Conyza Dicorides: Anew and Efficient Eco-Friendly Corrosion Inhibitor for Mild Steel in 1M HCl Solution

Narjes I. Khaled[1*], Abd-Alwahab A. Sultan[2], Hussein H. Ibrahem[3] and Moayad N. Khalaf[4]

[1]Technical College of Basrah, Petrochemical Department, Basrah-Iraq
[2]Southern Technical University / Basrah-Iraq.
[3] South oil company / Basrah-Iraq.
[4]Chemistry Department, College of Science, University of Basrah, P O Box 773, Basrah-Iraq
[*]E – mail: narjesibrahem@yahoo.com

Received: 27 Sep. 2014, Revised: 29 Oct. 2014, Accepted: 13 November 2014
Published online: 30 November 2014

Abstract

The inhibitory effects of the ethanol extract of *Conyza dioscoridis* (EECD) on the corrosion of mild steel in a 1 M HCl solution were investigated by weight loss measurements at the temperature range of 25 °C to 65 °C. Results showed that the inhibition efficiency increased with increasing EECD concentration and decreased with increasing temperature. The inhibition efficiency of 2 g/L EECD reached approximately 94.87% at 25 °C. The thermodynamic functions of dissolution, activation energy, and adsorption processes were calculated and discussed. The adsorption of the additive followed the Langmuir adsorption isotherm.

Keywords: Mild steel; Acid solution; Weight loss; Acid inhibition; Adsorption process; Corrosion inhibition.

1. Introduction

The corrosion of metallic materials in acidic solutions causes considerable costs. Several techniques have been applied to reduce metal corrosion. The use of inhibitors during acid pickling is a practical protection method against corrosion in acidic media. Most effective and efficient organic inhibitors are compounds containing heteroatoms, such as oxygen, nitrogen, sulfur, and phosphorus, which allow adsorption on metal surfaces [1, 2]. An effective inhibitor displaces water from the metal surface, interacts with anodic or cathodic reaction sites to retard the oxidation and reduction corrosion reaction, and prevents the transportation of water and corrosion active species on the surface.

Inhibitors that reduce corrosion on metallic materials have three types: inorganic, organic, and mixed material [3–6]. However, the applications of these inhibitors for corrosion control are limited by several factors, such as high cost, toxicity, low availability, and environmental unfriendliness. Thus, recent studies have focused on using natural products as corrosion inhibitors.

Naturally occurring substances as inhibitors of acid cleaning have attracted considerable attention as substitutes of synthetic organic inhibitors [7–10] because they are affordable, readily available, and ecologically friendly.

This study aims to investigate the inhibitory effects of the ethanol extract of *Conyza dioscoridis* (EECD), an affordable, eco-friendly, and naturally occurring substance, on the corrosion of mild steel in a 1 M HCl solution through weight loss measurements. The adsorption of EECD was investigated, and the thermodynamic adsorption parameters in the absence and presence of EECD were calculated and discussed.

2. Experimental

2.1 Materials and Solution

This study used rectangular mild steel coupons (53.5 cm × 1.8 cm × 0.3 cm) composed of 0.21% C, 0.05% Mn, 0.09% P, 0.05% S, 0.38% Si, 0.01% Al, and Fe. Each coupon had a hole with a diameter of approximately 3 mm near the upper edge.

An aggressive solution of 1 M HCl was prepared by diluting analytical-grade 37% HCl with doubly distilled water.

2.2 Inhibitor Preparation

Leaves of *C. dioscoridis* collected from Abu-AlKhaseeb, Basrah, Iraq were dried at room temperature and finely powdered.

Two extraction procedures were examined. These extraction procedures were performed using distilled water and ethanol at room temperature. Preliminary corrosion studies by weight loss measurements were performed to determine the optimal extraction procedure. The preliminary corrosion measurements showed that ethanol extraction was the same or more slightly efficient than the other procedure. Thus, this extraction procedure was adopted in this study.

Dry powdered plants (2 g) were soaked in 60 mL of ethanol at room temperature for 24 h and then filtered. The filtrate was added to an aqueous HCl solution to produce 1.0 L of stock solution in 1 M HCl. From the stock solutions, a series of diluted solution in 1 M HCl was prepared with different concentrations (0.2 g/L to 2 g/L).

