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Celery (Apium graveolens) Extract as Corrosion Inhibitor for carbon steel in 1 M HCl

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Abstract

Celery (Apium graveolens) was used as natural corrosion inhibitor of carbon steel in 1.0 M HCl. The results of weight loss method and polarization showed that the inhibition efficiency was increased by increasing the Celery (Apium graveolens) inhibitor doses and reached the maximum at 500 ppm. The inhibition action of the extract was discussed in view of Temkin adsorption isotherm. It was found that the adsorption of the extract on Carbon steel surface is a spontaneous process. The effect of temperature on the IE% was studied; the IE% was decreased with increased temperature. Also, it was found that the presence of extract increases the activation energy of the corrosion reaction. Furthermore, the thermodynamic parameters of the adsorption process were calculated.

Keywords: Corrosion inhibition, C-steel, Natural products

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1. Introduction:

Corrosion inhibitors in aqueous solutions mitigated the corrosion rate of metals [1, 2, and 3]. Inhibitor molecules were adsorbed onto the metal surface thus leaded up formation protective film [4, 5]. The adsorbed film worked as a barrier, which separated the metal surface from the corrosive medium and then decreased the corrosion reaction [6]. Organic compounds were containing oxygen, phosphorus, nitrogen, and sulphur atom [7.8]. They had protective effect and had good corrosion-inhibiting abilities. The inhibition efficiency of inhibitors increased in the order of: O < N < S < P.

The Synthetic compounds worked as good corrosion inhibitor [9], but these compounds had heavy metals and toxic effect on both human and environment. Heavy metals, chromates, phosphates, silicates, and materials were typical inhibitors for diminish corrosion of Carbon steel in aqueous solutions. These inhibitors had negative effect on environment such as toxicity, eutrophication, and environmental persistence. On the other hand, the removal of these materials from the environment was complicated and expensive.

So we refuged to Natural plants, these compounds considered environmentally friendly, it didn't contain heavy metals or other toxic compounds [10], Also it was inexpensive, renewable, and readily available. Natural plants in the shape of extracts, oils or pure compounds may play important part in keeping the environment healthier, safe and under pollution control.

2. Experimental:

2.1.1. Medium:

Solution of HCl was prepared by taking accurate volume of the pure acid and diluted of analytical grade 37 % HCl with bi-distilled water.

2.1.2. Celery phytochemistry

Celery (Apium graveolens) seeds contained several substances including volatile oils, flavonoids, coumarins, and linoleic acid. The essential oil of celery seed included d- limonene, selinene, sesquiterpene alcohols, sedanolide, and sedanonic anhydride [11, 12].

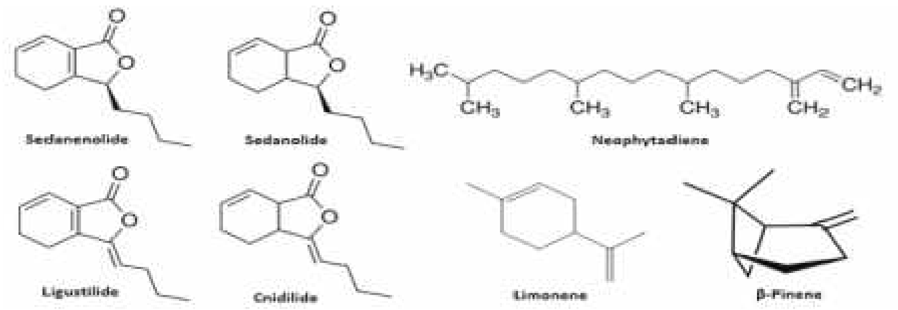

Fig (1): Major components in Celery

2.1.3. Extract Preparation:

Celery (Apium graveolens) used in this study was collected and washed to remove dust from dried Celery (Apium graveolens) plant. Then Celery (Apium graveolens) materials were grained to be the plant powders in homogeneous size. We take this powder and we boiled it in distilled water for two hours. Then we filtered the solution and the filtrate was evaporated to dryness. The residue was used for preparing a stock solution of high concentration. The Actual concentrations were prepared by dilution of the stock solution. All experiments were carried out at room temperature; 25 ^{0}C± 10 ^{0} C.

