Int. J. Electrochem. Sci., 7 **(2012)** 1997 - 2008

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Eco-friendly Corrosion Inhibitors: Adsorption and Inhibitive Action of Ethanol Extracts of Chlomolaena Odorata L. for the Corrosion of Mild Steel in H_2SO_4 Solutions

I.B. Obot[1,*], *E.E. Ebenso*[2], *Zuhair M. Gasem*[3]

[1] Department of Chemistry, Faculty of Science, University of Uyo, P.M.B 1017, Uyo, Akwa Ibom State, Nigeria.
[2] Department of Chemistry, School of Mathematical and Physical Sciences, North-West University (Mafikeng Campus) Private Bag X2046, Mmabatho 2735, South Africa.
[3] Department of Mechanical Engineering, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia.
[*]E-mail: proffoime@yahoo.com

Received: 11 February 2012 / *Accepted:* 27 February 2012 / *Published:* 1 March 2012

The corrosion inhibition of mild steel in 0.5 M H_2SO_4 by ethanolic extract from the leaves of *Chromolaena odorata L.* (LECO) has been studied as a possible source of green inhibitor using the gravimetric technique in the temperature range 303-333 K. Results obtained showed that the LECO functioned as a corrosion inhibitor for mild steel in the acidic environment. Inhibition efficiency increased with extract concentration but decreased with temperature. At a concentration as low as 5 %v/v of the extract, the percentage inhibition reached about 95 % at 303 K and 89 % at 333 K. The thermodynamic parameters for the adsorption of this inhibitor on the metal surface such as ΔG^{o}_{ads}, were calculated using the Langmuir adsorption isotherm. The activation (E_a) energy and the heat of adsorption (Q_{ads}) of the corrosion inhibition process suggest that the LECO molecules are physically adsorbed on the metal surface. The ethanolic *Chlomolaena odorata L.* leaves extract was found to be an excellent potential corrosion inhibitor because of the presence of essential oils, steroids, triterpenes, as well as the high content of a series of complex flavonoids, chalcones and flavones in the extract.

Keywords: Corrosion, Inhibition, *Chromolaena odorata L.*, Mild steel, Adsorption.

1. INTRODUCTION

The corrosion of metals in many industries, constructions, installations, and civil services such as electricity, water, and sewage supplies is a serious problem. In order to prevent or minimize corrosion, inhibitors are usually used especially in flow cooling systems. Organic, inorganic, or a mixture of both inhibitors can inhibit corrosion by using chemisorption and/or physisorption mechanism on the metal surface or reacting with metal ions and forming a barrier-type precipitate on its surface [1].

However, most of the corrosion inhibitors are synthetic chemicals, expensive and very hazardous to environment. Therefore, it is desirable to source for environmentally safe inhibitors [2–7]. It has been shown that natural products of plant origin contain different organic compounds (e.g. alkaloids, tannins, pigments, organic and amino acids, and most are known to have inhibitive action [8–15]. Other authors have also shown that the inhibitive effect of some plants solution extract is due to the adsorption of molecules of phytochemical present in the plant on the surface of the metal [16–19]. The review including extensive listing of various plants extracts as corrosion inhibitors has recently been published [20].

Among plant materials tested in our laboratory to date include *Pachylobus edulis* [21], *Gum arabic* [22], *Raphia hookeri* [23, 24], *Ipomoea involcrata* [25, 26]. Despite the great availability and varieties of plant materials only relatively few have been thoroughly investigated.

More recently, *Chromolaena odorata L.* leaves extract has been established as an eco-friendly corrosion inhibitor of acid corrosion of aluminium in 2 M HCl by our research group [27], using hydrogen evolution and thermometric techniques. Presently, to the best of my knowledge, there is no reported work on inhibitive effects of *Chromolaena odorata L.* extract on acid corrosion of mild steel in sulphuric acid solution.

This paper reports the adsorption and inhibitive efficacy of ethanolic extract of the leaves of *Chromolaena odorata L* in combating the menace of acid induce corrosion of mild steel in sulphuric acid using weight loss (gravimetric) technique at a temperature range of 303 – 333 K. Activation and thermodynamic parameters were effectively used to characterize the inhibition mechanism of the adsorption process.

2. MATERIALS AND METHODS

Tests were performed on a freshly prepared sheet of mild steel of the following composition (wt. %): 0.13% C, 0.18% Si, 0.39% Mn, 0.40% P, 0.04% S, 0.025% Cu, and bal. Fe. Specimens used in the weight loss experiment were mechanically cut into 5.0 cm x 4.0 cm x 0.8 cm dimensions, then abraded with SiC abrasive papers 320, 400 and 600 grit respectively, washed in absolute ethanol and acetone, dried in room temperature and stored in a moisture free dessicator before their use in corrosion studies [28].

