the two synthesized ligands. Tests were conducted under total immersion conditions in 100 ml of the aerated test solutions. To determine weight loss with respect to time, test coupons were retrieved after 24 h immersion time, scrubbed with a bristle brush, washed, dried, and reweighed. The weight loss was taken as the difference between the initial and final weights of the coupons. Weight loss measurements were done at 30 °C.

**RESULTS AND DISCUSSION**

**Mass spectroscopy:**

The mass spectra of CBT (Fig.1) (Scheme 3) show multi peak representing successive degradation of the ligand. The spectra show the peak m/e = 292.74 represent the molecular ion peak (C_{14}H_{11}ON_{2}SCl) with 39.57% abundance. The base peak 100% with m/e = 145.79.
Figure 1: Mass spectra of the prepared ligand (CBT)

Scheme 3: Suggested mass fragmentation patterns of the prepared ligand (CBT)

The mass spectra of PCBT (Fig. 2) (Scheme 4) show multi peak representing successive degradation of the ligand. The spectra show the peak m/e = 290.77 represent the molecular ion peak (C_{14}H_{11}ON_{2}SCl) with 52.7% abundance. The base peak 100% with m/e = 106.06.
Figure-2: Mass spectra of the prepared ligand (PCBT)

Scheme 4: Suggested mass fragmentation patterns of the prepared ligand (PCBT)

The mass spectra of Zn-CBT (Fig.3) (Scheme: 5) show multi peak representing successive degradation of the ligand. The spectra show the peak m/e = 510.94 represent the molecular ion peak (C_{18}H_{21}O_{7}N_{2}SCl) with 21.06% abundance. The base peak 100% with m/e = 52.62.
The mass spectra of Co-PCBT (Fig. 4) (Scheme: 6) show multi peak representing successive degradation of the ligand. The spectra show the peak m/e = 539.33 represent the molecular ion peak (C₁₈H₂₅O₉N₂SCl) with 22.52% abundance. The base peak 100% with m/e = 316.6.
Figure 4: Mass spectra of the prepared Co$^{II}$ complex of PCBT

Scheme 6: Suggested mass fragmentation patterns of the prepared Co (II) complex of PCBT

H$^1$NMR Spectroscopy:
For the ligand (CBT) fig.5 give two singlet signals, one at $\delta$ 11.78 ppm assigned to (S,1H, N8-H) and the other at $\delta$ 12.742 ppm assigned to(S,1H, N10-H) [22] (which were also identified by D$_2$O exchange). The multiplets observed at $\delta$ 7.293 – 8.098 ppm are attributed to the phenyl protons.
For ligand (PCBT) fig. 6 give two singlet signals, one at $\delta$ 11.58 ppm assigned to (S,1H, N8-H) and the other at $\delta$ 12.59 ppm assigned to (S,1H, N10-H) [22] (which were also identified by D$_2$O exchange).

The multiplets observed at $\delta$ 7.450 – 8.000 ppm are attributed to the phenyl protons.

**13C NMR spectroscopy:**

The $^{13}$C NMR spectra of the synthesized ligand (CBT) fig. 7 showed peaks at 180.219 ppm assigned to (C=O), 168.556 ppm assigned to (C=s), 135.357 ppm (C11), 133.239 ppm (C16), 131.858 ppm (C5), 129.483 ppm (C2) and at 128.793 ppm (C12), 128.261 ppm (C13), 128.110 ppm (C1 and C3), 126.167 ppm (C4 and C6).
The $^{13}$CNMR spectra of the synthesized ligand (PCBT) fig.8 showed peaks at 179.347 ppm assigned to (C=O), 168.207 ppm assigned to (C=S), 136.958 ppm to (C11) 133.133 ppm to (C14), 132.63 ppm to (C5), 130.257 ppm to (C2), 128.694 ppm to (C12, C16) and at 128.550 ppm (C1,C3), 126.167 ppm (C4 and C6).

