



Study of Anti-corrosion 1018 Carbon Steel in H₂SO₄ Using *Crescentia alata*, *Crataegus pubescens*, and *Jacaranda mimosaeifolia* as Green Corrosion Inhibitors

M. F. Meza Rodríguez¹, A. Rodríguez-Torres², A. Saldaña Heredia², J. Bhawsar³,
J. M. Colin de la Cruz¹, M. G. Valladares-Cisneros^{1*}

¹Facultad de Ciencias Químicas e Ingeniería, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Chamilpa, C.P. 62209, Cuernavaca, Morelos, México.

²Ingeniería Aeronáutica. Universidad Politécnica Metropolitana de Hidalgo. Boulevard de acceso a Tolcayuca 1009 Ex Hacienda San Javier, 43860, Tolcayuca, Hidalgo, México.

³Department of Chemistry, Medi-Caps University, Indore, 452001, (M.P.), India

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mg.valladares@uaem.mx;
Phone: +527773297039;
Fax: +527773297039

Abstract

The inhibitive behavior of three phytoextracts from *Crescentia alata*, *Crataegus pubescens* and *Jacaranda mimosaeifolia* have been studied as green corrosion inhibitors (GCI) in corrosion of AISI 1018 carbon steel in 0.5 M H₂SO₄ medium using weight loss method (WLM). The phytoextracts were studied individually employing WLM, it was used cylindrical AISI 1018 carbon steel coupons in a 0.5 M H₂SO₄ solution to determine the corrosion inhibition efficiency (CIE), in the absence and with 1000 ppm (w/v concentration) of each phytoextract respectively at 25 ± 2 °C in 36 h of resident time. The results show that *C. pubescens* was the best phytoextract, therefore it was evaluated at 250 to 1000 ppm and at three different immersion time 6, 12, and 24 h; to estimate the best concentration for green corrosion inhibition. The CIE increases when the concentration of *C. pubescens* increased. The best CIE was obtained at 1000 ppm, it produced 81 % of at 6 h as immersion time. The ΔG°_{ads} and Langmuir isotherm showed that the molecules of GCI have been adsorbed by physisorption.

1. Introduction

Many object, tools and structures have been manufactured and built by metals or steels. Likewise, all objects suffering deterioration over time. Corrosion is the deterioration of the metal by chemical attack or reaction with the oxygen present in the environment. However, corrosion has great economic impact on the world, is estimated that the economic cost to attend the problems occasioned by the corrosion problems have been estimated that correspond approximately 1 % of the world economy [1].

Derivate for their physicochemical properties of steel, it is widely employed in the construction and the manufactured buildings, machinery, and tools [2]. Some steel manufacturers have been employed organic synthetic inhibitors, common namely as corrosion inhibitors, with they cover metal pieces to protect them against of corrosion.

Corrosion inhibitor could be a substance or material at extremely low concentration that protects the metal against corrosion deterioration. Corrosion inhibitor covers the metal surface and produces a thin protective film, and it reduces the corrosion velocity [3, 4]. Corrosion inhibitors are widely used in different sectors because they have several advantages, such as: low cost, strong adaptability, simple

process, and economic efficiency [5]. Frequently, it has been observed that an effective corrosion inhibitor containing in their chemical structure heteroatom as N, S, or P [6].

Moreover, corrosion inhibitors can be sourced from different part of plants such as flowers, seeds, leaves, roots, and stems. These tissue plants have been extracted with different polarity solvents, the residue recover is namely phytoextract, and it contains natural organic compounds such as terpenoids, flavonoids, coumarins, tannins and alkaloids [7-9]. Several of these phytoextracts show good corrosion inhibition activities and efficiencies in acidic and basic media. Besides, they are safe, nontoxic, biodegradable, and good for the environment [6, 10].

Some natural compounds are highly effective green corrosion inhibitors. Polar natural compounds containing oxygen and nitrogen, nonpolar natural compounds having aromatic rings, aliphatic chains, heterocyclic rings, and functional moieties are abundant in phytoextracts. These natural compounds can get effectively absorbed on metal surface and thus protect it against corrosion without harming the environment like inorganic compounds [11, 12].

Some studies and research have been reported the activity of green corrosion inhibitor by phytoextracts such as the aqueous extract from fruit of *Garcinia indica*, it acts effectively on mild steel in 0.5 M and 1.0 M HCl [13]. *Tephrosia purpurea* leaves methanol extract was studied as corrosion inhibitor on mild steel in 1.0 M HCl solution and it has been found that the inhibition efficiency increases when the concentration of leaves extract increase [14].

Eucalyptus plant leaf ethanol extract was investigated as green corrosion inhibitor on the corrosion of mild steel in two aggressive solutions 0.5 M H₂SO₄ and 0.5 M H₃PO₄. The free energy of adsorption showed that the corrosion inhibition takes place by spontaneous physical adsorption of *Eucalyptus* leaf ethanol extract molecules on the mild steel surface. The data indicated that green corrosion inhibitor was more efficient in 0.5 M H₂SO₄ than in 0.5 M H₃PO₄ [15]. The corrosion inhibition of S300 steel in 1.0 M HCl was investigated, it has been used ethanol extract of *Cuminum cyminum*. The results shown that the green corrosion inhibition efficiency when the concentration of green inhibitor increase [16].

In the same way, others researches have been studied phytoextract as green corrosion inhibitor and the pure isolated compound from the phytoextract, such as *Piper nigrum* crude extract and piperine (major alkaloid present in the extract) were investigated as green corrosion inhibitors on carbon steel anti-corrosion efficiency in 1.0 M HCl. At the same concentrations *P. nigrum* crude extract got higher efficient than the pure piperine. The corrosion inhibition efficiencies were 97 % for the crude extract and 70 % for the pure piperine [17].

To contribute and increase the knowledge of green corrosion inhibitors, the present research shows the study of three different species; *Crescentia alata* and *Jacaranda mimosaeifolia*, both belong to the *Bignoniaceae* family, and *Crataegus pubescens* member of *Rosaceae* family (Figure 1), this study is about the anti-corrosion efficiency in AISI 1018 carbon steel under sulfuric acid.

Crescentia alata (*C. alata*) is a tree known in Mexico as cirián as common name. Important pharmacological activities have been reported for *C. alata*, such as anti-inflammatory, immunomodulatory, and insecticidal [18, 20]. From their fruits, it has been chemical identified and reported iridoids, chemically they are a special class of cyclopentanoid monoterpenes (Figure 1) [21].

Crataegus pubescens (*C. pubescens*), is a tree that currently develops between 1200 to 300 m at sea level, in the upper part of the cold-temperate hills. *C. pubescens* known in Mexico as tejocote as common name, in phytomedicine, it is used to treat respiratory system, and diabetic illness [22]. Antioxidant activity have been reported in which flavonoids can be highlighted [23]. Others natural compounds reported for *C. pubescens* are terpenes, proanthocyanins; and some flavonoids (Figure 3) [24].

