

# Improved corrosion resistance of mild steel in acidic solution

## 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl-1,10-phenathroline compounds

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### Abstract

The present study includes the appraisal of inhibitive performance of the 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl-1,10-phenathroline compounds as inhibitors on the corrosion behaviour of mild steel in 0.5 mol dm<sup>-3</sup> hydrochloric acid de-aerated solution at 313.15K were investigated using potentiostatic polarization method. Polarization curves indicate that both inhibitors were acting as mixed type inhibitors. The measurements show that inhibition efficiencies increase with increase in inhibitor concentration. This reveals that inhibitive actions of inhibitors were mainly due to adsorption on the mild steel surface and blocked the active sites. Adsorption of the 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl-1,10-phenathroline inhibitors follows Langmuir adsorption isotherm. Thermodynamic parameters of adsorption " $K_{ads}$ ,  $\Delta G_{ads}$ " of studied inhibitors were calculated using Langmuir adsorption isotherm. Differences in inhibition efficiency between the 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl-1,10-phenathroline inhibitors are correlated with their chemical structures. Furthermore, the mechanism of inhibition was discussed in the light of the chemical structure of the undertaken inhibitors.

### الخلاصة

إنّ الدراسة الحالية تضمّنت تقييم الأداء التثبيطي للمركبين ١، ٤ - داي ٢-(٥-اوكسيازول) - بنزين و ٤،٧- داي فينل - ١،١٠ - فينيثرولين التي استخدمت كمثبطات لتآكل الفولاذ المعتدل الصلادة في وسط حامضي من حامض الهيدروكلوريك الغير المهوى لدرجة حرارية مقدارها 313.15K ، وتمّ التحري عن السلوك الكهروكيميائي للأتموزج باستخدام تقينة المجهود ألكوني لتراكيز مختلفة من المواد المثبطة . تُشير منحنيات الاستقطاب على أن كلا المثبتين المدروسين يعملان وفق آلية التثبيط المزدوج للتفاعلات الكاثودية والانودية . ولقد بينت النتائج على أن كفاءة التثبيط تزداد بزيادة تركيز المادة المثبطة هذا يكشف بأنّ عملية التثبيط كانت بشكل رئيسي بسبب أمتزاز المادة المثبطة على سطح الفولاذ المعتدل الصلادة وأعاققت المواقع النشيطة كهربائياً من على سطح القطب . عملية أمتزاز المثبتين ١، ٤ - داي ٢-(٥-اوكسيازول) - بنزين و ٤،٧- داي فينل - ١،١٠ - فينيثرولين جرت وفق مبدأ لآنكامير للأمتزاز الحراري. وثابتت عملية الامتزاز والمتضمنة ثابت الامتزاز والطاقة الحرة للأمتزاز قد حُسبت من مبدأ لآنكامير للأمتزاز الحراري . التباين في كفاءة التثبيط لـ ١، ٤ - داي ٢-(٥-اوكسيازول) - بنزين و ٤،٧- داي فينل - ١،١٠ - فينيثرولين عُزيت إلى التركيب الكيميائي لكلا المثبتين وفضلاً عن ذلك بُيئت ميكانيكيات التفاعلات الكاثودية والانودية المترامنة.

### Introduction

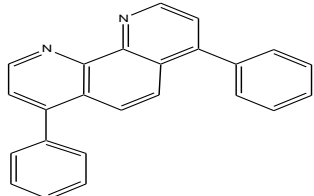
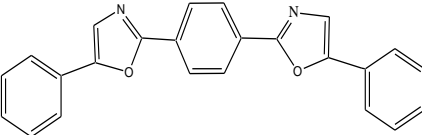
Corrosion is an electrochemical process by which the metallic structures are destroyed gradually through anodic dissolution (Uhling, 1985). Therefore, various attempts must be employed to prevent or retard this destructive process among methods under taken, application of inhibitors is one of the most practical and economical ones (Arshadi et al., 2004). Corrosion inhibitors are added to prevent metal dissolution during its surface cleaning from oxides and other adherent materials. Also, corrosion inhibitors may be liquids or powder form that effectively reduce the corrosion rate (Osman et al., 2003). Hydrochloric acid solutions are widely used for the pickling, cleaning, descaling etching of mild steel. The dissolution rate of the metal is quite high and the inhibition of these solutions with organic compounds, which retard the dissolution rate, is favored (Emergul and Atakol, 2003). There has been a growing interest in the use of organic compounds as inhibitors for the aqueous corrosion of metals (Bentiss et al., 2007). The study of corrosion processes and

their inhibition by organic compounds is a very active field of research (Bentiss, et al., 2007, 2005, 2003, 1998, 1994) . The influence of heterocyclic and other organic compounds containing nitrogen , like amino acids , on the corrosion of mild steel in acidic solutions have been investigated by several workers (Okafor et al. 2007, 2001, 1999, 1998, 1984). The inhibition efficiency of alkyl quaternary ammonium salts, 3,4-bis(n-pyridyl)-4-amino-1,2,5-triazoles, substituted benzothiazoles (Mernari et al., 1998) , thiophenol , phenol , 2,5-(bis(n-pyridyl)-1,3,4-thiadiazoles (El-Azhar et al., 2001), 2,5-bis(4-dimethylaminophenyl)-1,3,4-thiadiazole (Bentiss et al., 2001) and 2-mercaptothiazoline and acetylpyridinium chloride (Wang and Yin, 2001) on the corrosion inhibition of steel in acidic media has been studied . In the present paper , the efficiency of 1,4-Di-2-(5-phenyloxazolyl)-benzene(POPOP) and 4,7-diphenyl -1,10-phenanthroline (bathophenanthroline)(DPP) as inhibitors for the corrosion of mild steel in de-aerated of 0.5 mol dm<sup>-3</sup> hydrochloric acid is discussed on the basis of Tafel polarization data . Langmuir is tested for their potential relevance to describe the adsorption behaviour of the studied compounds , and differences in behaviour for the two compounds are explained within the frame of their structural properties .

