Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2017, 9(17):93-102
(http://www.derpharmachemica.com/archive.html)

Some Nitrogen Compounds as Corrosion Inhibitors for Steel in Acidic Solution

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ABSTRACT

The loss in weight of steel is set in acid solutions in presence of chloride and sulphate anions as aggressive ions and urea, phenylhydrazine and o-phenylenediamine as inhibiting compounds. The loss in weight will increase with the increasing concentration of chloride and sulphate ions and on raising the temperature of solution. The inhibition potency of the studied inhibiting compounds will increase within the order: urea>phenylhydrazine>o-phenylenediamine.

Keywords: Steel, Citric acid, Corrosion, Passivation, Weight loss, Inhibition

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INTRODUCTION

Iron and its alloys (e.g., steels) area unit continually exposed to the action of acids in industry [1]. Processes within which acids play a really necessary part are acid pickling, industrial acid cleanup, and cleanup of petroleum refinery instrumentality, oil well acidizing and acid descaling [1,2]. The exposures will be most severe however in several cases, corrosion inhibitors area unit wide utilized in the business to stop or to cut back the corrosion rates of antimonial materials in these media.

Corrosion is that the gradual physiochemical destruction of materials by the action of atmosphere. It's additionally referred to as the deterioration of materials or its properties due to reaction with its atmosphere. The word corrosion comes from the Latin word "corrodere", which implies to gnaw away. It always begins at the surface of a fabric and happens due to the spontaneous tendency of the materials to come to their physics stable state or to one of the forms within which they were originally found. Metals are usually vulnerable to corrosion as a result of most of them occur naturally as ores, that is that the most stable state of low energy and there's a web decrease in free energy ΔG from metallic to oxidized state [3].

Acid corrosion inhibitors notice huge application within the industrial field as parts in acid descaling, oiler acidizing, acid pickling, acid cleansing, etc. Most of the economical corrosion inhibitors employed in business are organic compounds having multiple bonds and hetero atoms like N, O, S through that they're adsorbable on the metal surface [4-11]. The influence of such organic compounds on the corrosion of steel in acidic media has been investigated by many researchers [12-14]. The inhibition property of those compounds is attributed to their molecular structure [15].

The aim of the current work is bothered with using weight loss measurements to shed additional light on the behavior of steel in acid solutions absent of-and containing increasing concentrations of chloride associate degreed sulfate ions as aggressive anions. The result of raising solution temperature within the vary (25-55°C) on the loss in weight of steel specimens are examined. The result of addition of skyrocketing concentrations of some organic compounds like urea, phenylhydrazine and o-phenylenediamine on this behavior is additionally investigated.

EXPERIMENTAL SECTION

The corrosion rate of steel was calculated by weight loss measurements. Experiments were performed using steel samples measuring 4 × 2 × 0.1 cm. These were cut from steel sheet that has the subsequent composition: Mn (0.89), C (0.32), Si (0.24), P (0.024), S (0.019) and Fe (98.507% mass). The corrosion rate was calculated on the premise of the geometrical expanse. The surface treatment enclosed sharpening by 0-, 00- and 000-grades of abrasive, degreasing with acetone, laundry with triple- water and drying between filter papers. The metal sheets were weighted and totally immersed in 250 cm^3 of the tested solution of acid with and absence of additives. All chemicals used were of BDH-quality. The cell used for weight loss measurements contains a double wall jacket through that, water at the adjusted temperature was circulated. Weight loss experiments were distributed in stagnant, naturally aerated solutions at a continuing temperature 25+0.1°C, except that associated with the effect of temperature.

The cell temperature was controlled using ultra thermostat kind polyscince (USA). Every set of measurements continual thrice to make sure reproducibity of the results. The influence of adding increasing concentrations of aggressive anions like NaCl and Na_2SO_4 on the corrosion rate of the steel electrode in 0.5 M citric acid solution was investigated. Increasing concentrations of urea, phenylhydrazine and 1,2-phenylenediamine were used as inhibitors. The percentage inhibitor efficiency (%IE) for steel in the presence of changed concentrations of each organic compound was calculated using the Equation:

$$\% \text{ Inhibitor Efficiency (IE)}=(1-R/R_o) \times 100 \qquad (1)$$

Where, R_o and R are the corrosion rates of steel in the absence and presence of each inhibitor, respectively.

RESULTS AND DISCUSSION

Effect of increasing concentrations of citric acid

The corrosion behavior of a metal in an aqueous solution was characterized by the extent to which it dissolved in the solution. This may be quantified by exploitation the straightforward relationship:

$$W=W_x-W_y \qquad (2)$$

Where, W=Weight of metal loss in the test solution, W_y=Weight of metal before exposure to the test solution, W_x=Weight of metal after exposure to the test solution.

