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Effect of Some Natural Products on the Corrosion Behavior of Mild Steel Exposed to 1.0m Hydrochloric Acid

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ABSTRACT

The effect of some natural product extracts (Punica Granatum Peel PG, Solenostemma Argel SA, Olibanum O, Datura Seeds DS and Datura Leaves DL) on the corrosion behavior of mild steel in 1.0M HCl was studied by electrochemical techniques (open–circuit potential, linear polarization resistance and Tafel plots polarization). It is clear, these extracts give inhibition in both anodic and cathodic slopes in Tafel polarization, that indicate these inhibitors used as mixed-type inhibitor. The thermodynamic adsorption isotherm was studied and falls into Langmuir isotherm indicating physisorption isotherm behavior. In addition, the surface morphology of mild steel samples without and with the inhibitors was examined using scanning electron microscopy.

Introduction

Corrosion [1] is a surface phenomenon known as the attack of metals or alloys by their environment as air, water or soil in chemical or electrochemical reaction to form more stable compounds. In some industries, mild steel is the material that is chosen in the storage tanks, fabrication of reaction vessel that corroded easily in the presence of acids. Acids used for remove scale, polishing and remove any deposits presented on the surface of metal and gives it cleaned surface, then, organic inhibitors that involve heterocyclic atoms (N, O, S and P) used for protect or minimize the cleaned surface from the attack of acids used [2]. A number of organic and synthetic compounds showed a good anticorrosive activity and most of them are extremely toxic to both human and environmental. These toxic affection has led to the utilization of natural products as anticorrosion agents which are eco-friendly and harmless. Lately, the researchers in the corrosion field have faced their studies for obtaining on eco-friendly inhibitors, which, safety, cheap and easy to obtain by simple methods of origin. Plants as green inhibitors are one of the important eco-friendly inhibitors, which have adopted the most works of researchers because plants have naturally synthesized chemical compounds that are acceptable environmentally [3-7]. Plant extracts [8], dried stems, leaves, seeds and other plants used in H_2SO_4 acid pickling baths. Animal proteins found in products of meat and milk industries used for retarding acid corrosion. The additives [8] used in acid, included flour, bran, yeast, a mixture molasses and vegetable oil, starch and hydrocarbons (tars and oils) are used as corrosion inhibitors. Recently began to consider the application of extracts of some common plant as a corrosion inhibitors as Onion, Garlic [9], Thyme [10] and Ginger [11] for mild steel in acid media. These extracts contain different hydroxyl organic, and nitrogen bearing compounds. The extraction of natural products Punica Granatum Peel involves (Tannins, Punicalin which known as Grananatine D, Punicalagen which known as C Grananatine, alkaloids such as Isopelletierine, N-Methylisopelletierine and Pseudopelletierine) [12], and it contains as much as three times the total amount of polyphenols [13], including condensed tannins [14], catechins, gallocatechins and prodelphinidins [15]. Solenostemma Argel involves Pollenium, Glipcosydes, and volatile oil Vlavonedaties such as (Campherol, Keristrine, Tannins, Cardinolates and some of antibiotic compounds and Argelosides and Kaempferol Glycosides [16-18]. Olibanum involves cortisones in large quantity, acidic resin (56%) soluble in alcohol and having the formula $C_{20}H_{32}O_4$, gum (similar to gum Arabic) 30–36%, Phellandrene [19], 3-acetyl-beta-boswellic acid (Boswellia sacra), alpha-boswellic acid (Boswellia sacra), 4-O-methyl-glucuronic acid (Boswellia sacra), incensole acetate [20]. Datura Seeds and Datura Leaves involve (alkaloids such as (Haeociamine, Haeocine, and Attribene), proteins and fatty compounds [21].

The aim of this study was to investigate the inhibitory effect of (Punica Granatum Peel (PG), Solenostemma Argel (SA), Olibanum (O), Datura Seeds (DS) and Datura Leaves (DL)) as a cheap, easily preparation, eco-friendly environmental and non-toxic on mild steel corrosion in 1.0 M hydrochloric acid. The electrochemical measurements were used to evaluate the inhibition efficiencies.

Experimental research methods

Preparation of Natural Products Extracts and Corrosives Media

An aqueous extract solution prepared by reflux 10 g of (Punica granatum PG, Solenostemma Argel SA, Olibanum O, Datura seeds DS and Datura leaves DL) in 100 ml of double distilled water for approximately 1 hour. The obtained was filtered to remove any contaminations. 1 ml of this filtrate evaporated up dryness and the residue was weighted [22]. Finally, 1.0M HCl solution was prepared as corrosive media by analytical method. Fig 1 illustrates the photographic shapes of the natural products used in this study

Characterization of Natural Products (PG, SA, O, DS and DL)

The solid plant extracts of PG, SA, O, DS and DL characterized by Fourier transform infrared (FTIR) spectroscopy. FTIR spectrum recorded in Jasco-FTIR-480 plus (Japan) which extended from 4000 to 400 cm^{-1}, using the KBr

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disk technique. The active substances and medical uses of the natural products, which used in this work, presented in the Table 1.

Preparation of test specimens and determination of properties

The mild steel specimens tested in the present paper were in the sheet form, supplied by the AL - EZZ Company in Alexandria, Egypt. The designation and analysis of the material by weight % is (C 0.175, Si 0.130, Mn 0.534, P 0.008, S 0.0094, Cr 0.0117, Mo 0.002, Ni 0.0188, Al 0.005, Co 0.0075, Cu 0.0047, Nb 0.003, Ti 0.002, V 0.005, W 0.172 and Fe 98.9). Prior immersion MS electrodes in the tested solutions were prepared by polishing with SiC paper up to 1200 grade, washing with distilled water and then Sterilization with alcohol about 5 minutes, washed again with distilled water then dried it using filter papers.

Electrochemical Cell (Corrosion Cell)

The corrosion cell used in potentiodynamic polarization involving three electrodes, mild steel as working electrode, Saturated Calomel Electrode (SCE) as reference electrode and a platinum wire used as counter electrode. The exposed area of working electrode to solutions was $1cm^2$.

Adopted Techniques and other calculations

The major electrochemical techniques used in this study were open circuit potential (OCP) and Potentiodynamic polarizations (linear polarization resistance (LPR) and Tafel plots polarizations (TP)) which carried out with model 352/252 corrosion measurement system, which consists of EG & G potentiostat/galvanostat model 273A driven by software from IBM computer. Measurements of polarization curves started after passed the immersed period (2hrs, 1 day, 2 days and 4 days) of mild steel electrodes for along 30 minutes to obtain on the steady state potential. The LPR measured from +20 mV up to -20 mV vs. E_{corr} and the TP measured from -250 mV up to +250 mV vs. E_{corr}. The scan rate for LPR and TP measurements were 0.166 mV/S and 0.3mV/S, respectively.

