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# Corrosion Inhibition of Mild Steel in Hydrochloric Acid Solutions by *Cajanus Cajan* and *Cymbopogon Citratus* Extracts

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## Abstract

*The corrosion inhibition studies of extracts of two African medicinal plants Cajanus cajan and Cymbopogon citratus on the corrosion of mild steel in hydrochloric acid environment were studied using gravimetric method. The extracts showed excellent corrosion inhibitive characteristics at higher concentrations and lower temperatures. Analysis of the results suggests the mechanism of inhibition to be adsorption; as the surface coverage data fits into Langmuir adsorption isotherm. Also, the thermodynamic and kinetic patterns of the corrosion inhibition suggest a spontaneous process through a combination physical and chemical adsorption processes.*

**Key Words**: *Adsorption, Acidic environment, Corrosion inhibition, Corrosion rate constant, Material half life.*

## Introduction

The consequence and cost of corrosion is enormous, from environmental degradation due to product spill from broken pipes, economic loss due to down times to corrosion allowance, etc. The

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cost of corrosion has been estimated at about 1-5 % of a nations GNP. The direct cost of corrosion in the United States was estimated at $276 billion (Koch *et at.*, 2002), hence the need and search of ways to mitigate corrosion. Different types of substances have been proposed as inhibitors of corrosion.

Traditional medicine makes use of phyto-substances because of the chemical characteristics inherent in these phyto-medicinal resources. Phyto-chemicals though most times are a mixture of chemical compounds in the crude extract, contain functional groups which could serve as adsorption site on a substrate. Corrosion inhibitors also most times function by adsorption on metallic substrate (Obot *et al.*, 2012, Arthur *et al.*, 2013). This is an important relationship between both.

Corrosion is an electrochemical process and particularly an oxidative process that is inevitable. In order to minimize corrosion, addition of corrosion inhibitors to corrosive environment is one of the veritable ways of controlling metallic corrosion (Rekkab *et al.*, 2012, Benali *et al.*, 2013 Znini *et al.*, 2012). There are different types of corrosion inhibitors. Organic type of corrosion inhibitors is similar to phyto-medicinal chemicals. As such these phyto medicinal compounds could serve as corrosion inhibitors. Phyto resources can serve as a better replacement for expensive and environmental toxic corrosion inhibitors because they are cheap, eco-friendly, and renewable.

This paper presents a study on the corrosion inhibition capacity of two plant resources:- *Cajanus cajan* (CAC) and *Cymbopogon citratus* (CYC). Both plants have been used in treating various ailments such as sickle cell anemia, malaria etc.( Dilipkumar *et al.*, 2011, Gagan *et al.*, 2011). The plant materials - CAC also known as "*Fiofio* or Pigeon pea" locally was obtained from Nsukka market, Enugu State, while CYC was harvested from gardens in Aladinma and Ikenegbu areas of Owerri, Imo State, Nigeria.

## METHODOLOGY

### Material preparation

The test mild steel specimens with elemental composition listed in Table 1 were obtained from the Engineering Workshop of the

University of Port Harcourt, Rivers State, where they were mechanically pressed into coupons of 1.5 × 2.0 ×0.3 cm. The quad shaped coupons were polished successively with coarse and smooth abrasive paper (up to 1000 grit), degreased in absolute ethanol, rinsed with distilled water, dried in acetone and weighed. The ready coupons were then stored in a dry desiccator. The entire reagent used were of analytical grade and were used without further purification.1 M HCl solution was used as the corrodent..

**Table 1. Elemental composition of the mild steel coupon**

| **Element** | **C** | **S** | **P** | **Si** | **Mn** | **Al** | **Fe** |
|---|---|---|---|---|---|---|---|
| **Composition (wt. %)** | 0.27 | 0.027 | 0.004 | 0.24 | 1.54 | 0.02 | Balance |

### Extract preparation

The already procured plant materials CAC and CYC were identified by the Department of Plant Science, University of Port Harcourt, Nigeria. The CAC seeds and CYC leaves were washed and air dried. The dried plant materials (CAC and CYC) were pulverized using ceramic mortar and an electric blender. About 500 g of the dried and grounded samples were soaked in absolute ethanol in a 1000 ml volumetric flask. Sufficient quantities of ethanol were added to cover the surface of the CAC and CYC samples. The flask was covered and left for 36 hours. The contents of the flasks were filtered and the filtrate concentrated with Rotary evaporator. The semi-dried residues were stored in an air tight analytical container. Appropriate quantities were subsequently weighed to make desired concentrations of experimental solutions.