**Figure-7: $^{13}$C NMR spectra of the ligand (CBT)**

**Figure-8: $^{13}$C NMR Spectra of PCBT**

**IR spectra:**

The characteristic IR bands of the thiourea ligands showed the expected frequencies of $\nu$ (C=O), $\nu$ (N-H), $\nu$ (C-N) and $\nu$ (C=S) and upon coordination of the metal center to ligand, these characteristic bands were found to be shifted to a lower frequency. This finding may be taken as an evidence for the coordination of the carbonyl oxygen and thionyl Sulphur atoms with the metal. The IR data of ligands and complexes are tabulated in Table1 and 2 [19, 20].
Electronic and magnetic properties of the prepared compounds

The stereochemistry of the metal ions in the complexes can be assigned via the electronic spectral measurements. The spectra of the ligands and their complexes in solid-state showed a number of bands in the UV-Vis region (200-800 nm) table 3, 4 [19, 20].

### Table 1: I.R bands of the synthesized ligand CBT and its complexes

| Cpd. | $\nu$ OH (H2O) | $\nu$ N-H | $\nu$ C-H Aromatic | $\nu$ OAc Assym. /Sym. | $\nu$ C=O | $\nu$ C=S | $\nu$ Ph-Cl | $\nu$ M-O | $\nu$ M-S |
|------|----------------|-----------|---------------------|------------------------|--------|--------|------------|--------|--------|
| CBT  | --             | 3312      | 3018                | --                     | 1669   | 1329   | 753        | --     | --     |
| CBT-Co | 3850           | 3310      | 3016               | 1435                   | 1666   | 1249   | 679        | 594    | 540    |
| CBT-Ni | 3700           | 3309      | 3016               | 1427                   | 1666   | 1242   | 678        | 594    | 509    |
| CBT-Cu | 3850           | 3371      | 3016               | 1442                   | 1597   | 1242   | 694        | 578    | 532    |
| CBT-Zn | 3448           | 3209      | 3008               | 1404                   | 1601   | 1288   | 686        | 617    | 501    |

### Table 2: I.R bands of the synthesized ligand PCBT and its complexes

| Cpd. | $\nu$ OH (H2O) | $\nu$ N-H | $\nu$ C-H Aromatic | $\nu$ OAc Assym. /Sym. | $\nu$ C=O | $\nu$ C=S | $\nu$ Cl | $\nu$ M-O | $\nu$ M-S |
|------|----------------|-----------|---------------------|------------------------|--------|--------|--------|--------|--------|
| PCBT | --             | 3251      | 3020                | --                     | 1670   | 1341   | 765    | --     | --     |
| PCBT-Co | 3742           | 3348      | 3148               | 1396                   | 1550   | 1273   | 679    | 609    | 501    |
| PCBT-Ni | 3850           | 3441      | 2993               | 1412                   | 1535   | 1250   | 686    | 609    | 509    |
| PCBT-Cu | 3700           | 3487      | 3148               | 1442                   | 1405   | 1273   | 694    | 625    | 501    |
| PCBT-Zn | 3850           | 3464      | 3009               | 1342                   | 1535   | 1250   | 686    | 609    | 501    |

### Table 3: Electronic Spectra, magnetic for CBT metal complex

| Cpd   | $\lambda_{max}$ nm | Assignments | $\mu_{eff}$(B.M) | Suggested Structure |
|-------|---------------------|-------------|------------------|---------------------|
| CBT   | 330 290 260         | (n-\pi*, C=O), (n-\pi*, C=N), (\pi-\pi*, aromatic ring) | --                | -                   |
| CBT-Co | 425-650         | 4T1g (F) $\rightarrow$ 4T1g(P) 4T1g (F) $\rightarrow$ 4T2g | 5.8              | Octahedral          |
| CBT-Ni | 450-750       | $^3$A_2g $\rightarrow$ $^3$T_1g (P) $^3$A_2g $\rightarrow$ $^3$T_2g | 2.9              | Octahedral          |
| CBT-Cu | 425-750        | 2B2 $\rightarrow$ 2E | 1.78            | Tetrahedral         |
| CBT-Zn | 560-720       | MLCT        | Di               | Tetrahedral         |
Table-4: Electronic Spectra, magnetic for PCBT metal complex