### Experimental details

The molecular structure and molecular weight of compounds for this study are given in table (1) :

**Table (1) : Details of the organic inhibitors used**

Name	Structure	Molecular Wt. ( g / mol )
4,7-diphenyl -1,10-phenanthroline ( DPP )		332.41
1,4-Di-2-(5-phenyloxazolyl)-benzene (POPOP)		364.41

The effects of these in table (1) on the corrosion rate of mild steel in de-aerated of 0.5 mol dm<sup>-3</sup> were studied to investigate the mechanism of inhibition. Hydrochloric acid , BDH analar grade was used for the preparation of the solutions. 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl -1,10-phenanthroline were Analar grade chemicals which have been obtained from BDH . All measurements were obtained on mild steel electrodes of the following composition as revealed by emission spectroscopy analysis: C 0.01 , Si 0.35, P 0.018, Cr 0.04, Mo 0.03 , Ni 0.017, Cu 0.02, Al 0.06 and Fe (balance) and dimensions (1×10×10) mm were used. The samples were polished to mirror finish, using emery paper following by aqueous alumina suspensions with particles size decreasing down to 0.05 μm on the soft cloth . After that, degreased by hot benzene and acetone. The metal was embedded in epoxy resin, to expose a geometrical surface of 1 cm<sup>2</sup> to electrolyte . A 200 ml of the test solution was transferred to the clean corrosion cell. Prior to immersion of the electrode, the solution was purged for a minimum of 1h with free nitrogen gas (purity 99.9%) to remove oxygen from solution (de-aerated solution) . After that , the electrode was

immersed 40 min in the electrolyte solution until a steady free corrosion potential as reached (steady state open– circuit potential  $E_{ocp}$ ). The potentials were with measured with reference to a saturated calomel electrode (SCE) , which a luggin probe positioned close to the electrode surface to minimize the Ohmic potential drop (Singh and Agarwal, 1979) connected to a potentiostatic ( type : potentiostatic Wenking HP , BANK INSTRUMENTES CORPORATION , GERMANY , Location : Ministry of science and Technology – unit , the researches of chemistry and petroleum , figure1 . and the block diagram for recording current versus potential curves have shown in figure 2). The platinum electrode was used as an auxiliary electrode . Platinum auxiliary electrode was used in the experiments due to its large surface area and high catalytic activity (Roberge; Green, 2000, 1965). The temperature of the solution was brought to the desired value by immersing the test cell in a controlled temperature water bath with a precision of  $\pm 0.1^{\circ}\text{C}$  , a temperature regular called Temp-unit , type PHYWE IP21, GERMANY, was used. The saturated calomel reference electrode was used throughout the whole work which it consisted of mercury , mercurous chloride and chloride ion . The reduction reaction which occurs in the calomel electrode may be represented as :  $\text{Hg}_2\text{Cl}_2 + 2\text{e} \leftrightarrow 2\text{Hg} + 2\text{Cl}^-$ , usually the electrode brought in contact with the electrolyte through a glass tubing as " Luggin probe". The tip of the Luggin probe is placed in the electrochemical cell very close to the working electrode through a Luggin probe bridge which was filled with electrolyte test solution . The platinization of platinum auxiliary electrode was made after cleaning the surface of the platinum electrode in hot aqua regia (3 parts concentrated HCl and 1 part concentrated  $\text{HNO}_3$ ), washing and the drying . The electrode was the platinitized by immersion in solution consisting 3 percent chloroplatinic acid and 0.02 percent lead acetate and electrolyzing at a current density  $40 \text{ mA/cm}^2$  for 5 minutes , and the polarity was reversed every minute . Occluded chloride removed by electrolyzing in a dilute (10 percent) sulphuric acid solution for 5 minute with a reversal in polarity every minute .The electrode was thereafter rinsed thoroughly and stored in distilled water (Yousif et al., 2001, 1972). The surface of the mild steel electrode was observed and analyzed by an MTI optical microscope , USA .

## Results and Discussion:

### A- The Polarization curves and efficiency of inhibition

Some of the polarization curves for mild steel electrode in  $0.5 \text{ mol dm}^{-3}$  hydrochloric acid de-aerated solution in absence and presence of 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl-1,10-phenathroline inhibitors with different concentrations at 313.15 K are shown in figure 3,4. Also, the electrochemical corrosion kinetic parameters obtained from these curves by extrapolation of Tafel lines (Roberge, 2000), anodic and cathodic Tafel slopes ( $B_a$  and  $B_c$ , respectively), corrosion potential ( $E_{corr}$ ), corrosion current density ( $I_{corr}$ ) and inhibition efficiency ( P% ) as function of two inhibitors concentrations are given in tables 2 , 3 at 313.15K . In this case , the inhibition efficiency is defined as follows :

$$\text{P\%} = \frac{I_{corr} - I_{corr(\text{inh.})}}{I_{corr}} \dots\dots\dots (1)$$

Where  $I_{corr}$  and  $I_{corr(\text{inh.})}$  are the corrosion current density values without and with the addition of inhibitors , respectively . It can be seen form figure 3 , 4 , both of anodic and cathodic current densities obtained in  $0.5 \text{ mol dm}^{-3}$  of hydrochloric acid solutions in the presence of 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl - 1,10-phenathroline inhibitors are lower than corrosion current densities obtained in acid solutions in the absence of inhibitors.  $E_{corr}$  values in the presence of inhibitors are shifted to negative direction ; this effect is more evident at higher concentrations.