### Gravimetric experiment

The experimental corrosion cells were set up using a glass hooks to suspend the pre-polished, dried and cleaned mild steel coupons inside six different 250 ml beakers containing about 180 ml 1 M HCl with different serial diluents of the extracts. The extract concentrations of both CAC and CYC ranged between 0.0 – 0.5 g/L. Thermo-stated water baths were used to maintain the corrosion temperatures at 303, 313 and 333 K for each additive set of experiments. Several researchers had earlier used this method (Khalid and Sisodia, 2011, Sangeetha *et al.*, 2011, Obot *et al.*, 2012). After 24 hours of immersion for the 303 K experiments and 4 hours for the 313 and 333 K experiments, the coupons were retrieved, washed with the aid of brittle brush inside water to remove corrosion products, degreased in absolute ethanol, dried in acetone and kept to air dry to a constant weight. Triplicate experiments were carried out to ensure reproducibility. The mean weight between the initial weight and weight after immersion was recorded as the weight loss. The experiments were allowed to run for between seven days to four hours except for instances the corrosion cell dried up.

## RESULTS AND DISCUSSION

### Weight loss, Corrosion inhibition efficiency and Corrosion rate.

The corrosion of mild steel in aggressive acid environment has been reported by many researchers (Singh and Quraishi, 2012, Karthik and Sundaravadivelu, 2013, Okafor *et al.*, 2014) .This rapid metallic degradation is attributable to the large potential difference between the metal and the aggressive environment. Figure 1, shows the rapid metallic weight loss due to 1 M HCl environment at 303 K while Figure 2, shows an even more increased rate of weight loss due to rise in temperature from 303 to 313 and 333 K.

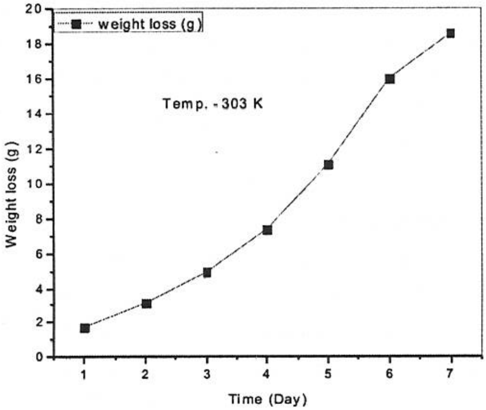

*Figure 1. Variation of weight loss with time at 303 K for the corrosion of Mild steel in 1 M HCl environment.*

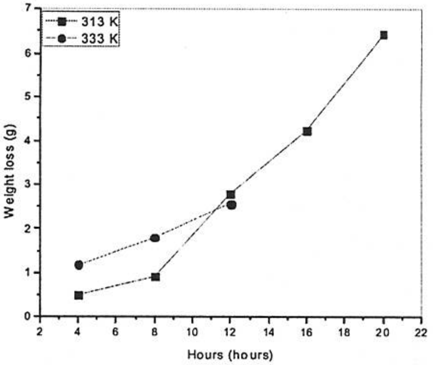

*Figure 2. Variation of weight loss with time at 313 and 333 K for the corrosion of Mild steel in 1 M HCl environment.*

The corrosion inhibition efficiencies in this work was evaluated using the relationship

$$IE\% = \left(1 - \frac{CR_{inh}}{CR_{blank}}\right) x100 \qquad (1).$$

where $CR_{inh}$ and $CR_{blank}$ represent either the weight loss or corrosion rates in inhibited and uninhibited solution, respectively.

Figures 3 to 5 depicts the corrosion inhibition efficiency for CAC and CYC for the corrosion of mild steel in 1 M HCl. Figure 3 A shows the variation of corrosion inhibition efficiency of CAC with time at 303 K for mild steel in 1 M HCl environment. The efficiencies of the various concentrations of CAC increased with time from day 1 to day 7 and also increased with increase in the concentration of the additive CAC. This trend has been previously reported (Kavipriya, *et al.*, 2013). Though there is pronounced difference in the corrosion inhibition efficiencies of the various concentrations of CAC, they tend to close gap between them with time. This may be attributed to the time taken for the inhibitors to stabilize at the surface of the metal. Bockris and Swinkels, Bockris and Swinkels, 1964 have proposed that the water molecules first get adsorbed at the metal/ electrolyte interface before they are displaced by the inhibitor molecules to get adsorbed at the metal surface. Figures 3B and 3C also indicates the continuous increase in the corrosion inhibition efficiency of CAC on the corrosion of mild steel in acidic environment as its concentration increased. However the corrosion inhibition efficiency decreased with rise in temperature from 303 to 313 K and to 333 K.