Jacaranda mimosaeifolia (*J. mimosaeifolia*) is an ornamental tree with attractive foliage and beauty purple flowers, known in Mexico as jacaranda and around the world known as blue trumpet tree as common name; leaves, flowers, and seeds are used in the state of Morelos to treat hypertension and amoebic infections [18, 22]. Important uses have been reported for *J. mimosaeifolia*, as hypotensive, immunomodulatory, and insecticidal [21-23]. The phytochemical compounds have been isolated while triterpenes, flavonoids, fatty acid, and anthocyanins (Figure 2) have been reported from *J. mimosaeifolia* [25-28]. All these compounds contained in chemical structures oxygen and π -electrons (aromatic rings) which may have a good interaction with the metal surface.

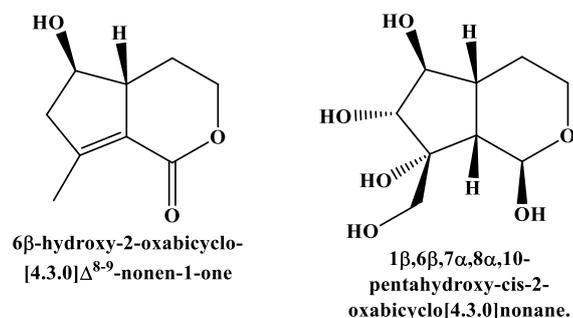


Figure 1. Natural compounds representatives of *Crescentia alata*, Iridoids.

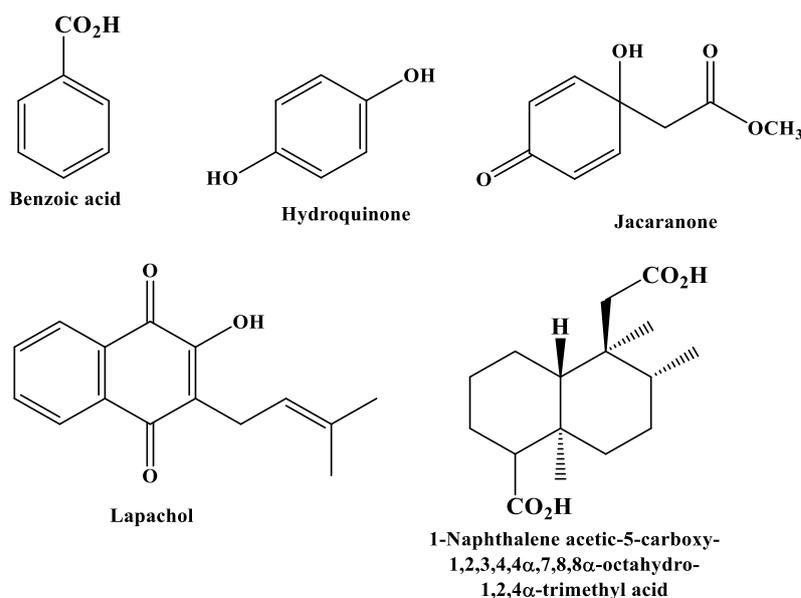


Figure 2. Natural compounds representatives of *Jacaranda mimosaeifolia*, Terpenes, hydroquinones, and acids

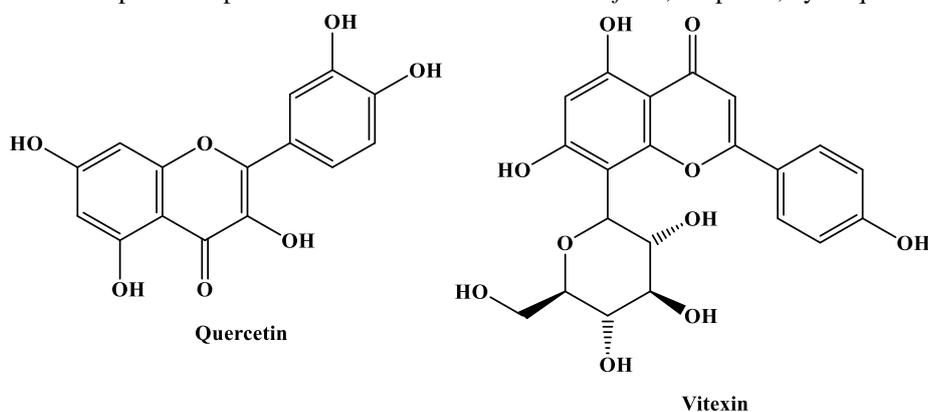


Figure 3. Natural compounds representatives of *Crataegus pubescens*, Flavonoids.

2. Material and Methods

2.1. Preparation AISI 1018 carbon steel electrodes

The metal studied in the gravimetric method was AISI 1018 carbon steel whose composition was C 0.14-0.20%, Mn 0.60-0.90%, P < 0.040%, S < 0.050%, and balance Fe. Cylindrical coupons of AISI 1018 carbon steel have been obtained from the steel bar with diameter of 0.6 cm, it was cut in small pieces sized 2.5 cm in height, each coupon was drilled at one end with the aid of a drill equipped with a 2.56 mm bit. Metallic surface of each coupon was polished uniformly with 120, 240, 320 and 600 grit SiC paper, washed with distilled water, and degreased with acetone.

2.2. Obtention of Green corrosion inhibitors

Fresh tissues from the vegetable species were collected in Morelos State, Mexico. Fruits of *C. alata* from Huautla downtown (+18.6326, -99.163) located in Tlaquiltenango. Flowers of *J. mimosaeifolia*, from Chamilpa (+18.9667, -99.25) ubicated in Cuernavaca City, and leaves of *C. pubescens* from Tres Marias downtown (+19.054, -99.241) located in Huitzilac (Figure 4).



Figure 4. Geographic distribution of vegetal species collected to studied as GCI

The leaves were dried at room temperature ($25\text{ }^{\circ}\text{C} + 2$) for three weeks in lightless and natural aeration. Afterwards, 500 g of dry leaves of each specie were macerated separately and individual using 1.0 L of methanol (99 %) at $25\text{ }^{\circ}\text{C}$ and the glass container was protected against sun light, covering it with Aluminium fold. The mixture leaves and dissolvent were left in stational conditions for 72 h. The liquid mixture macerate was filtered and the dissolvent was evaporated using a rotary evaporator. The dissolvent recovery was put in the glass container in contact with the respectively tissue of plant, and the processes was repeated two time more, for exhaustive extraction. Afterwards, for each specie was obtained the mixture of natural compounds as an organic vegetal residue dissolvent free, called “green corrosion inhibitor (GCI)”, more specifically the acronym name are Fruits of *C. alata* (GCIFCA), Flowers of *J. mimosaeifolia* (GCIFJM), and Leaves of *C. pubescens* (GCILCP).

2.3. Green corrosion inhibition

Different concentrations (0 - 1000 ppm) of each GCI were prepared before to evaluate through weight loss technique. Each GCI was prepared a stock solution at 2000 ppm, from this solution known, small volumes were added in each experiment to reach the concentration of GCI to evaluated.