The degree of dissolution depends on the surface area of the metal exposed and also the time of exposure; therefore the amount of corrosion was given with reference to area and time. The ensuing quantity, corrosion rate, is so a basic activity in corrosion science. Corrosion rates may analysis by measurement either the concentration of the dissolved metal in solution by chemical analysis or by measuring weight of a specimen before and after exposure and applying Equation 2. The latter is commonest technique. The weight-loss technique is sometimes most well-liked as a result of the number measured is directly associated with the extent of corrosion and does not rely on any assumptions about reactions occurring during corrosion.

Figure 1 show the weight loss-time curves for steel in increasing concentrations of citric acid solutions at 25°C. As shown during this figure, on increasing the concentration of acid solutions, the weight loss of steel samples is reduced. This implies that higher concentrations of citric acid retard the corrosion of steel and thus assist the passivation method [16]. The linear variation of weight loss with time in citric acid solutions indicates the absence of insoluble surface films throughout corrosion. Within the absence of any surface films, acid molecules could also be adsorbate onto the metal surface and thenceforth impede corrosion by forming complex with metallic element ions [17].

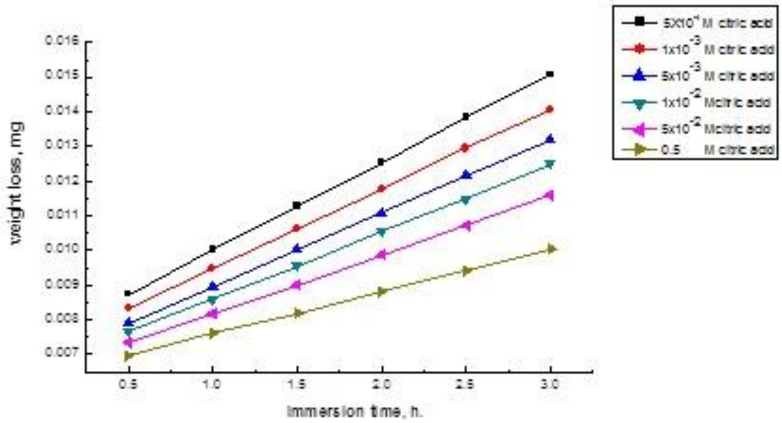

Figure 1: Variation of weight loss of steel with immersion time at different concentrations of citric acid at 298 K

Effect of temperature

Variation of loss in weight of steel in 0.5 M citric acid solution at completely different temperatures is additional examined. Figure 2 shows the influence of raising temperature (15-25°C) on the loss in weight of steel in 0.5 M citric acid solution. Review of the curves of this figure reveals that raising the solution temperature is amid increasing the loss in weight. It is quite clear that raising the temperature decreases the initial rate of passive film growth and/or enhances the corrosion of the steel and also the extent of corrosion promotion will increase with raising the temperature. This could be attributed to the decrease of solution viciousness and also the subsequent increase within the motion of ions with raising the solution temperature [18]. The corrosion rate of steel in naturally aerated 0.5 M citric acid solutions, at temperatures started from 25-55°C is plotted as a function of 1/T (K^{-1}) in Figure 3. From the Arrhenius plots of this figure; the free energy of activation of passive film thickening on steel surface is computed to be 6.3 kJ/mol. This very low value of energy of activation (<40 kJ/mol) indicates that the method of passive film thickening on the steel electrode is below diffusion management [19-21].

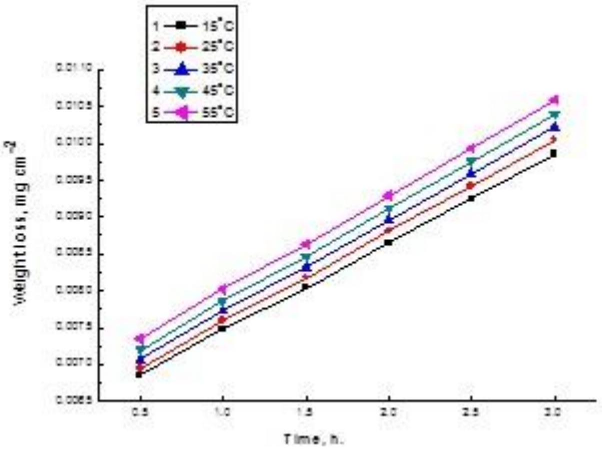

Figure 2: Variation of weight of steel electrode with immersion time in 0.5 M citric acid at different temperatures