These results suggest that two inhibitors can be classified as mixed - type inhibitors with a predominantly cathodic action (Yurt et al., 2006). As it is shown in figure 3, 4, the cathodic current – potential curves give rise to parallel Tafel lines, which indicate that hydrogen evolution reaction is activation controlled and that the addition of the 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl -1,10-phenathroline inhibitors does not modify the mechanism of this process (Kertit and Hammouti, 1996). The results demonstrate that the hydrogen reduction is inhibited and that the inhibition efficiency increases with inhibitor concentration. Furthermore, The values of  $B_c$  changed with increasing inhibitor concentration, which indicates the influence of the compounds on the kinetics of hydrogen evolution. In the anodic range the polarization curves of mild steel show that the addition of two inhibitors decreases current densities in a large domain of potential . Thus , the shift in the anodic Tafel slope  $B_a$  may be due to chloride ions or inhibitor models adsorb onto electrode surface (McCafferty and Hackerman, 1972). This result suggest that the two inhibitors act as a mixed- type inhibitors of the corrosion of mild steel in hydrochloric acid medium. It can be noticed that for potential higher than  $-14.2$  mv /SCE, the inhibitor start to desorb. This potential can be defined as the desorption potential. Similar behaviour have been already reported for other organic inhibitors (Yousif et al., 2005, 2000, 1990). This means, that the inhibition molecules of 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl -1,10-phenathroline inhibitors depend on electrode potential. The phenomenon may be due to the obvious metal dissolution, which leading to a desorption of 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl -1,10-phenathroline molecule from the electrode surface, in this case the desorption rate of the inhibitors is higher than its adsorption rate, so the corrosion current increases more obviously with rising potential (Aksut et al., 1982,1980). An interesting observation from figure 3 and tables 2 , 3 are that for low concentrations , the efficiency obtained with either inhibitor is almost identical . However , as the concentration increases , the 1,4-Di-2-(5-phenyloxazolyl)-benzene inhibitor generates a higher inhibition level than 4,7-diphenyl -1,10-phenathroline , and the advantage of the 1,4-Di-2-(5-phenyloxazolyl)-benzene inhibitor over 4,7-diphenyl-1,10-phenathroline increases with concentration. Several preliminary conclusions can be drawn from this behaviour. Firstly, the low-concentration behaviour suggests that intrinsic mild steel – inhibitor interactions are very similar at least in magnitude . Secondly, the fact that a discrepancy occurs and increases for higher concentrations may point to unfavorable interactions between the inhibitor molecules, which obviously become more important as number density increases. Thirdly , the inhibitor molecules are adsorbed on the mild steel–solution interface where the adsorbed molecules mechanically screen the coated part of the metal surface from the action of the corrodent . The inhibition efficiency values of the examined inhibitors follow the order: 1,4-Di-2-(5-phenyloxazolyl)-benzene > 4,7-diphenyl -1,10-phenathroline. The 1,4-Di-2-(5-phenyloxazolyl)-benzene inhibitor is the superior from the other inhibitor , this may be due to the highest molecular weight (Abd El-Maksoad, 2004) the presence of additional oxygen atoms which may be an additional adsorption center , thus the electron donating ability of the active sites increases and its adsorption on the mild steel surface increases .

## B- Adsorption isotherm

As it assumed that organic inhibitors establish their inhibition via inhibition the adsorption of the inhibitor onto the metal surface . The adsorption process of inhibitors are influenced by the chemical structures of organic compounds , the nature and surface charge of metal , the distribution of charge in molecule and the type of aggressive media (Saleh and Sham El-Di ,1981). One of the clearest examples there of is the observation of endothermic adsorption which indisputably identifies chemisorption, as physisorption is an intrinsically exothermic process (Hosseini and Ashadi, 2003). In the present investigation, Langmuir isotherm was assessed, having the following surface coverage – bulk concentration relationship (Durnie et al. ,1999 ):

$$\theta / 1 - \theta = K_{ads} \times C \text{ " Langmuir isotherm" .....(2)}$$

Where  $K_{ads}$  is the adsorption equilibrium constant ,  $K_{ads}$  must have the inverse dimension of concentration i.e.  $\text{dm}^3 \text{mol}^{-1}$  . As  $\theta$  is a dimensionless quantity " degree of surface coverage " , Taking into account the degree of surface coverage  $\theta$  , as a function of inhibitor concentration . The surface coverage values were calculated from the following equation ( Yurt and Ultas , 2006):

$$\theta = [1 - I_{corr ( inh. )} / I_{corr} ] \text{ .....( 3 )}$$

Where  $I_{corr ( inh. )}$  and  $I_{corr}$  are the correction current densities for with and without inhibitor . With regard to the Langmuir isotherm , it is convenient to rearrange equation , 2 . in following form :