The procedure for the preparation of the leaf extracts is similar to that reported recently by Okafor et al. [29]. *Chromolaena odorata L.* leaves were collected from Itak, Akwa Ibom State, Nigeria. They were dried in an N53C-Genlab Laboratory oven at 60 ^{o}C, and ground to powder form. About 10 g of the powder was extracted continually with 250 cm^3 of ethanol in a Soxhlet extractor. The resultant solution was kept for 24 h, filtered and stored. Appropraite concentration (0.5 M) of H_2SO_4 was prepared using deionized water in the absence and presence of various concentrations of LECO. The employed concentration range of LECO was 1 - 5 % v/v.

Weight loss measurements were conducted under total immersion using 250 mL capacity beakers containing 200 mL test solution at 303-333 K maintained in a thermostated water bath. The mild steel coupons were weighed and suspended in the beaker with the help of rod and hook. The coupons were retrieved at 2 h interval progressively for 10 h at 303 K and 10 h at 313-333 K, washed thoroughly in 20% NaOH solution containing 200 g/l of zinc dust with bristle brush, rinsed severally in deionized water, cleaned, dried in acetone, and re-weighed [30]. The weight loss, in grammes, was taken as the difference in the weight of the mild steel coupons before and after immersion in different test solutions determined using LP 120 digital balance with sensitivity of ± 0.1 mg. Then the tests were repeated at different temperatures. In order to get good reproducibility, experiments were carried out in triplicate. In this present study, the standard deviation values among parallel triplicate experiments were found to be smaller than ± 2 %, indicating good reproducibility.

The corrosion rate (ρ) in g cm^{-2} h^{-1} was calculated from the following equation [31]:

$$\rho = \frac{\Delta W}{At} \qquad (1)$$

where W is the average weight loss of three mild steel sheets, *A* the total area of one mild steel specimen, and t is the immersion time . With the calculated corrosion rate, the inhibition efficiency (*%I*) was calculated as follows [32]:

$$\%I = \left(\frac{\rho_1 - \rho_2}{\rho_1} \right) x100 \qquad (2)$$

Where ρ_1 and ρ_2 are the corrosion rates of the mild steel coupons in the absence and presence of LECO, respectively.

3. RESULTS AND DISCUSSION

3.1. Weight loss, corrosion rates and inhibition efficiency

The gravimetric method (weight loss) is probably the most widely used method of inhibition assessment [33]. The simplicity and reliability of the measurement offered by the weight loss method is such that the technique forms the baseline method of measurement in many corrosion monitoring programmes [34]. Several authors have reported on comparable agreement between weight loss technique and other well established techniques of corrosion monitoring such as polarization technique [35], electrochemical impedance spectroscopy [36], gasometric [37], thermometric [23] and atomic absorption spectroscopy [38]. Recently, weight loss method together with potentiodynamic polarization and electrochimical impedance spectroscopy were used to evaluate the corrosion inhibitive effect of cigarette butt on N80 steel at 90 ^{o}C in hydrochloric acid solution [39]. Results obtained for the three independent methods were in good agreement.

The anodic dissolution of iron in acidic media and the corresponding cathodic reaction has been reported to proceed as follows [40]:

$$Fe + A^{n-} \leftrightarrow (FeA^{n-})_{ads} \tag{3}$$

$$(FeA^{n-})_{ads} \leftrightarrow (FeA^{n-})_{ads} + ne^{-} \tag{4}$$

$$(FeA^{n-})_{ads} \rightarrow (FeA^{n+})_{ads} + ne^{-} \tag{5}$$

$$(FeA^{n+})_{ads} \leftrightarrow (Fe^{2+})_{ads} + A^{n-} \tag{6}$$

The cathodic hydrogen evolution:

$$Fe + H^{+} \leftrightarrow (FeH^{+})_{ads} \tag{7}$$

$$(FeH^{+})_{ads} + ne^{-} \rightarrow (FeH)_{ads} \tag{8}$$

$$(FeH^{+})_{asd} + H^{+} + ne^{-} \rightarrow Fe + H_2 \tag{9}$$

As a result of these reactions, including the high solubility of the corrosion products, the metal loses weight in the solution.