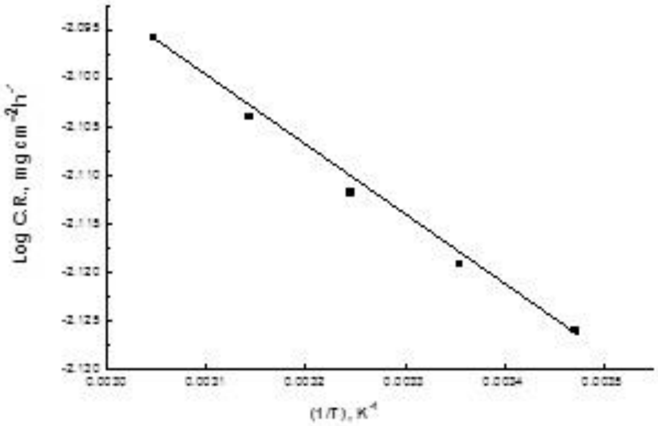

Figure 3: Arrhenius plot of Log C.R. of steel electrode with 1/T

Effect of adding increasing concentrations of Cl^- and SO_4^- anions

The straight lines in Figures 4 and 5 represent the variation of the loss in weight of the steel with immersion time in naturally aerated solutions of 0.5 M citric acid devoid of and containing increasing concentrations of NaCl and Na_2SO_4, severally. Inspection of those figures reveals that the losses in weight of the steel specimens within the presence of aggressive ions are markedly increased. Moreover, as the immersion time increased the loss in weight increased. For a similar concentration of aggressive anions, the loss in weight just in case of SO_4^- is bigger than Cl^- and so SO_4^- anions more corrosive in steel than Cl^- anions. On more increasing of the concentration of the aggressive anions, the loss in weight area unit markedly inflated. Because the concentration of the sulfate and chloride ions will increase, passive film destruction predominates passive film formation [22]. The influence of concentrations of aggressive anions on the corrosion rate of steel electrode in 0.5 M citric acid is illustrated in Figure 6. A sigmoidal S-shaped curves are obtained which reveal that the initiation of pitting corrosion on the steel by Cl^- and SO_4^- ions takes place by the means of an adsorption mechanism.

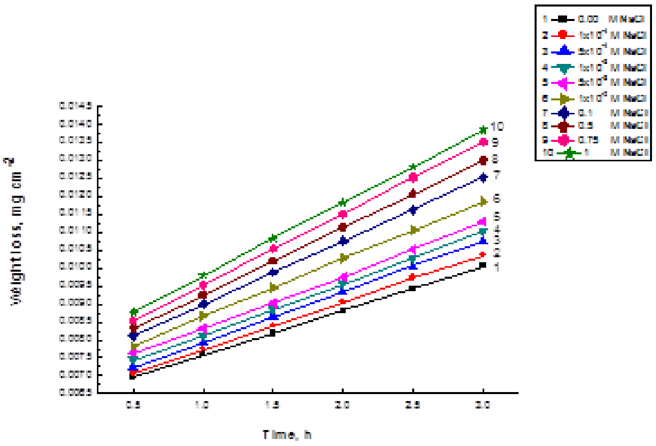

Figure 4: Variation of weight loss of steel electrode with immersion time in 0.5 M citric acid with different concentrations of NaCl at 298 K

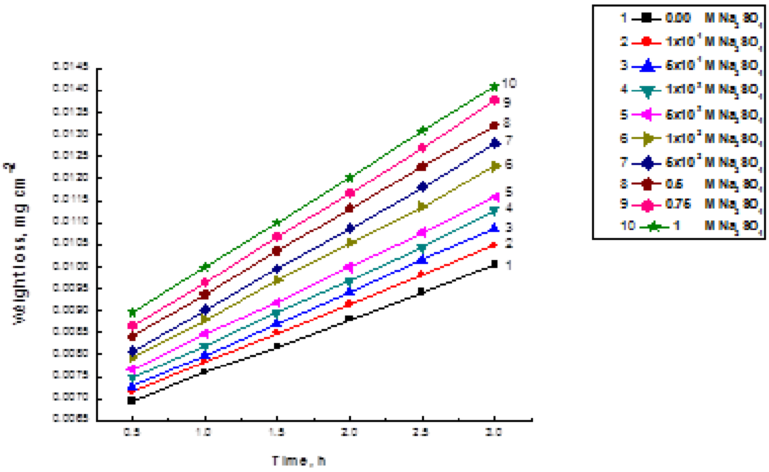

Figure 5: Variation of weight loss of steel electrode with immersion time in 0.5 M citric acid with different concentrations of Na_2SO_4 at 298 K