2.4. Electrolyte solution

The corrosive solution was 0.5 M H₂SO₄. Aggressive solution was made dissolving sulfuric acid (98% analytic grade) in distilled water.

2.5. Weight loss method

Weight loss experiments were performed with carbon steel rods at 25 ±2 °C immersed aggressive solution during 36 h and static conditions. Preparation and evaluation of the metallic coupons was carried out according to ASTM G1 and ASTM G31 [29, 30]. Each GIC were tested by triplicate. Concluded the immersion time, specimens were taken out of the glass cell, washed with distilled water, degreased with acetone, dried in warm air, and stored in a desiccator. Specimens were weighed in an analytical balance accuracy and highly precision of 0.01 mg, until constant weight. Weight loss measurements, ΔW, were calculated as follows:

$$\Delta W = \frac{(m_1 - m_2)}{A}$$

where m_1 is the mass of the specimen before corrosion, m_2 the mass of the specimen after corrosion, and A the exposed area of the specimen. Inhibition efficiency, IE , was calculated as follows:

$$IE (\%) = \frac{(\Delta W_1 - \Delta W_2)}{\Delta W_1} \times 100$$

where ΔW_1 correspond the weight loss without inhibitor, and ΔW_2 is the weight loss with inhibitor. Surface coverage (θ), and corrosion rates (CR) were calculated.

$$\theta = \frac{IE (\%)}{100}$$

$$CR = \frac{W_0}{AtD}$$

where, CR is corrosion rate (mm/y), W_0 is weight difference (g) before and after weight loss measurements; A correspond to exposed area of the specimen, t is the immersion time (h), and D is the density of the specimen (g/cm³). The weight loss values were used to plot adsorption isotherms such as Langmuir adsorption isotherm and to calculate the thermochemical parameters.

2.6. Surface morphology analysis

The study of the surface morphology for the AISI 1018 carbon steel immersed in sulfuric acid without and with GCI, it was carried out using a metallurgical microscope (40X-1600X Trinocular Dual-illumination).

3. Results and discussion

3.1. Preparation AISI 1018 carbon steel electrodes

The polish evolution of coupons of AISI 1018 carbon steel and the final coupon done is shown in the Figure 5.

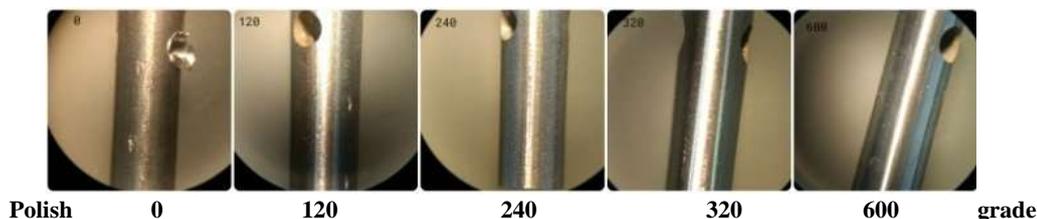


Figure 5. Polish evolution of coupons AISI 1018 carbon steel

3.2. Obtention of Green corrosion inhibitor

Green corrosion inhibitors were recovered after extraction processes. The free residues dissolvents have been looked dark green for *C. pubescens*, dark brown for *J. mimosaeifolia* and dark black for *C. alata*. Three of them GCI smelled slightly of wood.

3.3. Weight loss studies

The three GCI (*C. lata*, *C. pubescens* and *J. mimosaeifolia*) were tested individually at 1000 ppm for 36 h. The maximum immersion time reported where the green corrosion inhibitor is efficient in acid media, frequently it is not long time; so, do not exceed 36 h [31]. The green corrosion inhibition efficiency produced for three vegetable species studied are listed in Table 1. The effect produced on metal surface coupons after the use of GCI is showed in Figure 6. The microphotographs were taken before and after the inhibition corrosion tests, without and with the use of phytoextract as green corrosion inhibitors. The green corrosion inhibitor obtained through the natural compounds recovered from the phytoextract of fruits *C. alata* (GCIFCA) at 1000 ppm produced weak protection on 1018 carbon steel against to corrosion by 0.5 M sulfuric acid at 36 h. It is possible to observe in the Figure 3 that few damages were produced to coupon by the presence of GCIFCA into the electrolyte solution.

Table 1. Corrosion inhibition efficiency percentage using 1000 ppm of GCI on AISI 1018 carbon steel in 0.5 H₂SO₄ at 24 h

Inhibitor	IE (%)
GCIFCA	69.11 ± 0.47
GCILCP	79.94 ± 1.39
GCIFJM	74.78 ± 1.33

The major natural compound reported from *C. alata* are monoterpenes the kind of iridoids, for these compounds have been reported that in their chemical structures have been contained a ring kind of lactone, that is a 6-members or 5-member rings (Figure 7), the lactone ring are easier sensible and opened quickly by stress conditions likely acidic water solutions, that it forced the ring opened and the aldehyde resulted has not activity or the compound begging degrade [32, 33]. Green corrosion inhibitor recovered of methanol phytoextract from flowers *J. mimosaeifolia* (GCIFJM) has been produced 74.78 ± 1.33 % of protection to 1018 carbon steel in 36 h, this IE% was higher than *C. alata* produced. However, observing the respective microscopy image in Figure 6, is possible to distinguish multiples pitting, they look like big holes, and produced a porosity texture on the metal surface. There was greater deterioration of the metallic material than that observed in the blank.

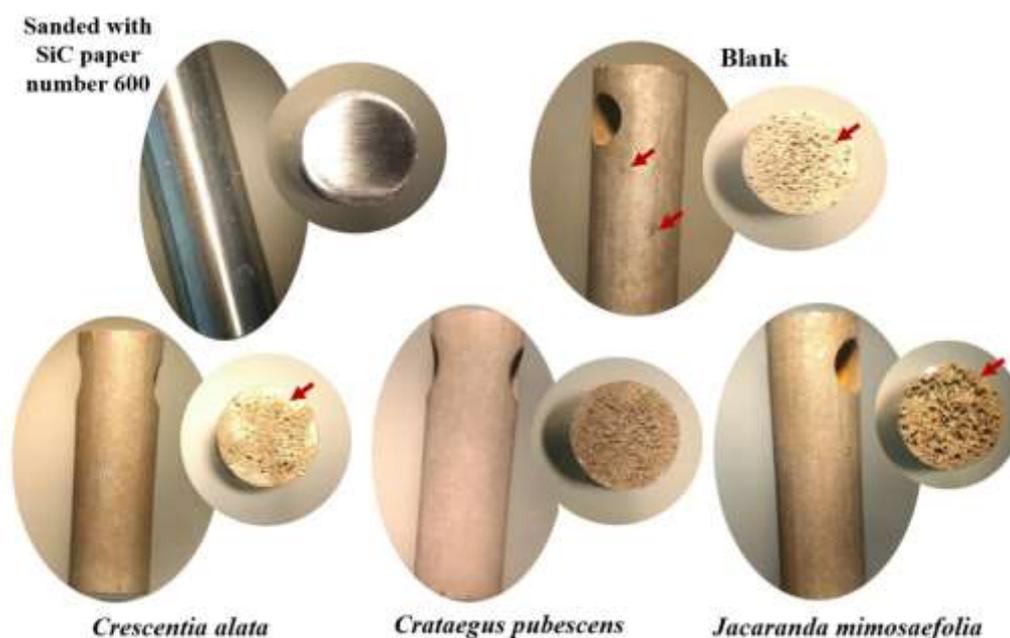


Figure 6. Coupons of AISI 1018 carbon steel before and after used green corrosion inhibitors in 0.5 M H₂SO₄ at 36 h immersion time at 25 ± 2 °C. (The red little arrows indicate some damage stand out)