2.3 Weight Loss Measurements

The mild steel coupons were ground and polished with emery paper up to 1200 grade, rinsed with distilled water, dried on a clean tissue paper, degreased by acetone for 5 s, and then air dried at room temperature. The coupons were weighed accurately and suspended vertically for 3 h in a 100 mL beaker that contains 1 M HCl with and without EECD at different concentrations. Then, the coupons were removed, rinsed with doubly distilled water and with ethanol, dried, and then weighed according to ASTM G1-71. The tests were repeated at different temperatures by using magnetic stirrer hot plates. To obtain good repeatability, the experiments were carried out twice, and the average weight loss of two readings was reported.

3. Results and Discussion

3.1 Effect of EECD Concentration

Corrosion rate (W) ($mg \cdot cm^{-2} \cdot h^{-1}$), inhibition efficiency (%IE), and degree of surface coverage (Θ) were obtained by weight loss measurements and by using the following equations at different concentrations of EECD immersed in 1 M HCl at 25 °C for 3 h.

$$\Theta = \frac{Wo - Wi}{Wo} \qquad (1)$$

$$\%IE = \Theta * 100 \qquad (2)$$

where W_O and W_i are the corrosion rates of the mild steel without and with EECD, respectively.

The corrosion rates of the mild steel in 1 M HCl containing EECD decreased as the concentration of EECD increased (Fig. 1). This result can be attributed to the increased adsorption amount and surface coverage of the

inhibitor on the mild steel with increasing concentration [11]. %IE increased as the concentration of EECD increased from 0.2 g/L to 2 g/L. The maximum %IE (94.87%) was obtained at 2 g/L and 25 °C (Fig. 2).

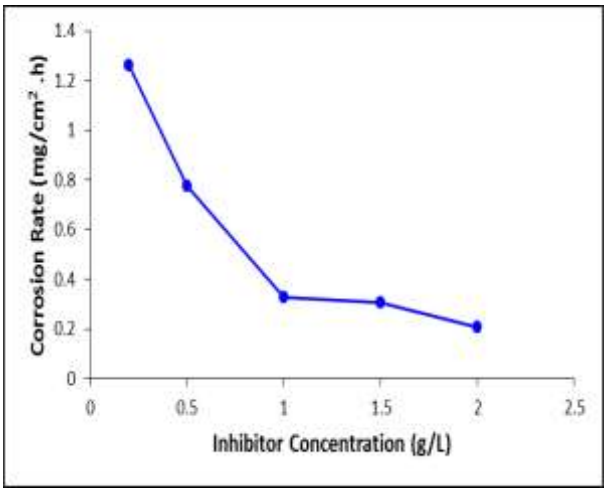

Fig.1. Variation of corrosion rates with concentrations of inhibitors in 1M HCl on mild steel surface at 25 °C.

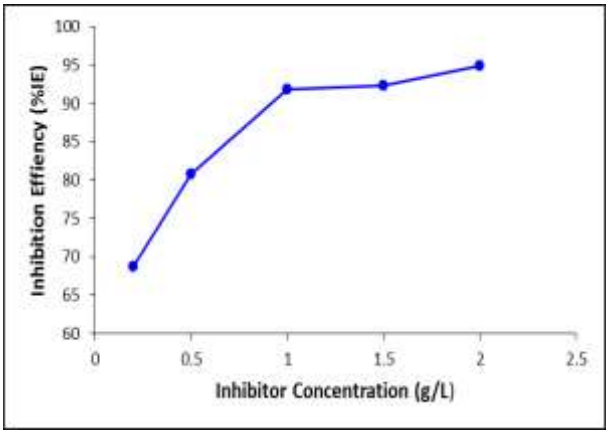

Fig.2. Variation of inhibition efficiency with concentrations of inhibitors in 1M HCl on mild steel surface at 25 °C.