Figure 4 A, shows the variation of corrosion inhibition efficiency of CYC with time at 303 K for the corrosion of Mild steel in 1 M HCl environment. The inhibition efficiency increased more distinctly as concentration of CYC increased. This pattern was repeated at higher temperatures of 313 and 333 K and depicted in Figures 4B and 4C. However the corrosion inhibition efficiency of CYC still decreased with rise in temperature from 303 to 313 K and to 333 K. Some other corrosion inhibitors have been reported to exhibit similar behaviour (Yatiman *et al.*, 2006 ).

Figure 5, shows, comparatively that both CAC and CYC have comparable corrosion inhibition efficiencies on the corrosion of Mild steel in Hydrochloric acid environment. However CYC showed higher corrosion inhibition efficiencies both at equivalent concentration and temperature. Also, the higher concentration of 0.5 g/L of both CAC and CYC showed more distinctly higher corrosion inhibition efficiency.

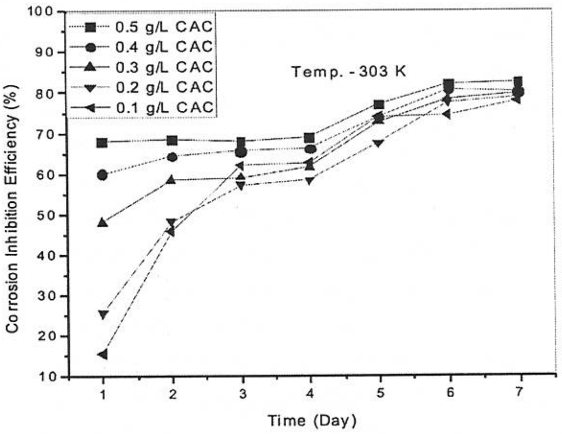

*Figure 3 A. Variation of corrosion inhibition efficiency with time for mild steel in HCl in the presence of CAC with time at 303 K.*

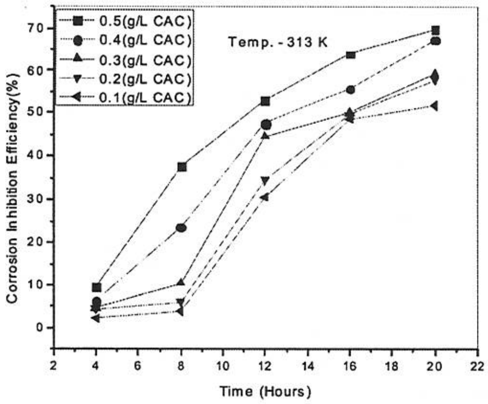

*Figure 3 B. Variation of corrosion inhibition efficiency with time for mild steel in HCl in the presence of CAC with time at 313 K.*

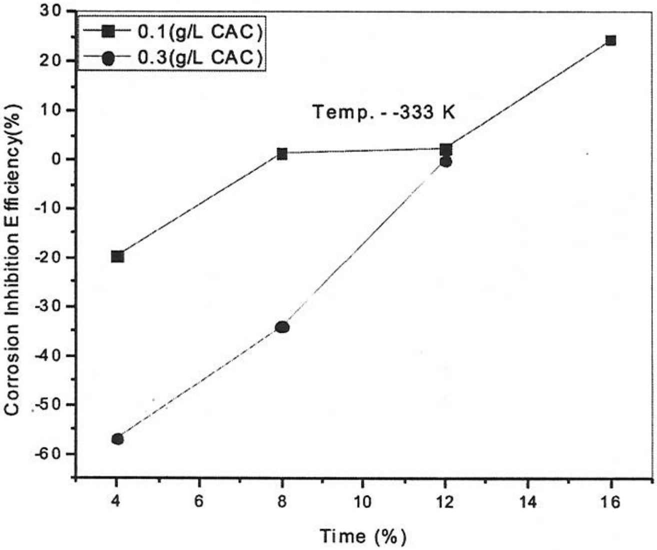

*Figure 3 C. Variation of corrosion inhibition efficiency with time for mild steel in HCl in the presence of CAC with time at 333 K.*

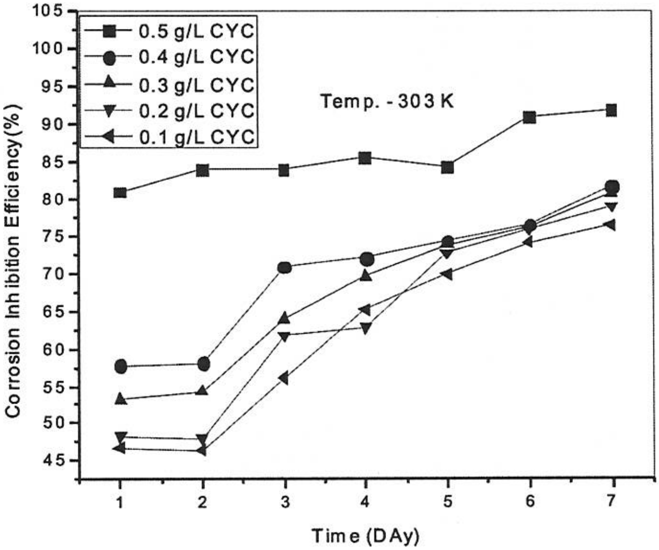

*Figure 4 A. Variation of corrosion inhibition efficiency with time for mild steel in HCl in the presence of CYC with time at 303 K.*