Fig (1). photographic shapes of natural products used in this study

Results and Discussion

FTIR of PG, SA, O, DS and DL

The data of absorption bands of PG, SA, O, DS and DL are listed in Table 2.

Open –Circuit Potential (OCP) Measurements

Fig. (2) shows the potential-time curves for mild steel exposed to 1.0 M HCl without and with different concentrations of (PG, SA, O, DS and DL) at exposure time 4 days (as it is the best exposure time). It is clear from these curves the steady state potential ($E_{s.s}$) for blank solutions curves shift to slightly negative direction than immersion potential (E_{im}) through the immersion times from 2hrs to 2 days but at 4 days $E_{s.s}$ shift to slightly positive potential than initial measuring potential (immersion time is the intial reading potential from measuring instrument after passed the tested period of time). On the other hand, at addition, concentrations of natural products extract to blank solution at mild steel electrode, $E_{s.s}$ shift to more noble direction than blank solutions which attributed to adsorption of inhibitor molecules on the active anodic and cathodic sites on the surface of mild steel. The data listed in Table 3 illustrated the values of $E_{s.s}$ and E_{im} for mild dteel electrode in corrosive media at addition the inhibitors at different exposure times and these data emphasize that $E_{s.s}$ shift to more positive direction than blank solutions, which attributed to blocking of the active sites on the anodic and cathodic reactions on the surface of metal.

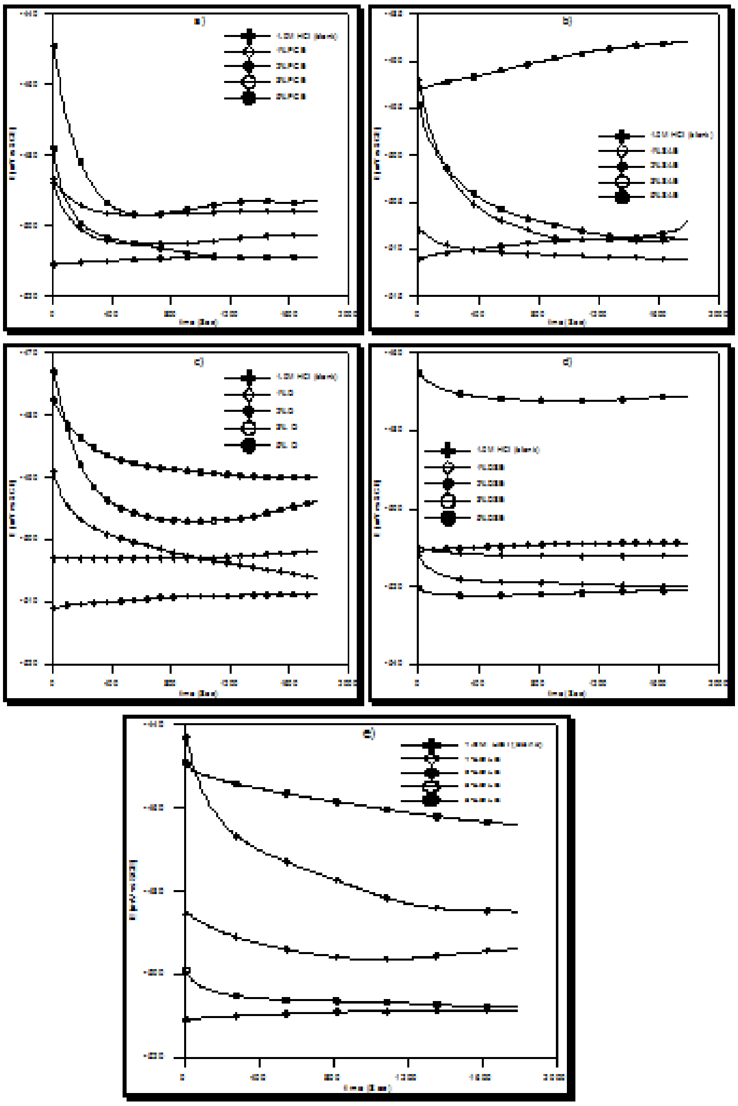

Fig (2). Potential-time curves for mild steel in 1.0M HCl at different concentrations of natural product extracts after exposure time 4days

Rate of Oxide Film Thickening

Abd El-Kader J.M. and A.M. Shams El-Din [23] have a theory of film thickening of the surface of metal and alloy based on OCP measurements. The essence of the theory is based on the idea that the potential is determined by simultaneous anodic (film formation) and cathodic (oxygen reduction) couple, in which the anodic reaction is the rate limiting. By representing the information in the form of potential–log (time) curves, straight lines were obtained satisfying the equation (1) [23]

$E = \text{constant} + 2.303\ (\delta / \beta) \log t$ ……………………… (1)

Where (E) electrode potential with respect to a saturated calomel electrode, (t) is the time from the moment of immersion in solution, δ is the rate of oxide film thickening per decade of time and β is given by equation (2):

$\beta = (nF / RT)\ \alpha\ \delta^{-}$…………………………………… (2)

Where (α) is a transference coefficient similar to that found in electrochemical kinetic rate expressions ($0.0 < \alpha < 1$), and (δ^{-}) is the width of the activation energy barrier to be traversed by the ion during oxide formation. The theory was utilized in the cases of oxide growth on nickel, titanium [24]; Fe-Cr alloys [25], and molybdenum steels [26].

It is apparent from the intercourse between the potential of the mild steel electrode versus the log of the immersion time until $E_{s.s}$ is confirmed (formation of oxide film on the surface of mild steel). This behaviour understood when one takes into consideration the physical properties of iron oxides, covering the metal surface. Consideration of the value of (δ^{-}) in Table 4 allows the following conclusion to be drawn:

(a) The rate of oxide film thickening (δ) for mild steel in 1.0M HCl solution at different exposure times varied between (0.025-0.242nm/log t).

(b) The rate of oxide film thickening for mild steel immersed in different concentrations of testing inhibitors at different times of exposure varied between (0.004 – 0.820 nm/log t).