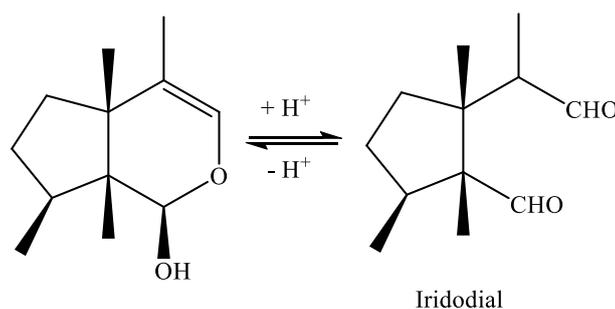


Figure 7. Iridoid interconversión.

Example the ring opens and closes in the iridoid to iridodial chemical structures.

A previous report shown that the green corrosion inhibitor recovered from ethanol extract of *J. mimosaeifolia* leaves, was used for corrosion inhibition of steel (C, 4.93%; Mn, 1.09%; Si, 1.78% and the remainder being Fe) immersed in 1.0 M HCl at room temperature during 6 h as immersion time, was obtained a corrosion inhibition efficiency of 92.1 % through weight loss method [34].

Both species *C. alata* and *J. mimosaeifolia* are *Bignoniaceae*s, few species from this family have been studied as corrosion inhibitors. Some examples about the *Bignoniaceae*s studied are *Podranea ricasoliana* leaves extract used at 8 % (v/v) on mild steel in 1.0 M HCl produced an inhibitory effect of 95.7 % by weight loss method in 3 h of immersion time [35]. *Anthocleista djalonesis* has been investigated as nontoxic corrosion inhibitor for mild steel in 0.5 M H₂SO₄. Through weight loss method was reported that 800 mg/L of green inhibitor produced 87 % of corrosion inhibition efficiency at 6 h as immersion time [36]. Chemical compounds presented into the leaves of *A. djalonesis* include an iridoid glucoside (djalonenoside), which is the major constituent of the plant [37].

In another hand, the highest green corrosion inhibition efficiency was showed by the green corrosion inhibitor recovered from the methanol phytoextract of *C. pubescens* leaves. GCILCP protected near to 80 % the 1018 carbon steel against the corrosion produced by 0.5 M sulfuric acid in 36 h. Figure 6 shows that this green inhibitor gives protection on metal surface, a minimum pitting could be observed on the

coupon. Thus, the corrosion inhibition activity of *C. pubescens* was explored in different concentrations and immersion times of residence.

The results obtained by weight loss method, using GCILCP at three different concentrations (250, 500 and 750 ppm) and three different times (6, 12 and 24 h), were corrosion inhibition efficiency (IE %), surface coverage (θ) and corrosion rate (CR) are shown in Tables 2 - 4. The effect produced on metal surface coupons after the use of GCILCP is showing in Figures 8 - 10. The microphotographs were taken before and after the inhibition corrosion tests, without and with the use of phytoextract as green corrosion inhibitor. The results show that the inhibition efficiency increases with the increment of the concentration of GCI, at 750 ppm of GCILCP the inhibition efficiency was close to 72 % at 6 h of immersion time (Table 2). In Figure 8 it can be observed that the coupon with 750 ppm, the metal surface shows uniform, compact and without pitting, thus, a corrosion protection is seen compared with the blank.

Table 2. Corrosion inhibition efficiency of GCILCP on AISI 1018 carbon steel in 0.5 M H₂SO₄ determined by weight loss in 6 h as immersion time at 25 ± 2 °C

<i>C. pubescens</i> [ppm]	Weight loss (mg/cm ²)	CR (mm/y)	Surface coverage (θ)	IE (%)
Blank	102.7	0.442		
250	46.8	0.202	0.542	54
500	38.1	0.165	0.627	63
750	28.8	0.124	0.719	72
1000	19.41	0.083	0.811	81



Figure 8. Corrosion inhibition efficiency of GCILCP on AISI 1018 carbon steel in 0.5 M H₂SO₄ determined by weight loss in 6 h as immersion time at 25 ± 2 °C

The results show that the green corrosion inhibition continued the tendency, the inhibitory efficiency increase when the green corrosion inhibitor concentration increases. However, inhibition efficiency

decreases according the immersion time increased during the tests (Table 3). In the Figure 9 observe the protection or damage on metal surface coupons after the tests. In blank coupon at 12 h can see non protection and pitting damage, the coupon at 750 ppm shown less pitting damage, but in the coupon treated with low corrosion inhibitor (250 ppm), it is possible to observe zones with pitting damage. And at 500 ppm GCILCP protects, and the aggressive solution produces uniform corrosion.

Table 3. Corrosion inhibition efficiency of GCILCP on AISI 1018 carbon steel in 0.5 M H₂SO₄ determined by weight loss in 12 h as immersion time at 25 +2 °C

<i>C. pubescens</i> [ppm]	Weight loss (mg/cm ²)	CR (mm/y)	Surface coverage (θ)	IE (%)
Blank	291.9	1.260		
250	198.9	0.860	0.318	32
500	179.9	0.780	0.384	38
750	97.8	0.420	0.650	65
1000	58.4	0.087	0.800	80