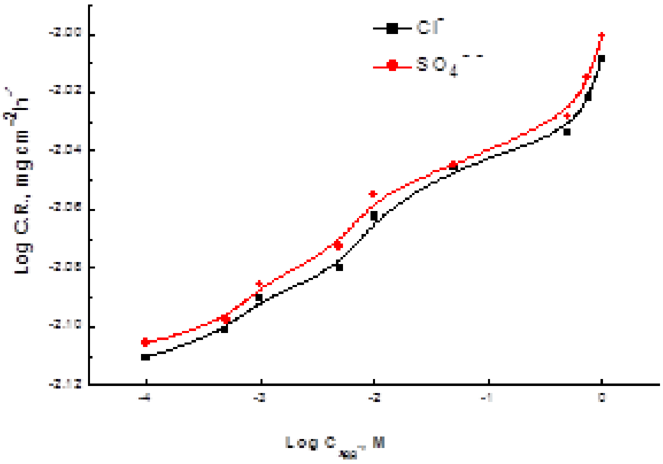

Figure 6: The dependence of corrosion rate of steel electrode in 0.5 M citric acid on the concentrations of aggressive anions after 1 h

Effect of adding some organic compounds

Behavior in absence of aggressive anions

The effect of addition of accelerating concentrations of urea, phenylhydrazine and 1,2-phenylenediamine on the loss in weight of steel in 5 × 10^{-4} M citric acid solution was examined. Figures 7-9, represent the influence of immersion time on the loss in weight of the steel specimens in naturally aerated 5 × 10^{-4} M citric acid solutions free of and containing increasing concentrations of urea, phenylhydrazine and o-phenylenediamine, respectively, at 25°C.

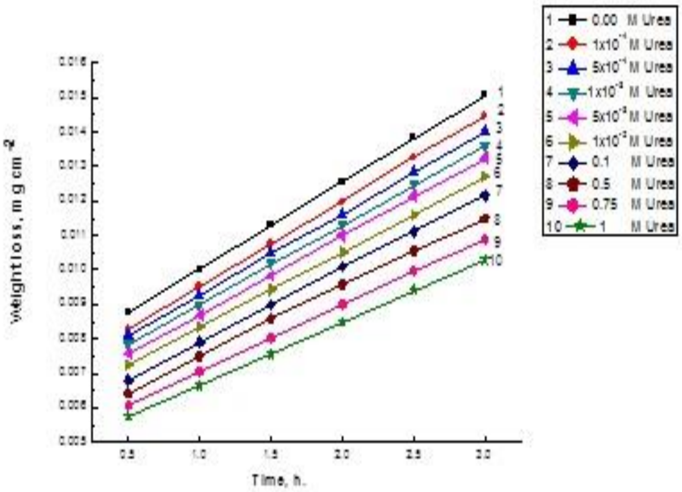

Figure 7: Variation of weight loss of steel electrode with immersion time in 5 × 10^{-4} M citric acid with different concentrations of urea at 298 K

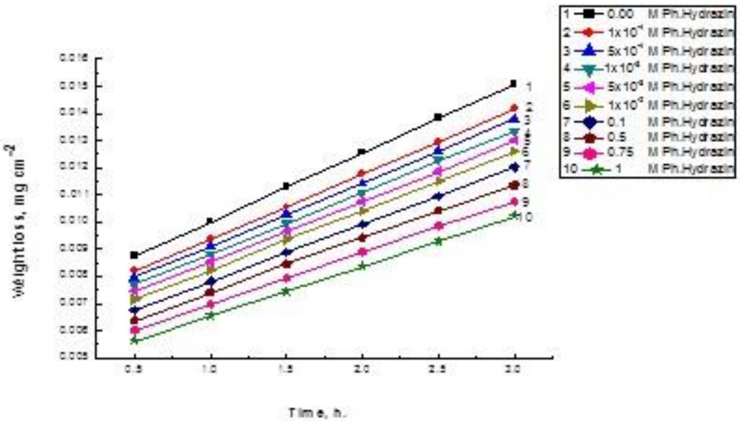

Figure 8: Variation of weight loss of steel electrode with immersion time in 5 × 10^{-4} M citric acid with different concentrations of phynylhydrazine at 298 K

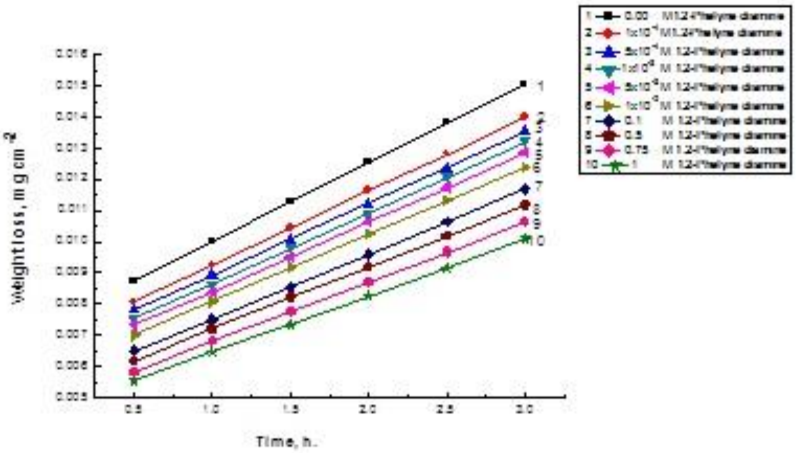

Figure 9: Variation of weight loss of steel electrode with immersion time in 5 × 10^{-4} M citric acid with different concentrations of 1,2-phene diamine at 298 K