2.2. Weight Loss Measurements:

Carbon steel was used for determination of weight loss, the corrosion rate (CR) and the percentage of inhibitor efficiency IE (%) were calculated according to the following equations [13]:

$$CR= \Delta m / At \quad (1)$$

$$IE\%= [(CR_{free}-CR_{lnh}) / CR_{free}] X100 \quad (2)$$

Where Δm (mg) is the mass loss, A (cm^2) is the area, (h) is the immersion time, CR_{free} and CR $_{(inh)}$ are the corrosion rates of carbon steel in the absence and presence of inhibitor.

2.3. Potentiodynamic Polarization:

Potentiostatic polarization experiments were carried out using a PS remote potentiostat with zum PS6 software for calculation of corrosion parameters (corrosion current density, corrosion potential and Tafel constants). Three-compartment cell with saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. For potentiostatic studies, a cylindrical rod embedded in araldite with exposed surface area of 0.5 cm^2 was used. The electrode was polished with different grades of emery papers, degreased with acetone and washed by distilled water before put in the test solution. A constant quantity of the test solution (80 ml) was taken in was taken in the polarization cell. The electrode was left in the test solution for 5 min. until it acquired its steady state potential. The potential was then swept until it acquired its steady state potential. The potential was then swept. The inhibition efficiency IE (%) was calculated from polarization measurements according to the relation given below [14]:

$$IE (\%) = [(I_{free}- I_{add}) / I_{free}] X100 \quad (3)$$

Where I_{free} and I_{add} are uninhibited and inhibited corrosion current densities, respectively. They are determined by extrapolation of Tafel lines to the respective corrosion potentials.

3. Result and Discussion:

The corrosion rates of the Carbon steel in 1.0 M HCl without and with different concentrations of Celery (Apium graveolens) extract. The results obtained are found in Table (1). The weight loss values expressed in mg/cm^2 are represented in Table; the table contained also calculation of inhibition efficiencies as well as its variation with the exposure time expressed in hour.

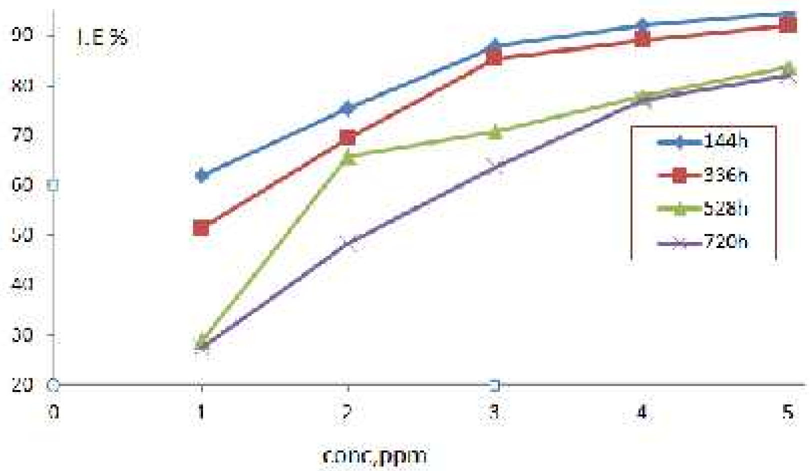

Fig (2): Relation between extract concentration and inhibition efficiency

Table (1): The weight loss values and inhibition efficiencies of carbon steel in1.0M HCl without and with different concentrations of Celery extract

Medium	t,(h)	144	336	528	720
free	wt-loss	43.69	68.55	99.6	123.66
100	wt-loss	16.63	33.27	70.84	89.63
	I.E%	61.88	51.46	28.86	27.49
200	wt-loss	10.65	20.89	34.05	63.71
	I.E%	75.62	69.52	65.80	48.46
300	wt-loss	5.31	9.86	29.03	44.80
	I.E%	87.84	85.61	70.84	63.76
400	wt-loss	3.46	7.49	21.91	28.08
	I.E%	92	89	77.99	77.28
500	wt-loss	2.32	5.32	16.11	22.14
	I.E%	94.62	92.2 3	83.82	82.09

From the data in Table (1) reveals that:

1.The weight loss in both free and inhibited acid solutions increases with increasing time.