$$C / \theta = C + 1 / K_{ads} \text{ .....(4)}$$

The linear relationship is observed when  $C / \theta$  is plotted as a function  $C$  , with a slope of ideally unity . In figure 4 , the proposed relation is plotted for both inhibitors . The expected linear relationship is well approximated in both cases ( correlation coefficients R square is very close for one for 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl -1,10-phenanthroline inhibitors ) and the line has a slope of 1.097 for 1,4-Di-2-(5-phenyloxazolyl)-benzene and of 1.1031 for 4,7-diphenyl -1,10-phenanthroline inhibitor . The deviation of the slope from unity is often interpreted as a sign that the adsorbing species occupy more or less than a typical adsorption site at the metal – solution interface ( Villami and Corio,1999) . However , it expresses the fact that the Langmuir isotherm is in many cases simple a model :

$$K_{ads} = e^{-\Delta G_{ads} / RT} \text{ ..... (5)}$$

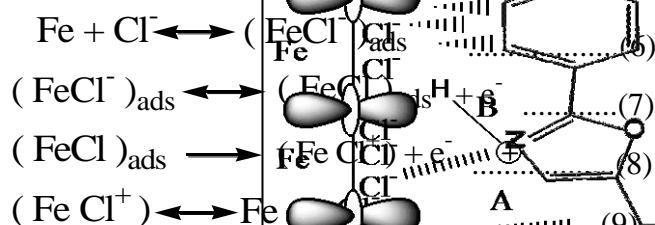
Where  $R$  is the universal gas constant and  $T$  is the absolute temperature , a value for the Gibbs energy of adsorption  $\Delta G_{ads} = -24.867 \text{ kJ mol}^{-1}$  can be calculated for 1,4-Di-2-(5-phenyloxazolyl)-benzene ( as  $K_{ads} = 14065.84 \text{ dm}^3 \text{mol}^{-1}$ ); for 4,7-diphenyl -1,10-phenanthroline inhibitor  $K_{ads} = 8424.931 \text{ dm}^3 \text{mol}^{-1}$  and  $\Delta G_{ads} = -23.533 \text{ kJ mol}^{-1}$  are found . Based on the Langmuir isotherm , one would consequently expect essentially identical adsorption characteristics, which is not experimentally observed in the inhibition efficiency versus concentration behaviour, figure 5. One of the assumption of the Langmuir formalism is that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites being occupied or not (Atkins, 2001). The slope of lines in figure 6 , differing from unity, together with the unexplained the protection efficiency versus the concentration behaviour, is a clear indication that at least on of these criteria is not met, which obviously is not surprising considering the relatively complex nature of the inhibitor molecules. These observations are excellent agreement with the inhibition efficiency–concentration, figure 3; for low concentration, and thus, low degrees of occupancy of the metal surface, the intrinsic adsorptive behaviour is uninfluenced by adsorbate–adsorbate interactions . As the concentration is augmented , these interactions have an increasing effect on the degree

of adsorption and thus, on the inhibition efficiency, although the intrinsic spontaneity of the adsorption process does not change.

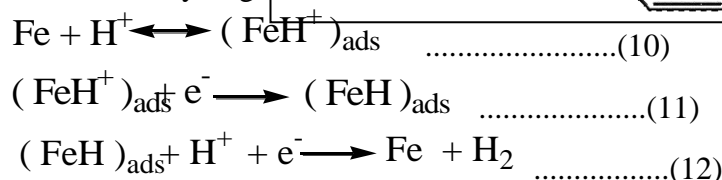
### C- The mechanism of inhibition

In order to predict the mechanism of inhibition onto metal surface, corrosion mechanism of metal must be known. In hydrochloric acid solution the following mechanism proposed for the corrosion of mild steel (Yurta et al., 2004).

The anodic dissolution mechanism of metal is:



The cathodic hydrogen evolution mechanism is:



If one considers the structures of the investigated compounds, table 1, several potential sources of inhibitor – metal interaction can be identified. In the case of 1,4-Di-2-(5-phenyloxazolyl)-benzene inhibitor, there are the free electron pairs on N and O, capable of forming a coordination  $\sigma$  – bond with Fe (Muller, 2006). Further, the double bonds in the molecule allow back donation of metal d – electrons to the  $\pi^*$  – orbitals, which is a type of interaction that cannot occur, e.g. with amines. And the  $\pi$  – electrons from the aromatic rings may interact with the metal surface. Furthermore, especially in acidic media, electrostatic interaction is possible between the negatively charge of iron surface (which may be brought about by specific adsorption of  $\text{Cl}^-$  anions) and the positively charged inhibitor, following protonation of its basic functionalities. In the case of 4,7-diphenyl -1,10-phenanthroline inhibitor, basically the same interactions can occur, with difference that no oxygen atoms. In view of the above, when mild steel is immersed in 0.5 mol dm<sup>-3</sup> hydrochloric acid containing 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl -1,10-phenanthroline inhibitors, two kinds of adsorption can be acting on steel surface and the adsorption mode shown in down paper: type A means the interaction between the aromatic rings, free electron pairs and the vacant low energy d – orbitals of Fe surface atoms, this process is called chemisorption. Type B shows the electrostatic interaction between the positively charge N atom and negatively charge  $\text{Cl}^-$  on mild steel surface, which is regard as physisorption.

#### D- Surface analysis by optical microscope

The surface analysis of the corroded electrodes in 0.5 mol dm<sup>-3</sup> hydrochloric acid in absence the inhibitors (A) and the presence of 1,4-Di-2-(5-phenyloxazolyl)-benzene (B) and 4,7-diphenyl -1,10-phenathroline(C) inhibitors have shown in figure 7 , The microscope reveals that , the surface is strongly damaged in the absence the inhibitors and show the pits . Thus , in the presence the inhibitors the microscope reveals there is a decrease in the corrosion site and pits over the surface of mild steel in figure 7 ( B,C) , it appears that the surface of the electrode was covered greatly by insoluble stable film of the inhibitor .