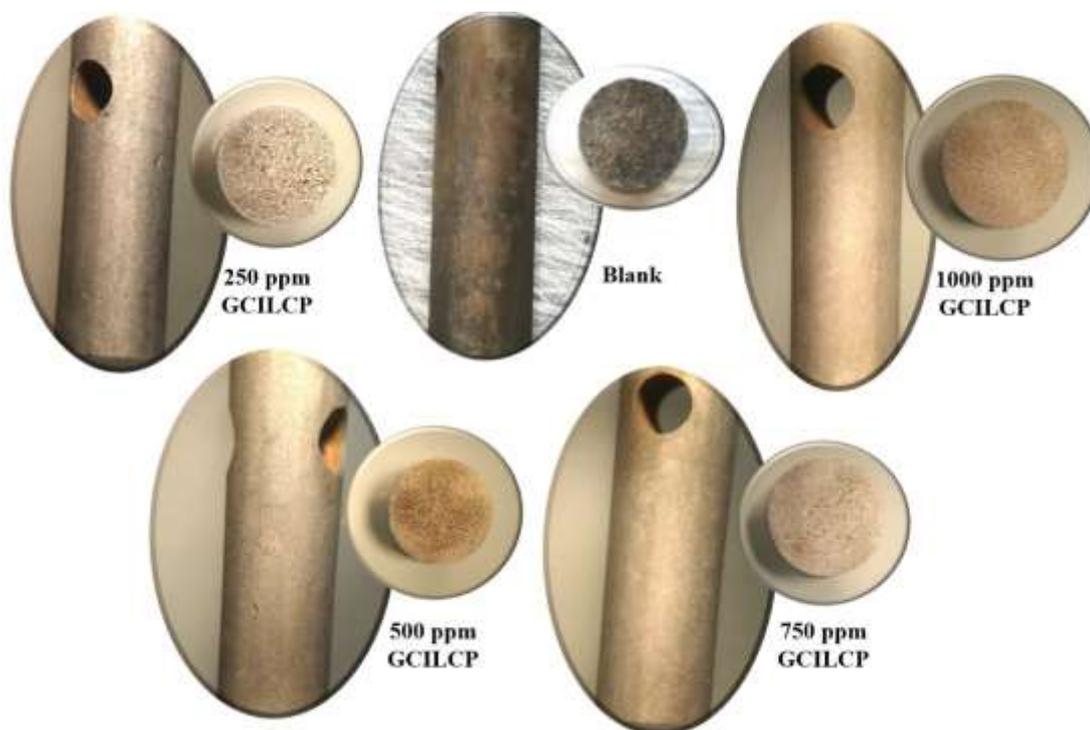


Figure 9. Corrosion inhibition efficiency of GCILCP on AISI 1018 carbon steel in 0.5 M H₂SO₄ determined by weight loss in 12 h as immersion time at 25 +2 °C

The results of green metal protection at 24 h (Table 4), shown that the corrosion inhibition efficiency increases with the increment of the concentration of GCI. Using 750 ppm of GCILCP the inhibition efficiency was close to fifty percent at 24 h of immersion time. The Figure 10 shows the protection and damage on metal surface coupons after the tests. Blank coupons immersed in aggressive solution for 24 h shown severe pitting damage. In the same figure the coupon treated with 750 ppm of GCILCP shows pitting damage, however, when the GCILCP is used in a low concentration (250 ppm) the metal surface coupon shows severe damage, observing a high corrosion on surface and even fracture.

Table 4. Corrosion inhibition efficiency of GCILCP on AISI 1018 carbon steel in 0.5 M H₂SO₄ determined by weight loss in 24 h as immersion time at 25 +2 °C

<i>C. pubescens</i> [ppm]	Weight loss (mg/cm ²)	CR (mm/y)	Surface coverage (θ)	IE (%)
Blank	650.2	2.820		
250	508.7	2.156	0.218	22
500	420.5	1.783	0.347	35
750	322.1	1.365	0.464	48
1000	130.7	0.088	0.799	80

The best protecting conditions for AISI 1018 carbon steel in H₂SO₄ through weight loss method was using 750 ppm GCILCP at 6 h to produce corrosion inhibition efficiency close to 72 %. Some species from *Rosaceae* family and belonging to the genus *Crataegus* have been studied as corrosion inhibitor. Apple tree belonging to the *Rosaceae* family, 500 ppm of apple fruit extract protected mild steel in 0.5 M HCl solution and produces 87.9 % of corrosion inhibition by spectroscopy electrochemical impedance (SEI) [38].



Figure 10. Corrosion inhibition efficiency of GCILCP on AISI 1018 carbon steel in 0.5 M H₂SO₄ determined by weight loss in 24 h as immersion time at 25 +2 °C

Crataegus oxycantha protects mild steel in 0.5 M HCl, 400 ppm of aqueous leaves extract produces 66 % of inhibition efficiency [39]. *Crataegus mexicana* gives green protection for AISI 1018 carbon steel in 0.5 M H₂SO₄, 500 ppm of methanol leaves extract produces 80 % of corrosion inhibition efficiency by SEI [40]. The natural products isolate and identified for the genus *Crataegus* are flavonoids, some others species their contained flavonoid have been studied as corrosion inhibition, the flavonoid extract form *Euphorbia guyoniana* was studied in the inhibitory effect on the corrosion of mild steel in H₂SO₄ medium, 1000 ppm of the flowers extract produced 78.92 % of corrosion inhibition efficiency [41].

3.5 Adsorption Isotherm

The surface coverage values obtained from the weight loss measurements were used to calculate Langmuir isotherm, which can provide the necessary information regarding the interaction between metal and green inhibitor [42], and though this analysis is possible to explore and understood how occurs the mechanism of green corrosion inhibition. The Langmuir isotherms at different immersion times were calculated with the surface coverage values obtained from the weight loss measurements, and the best fit was observed. The Langmuir adsorption isotherm can be expressed as follows:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

where C is the inhibitor concentration [ppm], θ is the surface coverage, and K_{ads} is the adsorption equilibrium constant. The plot shown in Figures 11-13 was obtained after graphing C/θ versus C used of GCILCP yielded straight line for each immerse time. Correlation coefficient obtained tends to unity, thus confirming the applicability of the Langmuir isotherm model [42] for the immersion time.

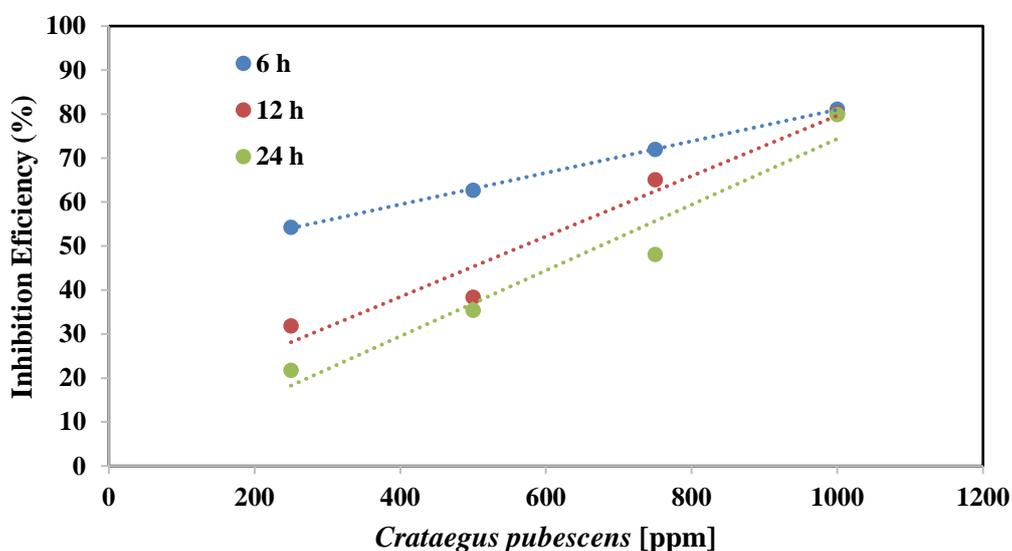


Figure 11. Inhibition efficiency (IE%) plots for GCI of AISI 1018 carbon steel in 0.5 M H₂SO₄ versus concentration of *Crataegus pubescens* in different immersion times