2.The inhibition efficiency of Celery (Apium graveolens) increases with increasing its concentration. Fig (2) represents the relation between inhibition efficiency and extract concentration.

3.The inhibition efficiency decreases as the exposure time is increased, the relation between exposure time and inhibition efficiency is represented in Fig (3).

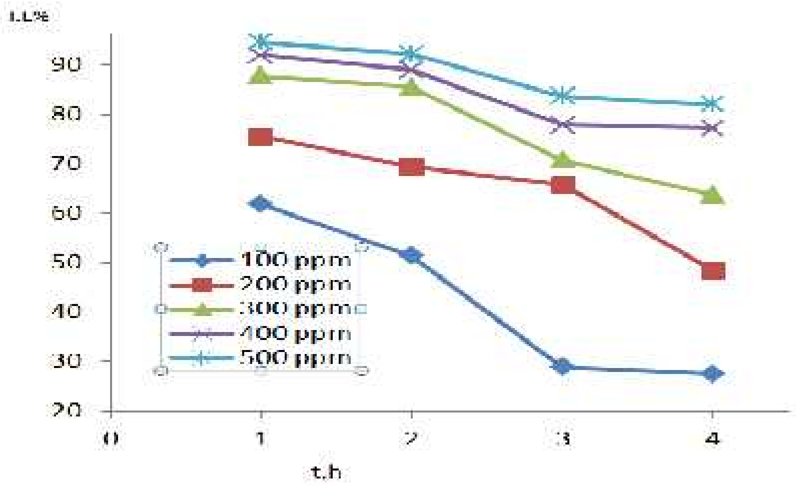

Fig (3): Relation between exposure time and inhibition efficiency for Celery

3.2. Adsorption Measurement:

The corrosion inhibition can be referred to the adsorption of the main components and phytochemicals molecules present within the Celery (Apium graveolens) extract on the metal surface. The adsorption of these compounds on the Carbon steel surface reduces the surface area available for corrosion. The values of surface coverage (θ= I.E% /100) for different concentrations of extract obtained from the weight loss Celery (Apium graveolens) measurements at 298 k. However, the slopes of these straight lines were not unity indicating a presence of some kind of interaction between the adsorbed molecules. It was found that all the used extracts follow Temkin adsorption isotherm. Figure (4) represents the relationship between logarithms of extract concentration (expressed in ppm) and the surface coverage. Straight line was obtained indicating an appropriate to Temkin isotherm. According to Temkin equation, the slope equal to (2.303RT/r) and its intercept equals to (2.303RT/r) log K'.

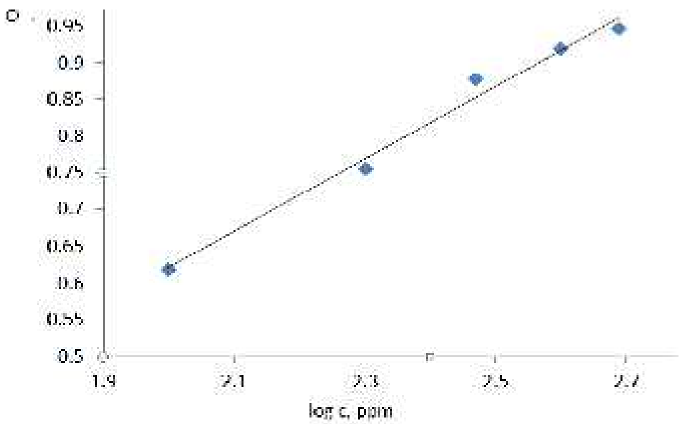

Fig (4): Temkin adsorption isotherm drawn using (ppm) concentrations of extracts in 1.0M HCl solution

The Temkin adsorption parameters (a) and (K) were calculated and represented in Table (2). Table (2) contains also the values of the standard free energy of adsorption (ΔGo_{ads}) calculated using the equation (4) [15].

