Adsorption assessment of the inhibitive effect of *Crateva adansonii* on low carbon steel in acidic medium

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Abstract
This paper outlines the unique role of *Crateva adansonii* (CA) leaf extract on low carbon steel in corrosive media. The defensive ability of *Crateva adansonii* extract was evaluated by gravimetric and gasometric techniques. The result of the experiment indicated that extract of *Crateva adansonii* exhibit perfectly well on the steel due photochemical species containing in the inhibitive extract thereby blocking both the anodic and cathodic site. The mixed Inhibitive effect of *Crateva adansonii* were investigated by the kinetic state. The adsorption studies of CA leaf extract obeyed the Langmuir, Freundlich, temkin isotherm but best fitted into Langmuir adsorption isotherm which characterised by physisorption. The range of $E_a$ values (from 46.09 kJ/mol to 60.58 kJ/mol) in the presence of the extract being higher than the free solution. Which suggests strong physical adsorption (physisorption).

Keywords: Weight loss, Adsorption isotherm, Coupons, physisorption, *Crateva adansonii*

1. Introduction
Metal in relation with the environment is a process that cannot be disregarded when the issue of corrosion and its effect comes to play. This effect has been seen when metal in the combined state tends to revert to its most stable natural state on exposure to certain environmental conditions. This effect of corrosion transition has drastically and technically affected a number of industries resulting in loss and damages with huge deficit [1-3]. A huge loss of investment have been ascertained as a result of metallic corrosion and degradation, an estimated value of 276 USD equivalent to 3.1 percent of the United States GDP also estimated [3]. Moreover, Corrosion has been a destructive phenomenon that affects almost all metal, in order words, corrosion inhibitor serve as a constructive organic phenomenon that prevent or combat depletion metal surface. Green inhibitors has been the most anticipated eco-friendly and of low cost products worldwide due to numerous heteroatoms that may established inhibitive properties. *Crateva adansonii* is popularly known as sacred garlic pea or temple plant (English) [4].The phytochemical study shows that *Crateva adansonii* manifests flavonoids, saponins, alkaloids, trepenoids and cardic glycosides [5]. The aim of this research work is to investigate adsorption assessment and inhibitive potency of *Crateva adansonii* on low carbon steel in corrosive media using Gravimetric and Gasometric techniques.

2. Materials and Method

| Table 1: Chemical composition of mild steel |
|------------------------------------------|
| Element | Fe | C | Si | Mn | Al | Cr | P | S | Ni |
| %Composition | 99.2 | 0.15 | 0.17 | 0.43 | 0.006 | 0.001 | 0.02 | 0.033 | 0.007 |

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2.5 kg of *Crateva adansoni* leave were accurately weighed on balance, which were washed, air dried for a period of 14 days and ground into powder. *Crateva adansoni* leaf was extracted by drenching the dried powder leaves in ethanol bath for 72 h. After which it was then filtered. Ethanol solvent was removed by rotary evaporation at 60-65°C temperature, thereby concentrating the crude extract to about 10% residue of the extract (219.5270 g). The residue was then left at room in an open air of a cool dry place. The prepared solution of the extract were accurately weighed of 0.08, 0.2, 0.4, 0.6 and 0.8 g into 200 ml of HCl for weight loss method.

### 2.1 Gasometric Method for *Crateva adansonii* Leaf Extract.

The gasometric method for corrosion monitoring of *Crateva adansonii* Leaf Extract on low carbon steel in corrosive media was carried out using gasometric apparatus at varying concentrations of 0.08, 0.2, 0.4, 0.6, 0.8 g/L of the leaf extract. Volume of gas evolved is observed with respect to time and the rate of evolution of gas is determined from the slope of volume of gas evolved versus time graph. The inhibition efficiency (I.E.) was then determined using equation 1 [8].

\[
I.E. (\%) = \frac{V_H - V_{HI}}{V_H} \times 100 \tag{1}
\]

Where:
- \( V_H \) = Volume of gas evolved without green corrosion inhibitor
- \( V_{HI} \) = Volume of gas with green corrosion inhibitor