Table 2 : Polarization parameters ; anodic Tafel slope  $B_a$  , cathodic Tafel slope  $B_c$  , corrosion potential  $E_{corr}$  , corrosion current density  $I_{corr}$  and inhibition efficiency P% for mild steel in 0.5 mol dm<sup>-3</sup> hydrochloric acid de – aerated solution with different concentration of the 1,4-Di-2- (5-phenyloxazolyl)-benzene inhibitor at 313.15K .

Concentration mol dm <sup>-3</sup>	$I_{corr}$ ( $\mu\text{A cm}^{-2}$ )	$-E_{corr}$ (mV/SCE)	$B_c$ mV dec <sup>-1</sup>	$B_a$ mV dec <sup>-1</sup>	P%
Blank	1204	16	52.2	20.3	-
$5 \times 10^{-4}$	168	20	51.1	21.5	85.971
$10^{-3}$	149	22	48.2	20.2	87.616
$5 \times 10^{-3}$	127	32	51.4	19.3	89.385
$10^{-2}$	117	33	47.6	18.3	90.232
$5 \times 10^{-2}$	112	35	33.1	17.2	91.038

Table 3 : Polarization parameters ; anodic Tafel slope  $B_a$  , cathodic Tafel slope  $B_c$  , corrosion potential  $E_{corr}$  , corrosion current density  $I_{corr}$  and inhibition efficiency P% for mild steel in 0.5 mol dm<sup>-3</sup> hydrochloric acid de – aerated solution with different concentration of the 4,7-diphenyl -1,10-phenathroline inhibitor at 313.15K .

Concentration mol dm <sup>-3</sup>	$I_{corr}$ . ( $\mu\text{A cm}^{-2}$ )	$-E_{corr}$ (mV/SCE)	$B_c$ mV dec <sup>-1</sup>	$B_a$ mV dec <sup>-1</sup>	P%
Blank	1204	16	52.1	20.3	-
$5 \times 10^{-4}$	175	17	47.3	21.3	85.423
$10^{-3}$	172	24	47.4	21.2	85.681
$5 \times 10^{-3}$	157	27	45.2	20.4	86.885
$10^{-2}$	127	28	48.6	19.6	89.385
$5 \times 10^{-2}$	114	29	42.2	17.7	90.481



Figure 1 : The potentiostatic Wenking for corrosion measurements .



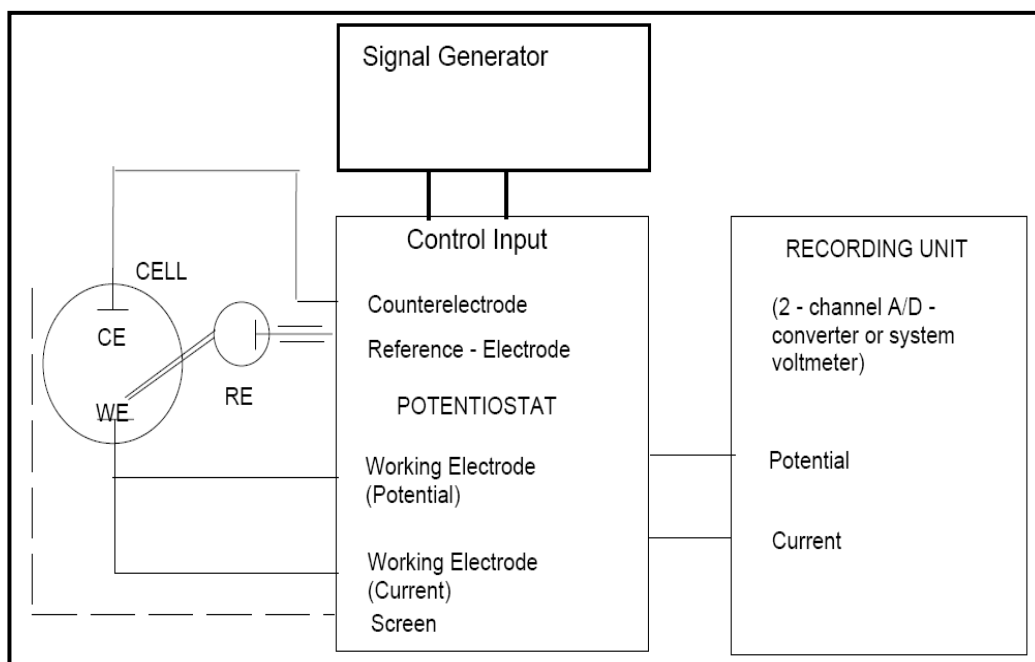


Figure 2 : The block diagram for recording current versus potential curves in potentiostatic Wenking for corrosion measurements show the polarization cell that it consist of from the (WE) working electrode , (CE) Platinum Auxiliary electrode or counter electrode and (RE) reference electrode . Also , the signal generator unit and the recording unit of current and potential .