$$logK' = -\log C_{H_2O} - \left(\frac{\Delta G^o_{ads}}{2.303\,RT}\right)$$

Table (2): The Temkin adsorption isotherm parameters drawn from Fig (4):

R^2	K'	-a	ΔG^o_{ads}, $KJ.mol^{-1}$
0.9856	5.520	2.33	14.16

3.3. Polarization Studies:

The potentiodynamic polarization curves of carbon steel in 1M HCl in absence and presence of various concentrations of Celery (Apium graveolens) shown in Fig (5). The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel slope (β_a) and cathodic Tafel slope (β_c) deduced from the curves are given in Table (3). Inspection of Fig (5) reveals that both the anodic and cathodic polarization curves shifted toward less current densities values and slightly [16] toward less negative potentials upon addition of Celery (Apium graveolens) extract. This result indicated the inhibitive action of Celery (Apium graveolens) extract toward corrosion in the acidic medium.

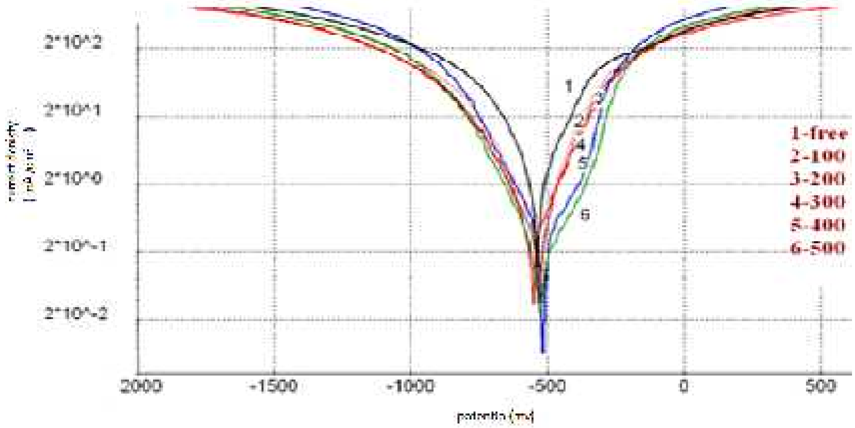

Fig (5): Polarization curves of carbon steel in 1M HCl in absence and presence of

Different concentrations of Celery extract

Table (3): Corrosion parameters of carbon steel in 1.0 M HCl solutions containing different concentrations of Celery extract at 25°

Conc, ppm	E_{corr} mV	β_a mV/ decade	$-\beta_c$ mV/ decade	I_{corr} mA/cm^2	IE%
free	524.14	119.84	156.74	1.18	-------
100	543.14	110.34	116.69	0.25	78.8
200	549.48	117.58	132.36	0.22 5	80.9
300	555.81	117.63	114.09	0.16	86.4
400	470.3	77.20	134.22	0.092	92.1
500	505.14	112.78	138.74	0.081	93.1

Inspection of the data of Table (3) showed that the inhibition efficiency increased with increasing extract concentration.

3.4. Effect of Temperature:

The effect of temperature on the corrosion rate of carbon steel in acid-free additives and in the presence of 500ppm of Celery (Apium graveolens) extract was studied in temperature range of 303 to 323 K using potentiodynamic Polarization measurements. The data listed in Table (4) show that E_{corr} shifted to more the negative values while values of I_{corr} increased with the increasing in temperature. On the other hand, the increases in temperature lead to a decrease in the inhibition efficiency and the best inhibition efficiency was obtained at 303K.

Table 4: Effect of temperature on the corrosion parameters of carbon steel in 1.0 M HCl and 1.0 M HCl + 500 ppm of Celery (Apium graveolens) extract.