### 3. Results and Discussion

#### Gasometric Method for *Crateva adansonii* Leaf (CA) Extract.

As shown in Figure 1 (a), as the extract concentration of *Crateva adansonii* increased from 0.08 g/L to 0.8 g/L at 300 minutes exposure time, the volume of hydrogen gas evolved decreased from 46.1 to 7.0 cm³ at 300 minutes exposure, the metal-phytoconstituent interaction showed that 0.8 g/L is the best concentration of the adsorption of the extract in corrosive media. This suggest that the inhibitive act of the *Crateva adansonii* leaf extract onto low carbon steel is concentration dependent [15]. Moreso, Figure 1 (b) shows that the addition of CA leaf extract with increases inhibition efficiency of the system. Further observation of I.E (%) values showed that samples with 0.8 g/L concentration of CA leaf extract possess the best performance with maximum I.E (%) value of 97.87%. The progression of inhibitor performance were established in Figure 4.39(b). This suggest that the inhibitive act of the *Crateva adansonii* leaf extract onto low carbon steel is concentration dependent [10].
Figure 1: shows, (a) the variation of an amount of gas evolved in (mL) with time and (b) Inhibition efficiency with time (5 h), at five different concentrations of CA leaf extract on low carbon steel in corrosive media at room temperature.

Regression Coefficient Values of *Crateva adansonii* leaf Extract Using Langmuir, Fredluich and Temkin Adsorption Isotherm.

Results shown on Table 2, Reveals the correlation coefficient value for the three tested adsorption isotherm (i.e. the Langmuir, Fredluich, Temkin). The result shows a clear linear relationship of Langmuir isotherm with regression close to unity at some certain temperature with maximum 0.9974, this suggests a strong adsorption of extract molecules (CA) leaf onto the metal interface [12]. And minimum of 0.6641 for the adsorption of CA leaf extract in 1.75 M HCl solution. Suggest a high rate of dissolution process at varied temperatures (303-333 K) which may weaken the ability of the adsorbed extract molecules on the metal interface as attested by [12].

Table 2: The Table Shows the Regression Coefficient Values of *Crateva adansonii* leaf Extract Using the Langmuir, Fredluich and Temkin Adsorption Isotherm Plots for 3-21h Exposure time at 303-333 K.

Adsorption Parameter from Langmuir isotherm for corrosion inhibition in the presence of different concentration of *Crateva adansonii* leaf extract

Regression values at table 3, which indicates that the values of $\Delta G^\circ_{adsl}$ are negative in all cases. The negative value indicate spontaneous adsorption of the inhibitor molecules. The lower value of $\Delta G^\circ_{adsl}$ (i.e. less than -20 kJmol$^{-1}$) are consistent with electrostatic interaction between the charged organic molecules and the charged metal which relatively also suggested that inhibitor (CA) leaf extract proposed the adsorption mechanism to be (physisorption) [10]. Generally, a high value of $K_{ads}$ manifests strong interaction between inhibitor and surface of the metal. Significantly, a large values of $K_{ads}$ manifests strong interaction between inhibitor and surface of the metal and imply more efficient and hence, better inhibition efficiency. In our present study, the higher values of $K_{ads}$ at temperature of 303 K, indicates strong adsorption of CA leaf extract onto the mild steel surface. Moreso, the equilibrium constant of the adsorption process $K_{ads}$ of the adsorbed CA leaf extract molecules tends to desorb from the metal interface at high temperature range of 313-333 K alongside with varied immersion time as attested by [13].
Table 3: Adsorption Parameter from Langmuir isotherm for corrosion inhibition in the presence of different concentration of *Crateva adansonii* leaf (CA) extract on low carbon steel in corrosive media at 303 K to 333 K.