| Cpd             | $\lambda_{\text{max}}$ (nm) | Assignments                                  | $\mu_{\text{eff.}}$ (B.M) | Suggested Structure |
|-----------------|-------------------------------|----------------------------------------------|---------------------------|---------------------|
| pCBT            | 325                           | (n–$\pi^*$, C=O), (n–$\pi^*$, C=N),          | --                        | -                   |
|                 | 277                           | ($\pi$–$\pi^*$, aromatic ring)              |                           |                     |
|                 | 258                           |                                               |                           |                     |
| PCBT-Co         | 425-650                       | $\rightarrow$ 4T1g(F) $\rightarrow$ 4T1g(P)  | 5.95                      | Octahedral          |
|                 |                               | 4T1g(F)→4T2g                                 |                           |                     |
| PCBT-Ni         | 450-750                       | $^2$A$_{2g}$$\rightarrow$ $^3$T$_1g$ (P)    | 3.9                       | Octahedral          |
|                 |                               | $^2$A$_{2g}$$\rightarrow$ $^3$T$_2g$        |                           |                     |
| PCBT-Cu         | 425-750                       | 2B2 $\rightarrow$ 2E                         | 1.89                      | Tetrahedral         |
| PCBT-Zn         | 560-720                       | MLCT                                         |                           |                     |

Measurement of Antioxidant activity:

The percentage of the DPPH radical scavenging activity of CBT and its Zn$^{II}$ complex was calculated and the results was tabulated in table 5 and expressed in figure 9.

Table-5: The percentage of the DPPH radical scavenging activity of CBT and its Zn$^{II}$ complex

| Sample concentration (µg/ml) | DPPH scavenging % (CBT) | DPPH scavenging % (CBT-Zn) |
|------------------------------|--------------------------|-----------------------------|
| 1440                         | 78.90                    | 4.09                        |
| 720                          | 70.77                    | 3.47                        |
| 360                          | 66.26                    | 1.01                        |
| 180                          | 35.03                    | 0.62                        |
| 90                           | 34.96                    | 0.44                        |
| 45                           | 34.81                    | 0.34                        |
| 22.5                         | 31.24                    | 0.16                        |
| 0                            | 0                        | 0                           |

Figure-9: The DPPH radical scavenging activity of CBT and its Zn$^{II}$ complex

The percentage of the DPPH radical scavenging activity of PCBT and its Co$^{II}$ complex was calculated and the results was tabulated in table 6 and expressed in figure 10.
Table-6: The percentage of the DPPH radical scavenging activity of PCBT and its Co^{II} complex

| Sample concentration (µg/ml) | DPPH scavenging % (PCBT) | DPPH scavenging % (PCBT-Co) |
|-----------------------------|--------------------------|-----------------------------|
| 1440                        | 58.49                    | 23.01                       |
| 720                         | 55.39                    | 18.63                       |
| 360                         | 53.81                    | 16.76                       |
| 180                         | 53.73                    | 7.83                        |
| 90                          | 50.69                    | 3.59                        |
| 45                          | 45.39                    | 1.97                        |
| 22.5                        | 16.28                    | 0.35                        |
| 0                           | 0                        | 0                           |

Figure-10: The DPPH radical scavenging activity of PCBT and its Co^{II} complex

For comparison purpose, the effect of ascorbic acid as standard antioxidant was evaluated and produced (IC_{50} ml) under the same conditions table 7 and figure 11.

Table-7: The percentage of the DPPH radical scavenging activity of Ascorbic acid

| Sample conc. (µg) | DPPH scavenging % |
|-------------------|-------------------|
| 30                | 80.10             |
| 25                | 76.99             |
| 20                | 70.84             |
| 15                | 54.70             |
| 10                | 16.50             |
| 5                 | 11.76             |
| 0                 | 0                 |
The reported results in terms of IC₅₀ value was recorded in Table 8.