Medium	Temp K	$-E_{corr}$ mV	β_a mV/decade	$-\beta_c$ mV/decade	I_{corr} mA/cm^2	IE%
1 M HCl	303	489.31	97.89	129.53	0.158	
	313	501.97	122.22	110.76	0.174	
	323	473.47	121.02	161.09	0.354	
Celery (Apium graveolens)	303	413.30	58	136.93	0.044	72.15
	313	419.63	79.50	150.27	0.0717	58.79
	323	413.30	73.79	157.25	0.252	28.1

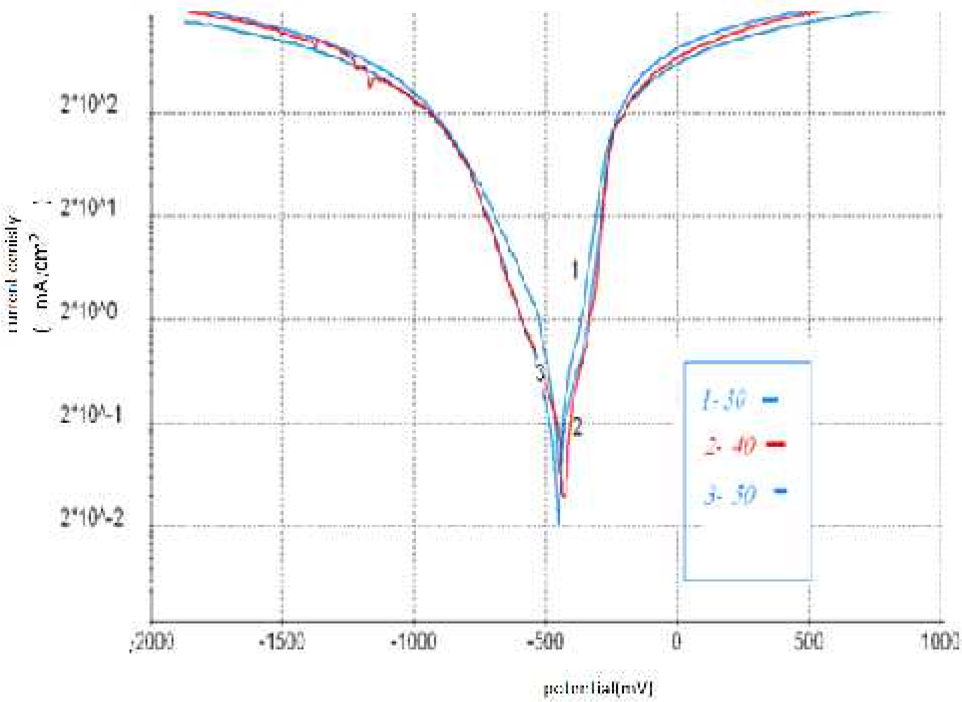

Fig (6): Potentiodynamic Polarization curves of carbon steel in 1 M HCL+500ppm of Celery extract at different temperatures at scan rate 10 mV/sec

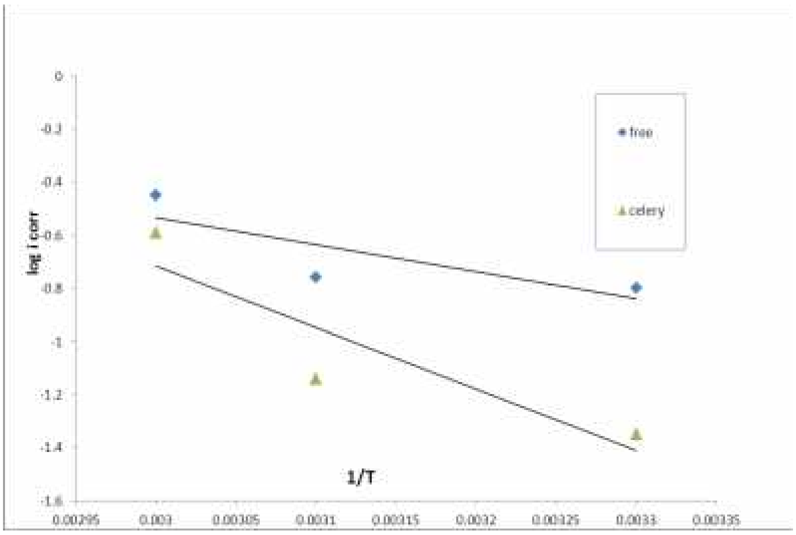

Fig (7): Arrhenius plot for corrosion of carbon steel in 1.0 M HCl solution, and 500 ppm of Celery extract + 1.0 M HCl