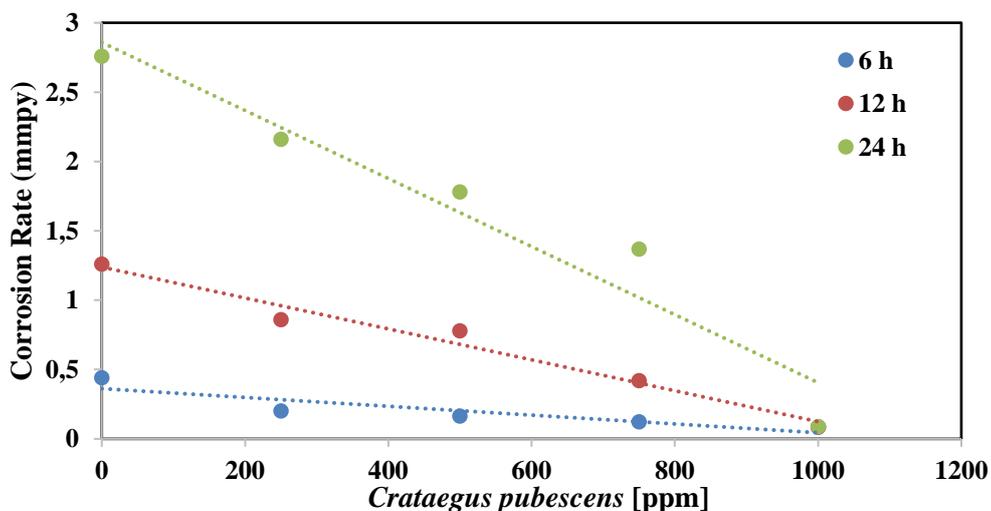


Figure 12. Corrosion rate (mmpy) plots for GCI of AISI 1018 carbon steel in 0.5 M H₂SO₄ versus concentration of *Crataegus pubescens* in different immersion times

The coverage surface increased according to the concentration of the GCILCP increased (Figure 13). The best coverage surface occurs using 1000 ppm of GCILCP in 6 h as immersion time.

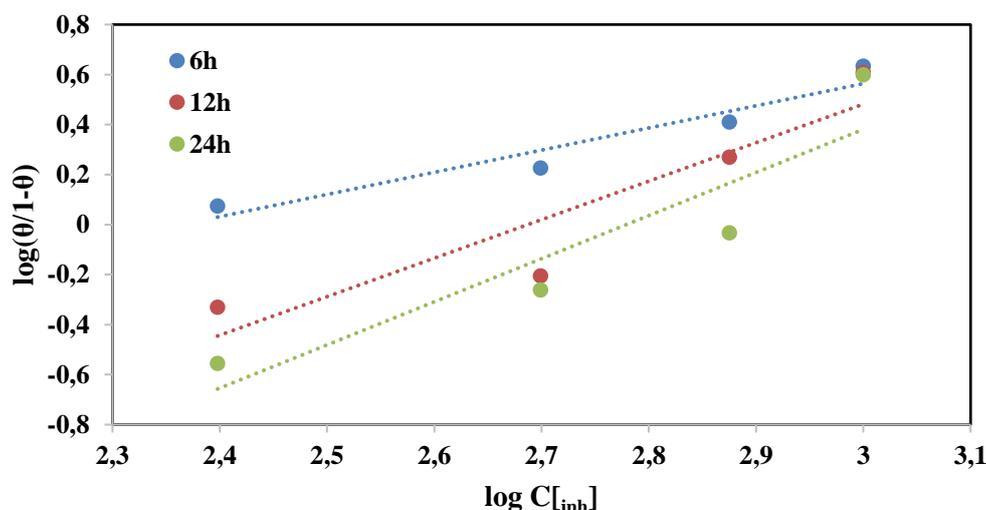


Figure 13. Langmuir adsorption isotherm plots for GCI of AISI 1018 carbon steel in 0.5 M H₂SO₄ versus concentration of *Crataegus pubescens* at different immersion times.

3.6 Free Energy

The free energies of adsorption, ΔG_{ads}^0 , were calculated from the equilibrium constant of adsorption in the different immersion time, using the following equation [42, 43]:

$$\Delta G_{ads}^0 = -2.303 RT \log[55.5 K_{abs}]$$

where the molar concentration of water in the solution is 55.5, R is the universal gas constant, and T is the absolute temperature (Table 5).

Table 5. Corrosion inhibition efficiency of GCILCP on AISI 1018 carbon steel in 0.5 M H₂SO₄ determined by mass loss in 24 h as immersion time at 25 ± 2 °C

Immerse time (h)	K _{ads} (l/g)	Slope	ΔG_{ads}^0 (KJ/mol)
6	1.1275	0.8869	- 10.255
12	0.6495	1.5396	- 8.888
24	0.5799	1.7244	- 8.067

Generally, values of ΔG_{ads}^0 around - 20 kJ/mol or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption), whereas those around - 40 kJ/mol or higher, involve charge sharing or transferring from organic molecules to the metal surface to form a coordinate type of bond [39]. The calculated free energy adsorption values, ΔG_{ads}^0 , show that the adsorption of kind molecules presents in the phytoextract (GCILCP) on the surface of the metal is a very feasible and spontaneous process. The values of Gibbs free energy in different concentration of GCI indicated in Table 5; shown the adsorption of GCILCP on the metal surface, therefore some natural organic molecules contained in GCILCP favor their physisorption.

Conclusion

The weight loss method confirmed the methanol leaves phytoextract from *Crataegus pubescens* acts as effective green corrosion inhibitor for AISI 1018 carbon steel in 0.5 M H₂SO₄ medium compare with *Crescentia alata* and *Jacaranda mimosaeifolia*, under the experimental conditions in which this investigation was fulfilment. The inhibition efficiency increases with the green inhibitor concentration increase. The maximum green inhibition efficiency for methanol leaves phytoextract *C. pubescens* was 81 % at 1000 ppm of in 6 h as immersion time. The surface coverage of AISI 1018 carbon steel increased with concentration of green inhibitor and the inhibition efficiency. Green corrosion inhibition obeys the Langmuir isotherm and occurs due to the adsorption of the natural molecules in the phytoextract on the mild steel surface.