Table 8: IC₅₀ values of Ascorbic acid and compounds under study

| Compound      | IC₅₀ (µg/mL) |
|---------------|-------------|
| Ascorbic Acid | 14.4        |
| CBT           | 250         |
| PCBT          | 84          |
| CBT-Zn        | -           |
| PCBT-Co       | -           |

**Corrosion Inhibition Measurements:**

Table 5 shows the calculated values of corrosion rate (mg cm⁻² h⁻¹), inhibition efficiency (ηₜₙ, %) and the degree of surface coverage (θ) for steel dissolution in 1.0 M HCl in the absence and presence of the surfactants under study. The values of corrosion rate were calculated from the following equation:

\[ K = \frac{\Delta W}{At} \]

Where \( K \) is the corrosion rate (mg cm⁻² h⁻¹), \( \Delta W \) is the loss of weight after corrosion (mg), \( A \) is the total area of the coupon (cm²), and \( t \) is the corrosion time (h). The degree of surface coverage (θ) and the inhibition efficiency, \( \eta \%), were calculated using the following equations[21]:

\[ \theta = \frac{K_o - K}{K_o} \times 100 \]

\[ \eta = \frac{K_o - K}{K_o} \times 100 \]

Where \( K_o \) and \( K \) are the values of the corrosion rate without and with addition of the inhibitor, respectively. From Table 9 we can find that:

- **For PCBT** the inhibition efficiency percentage (\( \eta \)), increases with increasing inhibitor concentration, which is due to the increase in the mass and charge transfer to the carbon steel surface leading to the adsorption of inhibitor molecules and reducing the metal dissolution. Also, more surface area (θ) is covered by increasing inhibitor concentration.

- **For the CBT** it was found that the corrosion rate increases by increase the concentration and so the inhibition efficiency percentage and surface area decreases by increase the concentration. This can be explained by that the chloride in the ortho position have more electron withdrawal effect than the para position in PCBT this leads to decrease the charge transfer to the carbon steel surface which leads to increase corrosion.
Adsorption Isotherm

According to corrosion studies it is important to know the relationship between the inhibitor molecules and the surface of the metal which obtained by the adsorption of these molecules on the metal surface by two different types of adsorption. Generally, adsorption of an inhibitor maybe classified as a physical adsorption and chemisorption. The main factors affecting the adsorption type are the electronic structure of the metal, the type of electrolyte and the chemical structure of the inhibitor. Furthermore, adsorption process take place when the water molecules (H₂O(sol)) which were previously adsorbed on the metal surface are replaced by the inhibitor molecules (Inh(ads)) present in the aqueous solution as follows:

\[ \text{Org} \text{(sol)} + x \text{H}_2\text{O} \text{(sol)} \rightarrow \text{Org} \text{(ads)} + x \text{H}_2\text{O} \text{(ads)} \]

Where x is the size ratio representing the number of water molecules replaced by one organic molecule. Different adsorption isotherm equations such as Freundlich, Langmuir, Frumkin, Flory-Huggins, Frumkin and Temkin can be applied to the resulted data resulted, but it was found that the data are more likely to fit with the Langmuir isotherm especially when the correlation coefficients (R²) for CBT and PCBT are 0.8119 and 0.0535 respectively figure 12 and 13. The Langmuir relation is as follow:

Langmuir Isotherm = \( C_{\text{inh}} / \theta = 1 / K_{\text{ads}} + C_{\text{inh}} \)

Where \( C_{\text{inh}} \) is the inhibitor concentration; \( K_{\text{ads}} \) is the equilibrium constant of the isotherm process and \( \theta \) is the degree of surface coverage. By plotting \( C_{\text{inh}}/\theta \) versus C, it was found that the slope of Langmuir adsorption isotherm for the three synthesized inhibitor PCBT at 30 °C was almost close to unity except a slight deviation took place which may be referred to the interaction between the adsorbed inhibitor molecules with each other[22, 23].Values of the equilibrium constant (\( K_{\text{ads}} \)) for inhibitor PCBT were 3.376 × 10³, 45.88 × 10² and 0.726 × 10¹ respectively, these values indicates how strong the adsorption force between the synthesized inhibitors and the surface of the metal. It is also known that the equilibrium constant (\( K_{\text{ads}} \)) is related to the Gibbs free energy according to the equation [24]:

\[ \Delta G_{\text{ads}}^{\circ} = -RT \ln (55.5 K_{\text{ads}}) \]

Where (55.5) is the molar concentration of water in solution expressed in mole/l, \( R \) (8.314) is the universal gas constant and \( T \) is the absolute temperature. Generally, when \( \Delta G_{\text{ads}}^{\circ} \) values are equal to -20 or higher it may be considered as (Physical adsorption), while values of -40 or lower are of the type (chemisorption)[25]. Calculated values of the Gibb's free energy for inhibitors MBT and PCBT were –30.58834 and -26.7168 KJ mol⁻¹ as tabulated in Table 10. So it is obvious that this values indicating that the adsorption processes were of chemically adsorption type on the surface of the carbon steel that also indicating an electron transfer process took place to form a coordination bond between the inhibitor molecules and the d-orbital of the iron molecules[26, 27].