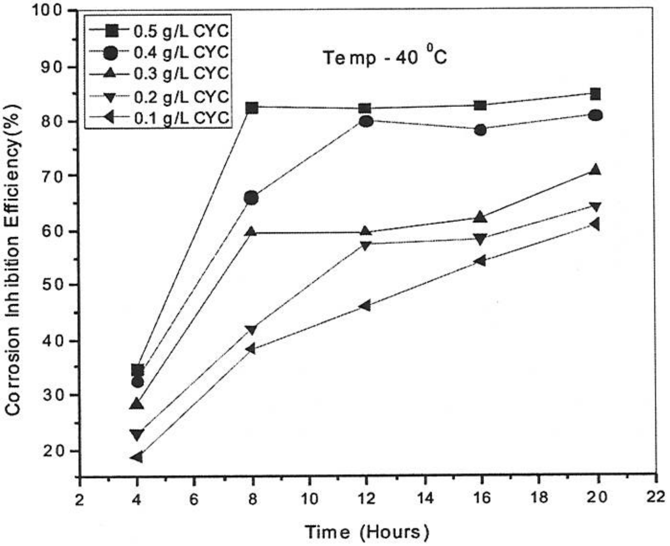

*Figure 4 B. Variation of corrosion inhibition efficiency with time for mild steel in HCl in the presence of CYC with time at 313 K.*

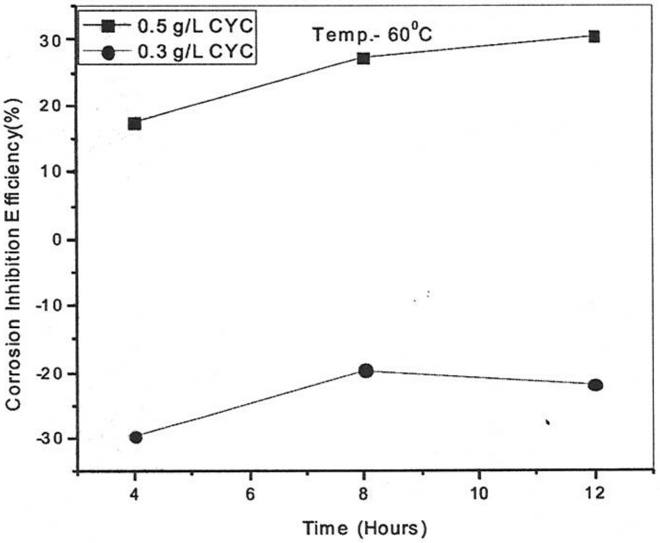

*Figure 4 C. Variation of corrosion inhibition efficiency with time for mild steel in HCl in the presence of CYC with time at 333 K.*

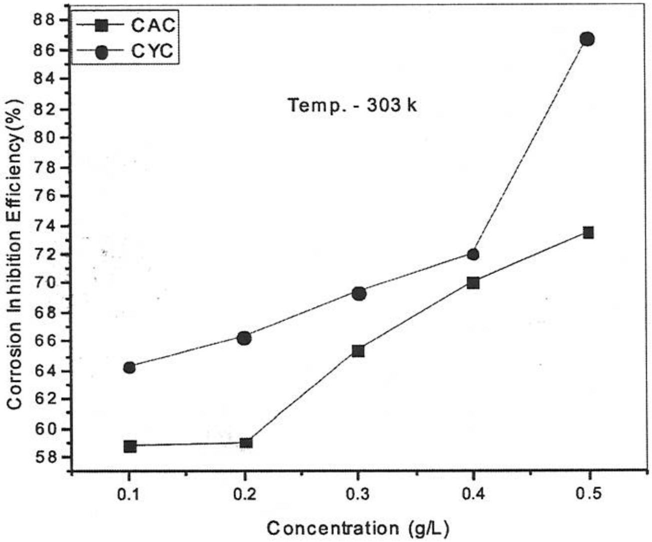

*Figure 5. Comparison of corrosion inhibition efficiency of CAC and CYC at various concentrations for the corrosion of mild steel in 1 M HCl environment.*

The corrosion rate (CR) for the corrosion of mild steel in Hydrochloric acid environment with various concentrations of CAC and CYC were calculated from the weight loss data using Equation 2 and the obtained data also plotted as a function of time and additive concentration in Figure 6.