In examining the effect of temperature on the corrosion process in the presence of the extract, the Arrhenius equation below was used [17]:

$$\log I_{corr} = \log A - \frac{E_a}{2.303\,RT}$$

Where I_{corr} represents the rate of corrosion reaction, A is Arrhenius factor and E_a is the apparent activation energy of the corrosion reaction. Plotting of log I_{corr} against 1/T gave straight lines, as shown in Fig (7). The values of apparent activation energies for corrosion reactions of carbon steel in different media are calculated from the slopes of these lines and represented in Table (5). Other activation parameters were calculated using the transition state equation:

$$\log\frac{I_{corr}}{T} = \left[\log\left(\frac{R}{hN}\right)\right] + \left[\frac{\Delta S^*}{2.303\,R}\right] - \frac{\Delta H^*}{2.303\,RT}$$

Where, R is the universal gas constant (8.314 J/mol.K), N is the Avogadro's number (6.02 x 1023), h is the Plank's constant (6.62 × 10-34m2 kg /s) where ΔS* and ΔH*are the entropy and the enthalpy changes activation corrosion for the transition state complex, respectively. Plotting log (I_{corr}/T) versus 1/T gives straight lines Fig (6) from which the activation parameters are determined and represented in

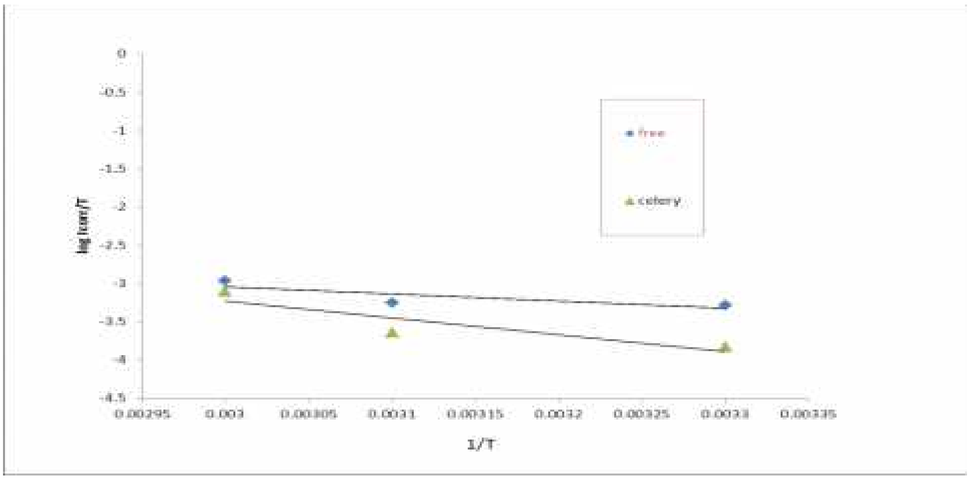

Fig (7): Transition state plot for corrosion of carbon steel in 1.0 M HCl and 1.0 M HCl solution + 500ppm of Celery extract.

The change in the activation free energy (ΔG*) of the corrosion process can be calculated by applying the famous equation:

$$\Delta G^* = \Delta H^* - T\,\Delta S^*$$

Table (5): Activation parameters of corrosion in1.0 M HCl and carbon steel and 1.0 M HCl solution + 500ppm of Celery extract

Medium	E_a kJ/mol	ΔH* kJ/mol	- ΔS* kJ/mol K	ΔG* kJ/mol
1 M HCl	19.7	17.91	0.1929	76.35
Celery (Apium graveolens)	44.44	42.53	0.1317	82.43

The values of ΔG* were positive indicating that the activated complex was not stable and the probability of its formation decreased somewhat with rise in temperature. So the corrosion rate increasing with increased temperature can be attributed to large number of corrosion species passing into an activated state with a less table configuration [18].