3.2 Adsorption Isotherm

The basic information of the interaction between EECD and the mild steel surface can be provided by the adsorption isotherm. Several attempts were performed to fit various isotherms, including Frumkin, Temkin, Freundlich, Bockris, Flory-Huggins, and Langmuir [12]. The results were best fitted by the Langmuir adsorption isotherm. According to this isotherm, the surface coverage (Θ) is related to the inhibitor concentration (*C*) by [13, 14]

$$\frac{\Theta}{1-\Theta} = K_{ads}.C \qquad (3)$$

Rearranging Eq. (3) yields

$$\frac{C}{\Theta} = \frac{1}{K_{ads}} + C \qquad (4)$$

A fitted straight line was obtained from the plots of C/Θ versus C with slopes close to 1 (Fig. 3). The parameters are listed in Table 1. The strong correlation ($R^2 > 0.99$) indicated that the adsorption of EECD on the mild steel surface followed the Langmuir adsorption isotherm. As shown in Table 1, the adsorption equilibrium constant (K_{ads}) value in L/g decreased with increasing temperature. This result indicated that EECD was easily and strongly adsorbed on the mild steel surface at relatively low temperatures. However, the adsorbed inhibitor desorbed from the mild steel surface at relatively high temperatures [15,16].

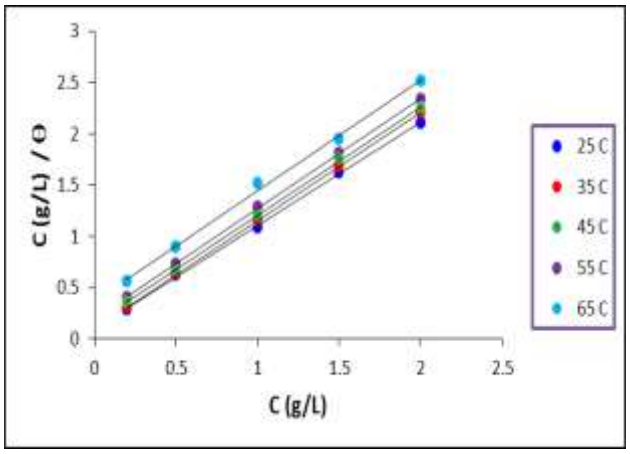

Fig.3. Langmuir adsorption isotherm model of (EECD) in 1M HCl on mild steel surface at different temperatures .

Table 1: Adsorption parameters for (EECD) obtained from Langmuir adsorption isotherm at different temperatures.

Additives	Temperature °C	Adsorption parameters			
		R^2	Slope	Intercept	K_{ads} (L/g)
(EECD)	25	0.9996	1.0078	0.0980	10.2040
	35	1.0000	1.0532	0.1015	9.8522
	45	0.9996	1.0566	0.1491	6.7069
	55	0.9998	1.0718	0.1973	5.0684
	65	0.9972	1.0771	0.3642	2.7457

3.3 Effect of Temperature on the Corrosion Inhibition of Mild Steel

The corrosion rate of the mild steel immersed in 1 M HCl for 3 h without EECD increased as the temperature increased from 25 ℃ to 65 ℃ (Fig. 4).

The effect of different temperatures (25 ℃ to 65 ℃) on the corrosion of the mild steel immersed in 1 M HCl for 3 h without and with EECD was determined. Results showed that the corrosion rate of the mild steel increased and the inhibition efficiency of EECD decreased as the temperature increased in all concentrations studied. This result can be ascribed to the desorption facilitated by the increase in temperature [17–19]. Thus, the behavior exhibited the physical adsorption of EECD on the mild steel surface.

At the optimum concentration (2 g/L), the inhibition efficiency decreased from 94.87% to 79.54% as the temperature increased from 25 ℃ to 65 ℃ (Fig. 5).

Table 2: Effect of temperature on the corrosion parameters of mild steel in 1M HCl at various concentration of (EECD) at 3 h.

Additives	Conc. (g/L)	Temp. (^{o}C)	Corrosion rate (mg. cm^{-2}. h^{-1})	%IE	Θ
Blank	0.0	25	4.0338	-	-
		35	4.7338	-	-
		45	5.5694	-	-
		55	6.7423	-	-
		65	7.6643	-	-
(EECD)	0. 2	25	1.2593	68.78	0.6878
		35	1.6474	65.19	0.6519
		45	2.5220	54.71	0.5471
		55	3.4016	49.54	0.4954
		65	4.9033	36.02	0.3602
	0.5	25	0.7762	80.75	0.8075
		35	0.9847	79.19	0.7919
		45	1.4135	74.62	0.7462
		55	2.1152	55.74	0.5574
		65	3.3915	66.12	0.6612
	1	25	0.3288	91.84	0.9184
		35	0.6457	86.35	0.8635
		45	0.9118	83.62	0.8362
		55	1.5101	77.60	0.7760