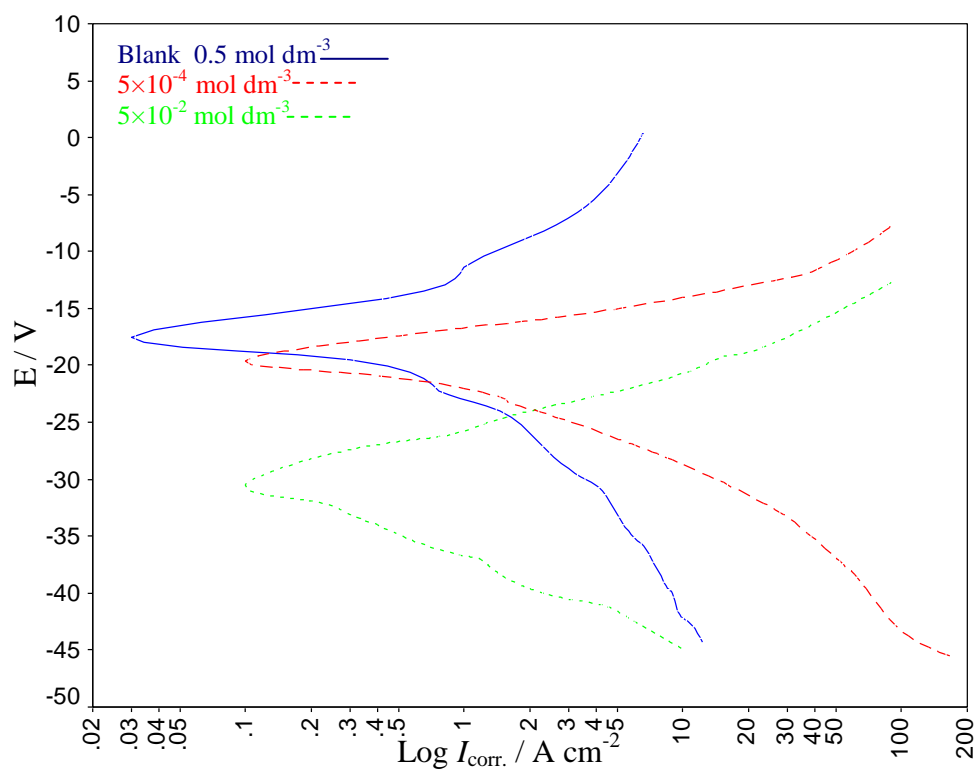


Figure 3 : Polarization curves for mild steel in  $0.5 \text{ mol dm}^{-3}$  hydrochloric acid de-aerated solution with different concentration of the 1,4-Di-2-(5-phenyloxazolyl)-benzene inhibitor at 313.15K .

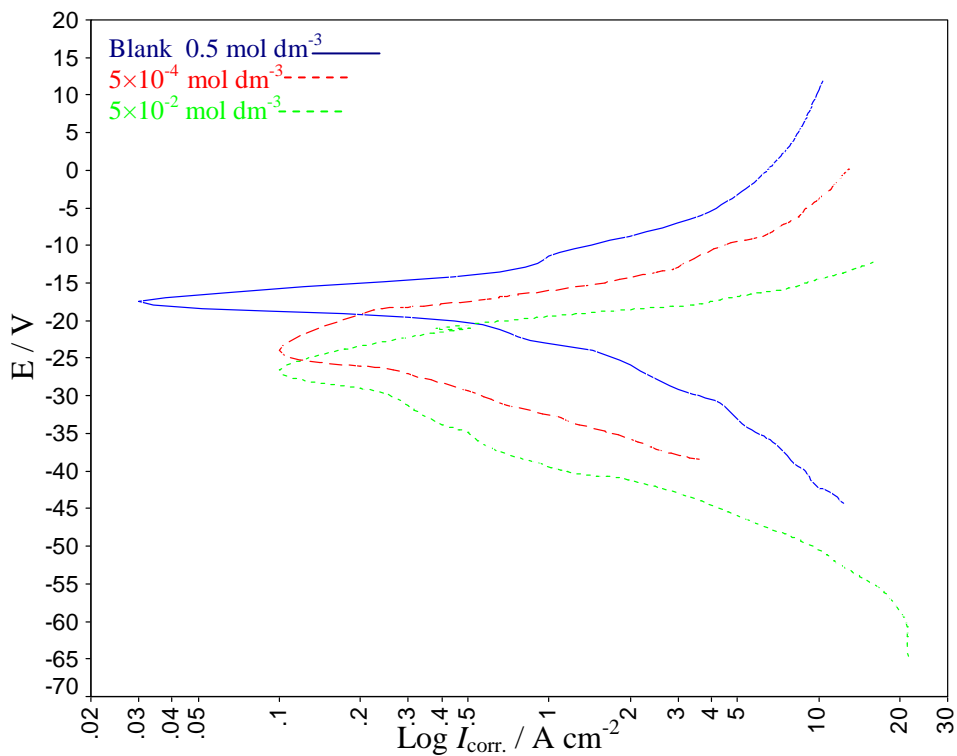


Figure 4 : Polarization curves for mild steel in  $0.5 \text{ mol dm}^{-3}$  hydrochloric acid de-aerated solution with different concentration of the 4,7-diphenyl -1,10-phenanthroline inhibitor at 313.15K .