Inspection of the curves in Figures 7-9 reveals that, in presence of those compounds, loss in weight of the steel specimens are reduced and as the degree of corrosion inhibition by those compounds becomes higher, the higher concentration of the inhibition action of those compounds depends on the amine groups (NH_2), the influence of molecular structure, inflexibility of π-delocalized system and inhibitor concentration [23,24]. Junter proposed that adsorption of the organic inhibitors in the main depends on some physicochemical properties of the molecule associated with its functional groups, to the imaginable steric effects and electronic density of donor atoms. Adsorption is thought also to depend on the possible interaction of p-orbitals of the inhibitor with d-orbitals of the surface atoms that induces larger surface assimilation of the substance molecules onto the surface of steel, resulting in the formation of a corrosion protective film [25]. It is apparent that adsorption of P-phenylenediamine (PPD) on the steel surface happens directly on the premise of donor acceptor between the lone pairs of the heteroatoms, the extensively delocalized electrons over the C6 ring of benzene, the PPD molecule and therefore the vacant d-orbitals of iron surface atoms [26]. The functional group responsible for PPD adsorption on metal surface is the lone pair of the nitrogen atom: iron ions on metal surface which act as a Lewis acid because they accept electrons from a donor group [27]. Phenylhydrazine, on the opposite hand, is assumed to inhibit the corrosion by the formation of phenylhydrazine-complex that is give rise to on the metal surface. Nevertheless, its lower inhibition efficiency could be attributed to its lower tendency to form its corresponding salt or to the presence of the benzene ring which lying parallel to the electrode surface affecting thus the p electrons interaction with the metal surface [28]. Urea has the ability to be a good corrosion inhibitor for the corrosion of steel and the inhibitive power of urea may be due to the presence of the nitrogen and the oxygen atoms in its structure which give it the ability to enhance the inner protective layer of γFe_3O_4 and/or forming a protective outer layer of urea–Fe^{+2} complex [29,30].

Behavior in presence of aggressive anions

Increasing concentrations of urea, phenylhydrazine and o-phenylenediamine are used to inhibit the pitting corrosion of the steel in naturally aerated 0.5 M citric acid solution in presence of 1 M Cl^- ions as pitting corrosion agent. The dependence of loss in weight of the steel specimens on immersion time and inhibitor concentration is used to elucidate this behavior. The curves in Figures 10-12 represent such behavior in presence of urea, phenylhydrazine and o-phenylenediamine compounds, respectively. Inspection of the curves in Figures 10-12 reveals that the action of those additives be influenced by their type and Concentration.

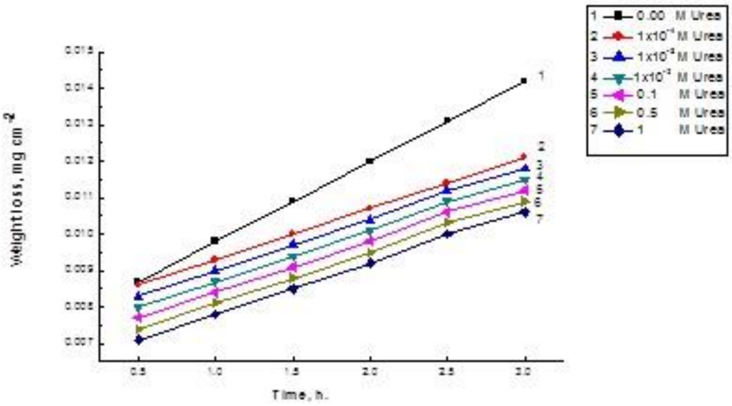

Figure 10: Variation of weight loss of steel electrode with immersion time in 0.5 M citric acid+1 M NaCl with different concentrations of urea at 298 K

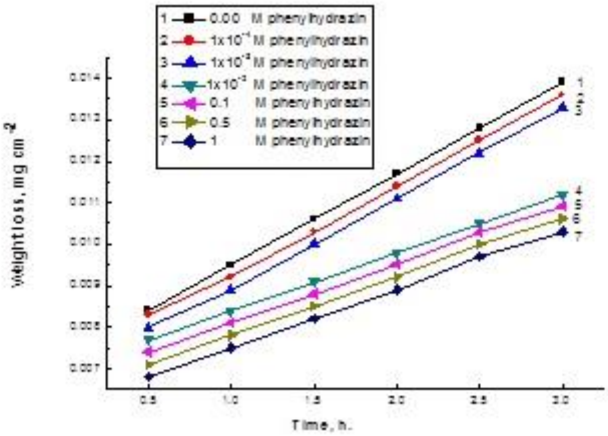

Figure 11: Variation of weight loss of steel electrode with immersion time in 0.5 M citric acid+1 M NaCl with different concentrations of phenylhydrazine at 298 K