	65	2.5965	66.12	0.6612
1.5	25	0.3067	92.39	0.9239
	35	0.5186	89.04	0.8904
	45	0.8169	85.33	0.8533
	55	1.1508	82.93	0.8293
	65	1.7474	77.20	0.7720
2	25	0.2067	94.87	0.9487
	35	0.4372	90.76	0.9076
	45	0.6203	88.86	0.8886
	55	0.9559	85.82	0.8582
	65	1.5677	79.54	0.7954

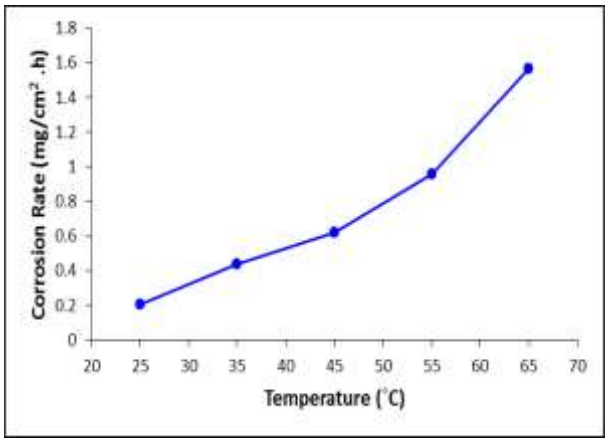

Fig.4. Variation of corrosion rate of mild steel in 1M HCl with temperature range (25 – 65) °C for 3 h immersion (for optimum concentration).

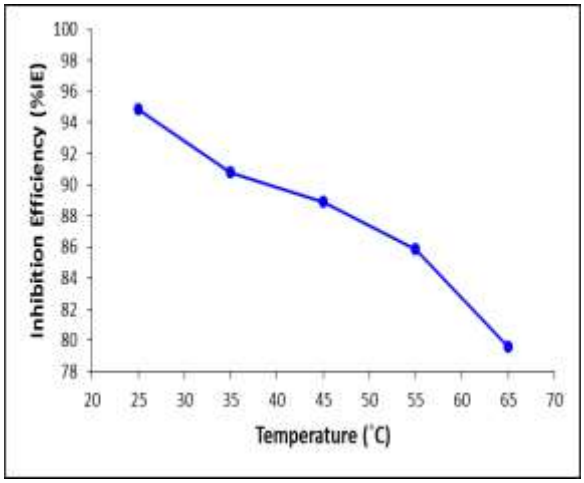

Fig.5. Variation of inhibition efficiency with the increase in the temperature on mild steel surface in 1M HCl at the optimum concentration of inhibitors (2 g/L) for 3 h immersion.

3.4 Thermodynamic Functions of the Adsorption Process

The constant of adsorption (K_{ads}) is related to the standard free energy of adsorption (ΔG^{o}_{ads}) in kJ mol^{-1} with the following equation [20, 21]:

$$\Delta G^{o}_{ads} = -R\ T\ Ln\ (C_{H2O}\ .\ K_{ads}) \quad (5)$$

The adsorption heat (ΔH^{o}_{ads}) and entropy (ΔS^{o}_{ads}) were calculated by using the thermodynamic basic equation [22, 23]:

$$\Delta G^{o}_{ads} = \Delta H^{o}_{ads} - T\Delta S^{o}_{ads} \quad (6)$$

Fig. 6 shows the variation in ΔG^{o}_{ads} versus T. A straight line was obtained. The slope yielded ΔS^{o}_{ads}, and the intercept led to ΔH^{o}_{ads}. All values of the thermodynamic parameters for the adsorption of EECD are listed in Table 3. These values provide valuable information about the mechanism of corrosion inhibition. The negative value of ΔG^{o}_{ads} suggested that the adsorption of inhibitor molecules on the mild steel surface was spontaneous. In general, the values of ΔG^{o}_{ads} up to −20 kJ mol^{-1} were consistent with the electrostatic interaction between the charged molecules and charged metal (physical adsorption), whereas those more negative than −40 kJ mol^{-1} involved sharing or charge transfer to form a coordinate bond (chemisorption) [24, 25]. In the present study, the ΔG^{o}_{ads} value for EECD was approximately −20 kJ mol^{-1}, indicating that the

adsorption mechanism of EECD on the mild steel surface in 1 M HCl solution was typical of physisorption.