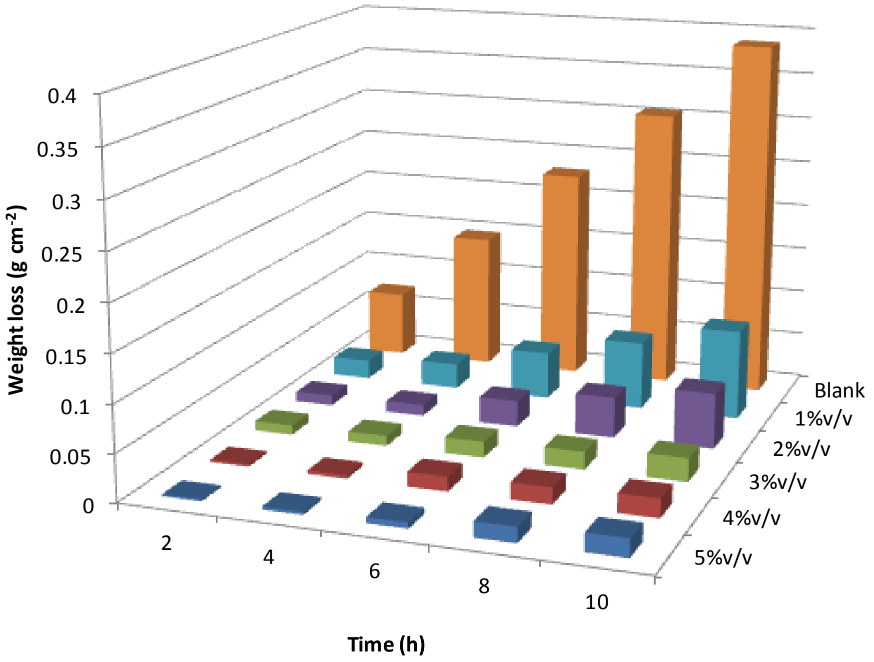

Figure 1. Effect of exposure time on weight loss of mild steel in 0.5 M H_2SO_4 at 303 K.

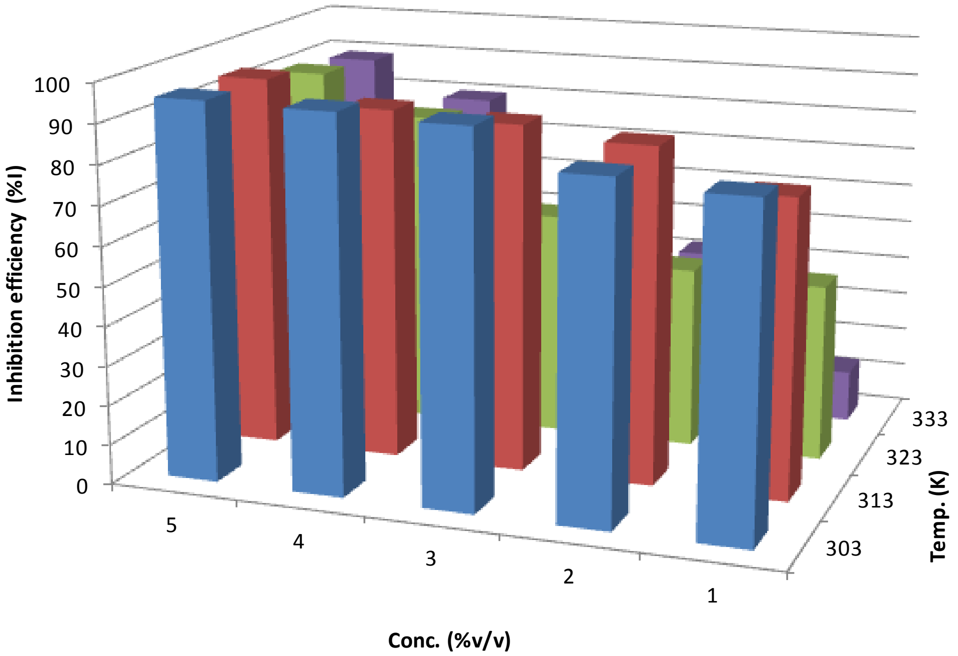

Figure 2. Variation of inhibition effeciency with concentration at different temperatures.

Table 1. Calculated values of inhibition efficiency for mild steel corrosion in 0.5 M H_2SO_4 in the presence of LECO at 303-333K

Concentration *(% v/v)*	Inhibition efficiency *(%I)*			
	303K	313K	323K	333K
1	82.47	75.26	44.94	13.07
2	84.54	85.06	46.18	42.09
3	93.81	87.84	57.37	52.03
4	94.85	89.27	80.99	79.94
5	95.36	94.92	90.76	89.14

The data obtained for the corrosion behaviour of mild steel in 0.5 M H_2SO_4 solution containing LECO within the concentration range of 1-5 %v/v from weight loss measurements are presented in Figs. 1 and 2, respectively, as well as Table 1. Fig. 1 shows the weight loss-time plots for mild steel in 0.5 M H_2SO_4 without and with different concentrations of LECO at 303 K. It is seen from the plots that the amount of material loss (g cm^{-2}) decreases significantly in the presence of LECO compared to the blank acid solution and was also found to be dependent on the concentration of the extracts. This indicates that LECO inhibit the corrosion of mild steel in 0.5 M H_2SO_4.