| TEMPERATURES | 303K | 313K | 323K | 333K |
|--------------|------|------|------|------|
| ADSORPTION PARAMETERS | K_{ads} | ΔG | R² | K_{ads} | ΔG | R² | K_{ads} | ΔG | R² |
| IMMERSION | | | | | | | | | | |
| TIME 3h (CA) | 10.6724 | 16.0823 | 0.9921 | 20.92050 | 18.3646 | 0.8666 | 10.4058 | 17.076 | 0.9793 | 2.05044 | 13.1076 | 0.993 |
| TIME 6h (CA) | 11.655 | 16.3042 | 0.9915 | 21.88184 | 18.4815 | 0.8720 | 3.54108 | 14.18 | 0.8257 | 2.40211 | 13.5458 | 0.9926 |
| TIME 9h (CA) | 11.6822 | 16.3101 | 0.9974 | 10.24590 | 16.5070 | 0.8744 | 5.50055 | 15.364 | 0.9428 | 2.04457 | 13.0996 | 0.931 |
| TIME 12h (CA) | 18.797 | 17.5082 | 0.9959 | 8.25764 | 15.9455 | 0.8831 | 9.28505 | 16.77 | 0.9871 | 1.59008 | 12.4036 | 0.6641 |
| TIME 15h (CA) | 15.625 | 17.0426 | 0.9974 | 6.87285 | 15.4679 | 0.9152 | 7.11238 | 16.054 | 0.9602 | 4.43262 | 15.2420 | 0.9916 |
| TIME 18h (CA) | 5.78369 | 14.5390 | 0.9967 | 5.35906 | 14.8204 | 0.9245 | 4.1425 | 14.602 | 0.8651 | 1.7963 | 12.7412 | 0.8523 |
| TIME 21h (CA) | 3.78788 | 13.4728 | 0.9863 | 4.29553 | 14.2448 | 0.9694 | 3.12598 | 13.846 | 0.7637 | 2.38493 | 13.5260 | 0.9657 |

The kinetics and thermodynamic parameters for *Crateva adansonii* leaf extract in corrosive media

The use of Arrhenius and transition state plots and equations are to establish the activation energy ($E_a$), enthalpy change ($ΔH$), and entropy change ($ΔS$) of the system. The value of $E_a$ for the uninhibited aqueous is 46.09 kJ/mol for CA leaf extract from Figure 3, shows that the activation energy ($E_a$) for CA leaf extract ranges from 46.09 kJ/mol - 60.58 kJ/mol (i.e. 0 to 0.8 g/L). From Table 4, it is found that $E_a$ values of the inhibited solutions are higher than in uninhibited solutions. It shows that values of $E_a$ enhanced with an increase in the inhibitor concentrations from (0.08 to 0.8 g/L), which is due to the deceleration of the corrosion rate of mild steel [16-18]. The result in Table 4 suggests that corrosion inhibition by the CA leaf extract is brought about by the increasing its activation energy. There is an increase in $E_a$ as a result of adsorption of the constituents on the mild steel surface making a barrier for mass and charge transfer and also an indicative of a lesser tendency to corrode [19-20]. The range of $E_a$ values (from 46.09 kJ/mol to 60.58 kJ/mol) are lower than the threshold value of 80 kJ/mol which suggests strong physical adsorption (physisorption). The value of the activation energy in the presence of inhibitor were higher than that of uninhibited solution [21-24]. A higher value of $E_a$ in inhibited solutions indicates a lower corrosion rate compared to that in its absence. The positive values of $ΔH^o$ in Table 4, reflects the endothermic behaviour of mild steel dissolution in hydrochloric acid media. The negative values of $ΔS^o$ in Table 4, suggest that the activation complex is the rate determining step that represents an association rather than dissociation step shown in Table 4. This mean that the activated molecules are in higher-order state than that of the initial state [25-27]. The kinetics and thermodynamic parameters for CA leaf extract in corrosive media are shown by Arrhenius plot (plotting log CR vs 1/T) shown in Figure 3.
Figure 3: Arrhenius plots of mild steel in corrosive media in the presence of different concentrations of *Crateva adansonii* at fixed immersion time of 21h.

The Transition state of Arrhenius plot (plotting log CR/T vs 1/T) using Erring’s equation to determine ΔH and ΔS shown in Figure 4 (change in enthalpy and entropy)

Figure 4: Transition state plots of low carbon steel in corrosive media in the presence of different concentrations of *Crateva adansonii* at fixed immersion time of 21h.

The kinetic-thermodynamic results as shown by the table using Arrhenius plot in the absence and presence of a different concentration of *Crateva adansonii* leaf extract.