Endothermic adsorption ($\Delta H^{o}_{ads} > 0$) can be attributed unequivocally to chemisorption, whereas exothermic adsorption ($\Delta H^{o}_{ads} < 0$) may involve either physisorption or chemisorption or a mixture of both processes [26, 27]. In the present study, the negative value obtained may introduce both chemisorption and physisorption processes. The negative value of ΔH^{o}_{ads} showed that the adsorption was exothermal with an ordered phenomenon ascribed by the negative values of ΔS^{o}_{ads}. This order may probably be explained by the possible formation of iron complex on the metal surface [28].

Table 3: Thermodynamic parameters for the adsorption of (EECD) on mild steel surface in 1M HCl at different temperatures.

Additives	Temp. °C	K_{ads} (L/g)	ΔG^{o}_{ads} (kJ mol^{-1})	ΔH^{o}_{ads} (kJ mol^{-1})	ΔS^{o}_{ads} (kJ mol^{-1} K^{-1})
(EECD)	25	10.2040	-22.8706	-27.887	-0.0168
	35	9.8522	-23.5483		-0.0140
	45	6.7069	-23.2960		-0.0144
	55	5.0684	-23.2647		-0.0140
	65	2.7457	-22.2513		-0.0166

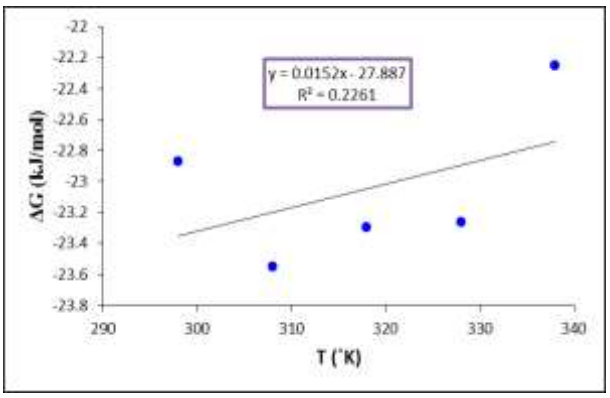

Fig. 6. The variation of ΔG^{o}_{ads} versus T.

3.5 Thermodynamic Activation Functions of the Corrosion Process

The adsorption phenomenon was successfully explained by thermodynamic parameters to further elucidate the inhibition properties of EECD. The kinetic model is also a useful tool to explain the mechanism by which EECD inhibits corrosion. The activation parameters for the corrosion process were calculated from Arrhenius equation [29, 30]:

$$W = A \exp\left(-\frac{Ea}{RT}\right) \qquad (7)$$

where E_a represents the apparent activation energy, R is the gas constant, A is the pre-exponential factor, and W is the corrosion rate obtained from the weight loss method.

Arrhenius plots for the corrosion rate of the mild steel are shown in Fig. 7. The E_a values for mild steel in 1 M HCl with EECD at different concentrations were calculated by linear regression between LnW and 1/T. The calculation results are shown in Table 4.

An alternative formulation of Arrhenius equation is [31, 32]

$$W = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S^{\circ}}{R}\right) \exp\left(\frac{-\Delta H^{\circ}}{RT}\right) \qquad (8)$$

where h is Plank's constant, N is Avogadro's number, R is the universal gas constant, ΔH°_{a} is the enthalpy of the activation, and ΔS°_{a} is the entropy of the activation.

Fig. 8 shows the plot of Ln (W/T) against 1/T. Straight lines were obtained with a slope of $-\Delta H^{\circ}_{a}/R$ and an intercept of $\mathrm{Ln}(R/Nh) + (\Delta S^{\circ}a/R)$ from which the values of ΔH°_{a} and

ΔS°_{a} were calculated. The calculation results are listed in Table 4.

As shown in Table 4, E_a and ΔH°_{a} varied in the same manner. The values of E_a were higher in the inhibited solutions than in the uninhibited solutions (13.6075 kJ mol^{-1}). In addition, the values of E_a increased as the inhibitor concentration increased from 0.2 g/L to 2 g/L (the increase in E_a decelerated the corrosion rate of the mild steel) [33].