Fig. 2 shows the variation of the inhibition efficiency with inhibitor concentration of LECO at different temperatures. Inspection of these data reveals that inhibition efficiency increases with increasing concentration of inhibitor. This suggests that the phytochemical components in the plant extracts are adsorbed on the mild steel-solution interface where the adsorbed molecules mechanically screen the coated part of the metal surface from the action of the corrodent. Similar views have been held by other researchers [10, 13]. Previous investigations revealed the presence of essential oils, steroids, triterpenes in *Chlomolaena odorata L* [27]. Suksamrarn et al. [41], reported the presence of four flavanones, isosakuranetin (5,7-dihydroxy-4'-methoxyflavanone), persicogenin (5,3'-dihydroxy-7,4'-dimethoxyflavanone) 5,6,7,4'-tetramethoxyflavanone and 4'-hydroxy-5,6,7-trimethoxyflavanone two chalcones, 2'-hydroxy-4,4',5',6'-tetramethoxychalcone and 4,2'-dihydroxy-4',5',6'-trimethoxychalcone, and two flavones, acacetin (5,7-dihydroxy-4'-methoxyflavone) and luteolin (5,7,3',4'-tetrahydroxyflavone) in *Chlomolaena odorata L.* (Fig.3).

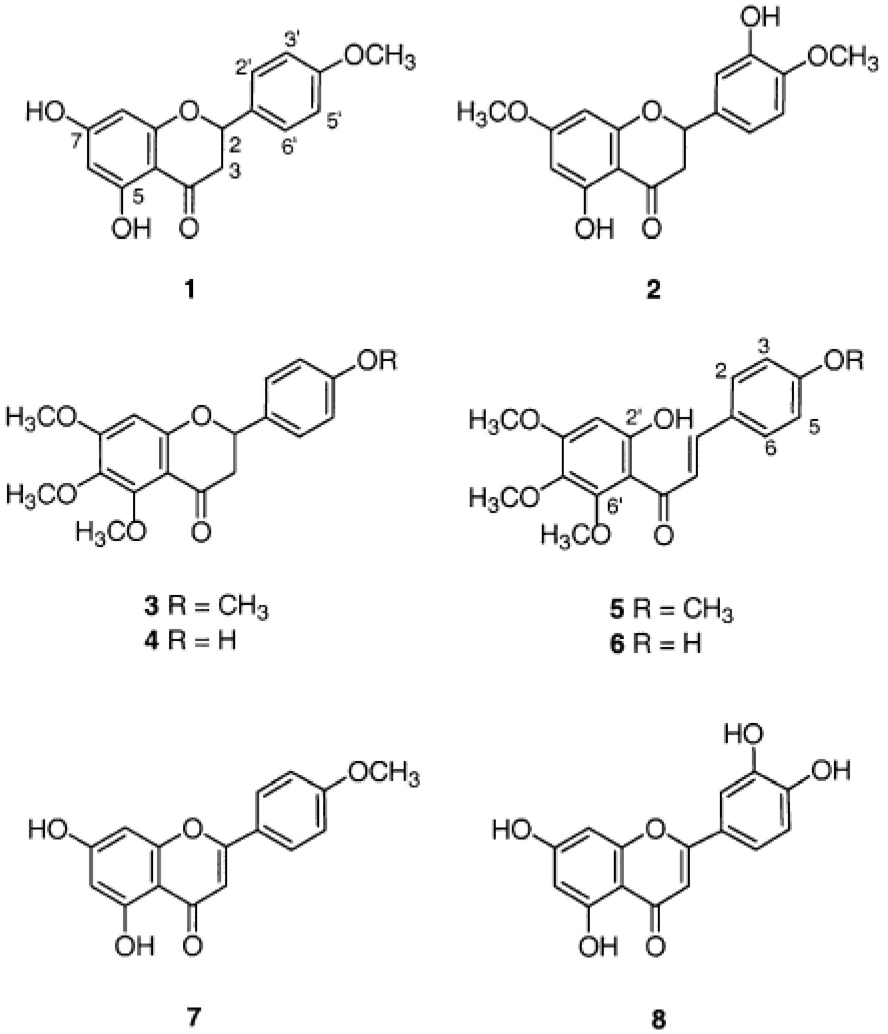

Figure 3. Four flavanones, isosakuranetin (5,7-dihydroxy-4'-methoxyflavanone) (**1**), persicogenin (5,3'-dihydroxy-7,4'-dimethoxyflavanone) (**2**), 5,6,7,4'-tetramethoxyflavanone (**3**) and 4'-hydroxy-5,6,7-trimethoxyflavanone (**4**), two chalcones, 2'-hydroxy-4,4',5',6'-tetramethoxychalcone (**5**) and 4,2'-dihydroxy- 4',5',6'-trimethoxychalcone (**6**), and two flavones, acacetin (5,7-dihydroxy-4'-methoxyflavone) (**7**) and luteolin (5,7,3',4'-tetrahydroxyflavone) (**8**) isolated from *Chromolaena odorata L.*

These compounds are heterogeneous organic compounds containing nitrogen, oxygen and sulphur or/and aromatic ring in their molecular structures. Organic heterogeneous compounds containing these elements have been reported to be efficient corrosion inhibitors [42 - 44]. Thus, the adsorption of these compounds on the surface of the metal is assumed to be mostly responsible for the inhibition of the corrosion reaction. However, the mutual effects of the phytochemical components of the extract may contribute to its high inhibition efficiency.