References

1. O. S. I. Fayomi, I. G. Akande, and S. Odigie. Economic impact of corrosion in oil sectors and prevention: An overview. *Journal of Physics: Conference Series*, 1378 (2019) 022037. <https://doi.org/10.1088/1742-6596/1378/2/022037>
2. M. Valladares-Cisneros, R. M. Melgoza-Aleman, and C. Cuevas-Arteaga. Inhibidores naturales en el control de la corrosión de materiales metálicos. *Inventio* 11 N°25 (2015) 11, 37-41.
3. F. Ravazzolo, and J. Vespignani. World steel production: A new monthly indicator of global real economic activity. *Canadian Journal of Economics*, 53 N°2 (2020) 743-766. <https://doi.org/10.1111/caje.12442>
4. C. Verma, L. O. Olasunkanmi, I. B. Obot, E. E. Ebenson, and M. A. Quraishi. 2, 4-Diamino-5-(phenylthio)-5H-chromeno [2, 3-b] pyridine-3-carbonitriles as green and effective corrosion inhibitors: gravimetric, electrochemical, surface morphology and theoretical studies. *RSC Adv.*, 6 (2016) 53933. <https://doi.org/10.1039/c6ra04900a>
5. M. Finsgar, A. Lesar, A. Kokalj, and I. Milosev. A comparative electrochemical and quantum chemical calculation study of BTAH and BTAOH as copper corrosion inhibitors in near neutral chloride solution. *Electrochim Acta*.53 N°28 (2008) 8287-8297. <https://doi.org/10.1016/j.electacta.2008.06.061>
6. B. E. Rani, and B. B. J. Basu. (2012). Green inhibitors for corrosion protection of metals and alloys: An overview. *International Journal of corrosion*, 380217 (2012). <https://doi.org/10.1155/2012/380217>
7. J. R. Vimala, A. L. Rose, and S. Raja. A study on the phytochemical analysis and corrosion inhibition on mild steel by *Annona muricata* L. leaves extract in 1 N hydrochloric acid. *Der Chemica Sinica*, 3 N°3 (2012):582-588.
8. L. T. Popoola. Progress on pharmaceutical drugs, plant extracts and ionic liquids as corrosion inhibitors. *Heliyon*, 5 N°2 (2019), e01143. <https://doi.org/10.1016/j.heliyon.2019.e01143>
9. M. Khan, M. M. S. Abdullah, A. Mahmood, A. M. Al-Mayouf, and H. Z. Alkhatlan. Evaluation of *Matricaria aurea* extracts as effective anti-corrosive agent for mild steel in 1.0 M HCl and isolation of their active ingredients. *Sustainability*, 11 N°24 (2019), 7174. <https://doi.org/10.3390/su11247174>
10. S. Marzorati, L. Verotta, and S. P. Trasatti. Green corrosion inhibitors from natural sources and biomass wastes. *Molecules*, 24 N°1 (2019). 48. <https://doi.org/10.3390/molecules24010048>
11. M. Chigondo, and F. Chigondo Recent natural corrosion inhibitors for mild steel: an overview. *J Chem.* 6208937 (2016) <https://doi.org/10.1155/2016/6208937>
12. S. Issaadi T. Douadi A. Zouaoui, S. Chafaa, M. A. Khan, and G. Bouet. Novel thiophene symmetrical Schiff base compounds as corrosion inhibitor for mild steel in acidic media. *Corros Sci.* 2011; 53 N°4 (2011) 1484-1488. <https://doi.org/10.1016/j.corsci.2011.01.022>
13. A. Thomas, M. Prajila, K. M. Shainy, and A. Joseph. A green approach to corrosion inhibition of mild steel in hydrochloric acid using fruit rind extract of *Garcinia indica* (Binda). *Journal of Molecular Liquids*, 312 N°15 (2020) 113369. <https://doi.org/10.1016/j.molliq.2020.113369>

14. T. K. Bhuvaneshwari, C. Jeyaprabha, and P. Arulmathi. Corrosion inhibition of mild steel in hydrochloric acid by leaves extract of *Tephrosia purpurea*. *Journal of Adhesion Science and Technology*, 34 N°22 (2020) 2424-2447. <https://doi.org/10.1080/01694243.2020.1766395>
15. A. M. Abdel-Gaber, H. T. Rahal, and F. T. Beqai. Eucalyptus leaf extract as a eco-friendly corrosion inhibitor for mild steel in sulfuric and phosphoric acid solutions. *International Journal of Industrial Chemistry* 11 (2020) 123-132. <https://doi.org/10.1007/s40090-020-00207-z>
16. S. A. Umoren, Z. M., Gasem, and I. B. Obot. Date palm (*Phoenix dactylifera*) leaf extract as an eco-friendly corrosion inhibitor for carbon steel in 1M hydrochloric acid solution. *Anti-Corros Methods and Materials*, 62 N°1 (2015) 19-28. <https://doi.org/10.1108/ACMM-10-2013-1302>
17. B. V. R. Assis, F. O. Meira, V. G. S. S. Pina, G. F. Andrade, R. G. O. Cotrim, E. D'Elia, and F. C. Souza. Efeito Inibitório do Extrato de Piper Nigrum L. sobre a Corrosão do Aço Carbono em Meio Ácido. *Rev. Virtual Quim.*, 7 N°5 (2015) 1830-1840.
18. C. Monroy-Ortiz, and P. Castillo España. Plantas medicinales utilizadas en el Estado de Morelos. 3rd Edition, Universidad Autónoma del Estado de Morelos, Morelos, Mexico, 2010.
19. V. da Silva Lima, R. da Conceição Santos, M. L. H. Ramos, R. E. da Silva, R. J. V. do Nascimento Nunes, R. M. Ramos, J. M. Feitosa, L. R. Dário Ferreira, J. da Silva Siqueira, and G. Cavalcante da Silva. Aspectos fitoquímicos e potencialidades biológicas da *Crescentia*: uma revisão narrativa. *Revista Eletrônica Acervo Saúde/Electronic Journal Collection Health*. 12 N°9 (2020) e3886-e3886. <https://doi.org/10.25248/reas.e3886.2020>
20. M. G. Valladares-Cisneros, M. Y. Ríos-Gómez, L. Aldana-Llanos, M. E. Valdes-Estrada, and M. Gutiérrez-Ochoa. Biological Activity of *Crescentia alata* (Lamiales: Bignoniaceae) Fractions on Larvae of *Spodoptera frugiperda* (Lepidoptera: Noctuidae). *Florida Entomologist*. 97 N°2 (2014) 770-777. <https://doi.org/10.1653/024.097.0259>
21. M. G. Valladares and M. Y. Rios. Iridoids from *Crescentia alata*. *J. Nat. Prod.* 70 N°1 (2007) 100-102. <https://doi.org/10.1021/np060499w>
22. M. S. Gachet, and W. Schuhly. Jacaranda – an ethnopharmacological and phytochemical review. *Journal of Ethnopharmacology*, 121 N°1 (2009) 14-27. <https://doi.org/10.1016/j.jep.2008.10.015>
23. J. A. Banderas-Tarabay, M. Cervantes-Rodriguez, M. Grada-Sanchez, M. Espindola-Lozano, E. Cuevas-Romero, A. Navarro-Ocana, and D. Mendez-Iturbide. Antioxidant-mediated protective effect of hawthorn (*Crataegus mexicana*) peel extract in erythrocytes against oxidative damage. *Afr. J. Food Sci.*, 9 N°5 (2015) 208-222. <https://doi.org/10.5897/AJFS2015.1269>
24. D. Kumar, V. Arya, Z. A. Bhat, N. A. Khan and D. N. Prasad. The genus *Crataegus*: chemical and pharmacological perspectives. *Revista Brasileira de Farmacognosia*, 22 N°5 (2012) 1187-1200. <http://dx.doi.org/10.1590/S0102-695X2012005000094>
25. P. Nicasio, and M. Meckes. Hypotensive effect of the hydroalcoholic extract from *Jacaranda mimosaeifolia* leaves in rats. *J. Ethnopharmacol.* 97 N°2 (2005) 301-304. <https://doi.org/10.1016/j.jep.2004.11.017>
26. L. Sidjui Sidjui, R. M. Kouipou Toghueo, E. Menkem Zeuko'o, C. D. Jiatsa Mbouna, V. Mahiou-Leddet, G. Herbette, F. Boyom Fekam, E. Ollivier and G. Ngosong Folefoc. Antibacterial Activity of the Crude Extracts, Fractions and Compounds from the Stem Barks of *Jacaranda mimosifolia* and *Kigelia africana* (Bignoniaceae). *Pharmacologia*, 7 (2016) 22-31. <https://doi.org/10.5567/pharmacologia.2016.22.31>
27. R. Naz, T. H. Roberts, A. Bano, A. Nosheen, H. Yasmin, M. N. Hassan, R. Keyani, S. Ullah, W. Khan, and Z. Anway. GC-MS analysis, antimicrobial, antioxidant, antilipoxygenase and cytotoxic activities of *Jacaranda mimosifolia* methanol leaf extracts and fractions. *PLoS ONE* 15 N°7 (2020) e0236319. <https://doi.org/10.1371/journal.pone.0236319>
28. F. A. Moharram, and M. S. A. Marzouk. A novel phenylethanoid dimer and flavonoids from *Jacaranda mimosaeifolia*. *Zeitschrift fur Naturforschung B*, 62 (2007) 1213-1220. <https://doi.org/10.1515/znb-2007-0918>
29. ASTM G 01-03, Standard practice for preparing, cleaning, and evaluating corrosion test specimens, ASTM Book of Standards. 3.02 (2003) West Conshohocken.