The positive values of ΔH°_{a} reflected the endothermic nature of mild steel dissolution. The values of ΔS°_{a} were higher in the inhibited solutions than in the uninhibited solutions. This result suggested that an increase in randomness occurred from the reactant to the activated complex [11, 33].

Table 4: Activation parameters for the dissolution of mild steel in 1M HCl with different concentrations of (EECD).

Additives	Conc. (g/L)	E_a (kJ mol^{-1})	ΔH°_{a} (kJ mol^{-1})	ΔS°_{a} (kJ$mol^{-1}K^{-1}$)	$E_a - \Delta H^{\circ}_{a}$
Blank	0.0	13.6075	10.9919	-195.5521	2.61
(EECD)	0. 2	28.5710	25.9546	-156.3979	2.61
	0.5	30.7135	28.1013	-153.6751	2.61
	1	41.4128	38.7989	-123.9043	2.61
	1.5	35.5864	32.9724	-143.9943	2.61
	2	40.2563	37.6416	-131.2032	2.61

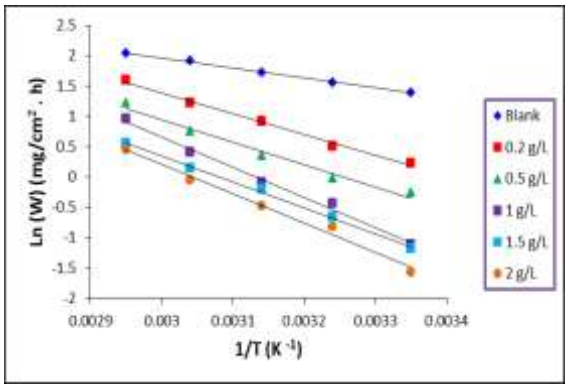

Fig. 7: Arrhenius plots of LnW versus 1/T for mild steel in 1M HCl solution with (EECD) at different concentrations.

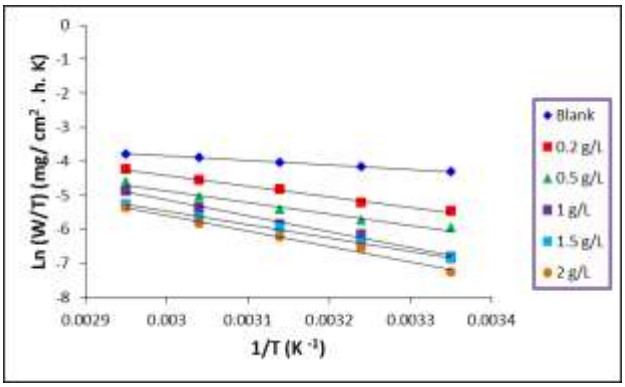

Fig. 8: Arrhenius plots of Ln (W/T) versus 1/T for mild steel in 1M HCl solution with (EECD) at different concentrations.

4. Conclusions

The following results can be drawn from this study:

1) EECD was a highly efficient inhibitor for mild steel in 1 M HCl solution, obtaining the highest inhibition efficiency of 94.87% at 2 g/L and 25 °C.

2) The inhibition efficiency increased with increasing EECD concentration and decreased with increasing temperature.

3) EECD was an adsorptive inhibitor, and its adsorption followed the Langmuir adsorption isotherm.

4) Thermodynamic adsorption parameters, such as ΔG^{o}_{ads}, ΔH^{o}_{ads}, and ΔS^{o}_{ads}, showed that EECD was adsorbed by a spontaneous exothermic process. In addition, a physisorption process can be suggested for the inhibitor.

5) EECD is an excellent, eco-friendly, and affordable corrosion inhibitor for mild steel coupons in 1 M HCl solution. Thus, EECD can

be used to replace toxic and expensive chemicals.

References

[1] M. Dahmani, A. Et – Touhami, S. S. Al – Deyab, B. Hammouti and A. Bouyanzer, "Corrosion inhibition of C38 steel in 1M HCl: a comparative study of black pepper extract and its isolated piperine" Int. J. Electrochem. Sci. 5, pp. 1060 – 1069, (2010).