### Table-9: Weight loss data for steel 1.0 M HCl without and with different concentrations of the ligands

| Inhibitor name | Conc.(M) | k (mg cm⁻² h⁻¹) | θ | ηw % |
|---------------|---------|----------------|----|-----|
| Blank         | 0x10⁻⁴  | 1.5916         | ---- | ---- |
| CBT           | 0.5 x10⁻³ | 1.5916         | 0   | 0   |
|               | 0.75x10⁻⁴ | 1.75           | -0.15 | -15 |
|               | 2.5x10⁻⁴ | 1.84           | -0.248 | -24.8 |
|               | 5 x10⁻⁴  | 2.083          | -0.3225 | -32.25 |
|               | 7.5 x10⁻⁴ | 2.173          | -0.4914 | -49.14 |
| PCBT          | 0.5 x10⁻⁴ | 1.563          | 0.0177 | 1.77 |
|               | 0.75x10⁻⁴ | 1.24           | 0.2199 | 21.99 |
|               | 2.5 x10⁻⁴ | 0.74           | 0.535 | 53.5 |
|               | 5 x10⁻⁴  | 0.705          | 0.557 | 55.7 |
|               | 10 x10⁻⁴ | 0.5            | 0.6858 | 68.58 |

### Table-10: Thermodynamic parameters using Langmuir adsorption isotherm on steel surface in 1.0 M HCl containing different concentrations of the ligands MBT and PCBT

| Inhibitor | Temp. ('k) | K_{ads} (KJ/mol) | \( \Delta G_{ads} \) (KJ/mol) | \( \Delta S_{ads} \) (J/mol.°K) | \( \Delta H_{ads} \) (KJ/mol) |
|-----------|------------|-----------------|-----------------|-----------------|-----------------|
| MBT       | 303        | 3376.074458     | -30.58834       | 0.304748049     | 61.75           |
| PCBT      | 303        | 726.2650946     | -26.7168        | 0.500414166     | 124.91          |
Enthalpy (ΔH_{ads}) and Entropy (ΔS_{ads}) of Adsorption:

Enthalpy and Entropy of adsorption can be calculated as follows:

\[ \ln K_{ads} = \left( \frac{\Delta H_{ads}}{RT} \right) + \text{const} \]

Where \( \Delta H_{ads} \) and \( K_{ads} \) are the adsorption heat and adsorptive equilibrium constant, respectively. Plotting \( \ln K_{ads} \) against \( 1/T \) gives straight link which slope is equal to \( \Delta H_{ads}/R \). Negative values of \( \Delta H_{ads} \) are shown in Table 10 indicating that the adsorption of inhibitors is exothermic in nature. Also, the negative values of \( \Delta H_{ads} \) show that the adsorption is exothermic with an ordered phenomenon ascribed by the negative values of \( \Delta S_{ads} \). This order may more probably be explained by the possibility of formation of iron complex on the metal surface [28, 29].

CONCLUSION

DMSO solution of the compounds under study showed good antioxidant potential by DPPH radical scavenging method when compared to standard ascorbic acid and IC_{50} value found to be 14.4 μg/ml for ascorbic acid, 250 μg/ml for CBT and 84 4 μg/ml for PCBT where the complexes show low activity. And then by study the anticorrosion activity of ligands CBT and PCBT showed that: PCBT has good inhibition efficiency as inhibitor for carbon steel dissolution in 1.0 M HCl solution, but CBT cannot be used as corrosion inhibitor. So, it can be said that some of thiourea derivatives can be useful for man health as antioxidants and economy as anticorrosive agents.

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