As shown from Table (5), the positive values of ΔH* indicated strong adsorption of the inhibitor on the surface. The values of entropy of activation ΔS* in the absence and presence of the Celery extract compound are negative, this can be achieved with loss in the degrees of freedom of the system by the formation of activated complex represents association during the process.

References:

[1] A. S. FoudaEmail author, H. E. Megahed,N. Fouad,N. M. Elbahrawy, Corrosion Inhibition of Carbon Steel in 1 M Hydrochloric Acid Solution by Aqueous Extract of Thevetia peruviana, Journal of Bio- and Tribo-Corrosion, 2 (2016) 16.

[2] SMA Hosseini, M. Salari, M. Ghasemi, 1-Methyl-3-pyridine-2-yl-thiourea as inhibitor for acid corrosion of stainless steel. Mater Corros 60(2009) 963–968.

[3] I. Ahamad and M. A. Quraishi, "Bis-(benzimidazol-2-yl) disulphide: An efficient water soluble inhibitor for corrosion ofmild steel in acid media", Corros. Sci., 51(2009) 2006-2013.

[4] M. Pardave, M. Romero, H. Hernandez, M. Quijano, N. Likhanova, J. Uruchurtu and J. Garcia, "Influence of the alkyl chain length of2-amino-5-alkyl-1,3,4-thiadiazole compounds on the corrosionsSci., 54(2012) 231-243.

[5] H. Ashassi-Sorkhabi, N. Ghalebsaz-Jeddi, F. Hashemzadeh, H. Jahani, Corrosion inhibition of carbon steel in hydrochloric acid by some polyethylene glycols. Electrochim Acta (2006).

[6] L. Herrag, B. Hammouti, S. Elkadiri, A. Aouniti, C. Jama, H. Vezin and F. Bentiss, "Adsorption properties and inhibition of mildsteel corrosion in hydrochloric solution by some newly synthesizeddiamine derivatives: Experimental and theoretical investigations" Corros. Sci., 52(2010), 3042-3051.

[7] A. Yildirim, MCetin, Synthesis and evaluation of new long alkyl side chainacetamide, isoxazolidine and isoxazoline derivatives as corrosion inhibitors. Corros Sci50(2008) 155–165

[8] Neha Patni, Shruti Agarwal, and Pallav Shah, Greener Approach towards Corrosion Inhibition, Chinese Journal of Engineering, 2013 (2013)10.

[9] L.Bammou, M. Mihit, R. Salghi, L. Bazzi, A. Bouyanzer, SS. Al-Deyab, B. Hammouti inhibition effect of natural artemisia oils towards tinplate corrosion in hcl solution: chemical characterization and electrochemical study. Int J Electrochem Sci 6(2011) 1454–1467.

[10] A. Y. El-Etre, M. Abdallah, ZE .El-Tantawy Corrosion inhibition of some metals using lawsonia extract. Corros Sci 47385–395.

[11] Wikipedia contributors. "Celery" Wikipedia, "The Free Encyclopedia". Wikipedia, The Free Encyclopedia, (28 May. 2016), 20:57 UTC, https://en.wikipedia.org/w/index.php?title=Celery&oldid=722543627

[12] https://examine.com/supplements/celery-seed-extract/.

[13] A. Y. El-Etre, "Inhibition of aluminum corrosion using Opuntia extract," Corrosion Science, 45(2003) 2485–2495.

[14] E. E. Oguzie, "Adsorption and corrosion inhibitive properties of Azadirachta indica in acid solutions," Pigment and Resin Technology, 35(2006) 334–340.

[15] A. E. Noor, Mat. Chem. and Phys., 114 (2009) 533.

[16] F. Hanna, G. M. Sherbini, and Y. Barakat, "Commercial fatty acid ethoxylates as corrosion inhibitors for steel in pickling acids," British Corrosion Journal, 24(1989) 269–272.

[17] R.T. Vashi and V.A. Champaneri, Ind. J. Chem. Technol., 4 (1997) 180.

[18] P. Muthukrishnan, B. Jeyaprabha, P. Prakash, Mild steel corrosion inhibition by aqueous extract of Hyptis Suaveolens leaves, InternationaJournal of Industrial Chemistry, (2014).

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