Potentiodynamic Polarization Measurements (linear and Tafel polarization)

Tafel plot polarization (TFP) or the anodic and cathodic polarization curves of mild steel in 1.0 M HCl solution without and with different concentrations of extracts (PG, SA, O, DS and DL) at exposure time 4 days (as it is the best exposure time where it gives highest inhibition efficiencies) are shown in Fig. (3). It was observed that both anodic and cathodic curves showed lower current density in the presence of inhibitor extract concentrations than those observed in solution without the inhibitor (blank solution). This indicates that inhibitors extracts retard or decrease corrosion process. The results shown in Fig. (3) also suggested that the studied inhibitors extracts affected on both anodic and cathodic corrosion processes, hence it reveals properties of a mixed-type inhibitor. The electrochemical parameters, i.e. Corrosion current density (I_{corr}), Tafel constants (anodic (β_a) and cathodic (β_c)), polarization resistance (R_P), corrosion rate (CR) and the inhibition efficiency (IE%) are listed in Tables 5 and 6. It is clear, that concentration of inhibitor has a varied influence on the values of both β_a and β_c of Tafel slopes indicating that inhibitor may change the mechanism of anodic and cathodic reactions and may regard the process of anodic dissolution. The data clearly indicate that the I_{corr} values decreased and R_P values increased in the presence of testing inhibitors extracts at various concentrations as expected. Referable to the inverse relationship between I_{corr} and R_P, with increasing concentration of the inhibitor, it can be taken for granted that the adsorption of the inhibitor molecules on metal surface makes a physical barrier to the mass and charge transfer, providing a high degree of protection to the metal surface. IE% values of mild steel in 1.0 M HCl solution containing different concentrations of inhibitor extracts were calculated from the Tafel plots polarization by I_{corr} data as using equation 3:

$IE\% = (I_{corr\,(uninh)} - I_{corr\,inhib.} / I_{corr\,(uninh)}) \times 100$ ……………..(3)

Where $I_{corr\,(uninh.)}$ and $I_{corr\,(inh.)}$ are the corrosion current density without and with inhibitor presence, respectively.

From the results we note, as the inhibitors extracts concentrations increase the R_P of metal corrosion increase, the CR decrease and the IE% increase that attributed to the adsorption of inhibitor molecules on the participating sites of the surface of mild steel electrode. We can concluded that the sequence of corrosive media used in this study effected at the presence of inhibitors extracts at 2 hrs, 1 day, 2 days and 4 days was arranged as (DLE (39.61%–58.51%) > DSE (37.87%–53.57%) > SAE (33.87%–51.84%) > PGE (33.18%–41.81%) > OE (17.77%–37.56%), DLE (83.48%–90.09%) > OE (73.93%–88.42%) > DSE (82.15%–86.62%) > SAE (72.96%–86.00%) > PGE (80.19%–83.72%), DLE (87.58%–97.15%) > DSE (89.48% –96.88%) > PGE (88.55%–94.21%) > SAE (82.24%–92.79%) > OE (83.82%–91.35%) and SAE (91.25%–99.71%) > DLE (90.80%–98.55%) > PGE (91.48%–98.40%) > DSE (92.40%–98.21%) > OE (91.35%–95.20%), respectively.

Fig. (4) shows time depedance of immersion times against corrosion rate CR, inhibition efficiency IE% and resistance polarization R_p, it reveals as the immersion time increase from 2 hrs to 96 hrs the R_p for corrosion metal in the tested solutions of natural product extracts increases that follows the CR of metal decreases and IE% increases to reach 99.71% for SAE at immersion time 4 days.

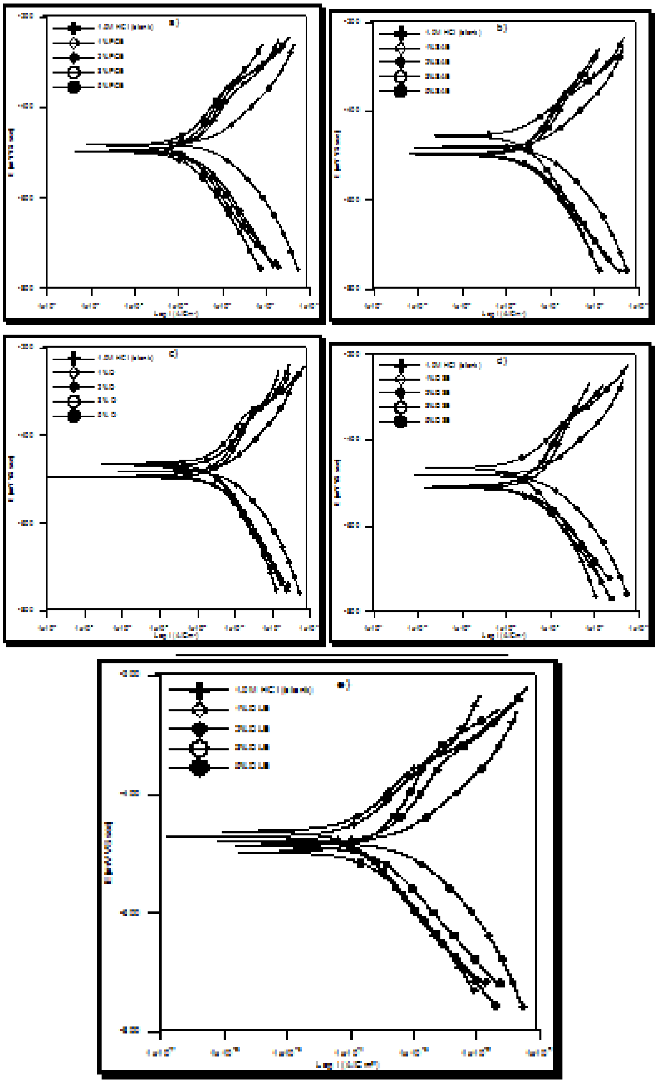

Fig (3). Tafel plots polarization curves of mild steel in 1.0M HCl at different concentrations of natural products extracts after exposure time 4days

Table (1). Active substances and its medical application of natural products used in this study.