[2] M. A. Amin, S. S. Abd El – Rehim, E. E. El – Sherbini and R. S. Bayoumi," The inhibition of low carbon steel corrosion in hydrochloric acid solutions by succinicacid part I. weight loss, polarization, EIS, PZC, EDX and ESM studies" Electrochim. Acta 52 ,pp. 3588 – 3599, (2007).

[3] J. Cruz, R. Martinez, J. Genesca and E. Garcia – Ochoa, "Experimental and theoretical study of 1 – (2 – ethylamino) – methylimidazoline as an inhibitor of carbon steel corrosion in acid media" J. Electroanalytical Chemistry 566 ,pp. 111 – 121, (2004).

[4] H. Ashassi – Sorkhabi and E. Asghari," Effect of hydrodynamic conditions on the inhibition performance of L – methionine as "green" inhibitor" Electrochim. Acta 54 ,pp. 162 – 167, (2008).

[5] A. S. Fouda and H. El – Dafrawy," Inhibitive effect of some pyrimidine derivatives on the cycle stressed specimens of stainless steel type 304 in acidic media" Int. J. Electrochem. Sci. 2 ,pp. 721 – 733, (2007).

[6] N. O. Eddy, S. A. Odemelam and A. O. Odiongenyi, "Ethanol extract of musa acuminate peel as an eco – friendly inhibitor for the corrosion of mild steel in H_2SO_4 " Advanced in Natural and Applied Sciences 2 ,pp. 35 – 42, (2008).

[7] J. Morris Princy, J. Christyezhilarasi, D. Kavitha and N. Sulochana," Natural product extract as eco – friendly corrosion inhibitor for commercial mild steel in 1M HCl – part II" J. Ind. Council Chem. 26 ,pp. 153 – 157, (2009).

[8] U. Garg and R. K. Tak," Inhibition of the corrosion of mild steel in acid media by naturally occurring acacia Senegal" E – Journal of Chemistry 7 ,pp. 1220 – 1229, (2010).

[9] M. Lebrini, F. Robert and C. Roos, "Alkaloids extract from palicourea guianensis plants as corrosion inhibitor for C38 steel in 1M hydrochloric acid medium" Int. J. Electrochem. Sci.6 ,pp. 847 – 859, (2011).

[10] P. Bothi and M. Gopolakrishnan, "Solanum tuberosum as an inhibitor of mild steel corrosion in acid media," Iran. J. Chem. Eng. 28 ,pp. 77 – 84, (2009).

[11] M. Abdallah, M. Al – Ages and S. A. Fouda, "Phenyl hydrazone derivatives as corrosion inhibitors for α – brass in hydrochloric acid solutions", Int. J. Electrochem. Sci. 14 ,pp. 336 – 352 (2009).

[12] A. O. James and O. Akaranta, "Corrosion inhibition of aluminum in 2 M hydrochloric acid solution by the acetone extract of red onion skin" African J. Pure and Applied Chemistry 3 ,pp. 262 – 168, (2009).

[13] N. O. Eddy, S. A. Odoemelam and A. J. Mbaba, "Inhibition of the corrosion of mild steel in HCl by sparfloxacin" African J. Pure and Applied Chemistry 2 ,pp. 132 – 138, (2008).

[14] S. M. Milic and M. M. Antonijevic, "Some aspect of copper corrosion in presence of benzotriazole and chloride ions" Corrosion Science 51 ,pp. 28 – 34,(2009).

[15] D. Zhang, Q. Cai, X. He, L. Gao and G. Kim, "The corrosion inhibition of copper in hydrochloric acid solutions by a tripeptide compound" Corrosion Science 51 ,pp. 2349 – 2354, (2009).

[16] Q. Qu, Z. Hao, L. Li, W. Bai, Y. Liu and Z. Ding," Synthethesis and evaluation of trishydroxymethyl – (2 – hydroxybenzylidenamino) – (methan as a corrosion inhibitor for colled rolled steel in hydrochloric acid" Corrosion Science 51 ,pp. 569 – 574, (2009).

[17] G. Lewist, "The corrosion inhibition of copper by benzimidazole" Corrosion Science 22 ,pp. 579 – 584, (1982).