From Fig. 2, it can also be shown that the inhibition efficiency decreases with an increase in temperature. Such behaviour can be interpreted in terms of the fact that the phytochemical molecules are physically adsorbed on the surface of metal [45], such that an increase in temperature resulted in the desorption of some adsorbed phytochemical molecules from the metal surface. Since, a physisorption mechanism is indicative of a weak adsorption bond, it may be possible that at higher temperatures, the decrease in inhibition efficiency may be a result of the increased agitation of the solution resulting from higher rates of hydrogen evolution, thereby reducing the ability of the molecules to be adsorbed on the surface of the metal [29].

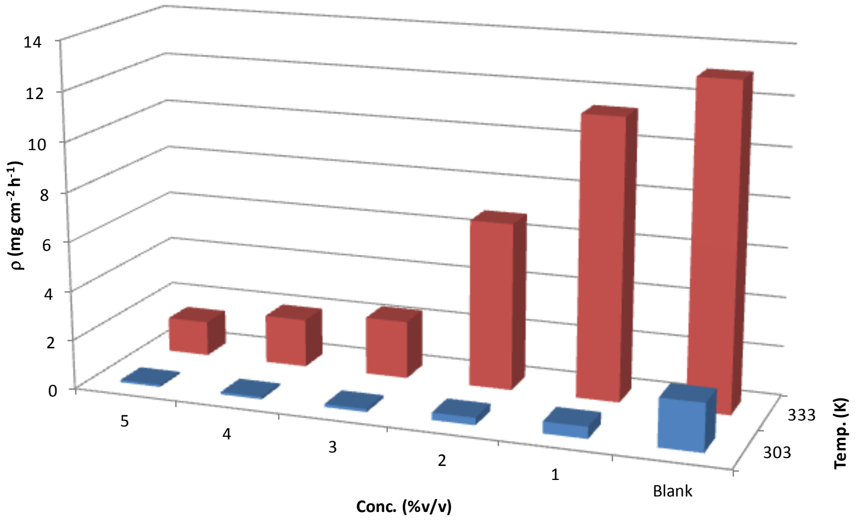

Figure 4. Variation of corrosion rate with inhibitor concentration for mild steel in 0.5 M H_2SO_4 containing LECO at 303 and 333 K.

The variation of corrosion rate with inhibitor concentration for mild steel in 0.5 M H_2SO_4 containing LECO at 303 and 333 K (Fig. 4) shows that the corrosion rate decreases markedly with increase in inhibitors concentration. The decrease may be attributed to the increase in the active (phytochemicals) ion in the corrosion inhibition process. Also from Fig. 3, it can be seen that corrosion rate increases with rise in temperature from 303 K to 333 K. Similar reports have been documented by several researchers [29, 36 - 38].

3.2. Effect of temperature

Temperature has a great effect on the rate of metal electrochemical corrosion. In case of corrosion in a neutral solution (oxygen depolarization) the increase in temperature has a favourable effect on the overpotential of oxygen depolarization and the rate of oxygen diffusion but it leads to a decrease of oxygen solubility. In case of corrosion in acidic medium (hydrogen depolarization), the corrosion rate increases exponentially with temperature increase because the hydrogen evolution overpotential decreases [46]. Therefore, in order to evaluate the stability of adsorbed layer/film of inhibitor on mild steel surface as well as activation parameters of the corrosion process of steel in acidic media, weight loss measurements were carried out in the range of temperature 303 – 333 K in the absence and presence of different concentrations of LECO during 10 h immersion time.

Thus in examining the effect of temperature on the corrosion process, the apparent activation energies (E_a) were calculated from the Arrhenius equation [27]:

$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (10)$$

where ρ_2 and ρ_1 are the corrosion rates at temperature T_1 and T_2 respectively, and R the molar gas constant. An estimate of heat of adsorption was obtained from the trend of surface coverage (θ) (%I = 100 × θ) with temperature as follows [27]:

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] x \left(\frac{T_{1X} T_2}{T_2 - T_1}\right) kJmol^{-1} \qquad (11)$$

where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2, The calculated values for both parameters are given in Table 2.

Table 2. Calculated values of activation energy, E_a (kJ mol^{-1}) and heat of adsorption, Q_{ads} (kJ mol^{-1}) for LECO for mild steel corrosion in 0.5 M H_2SO_4.

Conc. (% v/v)	E_a (kJ mol^{-1}) 30-60 °C	Q_{ads} (kJ mol^{-1}) 30-60 °C
Blank(0.5 M H_2SO_4)	53.37	-
1	88.52	-57.75
2	87.24	-34.03
3	78.26	-18.98
4	88.23	-26.79
5	77.15	-17.63

Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies with and without inhibitor gives some insight into the possible mechanism of inhibitor adsorption. Popova et al. [46] reported that a decrease in inhibition efficiency with a rise in temperature with a corresponding increase in corrosion activation energy in the presence of an inhibitor compared to its absence is frequently interpreted as being suggestive of physical adsorption. It has been suggested that adsorption of an organic inhibitor can affect the corrosion rate by either decreasing the available reaction area (geometric blocking effect) or by modifying the activation energy of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process [47]. The E_a values support the earlier proposed physisorption mechanism.