Scientific name	Active substances	Medical applications
Punica Granatum peel PG	PG peel contains glycosides, alkaloids, tannins, phenols, resine, saponins, terpenes, coumarines and Filavovidat. Where the percentage of organic material (25% - 28% tannins) .oahm compound in this chemical group compound, (Punicalin) which is known as GrananatineD) and Bionakallagen compound whic h is known as rananatine (GG), and it contains as much as three times the total amount of polyphenols, including condensed tannins, catechins, gallocatechins and prodelphinidins.	Treatment of the following diseases: 1) Gastric ulcer 2) Tonsillitis 3) Excessive sweating all over the body 4) Haemorrhoids 5) Worms
Solenostemma argel SA	SA involves Pollenium, Glipcosydes, and volatile oil Vlavonedaties such as (Campherol, Keristrine, Tannins, Cardinolates and some of antibiotic compounds and Argelosides and Kaempferol Glycosides.	Treatment of the following diseases: 1) The kidneys and liver 2) Sensitivity, special sensitivity of chest diseases trachea 3) Colic, intestinal diseases and cases of colds and infections of the urinary channel 4) Neurology 5) Stomach cancer
Olibanum O	O involves cortisones in large quantity, acidic resin (56%) soluble in alcohol and having the formula $C_{20}H_{32}O_4$, gum (similar to gum Arabic) 30–36%, Phellandrene, 3-acetyl-beta-boswellic acid (Boswellia sacra), alpha-boswellic acid (Boswellia sacra), 4-O-methyl-glucuronic acid (Boswellia sacra), incensole acetate.	Treatment of the following diseases: 1) Infections of the chest, throat, cough and expel phlegm 2) The stomach, indigestion and inflammatory bowel 3) Leukaemia 4) Heart Disorders 5) Kidney weakness and wasting
Datura seeds DS & Datura leaves DL	DS & DL involve (alkaloids such as (Haeociamine, Haeocine and Attribene), proteins and fatty compoun ds.	Treatment of the following diseases: 1)asthma 2) antispasmodic 3) pain relief (hypnotic) are also used in Expansion of the eye pupil and stimulant for the central nervous system

Table (2). FTIR transmittance spectra of (PG, SA, O, DS and DL) and their identification

Natural products	Peaks from FT-IR spectra	Possible groups
PG	1363	C–N stretch
	1508	aromatic–C═C–stretch
	1617.6	–C═N–
	1735.19	›C═O ester
	2928.8	CH- aliphatic
	3389	-NH or -OH gp. stretch
SA	1051	-OH gp. stretch
	1321.8	C–N stretch
	1441.1	–C–N–H–bend
	1655.5	–C═N–
	2922.9	CH- aliphatic
	3400.8	-NH gp. stretch
O	666.8	≡ CH- bending
	1039.5	-OH gp. stretch
	1241.5	–O–SO_2–O–
	1377.7	C–N stretch
	1456.8	–C–N–H–bend
	1740	›C═O ester
	2923.4	CH- aliphatic
	3431	-NH gp. stretch
DS	722.7	≡ CH- bending
	1372.9	C–N stretch
	1463	–C–N–H–bend
	1650.9	–C═N–
	1746	›C═O ester
	2925.7	CH- aliphatic
	3009	CH-aromatic
	3403	-NH gp. stretch
DL	1077.4	-OH gp. stretch
	1325	C–N stretch
	1647	C═N– or C═C–
	2928	CH- aliphatic
	3386	-NH or –OH gp. stretch

Table (3). Values of E_{im} and $E_{s.s}$ (mV) for mild steel in 1.0M HCl and different concentrations of natural product extracts at different exposure times

Test Solution	C V/V%	2hr		1day		2days		4days	
		$-E_{im}$	$-E_{s.s}$	$-E_{im}$	$-E_{s.s}$	$-E_{im}$	$-E_{s.s}$	$-E_{im}$	$-E_{s.s}$
HCl	1.0M	510	513	502	506	490	504	511	509
PG	1	478	498	510	497	506	509	486.6	496
	2	455	476	465	486	492	503	488	503
	3	479	489	518	523	492	496	449	493
	5	470	486	485	499	491.7	491	478	509
SA	1	456	486	432.3	462	508	509.1	508	511
	2	464	475	490	490	472	485	492	509
	3	476	488	445.1	490.1	480	510	494	508.7
	5	457	483	475.5	486	468	504	492	488
O	1	470	502	500	489	477.9	495.5	503	502
	2	484	503	483	500	489	506	489	506
	3	489	499	498	502	510	490	473	494
	5	463	481	483	495	496	498	477	490
DS	1	435	486	503	504	513	511	510	512.3
	2	439	481	499.3	513.8	519.1	515	512	520
	3	482	511	466	498	510	524	520.5	521
	5	421	456	508	522	511.3	514.8	465.3	471
DL	1	439	475	480	498	415	487	443	485
	2	430	478	476	490	460	490	485	494
	3	441	478	454	491	483	480	499	508
	5	390	446	432	476	427	449	449	464

Table (4). Values of slopes of E (mV) vs. log t lines and the rate of oxide film thickening (δ^-) (nm\log t) for corresponding the mild steel in different concentrations of natural products extracts at 1.0M HCl.

Test solution	**C** V/V%	**Slope**				**Rate (nm/log t)δ^-**			
		2hrs	**1day**	**2days**	**4days**	**2hrs**	**1day**	**2days**	**4days**
HCl	1.0M	0.991	3.142	9.523	6.776	0.025	0.080	0.242	0.172
PGE	1	7.345	3.620	2.941	0.702	0.187	0.092	0.075	0.018
	2	10.366	16.158	4.782	11.701	0.264	0.411	0.122	0.298
	3	2.243	3.107	3.962	31.976	0.057	0.079	0.101	0.814
	5	6.895	8.162	0.466	17.628	0.175	0.208	0.012	0.449
SAE	1	12.755	6.778	1.439	1.570	0.325	0.172	0.037	0.040
	2	5.428	2.777	8.839	9.015	0.138	0.071	0.225	0.229
	3	3.223	24.081	14.251	6.151	0.082	0.613	0.363	0.157
	5	11.189	6.620	17.669	0.741	0.285	0.168	0.450	0.019
OE	1	11.273	3.596	12.723	1.331	0.287	0.092	0.324	0.034
	2	10.117	10.634	7.865	6.814	0.257	0.271	0.200	0.173
	3	3.519	2.006	13.583	14.961	0.090	0.051	0.346	0.381
	5	7.556	6.221	1.134	6.049	0.192	0.158	0.029	0.154
DSE	1	17.591	3.619	0.373	1.179	0.448	0.092	0.009	0.030
	2	9.376	16.158	0.868	4.335	0.239	0.411	0.022	0.110
	3	7.942	3.106	8.761	1.117	0.202	0.079	0.223	0.028
	5	15.062	8.1	2.920	3.830	0.383	0.208	0.074	0.097
DLE	1	12.755	5.15625	32.209	1.569	0.325	0.131	0.820	0.040
	2	5.428	7.847	19.272	9.015	0.138	0.200	0.490	0.229
	3	3.223	22.220	0.171	6.151	0.082	0.565	0.004	0.157
	5	11.189	15.953	11.942	0.741	0.285	0.406	0.304	0.019