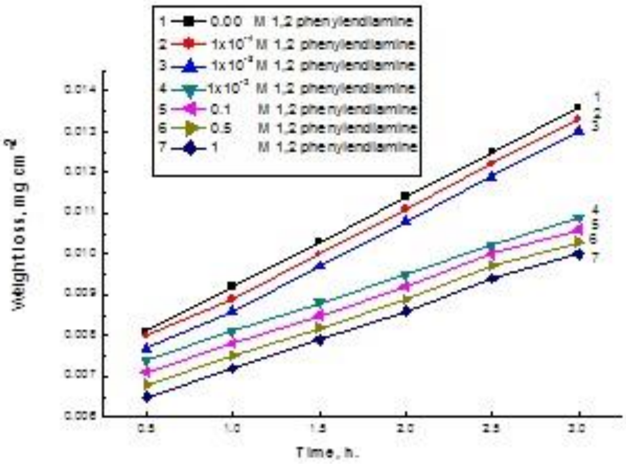

Figure 12: Variation of weight loss of steel electrode with immersion time in 0.5 M citric acid+1 M NaCl with different concentrations of 1,2-phenylendiamine at 298 K

Accordingly, in presence of these compounds, the loss in weight of steel specimens decreases with increasing the additives concentration. This behavior could be attributed to a competitive process, including passive film healing and thickening by the inhibitor compounds and passive film damage by the aggressive Cl^- ions. The dependency of corrosion rate of steel on the concentrations of these additives is presented in Figure 13. Figure 13 represents the variation of the corrosion rate, C.R., of the steel electrode, in 0.5 M citric acid+1 M Cl^- ions, as a function of molar concentration of the added inhibitive compounds on a double logarithmic scale. Straight line relationships are obtained indicating the domain of passive film destruction and initiation of pitting corrosion in presence of the inhibiting compounds in lower concentrations. Once the concentration of those compounds increased, passive film repair and thickening predominates passive film destruction and passivation of steel surface takes place.

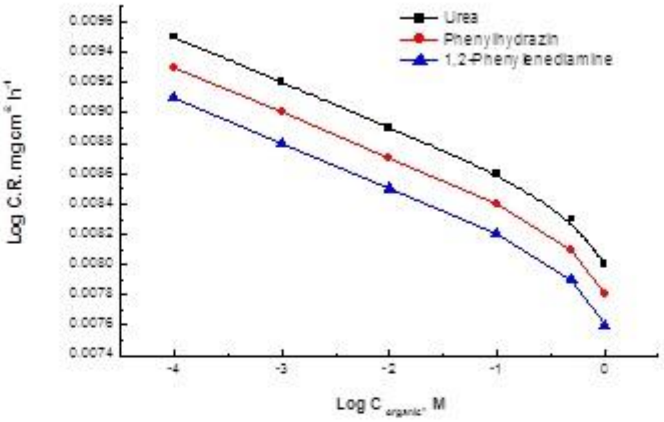

Figure 13: The dependence of corrosion of steel in 0.5 M citric acid+1 M NaCl on the concentrations of organic compounds used at 298 K

The inhibition efficiencies (% IE) of the used organic compounds are determined by using the Equation:

$$\%\text{Inhibition Efficiencies (IE)}=[(R_o-R_o')/R_o] \times 100 \qquad (3)$$

Where, R_o and R_o' are the corrosion rate of steel in the absence and presence of the organic compounds, respectively at given time period and temperature. The variation of inhibition efficiency with the concentration of these organic compounds is calculated and shown in Table 1.

Table 1: Variation of Inhibition Efficiencies of steel immersed in 0.5 M citric acid solution+1 M Cl^- ions in presence of different organic compounds with their concentrations, at 25°C (Immersion time=1 h)

Conc., M	**%IE**		
	Urea	**Phenylhydrazine**	**1,2-phenylendiamine**
1×10^{-4}	3.061	5.102	7.142
1×10^{-3}	6.122	8.163	10.204
1×10^{-2}	9.183	11.224	13.265
0.1	12.244	14.285	16.326
0.5	15.306	17.346	19.387
1	18.367	20.408	22.449

From the values of inhibition efficiencies of Table 1, one can conclude that, for all organic compounds used, the inhibition efficiency increases with increasing of concentration and for the same concentration of these organic compounds, the order of the inhibition efficiencies is decreased in the following: (The highest) o- phenylenediamine>phenylhydrazine>urea (the lowest).