It was found that the adsorption of LECO species on the mild steel surface is an exothermic process associated with negative values of adsorption heat (Q_{ads}). This result indicates that the degree of surface coverage decreased with rise in temperature, supporting the earlier proposed physisorption mechanism [47].

3.3. Adsorption isotherm and thermodynamic study

Basic information on the interaction between the inhibitor and the mild steel surface can be provided by the adsorption isotherm. For this purpose, the values of surface coverage at different concentrations of LECO in acid media in the temperature range (303 – 333 K) have been used to explain the best isotherm to determine the adsorption process. The adsorption of an organic adsorbate on to metal-solution interface occurs by a substitutional adsorption process between organic molecules in the aqueous solution $Org_{(sol)}$ and the water molecules on the metallic surface $H_2O_{(sol)}$ [48]:

$$Org_{(sol)} + xH_2O_{(ads)} \rightarrow Org_{(ads)} + xH_2O_{(sol)} \tag{12}$$

where $Org_{(sol)}$ and $Org_{(ads)}$ are the organic molecules in the aqueous solution and adsorbed on the metallic surface, respectively, $H_2O_{(ads)}$ is the water molecules on the metallic surface, and x is the size ratio representing the number of water molecules replaced by one molecule of organic adsorbate.

Several isotherms including Frumkin, Langmuir, Temkin, Freundlich, Bockris-Swinkels and Flory-Huggins isotherms were employed to fit the experimental data. It is found that the adsorption of studied extract on steel surface obeys the Langmuir adsorption equation [49]:

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{13}$$

where C is the concentration of extract, K the adsorption equilibrium constant, and θ is the surface coverage.

Table 3. Some parameters from Langmuir isotherm model for mild steel in 0.5 M H_2SO_4 in the presence of LECO.

Temperature (K)	Slope	K (L ml^{-1})	(R^2)	ΔG^o_{ads} (kJ mol^{-1})
303	0.96	2.73	0.998	-12.64
313	0.98	3.58	0.999	-13.77
323	0.97	2.65	0.997	-13.40
333	1.06	2.67	0.964	-13.83

Plots of C/θ against C yield straight lines as shown in Fig. 5, and the corresponding linear regression parameters are listed in Table 3. Both linear coefficient (R^2) and slope are close to 1, indicating the adsorption of LECO on steel surface obeys Langmuir adsorption isotherm.