Table (5). Polarization parameters for mild steel in 1.0M HCl at different concentrations of natural product extracts after exposure times 2hrs and 1 day

Tested Solution	C	R_P (Ω)	$ß_a$ mV\decade	$ß_c$ mV\decade	E_{corr}- (mV)	I_{corr} (µA/Cm^2)	C.R (may)	I.E (%)	Surface coverage(θ)
2hr									
HCl 1.0 M	------	44.13	122.2	100.6	487.3	213.1	196.49	-----	-----
PG	1	45.07	82.69	83.30	495.5	142.4	131.30	33.18	0.332
	2	47.1	106.4	123.1	470	131.1	120.88	38.48	0.385
	3	52.8	109.8	124.1	479.03	126.1	116.27	40.83	0.408
	5	63.5	102.3	113.2	470.1	124.0	114.33	41.81	0.418
SA	1	82.6	109.7	108.5	742.5	141.2	130.19	33.74	0.337
	2	93.0	107.7	122.9	476.7	132.4	122.08	37.87	0.379
	3	97.2	91.14	107.9	492.6	117.6	108.43	44.81	0.448
	5	101.0	98.05	115.36	474.5	102.62	94.62	51.84	0.518
O	1	45.22	113.2	123.4	494	175.24	161.58	17.77	0.178
	2	65.70	73.78	66.66	488.5	150.21	138.50	29.51	0.295
	3	90.19	93.35	114.1	484.2	142	130.93	33.36	0.334
	5	104.6	87.37	127.5	459.5	133.06	122.69	37.56	0.376
DS	1	47.08	114.5	139.5	467.7	132.4	122.08	37.87	0.379
	2	46.5	98.20	112.2	480.8	121.9	112.40	42.80	0.428
	3	51.3	62.23	66.33	465.5	103.7	95.62	51.34	0.513
	5	59.25	54.26	64.28	459	98.56	90.88	53.75	0.537
DL	1	68.90	103.4	117.8	464.6	128.7	118.67	39.61	0.396
	2	79.61	105	112.2	477.6	116.9	107.79	45.14	0.451
	3	141.4	87.12	104.4	469.7	102.9	94.88	51.71	0.517
	5	155.3	69.27	88.88	454	88.41	81.52	58.51	0.585
1day									
HCl 1.0 M	----	35.3	110.1	129.2	489	702	647.27	…...	....
PG	1	54.1	157.13	166.25	482	139.1	128.26	80.19	0.802
	2	58.1	114.13	119.6	490	125.2	115.44	82.17	0.822
	3	61.5	91.02	80.31	493.6	123.4	113.78	82.42	0.824
	5	75.7	119.4	127.3	566.5	114.3	105.39	83.72	0.837
SA	1	93.8	125.5	142.5	460	189.8	175.00	72.96	0.730
	2	111.3	50.7	51.56	471	125.0	115.25	82.19	0.822
	3	119.5	87.14	120.7	468.2	109.1	100.59	84.46	0.845
	5	125.4	39.19	41.49	471.3	98.31	90.65	86.00	0.860
O	1	50.20	98.60	135.9	462.2	183.02	168.75	73.93	0.739
	2	77.12	101.9	119.2	478.7	131.7	121.43	81.24	0.812
	3	99.30	70.85	59.32	492.4	116.0	106.96	83.48	0.835
	5	107.2	38.30	57.17	475	81.30	74.96	88.42	0.884
DS	1	48.1	42.33	47.58	489.1	125.32	115.55	82.15	0.821
	2	49.2	33.35	38.89	507.1	118.09	108.88	83.18	0.832
	3	55.7	116.9	123.1	460.5	99.73	91.95	85.79	0.858
	5	66.2	140.91	41.62	507.1	93.9	86.58	86.62	0.866
DL	1	106.3	82.40	73.17	486.4	116	106.96	83.48	0.835
	2	117.8	67.38	65.02	490.3	94.29	86.94	86.57	0.866
	3	157.2	104	107.2	483.5	87.1	80.31	87.59	0.876
	5	168.0	65.73	74.62	465.7	69.6	64.17	90.09	0.901

Table (6). Polarization parameters for mild steel in 1.0M HCl at different concentrations of natural products extracts after exposure times 2days and 4 days by using Tafel polarization method

Tested Solution	C	RP (Ω)	ßa mV\decade	ßc mV\decade	E_{corr}- (mV)	I_{corr} (μA/Cm^2)	C.R (may)	I.E (%)	Surface coverage (θ)
2 days									
HCl 1.0 M	----	28.26	103.8	142.4	467.2	890	820.61	------	-------
PG	1	70.2	108.82	116.50	784.5	101.9	93.96	88.55	0.886
	2	76.3	16.96	20.13	486.5	82.7	76.25	90.71	0.907
	3	77.7	37.31	24.40	490	58.25	53.71	93.46	0.935
	5	79.7	41.21	47.03	483	51.56	47.54	94.21	0.942
SA	1	108.03	102.50	158.07	493.2	158.07	145.75	82.24	0.822
	2	113.15	79.75	76.14	493.5	110.60	101.98	87.57	0.876
	3	127.1	69.37	74.23	503.1	91.95	84.78	89.67	0.897
	5	139.04	41.41	47.24	491.1	64.16	59.16	92.79	0.928
O	1	69.50	126.0	141	486.4	144.02	132.79	83.82	0.838
	2	85.02	47.6	47.96	476.9	120.2	110.83	86.49	0.865
	3	102.13	21.56	22.01	452.7	62.18	57.33	93.01	0.930
	5	114.23	25.62	24.03	480.7	76.97	70.97	91.35	0.914
DS	1	54.5	38.32	31.21	501.2	93.60	86.30	89.48	0.895
	2	57.2	21.72	25.13	486	64.90	59.84	92.71	0.927
	3	60.0	27.90	22.11	508.5	58.44	53.88	93.43	0.934
	5	89.02	15.58	17.06	508.9	27.75	25.59	96.88	0.969
DL	1	130.9	124.3	121.3	486.4	110.5	101.88	87.58	0.876
	2	149.02	59.72	56.98	491.6	80.21	73.96	90.99	0.910
	3	168.13	61.22	69.46	477.6	78.82	72.67	91.14	0.911
	5	174.05	18.19	19.89	459.5	25.33	23.36	97.15	0.972
4 days									
HCl 1.0 M	----	17.2	131.1	148.7	481	1122	1034.5	------	------
PG	1	78.3	53.15	34.32	494.2	95.58	88.13	91.48	0.915
	2	79.5	26.83	27.89	496.2	46.35	42.74	95.87	0.959
	3	82.35	27.15	13.37	483	24.1	22.22	97.85	0.979
	5	89.58	18.60	16.62	479.9	17.92	16.52	98.40	0.984
SA	1	141.7	51.79	46.71	499	98.17	90.52	91.25	0.913
	2	158.21	22.52	22.96	496.4	53.17	49.02	95.26	0.953
	3	175.5	20.13	21.41	499.3	48.74	44.94	95.66	0.957
	5	190.17	14.30	14.16	486.3	3.22	2.97	99.71	0.997
O	1	108.90	20.98	42.43	490	97.03	89.47	91.35	0.914
	2	119.30	16.41	18.42	496	80.55	74.27	92.82	0.928
	3	124.06	21.56	22.01	452.7	62.18	57.33	94.46	0.945
	5	135.11	25.86	31.30	464	53.82	49.62	95.20	0.952
DS	1	59.1	41.3	60.42	505.8	85.23	78.59	92.40	0.924
	2	63.04	22.56	24.67	588.3	55.03	50.74	95.10	0.951
	3	67.8	24.48	22.45	511.3	41.82	38.56	96.27	0.963
	5	95.26	18.18	19.93	464	20.03	18.47	98.21	0.982
DL	1	140.0	99.89	103.8	472	103.2	95.15	90.80	0.908
	2	152.5	61.22	69.46	477.6	78.82	72.67	92.98	0.930
	3	173.9	82.3	118.4	462.7	69.02	63.64	93.85	0.938
	5	180.3	22.23	17.5	488	16.25	14.98	98.55	0.986