Figure 14, Scanning Electron Microscope (SEM), micrographs of steel electrode surface after immersion for a period of 6 h in (A) 0.5 M citric acid (free) and (B) 0.5 M citric acid in+0.1 M Cl^- ions and (C) 0.5 M citric acid in+0.1 M Cl^- ions+1 M o-phenylenediamine.

Inspection of these micrographs shows only the abrasion lines in aggressive ion free citric acid solutions, Figure 14(A). However, in the presence of chloride ions, Figure 14(B), fine pits were formed, some of which expanded equally laterally as well as inwardly to give some large attacked areas. Inside these large areas traces of the corrosion products are observed. On the other hand, Figure 14(C), in presence of o-phenylenediamine, as an example of organic inhibitors used, the number and size of the pits formed are remarkably decreased relative to that observed in inhibitor free solutions and there are with no large corroded areas.

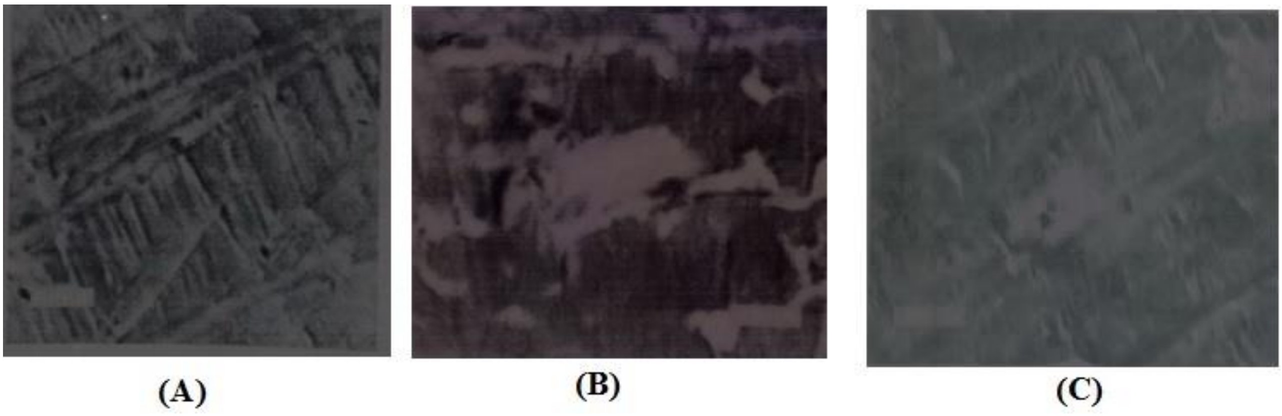

Figure 14: SEM micrographs of steel electrode surface after immersion for a period of 6 h in (A) 0.5 M Citric acid (free) and (B) 0.5 M Citric acid in+0.1 M Cl^- ions and (C) 0.5 M Citric acid in+0.1 M Cl^- ions+1 M o-phenylenediamine

Adsorption isotherms

The inhibition process of organic molecules can be taken place by adsorption of these molecules on the metal surface. Theoretically, adsorption process can be considered as a single substitution process in which an inhibitor molecule, $I_{(aq)}$, in the aqueous phase substitutes an "n" number of water molecules adsorbed on the metal surface [31].

$$I_{(aq)}+n\ H_2O_{(sur)}\ I_{(sur)}+x \ \rightarrow \ H_2O_{(aq)} \qquad (4)$$

Where, n is known as the size ratio and simply equals the number of adsorbed water molecules replaced by a single inhibitor molecule. Adsorption depends on the structure of the matter, the kind of the metal and also the nature of its surface, the character of the corrosion medium and its pH value, the temperature and also the electrochemical potential of the metal/solution interface. Adsorption provides additionally info regarding the interaction among the adsorbable molecules themselves, as well as, their interaction with the metal surface.

Actually an adsorbed molecule could build the surface harder or easier for an additional another molecule to become attached to a neighboring site and multilayers could happen. There may be more or less than one inhibitor molecule per surface site. Finally, varied surface sites may have variable degrees of activation. For these reasons a lot of mathematical adsorption isotherm expressions have been established to take into consideration. Adsorption isotherm equations can be represented by [32]:

$$f\,(\theta, x)\ \exp\,(-a, \theta)=KC \qquad (5)$$

Where, f (θ, x) is the configurationally factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm and is a molecular interaction parameter depending upon molecular interactions in the adsorption layer and the degree of heterogeneity of the surface. All adsorption processes include the equilibrium constant of the adsorption process, K_{ads}, which is related to [33] the standard free energy of adsorption ($\Delta G°_{ads.}$) by:

$$K_{ads}=1/55.5\ \exp\,(-\Delta G°_{ads.}/RT) \qquad (6)$$

Where, R is the universal gas constant and T is the absolute temperature. A number of mathematical relationships for the adsorption isotherms are advised to suit the experiment knowledge of this work. The Langmuir adsorption isotherm [34] is represented by the following Equation:

$$\theta/(1-\theta)=K_{ads}C \qquad (7)$$

Where, K_{ads} is the equilibrium constant of the adsorption process, C is the inhibitor concentration in the bulk of the solution and θ is the surface coverage. The surface coverage, θ, is the fraction of the surface covered by the inhibitor molecules, and can be calculated from the following Equation:

$$\theta=[1-(W_o'/W_o)] \qquad (8)$$

Where, W_o and W_o' are the weight losses in the absence and presence of inhibitor, respectively. Plots of C/θ *vs*. C (Langmuir adsorption plots) for adsorbed organic compounds on the surface of steel in 0.5 M citric acid+1 M NaCl at 25°C are shown in Figure 15. The data give straight lines with maximum value of correlation coefficient indicating that Langmuir's isotherm is valid for these systems [35].

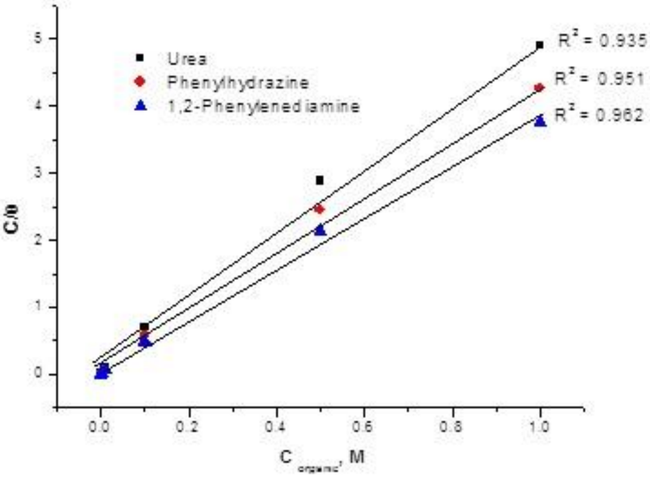

Figure 15: Langmuir adsorption isotherm of the investigated organic compounds for steel in 0.5 M citric acid+1 M NaCl at 298 K

The value of K_{ads} and $\Delta G°_{ads}$ for organic compounds are calculated and recorded in Table 2.

Table 2: Equilibrium constant (K_{ads}), activation free energy of adsorption ($\Delta G°_{ads}$) and correlation coefficient (R^2) for adsorption of inhibitors on steel in 0.5 M citric acid+1 M NaCl, at 25°C

Inhibitors	Langmuir isotherm		
	$K_{ads} \times 10^2$ (M^{-1})	$-\Delta G°_{ads.}$ (KJ/mol^{-1})	R^2
1,2-phenylendiamine	11.11	17.370	0.962
phenylhydrazine	6.66	16.103	0.951
Urea	5.37	15.572	0.945

In all cases, the value of R^2 is approximately equal unity indicating the applicability of Langmuir adsorption isotherm to the used organic compounds. The low negative values of $\Delta G°_{ads}$ (<-40 kJ/mol) indicate that these organic compounds are physically adsorbed on steel surface. The values of K_{ads} were found to run parallel to the %IE; o-phenylenediamine>phenylhydrazine>urea. This result reveals the increasing of adsorption ability, due to structural formation, on the metal surface [36].

SUMMARY AND CONCLUSION

In this work, the weight loss measurement is employed to analyze the behavior of steel in naturally aerated citric acid solutions in absence and presence of both each the aggressive and also the inhibitive organic compounds.

- The loss in weight of steel electrode decreases with increasing the concentration of citric acid and will increase on rising of solution temperatures.
- The free activation energy of passive film thickening on steel surface is computed to be 6.3 kJ/mol.
- On addition of increasing concentrations of NaCl and Na_2SO_4, the loss in weight of the steel specimens are markedly increased, moreover as the immersion time increased the loss in weight increased. For the same concentration of aggressive anions, the loss in weight in case of SO_4^- is greater than Cl^- and hence SO_4^- anions more aggressive than Cl^- anions.
- In presence of organic compounds, the loss in weight of steel specimens decreases on increasing the additives concentration.
- The (%IE) increases with increasing the concentration of organic compounds.
- At one and the same concentration of these organic compounds, the inhibition efficiency decreases in the order; (the highest) o-phenylenediamine>phenylhydrazine>urea (the lowest).
- The adsorbability constant and the free energy of repassivation for the respective inhibiting compounds are calculated, the low negative values of $\Delta G°_{ads}$ indicate that these organic compounds are weakly adsorbed on steel surface.

ACKNOWLEDGEMENT

The authors appreciate the financial support and facilities provided by the University of Zagazig to finish this work.

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