**Table 4:** Activation parameters for low carbon steel in aqueous medium containing corrosive media in absence and presence of different concentration of *Crateva adansonii* leaf extract
4. Conclusion
The inhibitive influence CA ethanolic leaf extract on the corrosion of low carbon steel in corrosive media was studied by Gasometric at room temperature, weight loss method at (303-333 K). The corrosion inhibition of CA leaf extract is attributed to the adsorption of any of the phyto-chemical components on the mild steel surface. The adsorption of CA leaf extract on low carbon steel from aqueous medium obey Langmuir, Temkin and Freundlich adsorption isotherms but, Langmuir isotherm is the best fit for these inhibitors. The free energy $\Delta G_{ads}^{o}$ values for the adsorption processes indicates strong, spontaneous adsorption of CA leaf extract on the mild steel surface. CA leaf extract is brought about by the increasing its activation energy. The increase in activation energy ($E_a$) his as a result of a physical adsorption process (physisorption).

5. Recommendation
Weight loss and Potentiodynamic polarization studies the action of the inhibitors should be studied in other aggressive media.
SEM analysis of this studies should be carried out on both the protected and unprotected metal interface.

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References
[1] Scendo, M. (2007). The effect of purine on the corrosion of copper in chloride solutions. Corrosion science, 49(2), 373-390.
[2] Alaneme, K. K., Olusegun, S. J., and Adelowo, O. T. (2016). Corrosion inhibition and adsorption mechanism studies of Hunteria umbellata seed husk extracts on mild steel immersed in acidic solutions. Alexandria Engineering Journal, 55(1): 673-681.
[3] Alam, S., Albareti, F. D., Prieto, C. A., Anders, F., Anderson, S. F., Anderton, T., and Basu, S. (2015). The eleventh and twelfth data releases of the Sloan Digital Sky Survey: final data from SDSS-III. The Astrophysical Journal Supplement Series, 219(1), 12.
[4] Ajanaku, C. O., Ajani O. O., Ataboh J. U., Mordi R. C., Olugbuyiro J. A. O., Owoeye T. F. write in full (2016). Phytochemical screening and Antimicrobial Studies of Crateva adansonii Leaf Extract. Journal of Physical and Life Sciences, 24(2): 35-41.
[5] Ajanaku, K. O., Aladesuyi, O., Ajanaku, C. O., Adedapo, E. A., Akinsiku, A. A., and Sodiya, F. E. (2015). Adsorption properties of Azadirachta indica extract on corrosion of aluminium in 1.85 M hydrochloric acid. Journal of The International Association of Advanced Technology and Science, 16(4): 1-11.
[6] Satapathy, A. K., Gunasekaran, G., Sahoo, S. C., Amit, K., & Rodrigues, P. V. (2009). Corrosion inhibition by Justicia gendarussa plant extract in hydrochloric acid solution. *Corrosion science*, 51(12), 2848-2856.

[7] Eddy, N. O. (2009). Inhibitive and adsorption properties of ethanol extract of Colocasia esculenta leaves for the corrosion of mild steel in H2SO4. *International Journal of Physical Sciences*, 4(4), 165-171.

[8] Okafor, P. C., Osabor, V. I., & Ebenso, E. E. (2007). Eco-friendly corrosion inhibitors: inhibitive action of ethanol extracts of Garcinia kola for the corrosion of mild steel in H2SO4 solutions. *Pigment & Resin Technology*, 36(5), 299-305.

[9] Odeja, O., Obi, G., Ogwuche, C. E., Elemike, E. E., & Oderinlo, Y. (2015). RETRACTED ARTICLE: Phytochemical Screening, Antioxidant and Antimicrobial activities of Senna occidentalis (L.) leaves Extract. *Clinical Phytoscience*, 1(1), 6.

[10] Rani, P. D., and Selvaraj, S. (2011). Influence of Ocimum tenuiflorum extract on mild steel in acid environment. *Asian Journal of Research in Chemistry*, 4(2), 211-216.

[11] Singh, H., Sharma, R., Joshi, M., Garg, T., Goyal, A. K., & Rath, G. (2015). Transmucosal delivery of Docetaxel by mucoadhesive polymeric nanofibers. *Artificial cells, nanomedicine, and biotechnology*, 43(4), 263-269.