Table (7). Values of Langmiur adsorption parameters at exposed mild steel to different natural product extracts in 1.0 M HCl.

Inhibitor	Immersion time	Slope ≈	$LogK_{ads}$	R^2	$-\Delta G_{ads}$.$kjmol^{-1}$
PG	2hrs	2.238	1.36	0.999	17.72
	1 day	1.180	2.36	0.999	23.42
	2 days	1.028	2.03	0.999	21.63
	4 days	0.997	2.27	0.999	22.76
SA	2hrs	1.631	1.17	0.988	16.65
	1 day	1.114	2.04	0.998	21.60
	2 days	1.042	2.11	0.999	22.01
	4 days	0.980	2.25	0.999	22.80
O	2hrs	1.970	2.99	0.998	14.46
	1 day	1.075	1.81	0.999	20.29
	2 days	1.062	2.19	0.999	22.43
	4 days	1.038	2.49	0.999	24.13
DS	2hrs	1.633	1.25	0.999	17.08
	1 day	1.135	2.29	0.999	23.03
	2 days	1.010	2.17	0.999	22.36
	4 days	1.0015	2.33	0.999	23.24
DL	2hrs	1.478	1.06	0.999	19.07
	1 day	1.087	2.59	0.999	24.70
	2 days	1.001	2.41	0.999	23.70
	4 days	0.991	2.51	0.999	24.26

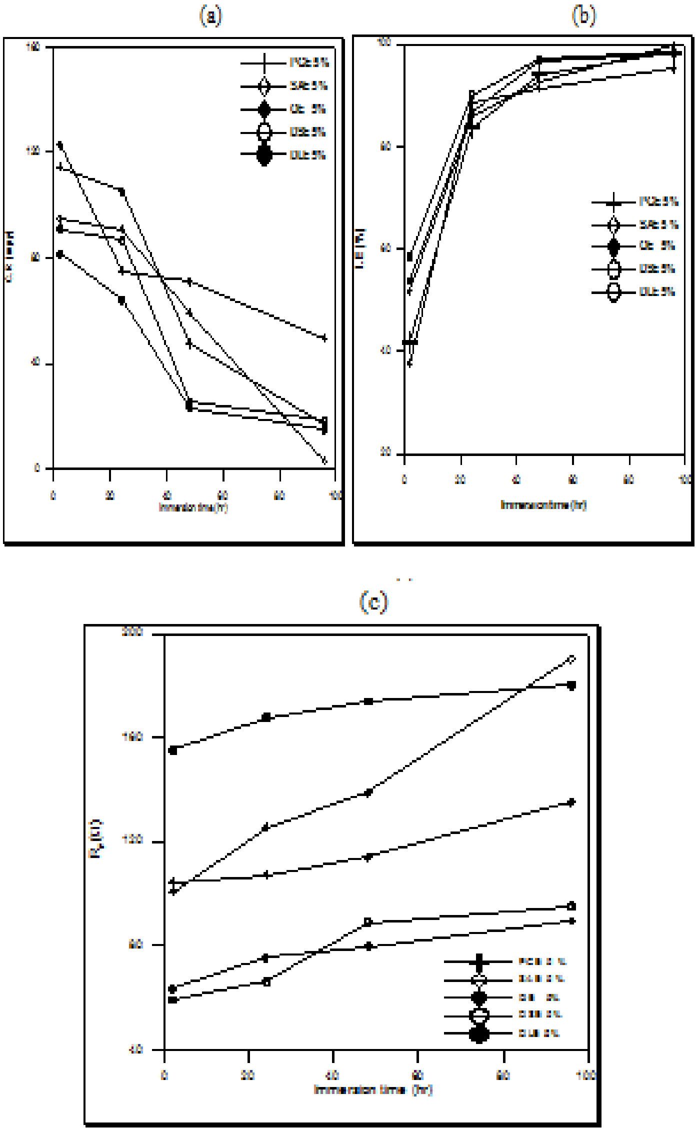

Fig (4). Time dependence of a) corrosion rate, b) inhibition efficiency and c) resistance polarization for mild steel exposed to natural product extracts at 1.0 M HCl

Adsorption Isotherm Calculations

It is a general assumption that, the adsorption of the organic inhibitors at the metal interface is the first step in the mechanism of inhibitors action. Organic molecules may adsorb on the metal surface in four types: i) electrostatic interaction between the charged molecules and the charged metal surface. ii) Interaction of uncharged electron pairs in the molecules and metal. iii) Interaction of π-electrons with metal. IV) A combination of the type (i) and (iii). Calculation of adsorption isotherm is one of the important methods that represent the interaction between the molecules of inhibitor and the metal surface, the Langmuir model agrees more with the experimental results obtained in this study by applying the following equation (4)

$$\theta /1- \theta = KC \quad (4)$$

The previous equation (4), may be modified into the equation (5)

$$C/ \theta = 1/K_{ads.} + C \quad (5)$$

Where, (θ) surface coverage obtained from θ = IE% /100, (C) concentration of inhibitor and K_{ads} is equilibrium constant of adsorption. Adsorption free energy ΔG_{ads} can be calculated by using equation (6) [27]

$$\Delta G_{ads} = -2.303RTlog\ (55.5K)\ldots\ldots\ldots\ldots \quad (6)$$

The free energy of adsorption values, ΔG_{ads} of natural product extracts (PG, SA, O, DS, and DL) of mild steel in 1.0M HCl at exposure time 4days were calculated using the slope and the ordinate axis intercept of the straight lines as shown in Fig. (5).