$$CR_{(\text{mm per year})} = 87.6\text{“}w/DAT \qquad (2)$$

“w is the weight loss, D the density of steel (g/cm$^3$), A the area of the coupon in (cm$^2$) and exposure time (h) (Shanmugam *et al.*, 2013). Figures 6A and 6B shows the variation of the corrosion rates of various concentrations of CAC and CYC against time respectively. Both CAC and CYC showed a general decrease in corrosion rate with time. The corrosion rates also decreased with increased additive concentrations (Oguzie, 2005, Shanmugam *et al.*, 2013). Also similar to corrosion inhibition efficiency pattern, the 0.5 g/L of both CAC and CYC showed clearly distinct corrosion rate trend.

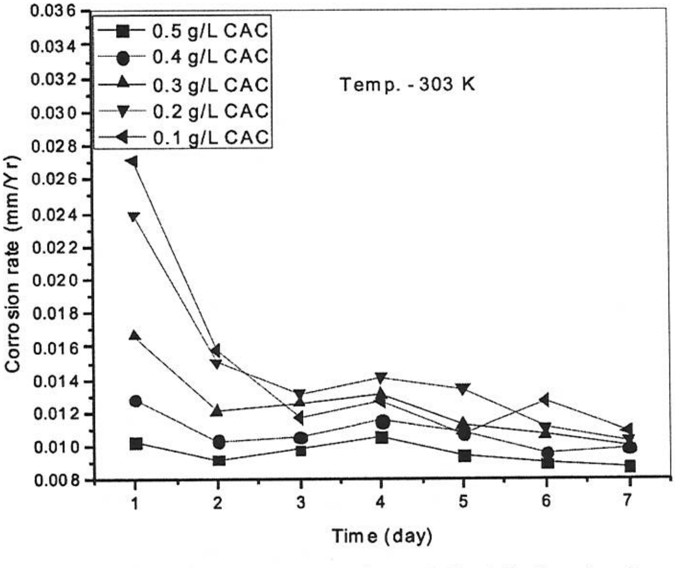

*Figure 6 A. Variation of corrosion rate (mm/Yr) with time for the corrosion of mild steel in HCl in the presence of CAC at 303 K.*

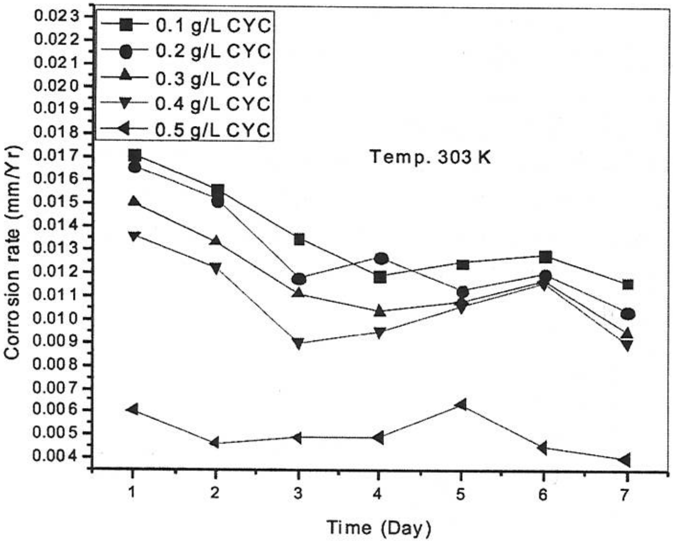

*Figure 6 B. Variation of corrosion rate (mm/Yr) with time for the corrosion of mild steel in HCl in the presence of CYC at 303 K..*

## Corrosion rate constant and Material half life

The corrosion rate constant (k) and material half-life ($t_{1/2}$) for the corrosion inhibition of the corrosion of mild steel in acidic environment using CAC and CYC were calculated from the weight loss data for first order reaction.

$$K = \frac{2.303}{t} \log \frac{w_i}{w_f} \tag{3}$$

The material half-life $t_{1/2}$ was calculated from k;

$$t_{\frac{1}{2}} = \frac{0.693}{k} \tag{4}$$

Where $w_i$ and $w_f$ are initial and final weights respectively. The plots of k versus concentration of CAC and CYC (Figure 7) and $t_{1/2}$ versus concentrations of CAC and CYC (Figure 8) respectively show that k varied inversely with concentrations of CAC and CYC, while the half-life varied directly with concentrations of CAC and CYC. Therefore the corrosion rate constant k was the inverse of the material half-life ($t_{1/2}$). The material half-life $t_{1/2}$ of the corrosion reaction was higher in inhibited solutions compared to the uninhibited system and increased generally with increase in CAC and CYC concentrations. This implies that the introduction of CAC and CYC reduced the tendency of the mild steel specimen to undergo corrosion reaction in Hydrochloric acid, confirming the corrosion inhibiting capacity of the additives. CYC showed a comparative higher $t_{1/2}$ than CAC at all concentrations and could be related to its higher corrosion inhibition efficiency.