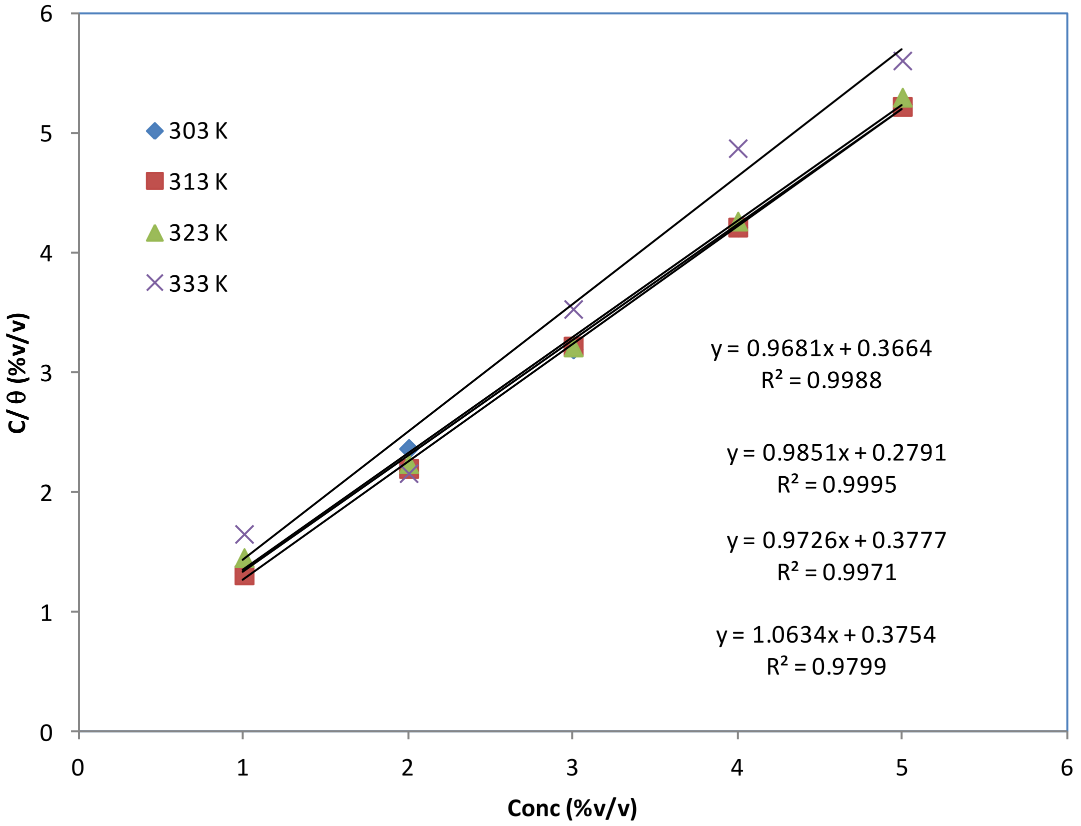

Figure 5. Langmuir adsorption isotherm plots for LECO on mild steel in 0.5 M H_2SO_4.

K is related to the free energy of adsorption ΔG^o_{ads} by the equation [50]:

$$K = \frac{1}{C_{water}} \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \qquad (14)$$

where C_{water} is the concentration of water expressed in ml/L, R is the molar gas constant ($J\ mol^{-1}K^{-1}$) and T is the absolute temperature *(K)*. It must be noted that the concentration unit of water molecules must be similar to that of inhibitor, because this is a common mistake in many corrosion inhibition literatures that used natural products as inhibitors. Most of the literatures used concentration of water in the molar unit (55.5 M at 25 ^oC), while they expressed their inhibitors concentration in mass/volume or volume/volume %, which leads to uncorrected values for ΔG^o_{ads}.

The values of ΔG^o_{ads} were also listed in Table 3. The negative values of ΔG^o_{ads} suggest that the adsorption of LECO is a spontaneous process. Generally speaking, values of ΔG^o_{ads} up to -20 kJ mol^{-1} indicate the electrostatic attraction between the charged metal surface and charged organic molecules in the bulk of the solution (physisorption). Those around -40 kJ mol^{-1} or smaller involve charge sharing or charge transfer between the metal and the organic molecules (chemisorption) [51]. Accordingly, the values of ΔG^{o}_{ads}obtained in the present study are below -20 kJ mol^{-1} and is therefore consistent with physisorption mechanism.

4. CONCLUSIONS

1. Leaves extract of *Chromolaena odorata L.* (LECO) was found to be an effective inhibitor for the corrosion of mild steel in 0.5 M H_2SO_4.
2. Gravimetric measurements revealed that inhibition efficiency reached 95 % at a concentration as low as 5 %v/v of the extract. Furthermore, Inhibition efficiency increased with extract concentration but decreased with temperature.
3. Adsorption of inhibitor species was found to follow Langmuir isotherm model and the adsorption free energy calculated shows the spontaneous adsorption of inhibitor species onto the mild steel surface.
4. Physical adsorption mechanism of LECO species on steel surface in 0.5 M H_2SO_4 is proposed following the trend of extract adsorption with solution temperature. The activation (E_a) energy and the heat of adsorption (Q_{ads}) of the corrosion inhibition process calculated also corroborated this assertion.

References

1. A. Nahle, I. Abu-abdoun, I. Abdel-Rahman, M. Al Khayat, *Int. J. Corros*. (2010) doi: 10.1155/2010/460154.
2. M. Bouklah and B. Hammouti, *Portugaliae Electrochimica Acta.* 24 (2006) 457.
3. E.E. Oguzie, *Pigment & Resin Tech*. 34(6) (2005) 321.
4. P.C. Okafor, U.J. Ekpe, E.E. Ebenso, E.M. Umoren and K.E. Leizou, *Bull. Electrochem.* 21(8) (2005) 347.
5. E.E. Oguzie and E.E. Ebenso, *Pigment & Resin Tech*. 35(1) (2006) 30.
6. A.Y. El-Etre and Z. El-Tantawy, *Port. Electrochim. Acta* 24 (2006) 347.
7. E.E. Oguzie, *Pigment & Resin Tech*. 35(6) (2006) 334.
8. H. Ashassi-Sorkhabi and D. Seifzadeh, *Int. J. Electrochem. Sci*. 1 (2006) 92.
9. A.A. Rahim, E. Rocca, J. Steinmetz, M.J. Kassim, R. Adnan and M. Sani Ibrahim, *Corros. Sci.* 49 (2007) 402.
10. E.E. Oguzie, *Mater. Chem. Phys*. 99(2–3) (2006) 441.
11. E.E. Oguzie, *Corros. Sci*. 49 (2007) 1527.
12. Z. Ghasemi and A. Tizpar, *Appl. Surf. Sci*. 252 (2006) 3667.
13. A.M. Abdel-Gaber, B.A. Abd-El-Nabey, I.M. Sidahmed, A.M. El-Zayady and M. Saadawy, *Corros. Sci.* 48(9) (2006) 2765.
14. C.A. Loto, *Corros. Prev. & Control.* 48(1) (2001) 38.
15. A.Y. El-Etre, *J. Colloid & Interface Sci.* 314 (2007) 578.
16. C.A. Loto, *Corros. Prev. & Control*. 50(1) (2003) 43.
17. A.Y. El-Etre, *Appl. Surf. Sci.* 252 (2006) 8521.