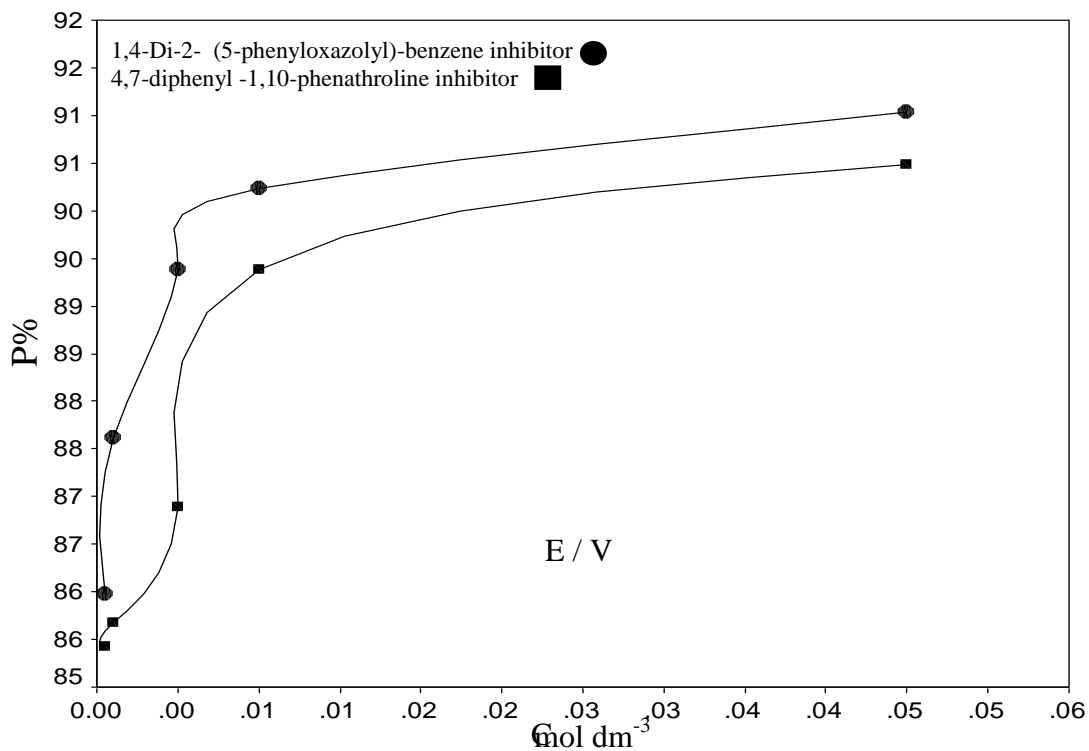


Figure 5 : Corrosion inhibition efficiency of mild steel in  $0.5 \text{ mol dm}^{-3}$  hydrochloric acid de-aerated solution at 313.15K upon addition of 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl -1,10-phenanthroline inhibitors.

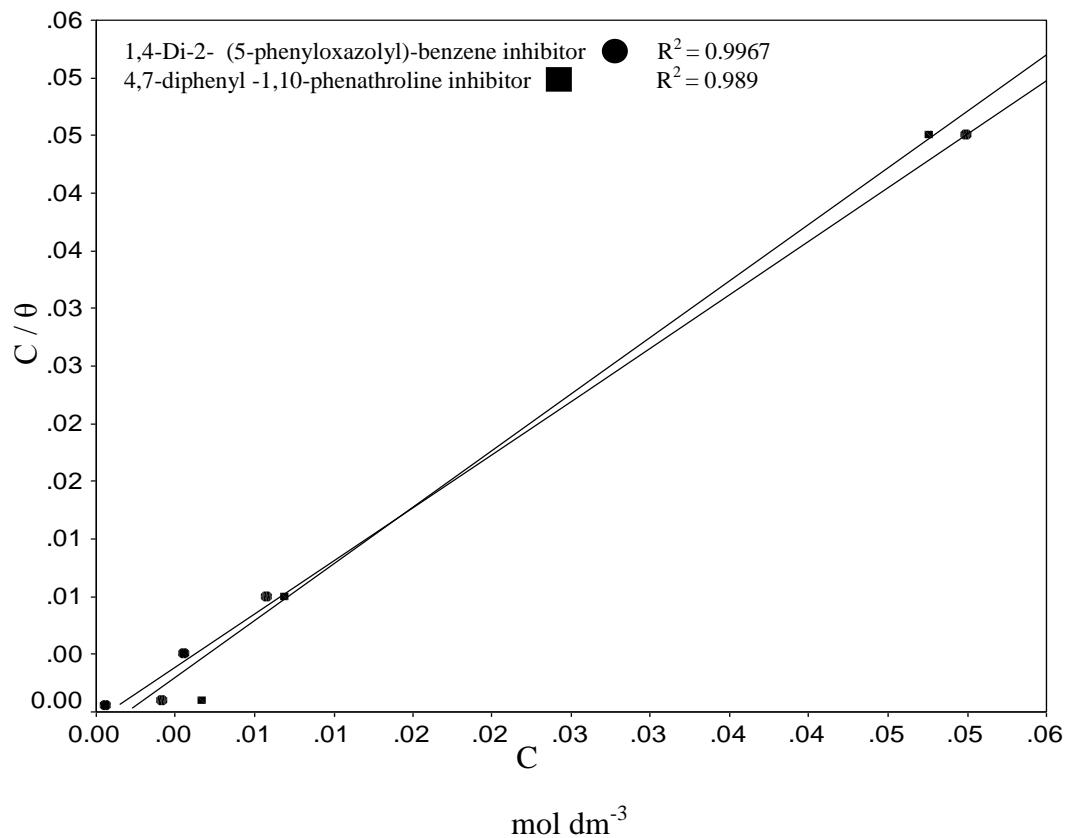
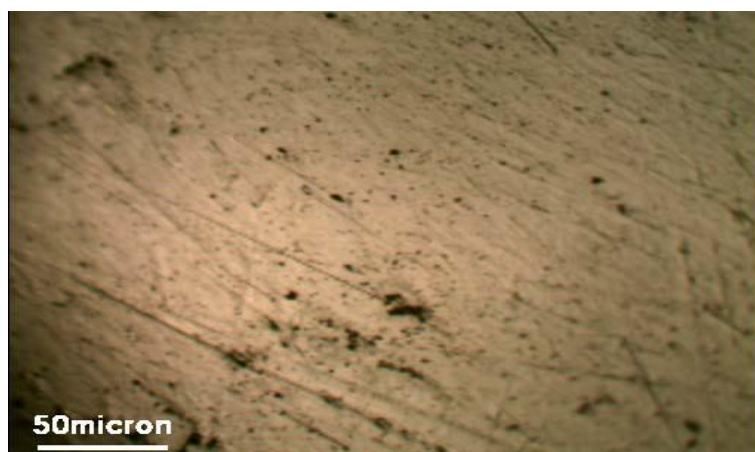
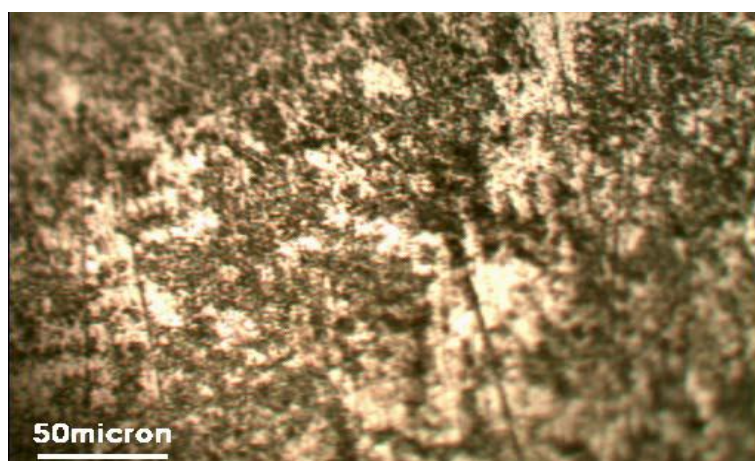