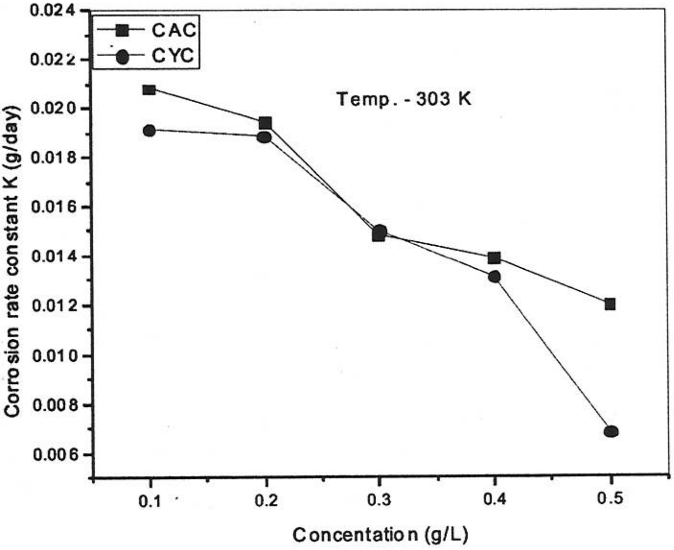

*Figure 7. Comparison of corrosion rates constant (g/day) of CAC and CYC at various concentrations for the corrosion of mild steel in 1 M HCl environment at 303 K.*

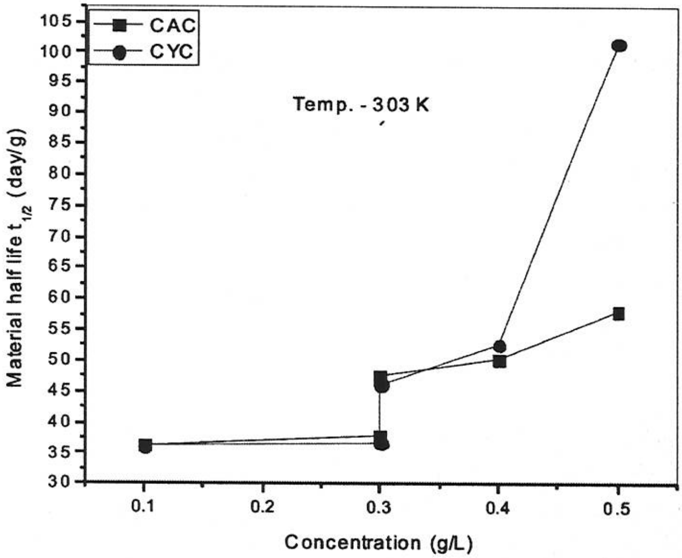

*Figure 8. Comparison of corrosion material half-life ($t_{1/2}$) of CAC and CYC at various concentrations for the corrosion of mild steel in 1 M HCl environment at 303 K.*

## Adsorption behavior

The adsorption of chemical specie on a substrate is largely dependent on the nature of the chemical specie and the substrate in addition to the thermodynamic and kinetic parameters at and near the interface. Corrosion inhibitors function by reducing or blocking of corrosion active sites on the metal surface which is a function of the inhibitors surface coverage on the metallic surface. It has been severally reported that corrosion inhibitors inhibit corrosion by been adsorbed on the metal surface (Abiola *et al.*, 2004, Ebenso *et al*, 2004., Oguzie *et al.*, 2004). The establishment of an adsorption isotherm gives an insight into the adsorption behaviour at the metal/ solution. In this study the values of surface coverage (è) at various concentrations (C) of CAC and CYC was determined using equation 5 and tabulated in Table 2.

$$\theta = IE\%/100 \qquad (5)$$

Where IE% is the corrosion inhibition efficiency.

The plots of C/θ versus C for both CAC and CYC were approximately linear, confirming their fit to the Langmuir adsorption isotherm thereby suggesting that both additives inhibited the corrosion of mild steel in acidic environment by adsorption on to the metallic surface as shown in Figure 9.

The free energy of adsorption, “$G_{ads}$ of CAC and CYC were calculated using the relationship:

$$\Delta G_{ads} = -2.303RT\log\left[\frac{55.4\theta}{Co(1-\theta)^{n}}\frac{\{\theta+(1-\theta)n\}^{n-1}}{n^{n}}\right] \qquad (6)$$

Where Co is the concentration of inhibitor in the bulk of the solution; n is the size factor (9 for flat adsorption on the surface and 3 in the perpendicular direction to the surface). The negative values of $\Delta G_{ads}$ (Table 2) suggest spontaneous adsorption of CAC and CYC on the mild steel surface in hydrochloric acid (Atkins and Paula, 2002).