18. [E.E. Oguzie, Y. Li and F.H. Wang, *J. Colloid & Interface Sci*. 310 (2007) 90.
19. E.E. Oguzie, A.I. Onuchukwu, P.C. Okafor and E.E. Ebenso, *Pigment & Resin Tech*. 35(2) (2006) 63.
20. B. E. Rani, B. J. Basu, *Int. J. Corros*. doi: 10.1155/2012/380217.
21. S. A. Umoren, I. B. Obot, *E-J Chem*. 5 (2008) 355.
22. S. A. Umoren, I. B. Obot, E. E. Ebenso, P. C. Okafor, O. Ogbobe, E. E. Oguzie, *Anti-Corros. Meth. & Mater*. 55 (2006) 227.
23. S. A. Umoren, I. B. Obot, E. E. Ebenso, N.O. Obi-Egbedi, *Desalination* 247 (2009) 561.
24. S. A. Umoren, I. B. Obot, N.O. Obi-Egbedi, *J. Mater. Sci*. 44 (2009) 274.
25. I. B. Obot, N. O. Obi-Egbedi, S. A. Umoren, E. E. Ebenso, *Int. J. Electrochem. Sci.* 5 (2010) 994.
26. I. B. Obot, N. O. Obi-Egbedi, *Port. Electrochim. Acta* 27 (2009) 517.
27. I. B. Obot, N. O. Obi-Egbedi, *J. Appl. Electrochem.* 40 (2010) 1977.
28. I.B. Obot, N.O. Obi-Egbedi, *Mater. Chem. Phys*. 122 (2010) 325.
29. P. C. Okafor, V. I. Osabor, E. E. Ebenso, *Pigm & Res. Technol*. 36 (2007) 299.
30. I. B. Obot, N. O. Obi-Egbedi, A.O. Eseola, *Ind. Eng. Chem. Res.* 50 (2011) 2098.
31. I.B. Obot, and N.O. Obi-Egbedi, *Curr. Apl. Phys.* 11 (2011) 382-392.
32. I.B. Obot, N.O. Obi-Egbedi, *Corros. Sci.* 52 (2010) 198.
33. A.A. Khadom, A.S. Yaro, Kadum, A.H, *J. Taiwan. Inst. Chem. Engr*. 41 (2010) 122.
34. A.A. Rahim, J. Kassim, *Recent. Patents Mater. Sci*. 1 (2008) 223.
35. S.K. Shukla, A.K. Singh, I. Ahamad, M.A. Quraishi, *Mat. Lett*. 63 (2009) 819.
36. S.K. Shukla, M.A. Quraishi, *Corros. Sci*. 51 (2009) 1007.
37. S.A. Umoren, I.B. Obot, *Surf. Rev. Lett*. 15(3) (2008), 277.
38. Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, H. Hannache, *Desalination* 247 (2009) 175.
39. J. Zhao, N. Zhang, C. Qu, X. Wu, J. Zhang, X. Zhang, *Ind. Eng. Chem. Res*. 49 (2010) 3986.
40. M. A. Quraishi, A. Singh, V. K. Singh, D. K. Yadav, A. K. Singh, *Mater. Chem. Phys.* (2010), doi: 10.1016/j.matchemphys.2010.02.066.
41. A. Suksamrarn, A. Chotipong, T. Suavansri, S. Boongird1, P. Timsuksai, S. Vimuttipong, A. Chuaynugul, *Arch. Pharm. Res*. 27 (2004) 507.
42. L. Wang, *Corros. Sci.* 48 (2006) 608.
43. J.J. Fu, S.N. Li, L.H. Cao, Y.Wang, L.H. Yan, L.D. Lu, *J. Mater. Sci*. 45 (2010) 979.
44. N.O. Obi-Egbedi, I.B. Obot, M.I. El-khaiary, *J. Mol. Struct*. 1002 (2011) 86.
45. I.B. Obot, and N.O. Obi-Egbedi, *Colloids & Surf.A: Physicochem. Eng. Aspects* 330 (2008) 207.
46. A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros. Sci*. 45 (2003) 33.
47. I. B. Obot, N. O. Obi-Egbedi, S. A. Umoren, *Corros. Sci.* 51 (2009) 276.
48. G. K. Gomma, M. H. Wahdan, *Mater. Chem. Phys*. 39 (1994) 420.
49. S. D. Deng, X. H. Li, H. Fu, *Corros. Sci*. 53 (2011) 822.
50. E. A. Noor, *Mater. Chem. Phys*. (2011), doi: 10.1016/j.matchemphys.2011.08.001
51. S. A. Umoren, *J. Appl. Polym*. Sci. 119 (2011) 2072.