The deducted values summarized in Table 7. Generally, values of ΔG_{ads} have ranged from -14.46 to 24.70 kjmol^{-1}. Values of ΔG_{ads} in the order -20 kjmol^{-1} or lower indicate the electrostatic interaction between organic charged molecules and the charged metal. Also, these values indicating that natural products (PG, SA, O, DS, and DL) are physically adsorbed on the metal surface, while those around -40 kjmol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to from a co-ordinate type of bond (chemisorption) [28]. The large negative values of ΔG_{ads} indicated that, the adsorption reaction proceeds spontaneously and accompanied by highly efficient adsorption.

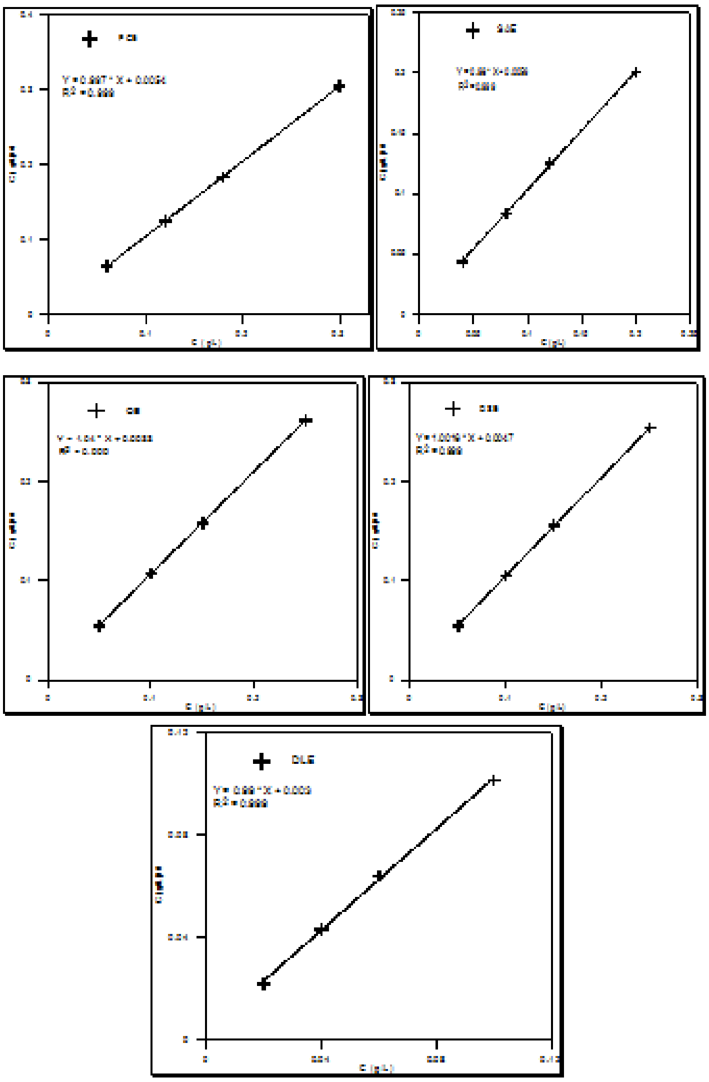

Fig (5). Langmuir adsorption isotherm for adsorption of natural product extracts on the surface of mild steel in 1.0 M HCl after 4 days.

Scanning Electron Microscope (SEM)

SEM is one of the methods, which explain the behaviour of metal surface against corrosive and inhibitor substances, Fig. (6A) represented the morphology of MS surface before immersion in any solutions and it appears as smoothing surface except some scratching due to polishing before using the metal in experiments. Fig. (6B) represents the surface exposed to corrosive media 1.0M HCl at 24 hr, and the surface damage because of deterioration of metal surface. In addition, 5% of the inhibitor SA at corrosive media which shown in Fig (6C), causes formation of layer of inhibitor molecules formed or adsorbed on the surface of metal, that show hat the molecules of inhibitor act as a defence for corrosive media to attack the surface of metal.

Conclusion

All tested natural products inhibitors give best values of IE% for mild steel in 1.0M HCl solution, and the IE% increased as the concentration of inhibitor increased, the adsorption type of these inhibitors on the surface of mild steel is physisorption and the adsorption isotherm follows Langmuir isotherm.

The following conclusions summarized from the present study as:

i. All tested inhibitors decrease the corrosion rate of mild steel in 1.0M HCl as dependent concentration.

ii. All tested natural product extracts inhibit the corrosion rate through adsorption that following Langmuir isotherm. The values of ΔG_{ads} were indicative of the physisorption.

iv. The used inhibitors follow mixed type inhibitor for testing corrosive media

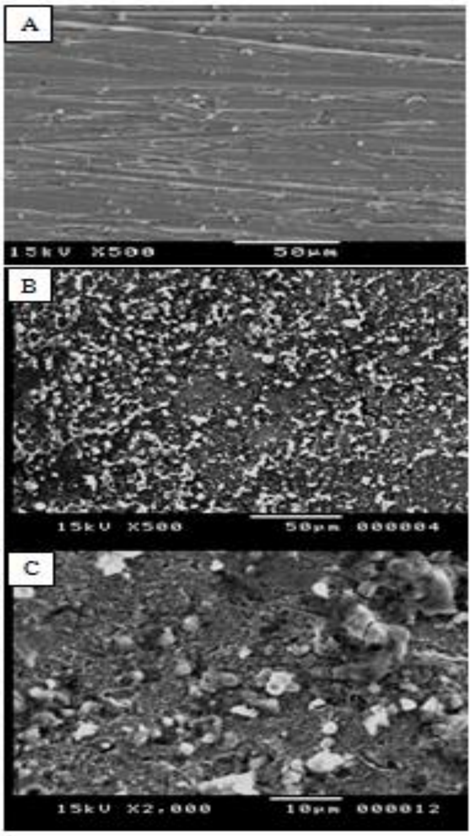

Fig (6). SEM of polished mild steel surface (A), mild steel+1.0M HCl (B) and mild steel+1.0M HCl + 5% SAE (C)

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References

[1] H.H.Uhlig,"Corrosion and Corrosion Control", John Wiley and Sons Inc., 2nd Ed. New York (1971).