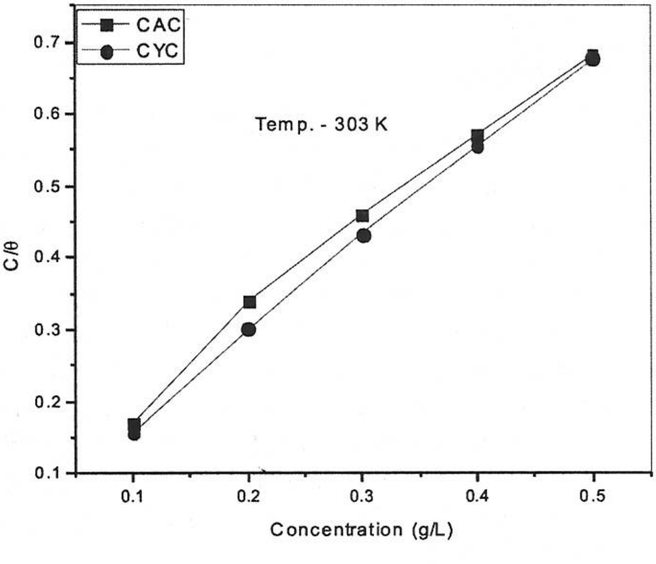

*Figure 9. Langmuir isotherm for adsorption of CAC and CYC on mild steel*

**Table 2: Calculated values of Gibbs free energy of adsorption and average surface coverage for corrosion inhibition of mild steel by CAC and CYC in pipeline Hydrochloric acid.**

| Conc. (g/L) | $\Delta G_{ad}$ (CAC) | $\Delta G_{ad}$(CYC) | θ (CAC) | θ(CYC) |
|---|---|---|---|---|
| **0.1** | -46.16 | -44.44 | 0.87 | 0.64 |
| **0.2** | -40.06 | -39.21 | 0.72 | 0.66 |
| **0.3** | -34.44 | -34.26 | 0.69 | 0.69 |
| **0.4** | -29.57 | -30.20 | 0.66 | 0.72 |
| **0.5** | -24.69 | 30.31 | 0.62 | 0.87 |

## Conclusion

Extracts of *Cajanus cajan* and *Cymbopogon Citratus* were found to inhibit the corrosion of mild steel in acidic environment. The action of both was attributed to proceed through adsorption spontaneously on the steel surface. The corrosion inhibition capacity of both additives increased with increase in their concentration and decreased with rise in temperature. The corrosion inhibitive behaviour of both extracts was attributed to the multi phyto chemical constituent of the crude extracts.

## Acknowledgement

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## References

Abiola, K. O., Oforka N. C., Angaye S. S. (2004). Corrosion behaviour of aluminium in hydrochloric acid solution containing mercaptoacetic acid. *Materials Letters* 58, 3461 - 3466.

Arthur, D. E., Jonathan A., Ameh P. O., Anya C. (2013). A review on the assessment of polymeric materials used as corrosion inhibitor of metals and alloys, *Internl J. Industrial Chemistry* 4 2013 2.

Atkins, P. and J. Paula (2002). Atkins Physical Chemistry, Oxford University press, seventh edition, 984-990.

Benali, O., Benmehdi H., Hasnaoui O., Selles O., Salghi R (2013). Green corrosion inhibitor: inhibitive action of tannin extract of Chamaerops humilis plant for the corrosion of mild steel in 0.5 M $H_2SO_4$, *J. Mater. Environ. Sci.* 4 (1), 127-138.

Bockris, J. O. M., Swinkels, D. A. J. (1964). Adsorption of n-Decylamine on solid Metal electrodes, *J. Electrochem. Soc.* 111, 736-743.

Cang, H., Fei Z., Shao J., Shu W., Xu Q. (2013). Corrosion inhibition of mild steel by Aloes Extract in HCl solution medium. *Int. J. Electorchem. Sci.* 8, 720-734.

Ebenso, E. E., Ibok, U. J., Ekpe, U. J., Umoren, S., Jackson, E., Abiola, K. O., Oforka, N. C., and Martinez, S. (2004). Corrosion Inhibition studies of some plant extracts on Aluminium in acidic medium. Transaction of the SAEST, 39, pp 117 - 123.

Hasan, S. K, Sisodia, P. (2011). Paniala (*flacourtia jangomas*) plant extract as eco friendly inhibitor on the corrosion of mild steel in acidic media, Rasayan *J. Chem.*.4 (3) 548-553.