30. ASTM G 31-72, Standard practice for laboratory immersion corrosion testing of metals, ASTM Book of Standards. 3.02 (2004) West Conshohocken.
31. A. Fateh, M. Aliofkhaezai, and A. R. Rezvanian. Review of corrosive environments for copper and its corrosion inhibitors. *Arabian Journal of Chemistry* 13 N°1 (2020) 481-544. <http://dx.doi.org/10.1016/j.arabjc.2017.05.021>
32. R. Kouda, F. Yakushiji. Recent advances in iridoid chemistry: Biosynthesis and chemical synthesis. *Chem. Asian J.* (2020) <https://doi.org/10.1002/asia.202001034>
33. F. Wang, Y. Zhang, S. Wu, Y. He, Z. Dai, S. Ma, and B. Liu. Studies of the structure-antioxidant activity relationships and antioxidant activity mechanism of iridoid valepotriates and their degradation products. *PLoS ONE*, 12 N°12 (2017) e0189198. <https://doi.org/10.1371/journal.pone.0189198>
34. K. Rose, M. Sukumaran, K. Devarayan, G. Mayakrishnan and S. Arumugam. Physicochemical Evidence for the Adsorption of Extract of *Jacaranda mimosifolia* on Steel Against Corrosion in Acid Medium. *Orient. J. Chem.*, 32 N°4 (2016) 2147-2153.
35. M. N. Fathima, A. Prithiba, S. Leelavathi, and R. Rajalakshmi. Investigation of *Podranea ricasoliana* Leaves Extract as Green Corrosion Inhibitor for Mild Steel in 1M HCl. *International Journal of Advanced Scientific Research and Management*, 1 N°4 (2016) 122-130.
36. C. E. Ogukwe, C. O. Akalezi, M. A. Chidiebere, K. L. Oguzie, Z. O. Iheabunike, and E. E. Oguzie. Corrosion inhibition and adsorption of *Anthocleista djalonensis* leaf extract on the acid corrosion of mild steel. *Portugaliae Electrochimica Acta*, 30 N°3 (2012) 189-202. <http://dx.doi.org/10.4152/pea.201203189>
37. P. A. Onocha, D. A. Okorie, J. D. Connolly, and D. S. Roycroft. Monoterpene diol, iridoid glucoside and dibenzo- α -pyrone from *Anthocleista djalonensis*. *Phytochemistry*, 40 N°4 (1995) 1183-1189. [https://doi.org/10.1016/0031-9422\(95\)00121-M](https://doi.org/10.1016/0031-9422(95)00121-M)
38. S. Umoren, I. B. Obot, Z. Gasem, and N. A. Odewunmi. Experimental and theoretical studies of red apple fruit extract as green corrosion inhibitor for mild steel in HCl solution. *Journal of Dispersion Science and Technology*, 36 N°6 (2015) 789-802. <https://doi.org/10.1080/01932691.2014.922887>
39. R. S. Al-Moghrabi, A. M. Abdel-Gaber, and H. T. Rahal. A comparative study on the inhibitive effect of *Crataegus oxyacantha* and *Prunus avium* plant leaf extracts on the corrosion of mild steel in hydrochloric acid solution. *Int J Ind Chem* 9 (2018) 255–263. <https://doi.org/10.1007/s40090-018-0154-3>
40. A. Rodríguez-Torres, M. G. Valladares-Cisneros, C. Cuevas-Arteaga, and M. A. Veloz-Rodríguez. Study of green corrosion inhibition on AISI 1018 carbon steel in sulfuric acid using *Crataegus mexicana* as eco-friendly inhibitor. *J. Mater. Environ. Sci.*, 10 2 (2019) 101-112.
41. S. Chihi, N. Gherraf, B. Alabed, and S. Hameurlain. Inhibition effect of flavonoid extract of *Eurphasia guyoiana* on the corrosion of mild steel in H₂SO₄ medium. *J Fundam Appl Sci.*, 1 2 (2009) 31-19. <https://doi.org/10.4314/jfas.v1i2.4>
42. A. Singh, E. E. Ebenso, and M. A. Quraishi. Theoretical and electrochemical studies of *Cuminum cyminum* (Jeera) extract as green corrosion inhibitor for mild steel in hydrochloric acid solution. *Int J Electrochem Sci.*, 7 (2012) 8543-8559.
43. J. Bhawsar, P. K. Jain, P. Jain. Experimental and computational studies of *Nicotiana tabacum* leaves extract as green corrosion inhibitor for mild steel in acidic medium. *Alex Eng J.*, 54 N°3 (2015) 769-775

(2020) ; <http://www.jmaterenvirosci.com>