[2] Senthil Kumar, A.N., Tharini, K., Sethuraman, M.G., "Corrosion inhibitory effect of few piperidin-4-one oximes on mild steel in hydrochloric medium". Surf. Rev. Lett. 16 (2009) 141–147.

[3] O.K. Abiola, J.O.E. Otaigbe, O.J. Kio, Gossipium hirsutum L. extracts as green corrosion inhibitor for aluminum in NaOH solution, Corrosion Science 51(2009) 1879–1881.

[4] A.M. Abdel-Gaber, E. Khamis, H. Abo-ElDahab, Sh. Adeel, Inhibition of aluminium corrosion in alkaline solutions using natural compound, Materials Chemistry and Physics 109 (2008) 297–305.

[5] A. Ostovari, S.M. Hoseinieh, M. Peikari, S.R. Shadizadeh, S.J. Hashemi, "Corrosion inhibition of mild steel in 1 M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawsone, Gallic acids, -DGlucose and Tannic acid)", Corrosion Science 51 (2009) 1935–1949.

[6] A.M. Abdel-Gaber, B.A. Abd-El-Nabey, M. Sadawy, "The role of acid anion on the inhibition of the acidic corrosion of steel by Lupine extrac", Corrosion Science 51 (2009) 1038–1042.

[7] O.K. Abiola, N.C. Oforka, E.E. Ebenso, N.M. Nwinuka, "Eco-friendly corrosion inhibitors: the inhibitive action of Delonix Regia extract for the corrosion of aluminum in acidic media", Anti-Corrosion Methods and Materials 54 (2007) 219–224.

[8] Putilova, S.Balezin, V.Barannik; "Metallic Corrosion Inhibitors" Pergamon Press, New York (1960).

[9] K.S.Parikh, K.J.Joshi; " Natural compounds onion, garlic and bitter gourd as corrosion inhibitors for mild steel in hydrochloric acid" Tans. SAEST 39 (2004) 29-35

[10] Chetouani, B.Hamounti; " Corrosion inhibition of iron in hydrochloric acid solutions by naturally henna" Bulletin of Electrochemistry, 19 (2003) 23-25.

[11] U.R.Evans; "The Corrosion and Oxidization of Metals" Edward Arnold, London (1960)

[12] Sharrif Moghaddasi Mohammad, Hamed Haddad Kashani, "Chemical composition of the plant Punica granatum L. (Pomegranate) and its effect on heart and cancer" Journal of Medicinal Plants Research Vol. 6(40) (2012) pp. 5306-5310.

[13]- Singh R. P.; Chidambara Murthy, K. N.; Jayaprakasha, G. K.. "Studies on the Antioxidant Activity of Pomegranate (Punicagranatum) Peel and Seed Extracts Using in Vitro Models".Journal of Agricultural and Food Chemistry, 50 (1) (2002) 81–86.

[14]- C. Ben Nasr, N. Ayed and M. Metche, "Quantitative determination of the polyphenolic content of pomegranate peel". Zeitschrift für Lebensmittel-Untersuchung und Forschung, , Volume 203(4) (1996) 374-378,

[15]- Plumb GW, De Pascual-Teresa S, Santos-Buelga C, Rivas-Gonzalo JC and Williamson G. "Antioxidant properties of gallocatechin and prodelphinidins from pomegranate peel". Redox Rep. 7 (41) (2002) 41-46.

[16] R. E. Shafek, N. H. Shafek, H. N. Michael, " Antibacterial and antioxidants activities of two new Kaempferol glycosides isolated from solenostemma argel stem extract", Asian journal of plant sciences, 11 (3)(2012)143-147.

[17] Sayadat El Tigani, Shaza S. Ahmed, "Solenostemma argel Tissue Culture for Production of Secondary Metabolites" Journal of Genetic Engineering and Biotechnology" 7(1) (2009)19-23.

[18] Angela Perrone , Alberto Plaza , Simona Francesca Ercolino , Arafa I. Hamed , Luca Parente , Cosimo Pizza, Sonia Piacente, " 14,15-Secopregnane Derivatives from the Leaves of Solenostemma argel" , J. Natural Products,69 (1) (2006) pp 50–54.

[19] Harvey Wickes Felter, M.D., John Uri Lloyd, Phr. M., Ph. D. ". Henriette's Herbal Homepage. www.henriettes-herb.com. Retrieved 2009-01-14. King's American Dispensatory, 1898

[20] Jim Duke "Farmacy Query". Green Farmacy Garden, www.ars-grin.gov. Retrieved 2009-01-14.

[21] Mendel Friedman , Carol E. Levin, "Composition of jimson weed (Datura stramonium) seeds" J. Agricultural and Food Chemistry, 37 (4) (1989) pp 998–1005

[22] A.M. Abdel-Gaber, B.A. Abd-El-Nabey, I.M. Sidahmed, A.M. El-Zayady, M. Saadaw, " Inhibitive action of some plant extracts on the corrosion of steel in acidic media" Corrosion Science 48 (2006) 2765–2779

[23] Abd El-Kader J.M., A.M. Shams El-Din, "Film Thickening on Nickel in Aqueous Solution in Relation to Anion Type and Concentration", British Corros. J. 14 (1979) 40

[24] Abd El-Kader J.M.; F.M. Abd El-Wahab; M.G. A. Khedr, H.A. El-Shayeeb, "Oxide Film Thickening on Titanium in Aqueous Solutions in Relation to Anion Type and Concentration", Br. Corros. J., 16 (1981) 111-114.

[25] Abd El-Kader M.; F.M. Abd El-Wahab; M.G. A. Khedr, A.M. Shams El-Din, "Oxide film thickening on the surface of iron-chromium alloys in relation to anion type and concentration" Mater. Chem.7 (1982) 313-329.

[26] Shams El-Din A.M., N.J. Panl,. "Oxide film thickening on some molybdenum-containing stainless steels used in desalination plants", Desalination, 69 (1988) 251-260.

[27] Olivares O., N. Likhanova, B. Gómez, J. Navarrete, M. Llanos-Serrano, E. Arce, J. Hallen,. "Electrochemical and XPS studies of decylamides of α-amino acids adsorption on carbon steel in acidic environment", Appl. Surf. Sci. 252 (2006) 2894–2909.

[28] A. Y. El-Etre, “Inhibition of Acid Corrosion of Carbon Steel Using Aqueous Extract of Olive Leaves,” Journal of Colloid and Interface Science, Vol. 314 No. 2 (2007) pp. 578-583.