Karthik, G., Sundaravadivelu, M. (2013). Inhibition of Mild Steel Corrosion in Sulphuric Acid Using Esomeprazole and the Effect of Iodide Ion Addition, SRN Electrochemistry, Volume 2013 Article ID 403542, 10 pages, http://dx.doi.org/10.1155/2013/403542.

Kavipriya, K., Sathiyabama, J., Rajendran S, Nagalakshmi, R. (2013). The inhibitive effect of diethylenetriaminepentamethylene phosphonic acid on the corrosion of carbon steel in sea water, *Eur. Chem.* Bull 2 (7), 423-429.

Koch, G. H, Michiel, P. H., Brongers, C. C., Thompson, N. G., Virmani, Y. P., Payer, J. H. (2002). Corrosion Costs and Preventive in the United States. NACE international (http://events. Race.org/ publications/images. cocorr/cssupp.pdf ).

Ngobiri, N. C., Oguzie, E. E., Oforka, N. C., Akaranta, O. (2015). Comparative study on the inhibitive effect of Sulfadoxine–Pyrimethamine and an industrial inhibitor on the corrosion of pipeline steel in petroleum pipeline water. *Arabian J. Chemistry,* http://dx.doi.org/10.1016/j.arabjc.2015.04.004

Obot, I. B., Ebenso, E. E., Gasem, Z. M., (2012). Eco-friendly corrosion inhibitors: Adsorption and Inhibitive action of ethanol extracts of Chlomolaene odorata L. for the corrosion of mild steel in $H_2SO_4$ solutions, *Int. J. Electrochem Sci.* 7, 1997-2008.

Oguzie E. E. (2005). Inhibition of acid corrosion of mild steel by telfaria occidentalis, *J. Pigment and Resin Technology,* 34 (6) 231.

Oguzie, E. E. (2004). Influence of halide ions on the inhibitve effect of Congo red dye on the corrosion of mild steel in sulphuric acid solution. *Materials Chemistry and physics* 87, 212 - 217.

Okafor, P. C., Odoh, U. C., Ikeuba, A. I., Ekpe, U. J., Obono, O. E., (2014). The inhibition of mild steel corrosion by extracts from seeds of Myristica fragrance, Monodora mystica and Parkia biglobosa in sulphuric acid solution, *ASUU J. Sci*. 2 (1) 34-46.

Pal D., Mishra P., Sachan N., Ghosh A. K., (2011). Biological activities and medicinal properties of Cajanus cajan, *J. Adv. Pharm Technol and Res*. 2 (4), 207-214.

Rekkab S., Zarrok H., Salghi R., Zarrouk A., Bazzi L., Hammouti B., Kabouche Z., Touzani R., Zougagh M., (2012). Green corrosion inhibitor from essential oil of *eucalyptus globulus* (Myrtaceae) for C38 steel in sulfuric acid solution, *J. Mater. Environ. Sci.* 3 (4) 613-627.

Sangeetha M., Rajendran S., Sathiyabama J., Krishnaveni A., Shanthy P., Manimaran N., Shyamaladevi B., (2011). Corrosion inhibition by an aqueous extract of *Phyllanthus amarus,* Portugaliae Electrochimica acta 29 (6), 429-444.

Shah G., Shri R., Panchal V., Sharma M., Singh B., Mann A. S., (2011). Scientific basis fot the therapeutic use of Cymbopogon Citratus and Occimum gratisssium. *J. Adv. Pharm Technol. Res.* 2 (1) 3-8.

Rajendran S., Thangavelu C., Angamuthu A., Jayakumar S., (2013). Inhibition of corrosion of Aluminium in alkaline medium by Glutaric acid in conjunction with Zinc sulphate and Diethylene triamine penta (Methylene phosphonic acid), *Arch. Appl. Sci. Res.* 5 (1), 202-212.

Singh A. K., Quraishi M. A., (2012). Study of Some Bidentate Schiff Bases of Isatin as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution, *Int. J. Electrochem. Sci.* 7, 3222 – 3241.

Yatiman P., Surdia N. M., Purwadaria S., Ariwahjoedi B., Suratman R., (2006). Application of Benzotriazole as Corrosion Inhibitor of API 5L X65 carbon steel in Sodium chloride solution, *Indonesian J. Materials Sci.* 7, (3), 75 – 79.

Znini M., Majidi L., Bouyanzer A., Paolini J., Desjobert J. M., Costa J., Hammouti B., (2012). Essential oil of Salvia aucheri mesatlantica as a green inhibitor for the corrosion of steel in 0.5 M $H_2SO_4$, *Arabian J. Chemistry* 5, 467–474.