[12] El-Rehim, S. A., Ibrahim, M. A., & Khaled, K. F. (1999). 4-Aminoantipyrine as an inhibitor of mild steel corrosion in HCl solution. *Journal of Applied Electrochemistry*, 29(5), 593-599.

[13] Zerga, B., Attayibat, A., Sfaira, M., Taleb, M., Hammouti, B., Touhami, M. E., ... & Rais, Z. (2010). Effect of some tripodal bipyrazolic compounds on C38 steel corrosion in hydrochloric acid solution. *Journal of applied electrochemistry*, 40(9), 1575-1582.

[14] Ansari, K. R., Quraishi, M. A., & Singh, A. (2015). Isatin derivatives as a non-toxic corrosion inhibitor for mild steel in 20% H2SO4. *Corrosion Science*, 95, 62-70.

[15] Eduok, U. M., Umoren, S. A., & Udoh, A. P. (2012). Synergistic inhibition effects between leaves and stem extracts of Sida acuta and iodide ion for mild steel corrosion in 1 M H2SO4 solutions. *Arabian Journal of Chemistry*, 5(3), 325-337.

[16] Oguzie, E. E. (2007). Corrosion inhibition of aluminium in acidic and alkaline media by Sansevieria trifasciata extract. *Corrosion science*, 49(3), 1527-1539.

[17] Noor, E. A., & Al-Moubaraki, A. H. (2008). Thermodynamic study of metal corrosion and inhibitor adsorption processes in mild steel/1-methyl-4 [4’-(X)-styril pyridinium iodides/hydrochloric acid systems. *Materials Chemistry and Physics*, 110(1), 145-154.

[18] Perumal S, Muthumanickam S, Elangovan A, Karthik R, Mothilal KK (2017) Bauhinia tomentosa leaves extract as green corrosion inhibitor for mild steel in 1M HCl medium. J Bio- Tribo-Corros 3(2):13

[19] Fayomi OSI, Abdulwahab M (2012) Degradation behaviour of aluminium in 2M HCl/HNO3 in the presence of arachis hypogaeae natural oil. Int J Electrochem Sci 7:5817–5827

[20] Fayomi OSI, Akande IG, Oluwole OO, Daramola D (2018) Effect of water-soluble chitosan on the electrochemical corrosion behaviour of mild steel. Chem Data Collect 17–18:321–326

[21] Elgahawi H, Gobara M, Baraka A, Elthalabawy W (2017) Eco-friendly corrosion inhibition of AA2024 in 3.5% NaCl using the extract of Linum usitatissimum seeds. J Bio- Tribo-Corros 3(4):55
[22] Haque J, Verma C, Srivastava V, Quraishi MA, Ebenso EE (2018) Experimental and quantum chemical studies of functionalized tetrahydropyridines as corrosion inhibitors for mild steel in 1 M hydrochloric acid. Results Phys 9:1481–1493

[23] Fayomi OSI, Abdulwahab M, Durodola BM, Joshua TO, Alao AO, Joseph OO, Inegbenebor AO (2013) Study of the electrochemical behavior and surface interaction of AA6063 Type Al–Mg–Si alloy by sodium molybdate in simulated sea water environment. Int J Manag Inf Technol Eng 1(3):159–166

[24] Fayomi OSI (2014) The inhibitory effect and adsorption mechanism of roasted *Elaeis guineensis* as green inhibitor on the corrosion process of extruded AA6063 Al–Mg–Si alloy in simulated solution. Silicon 6(2):137–143

[25] Kumari M (2017) Use of hexamine as corrosion inhibitor for carbon steel in hydrochloric acid. Int J Adv Educ Res 2(6):224–235

[26] Verma C, Chauhan DS, Quraishi MA (2017) Drugs as environmentally benign corrosion inhibitors for ferrous and nonferrous materials in acid environment: an overview. J Mater Environ Sci (JMES) 8(11):4040–4051

[27] Zakaria K, Negm NA, Khamis EA, Badr EA (2016) Electrochemical and quantum chemical studies on carbon steel corrosion protection in 1 M H₂SO₄ using new eco-friendly Schiff base metal complexes. J Taiwan Inst Chem Engineers 61:316–326