[18] M. Amin, S. Abd El – Rehim, E. El- Sherbini And R. Bayoumi, "Chemical and Electrochemical (AC and DC) Studies on the corrosion inhibition of low carbon steel in 1.0 m Hcl solution by succinic acid – temperature effect, activation energies and thermodynamics of adsorption" Int. J. Electrochem. Sci. 3 ,pp. 199 – 215, (2010).

[19] A. Sultan, A. Ateik, A. Abduallah and A. Al – Mowali, "Ziziphus leaves extract as corrosion inhibitor for mild steel in 3.5 M NaCl" The Iraqi Journal for Mechanical and Material Engineering, special issue (A), pp. 75 – 82, (2010).

[20] J. Aljourani, K. Raeissi and M. Golozar, "Benzimidazole and it's derivatives as corrosion inhibitors for mild steel in 1M HCl solution" Corrosion Science 51,pp. 1836 – 1843, (2009).

[21] A. Elbribri, M. Tabyaoui, H. El Attari, K. Boumhara, M. Simiti and B. Tabyaoui, "Temperature effects on the corrosion inhibition of carbon steel in 1M HCl solution by methanolic extract of euphorbia falcate" L, Mater. Environ. Sci. 2,pp.156 – 165, (2011).

[22] G. Quartarone, M. Battilana, L. Bonaldo and T. Tortato, "Investigation of the inhibition effect of indole – 3 carboxylic acid on the copper corrosion in 0.5M H_2SO_4" Corrosion Science 50 ,pp. 3467 – 3474, (2008).

[23] A. M. Badiea and K. N. Mohana, "Effect of temperature and fluid velocity on corrosion mechanism of low carbon steel in presence of 2 – hydrazine – 4,7 – dimethylbenzothiazole in industrial water" Corrosion Science 51 ,pp. 2231 – 2241, (2009).

[24] L. Herrag, A. Chetouani, S. Elkadiri, B. Hammouti and A. Aouniti, "Pyrazole derivatives as corrosion inhibitors for steel in hydrochloric acid" Portugaliae Electrochimica Acta 26 ,pp. 211 – 220, (2008).

[25] S. Kumar and M. Quraishi, "Cefotaxime sodium: a new and efficient corrosion inhibitor for mild steel in hydrochloric acid solution" Corrosion Science 51 ,pp.1007 – 1011, (2009).

[26] S. Zhang, Z. Tao, W. Li and B. Hou, "The effect of some triazole derivatives as inhibitors for the corrosion of mild steel in1M hydrochloric acid" Applies Surface Science 255 ,pp. 6757 – 6763, (2009).

[27] G. Gao and C. Hao, "1,3 – bis – diethylamino – propan – 2 ol as volatile corrosion inhibitor for brass" Corrosion Science 49 ,pp. 3479 – 3493, (2007).

[28] E. Ebenso, H. Alemu, S. Umoren and I. Obot, "Inhibition of mild steel corrosion in sulphuric acid using alizarin yellow gg dye and synergistic iodide additives" Int. J. Electrochem. Sci. 3 ,pp. 1325 – 1339, (2008).

[29] K. M. Mohana and A. M. Badiea, "Effect of sodium nitrite – borax blend on the corrosion rate of low carbon steel in industrial water medium" Corrosion Science 50 ,pp. 2939 – 2947, (2008).

[30] S. A. Refaey, F. Taha and A. M. Abd El – Malak, "Corrosion and inhibition of 316 L stainless steel in neutral media by 2 – mercaptobenzimidazole" Int. J. Electrochem. Sci. 1 ,pp. 80 – 91, (2006).

[31] L. Larabi, O. Benali and Y. Harek, "Corrosion inhibition of copper in 1 M HNO_3 solution by n – phenyl oxalic dihydrazide and oxalic n- phenylhydrazide n - phenylthiosemicarbazide" Portugaliae Electrochimica Acta 24 ,pp. 337 – 346, (2006).

[32] F. S. De Souza and A. Spinelli, "Caffeic acid as a green corrosion inhibitor for mild steel" Corrosion Science 51 ,pp. 642 – 649, (2009).

[33] F. Bentiss, M. Lebrini and M. Lagrenee, "Thermodynamic characterization of metal dissolution and inhibitor adsoirption processes in mild steel / 2,5 – bis(n – thienyl) – 1,3,4, thiadiazole / hydrochloric acid system" Corrosion Science 47 ,pp. 2915 – 2931, (2005).