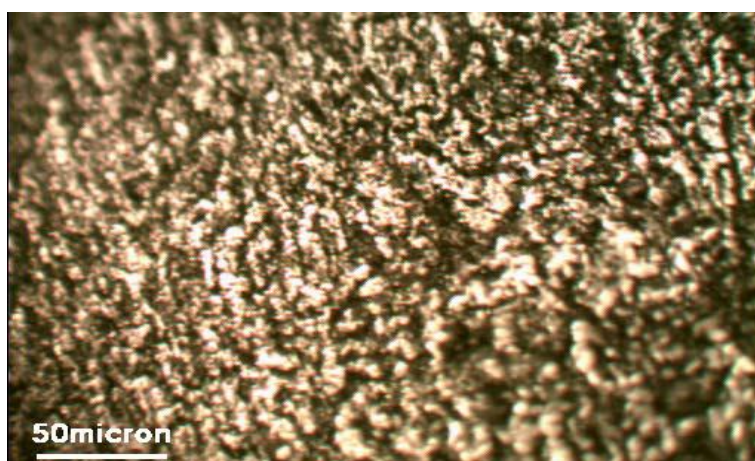
Figure 6 : Langmuir isotherm plots for 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl-1,10-phenanthroline inhibitors on mild steel in 0.5 mol dm<sup>-3</sup> hydrochloric acid de-aerated solution at 313.15K .



A



B



C

Figure 7 : Optical microscopic analysis of the electrode surface in 0.5 mol dm<sup>-3</sup> hydrochloric acid in absence the inhibitors (A) and the presence of  $5 \times 10^{-2}$  mol dm<sup>-3</sup> 1,4-Di-2-(5-phenyloxazolyl)-benzene (B) and 4,7-diphenyl -1,10-phenanthroline(C) inhibitors , respectively .

## Conclusi

A systematic study of the inhibition of the corrosion of mild steel electrode in 0.5 mol dm<sup>-3</sup> hydrochloric acid de-aerated solution at 313.15K by 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl -1,10-phenathroline inhibitors by electrochemical method " technique of three electrodes " led to following conclusions :

- 1- The 1,4-Di-2-(5-phenyloxazolyl)-benzene and 4,7-diphenyl -1,10-phenathroline inhibitors are excellent for mild steel corrosion in hydrochloric acid solution at 313.15K , generating inhibition efficiencies in the order of 91% at a concentration  $5 \times 10^{-2}$  mol dm<sup>-3</sup> . As the concentration increases , the 1,4-Di-2-(5-phenyloxazolyl)-benzene inhibitor shows an increasing inhibitive advantage over 4,7-diphenyl -1,10-phenathroline inhibitor .
- 2- The polarization curves appears the Tafel behaviour indicates that both inhibitors are of a mixed - type inhibitor .
- 3- The inhibition action of the both inhibitors is mainly due to their adsorption on the mild steel electrode surface . Adsorption process obey Langmuir adsorption isotherm at 313.15K .
- 4- The thermodynamic parameters ( $K_{ads}$  ,  $\Delta G_{ads}$ ) of adsorption for the studied inhibitors are calculated from their adsorption isotherms . The negative values of free energy of adsorption indicated that the adsorption of the inhibitor molecule is a spontaneous process .
- 5- The mechanism of their inhibitor via chelate formation between adsorbed inhibitor molecules and surface metal atoms leading to a thicker and more protective surface film

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