Study of the Functional Groups Associated with the Corrosion Inhibition of Stainless Steel Arch Bar in Acidic Medium by *Khaya Grandifolia Gum* Exudate

Naziru Imam*, Isreal I. Omoniyi, and Paul Ameh

Abstract: *The corrosion inhibition of stainless steel arch bar (an implant used for maxillo-mandibular fixation in dentistry) by Khaya grandifolia gum exudates in 1.00 x 10^{-4} moldm^{-3} HCl solution and pH of 4.0 was studied using weight loss method (gravimetric analysis). The corrosion rate decreased in the presence of the gum exudate while the inhibition efficiency was observed to increase with an increase in the concentration of the gum exudate. Variation of the inhibition efficiency with time showed a decreasing trend, FTIR analysis of the gum exudate (crude and in HCl) showed the presence of some functional groups that might have been used in adsorbing the inhibitor unto the surface of the metal. The observed functional groups included OH stretch, C=C, C=N, or C=O functional groups and C-C, C-N, and C-O due to carboxylic acid stretching or alcohol bonds in the gum. Surface analysis showed remarkable improvement on the surface, in the presence of the inhibitor than in its absence.*

Naziru Imam*
Department of Industrial Chemistry, Federal University Oye-Ekiti, Nigeria
Email: naziruimam2@gmail.com
Orcid id: 0000-0003-4864-7041

Isreal K. Omoniyi
Department of Chemistry, Ahmadu Bello University,
Zaria, Kaduna State, Nigeria
Email: israelflourish@yahoo.com

Paul Ocheje Ameh
[3]Department of Chemistry, Nigerian Police Academy
Wudil, Kano State, Nigeria
Email: amehpaul99@gmail.com
Orcid id: 0000-0002-7050-6715

1.0 Introduction

Corrosion is a major challenge in industries where metals are in contact with an aggressive medium, which implies that there must be adequate measures to control the rate at which valuable metals in industries wear off through corrosion (Namrata *et al.,* 2017). Studies on corrosion have revealed a wealth of knowledge on the choice of corrosion inhibitors, especially green corrosion inhibitors, which are eco-friendly, cost-effective, biodegradable and easily available (Loto *et* al., 2011; Umoren, 2009). Consequently, some plant extracts have been investigated and found to be effective corrosion inhibitors (ref) Studies on the use of some gums including *Daniella oliverri* gum exudate (Eddy *et al*., 2012a), *Ficus platyphylla g*um exudates (Eddy *et al*., 2012b), *Ficus benjamina* gum exudate (Eddy *et al*., 2011), *Anogessius leocarpus* gum exudate (Ameh *et al*., 2012), *albizzia lebecck* gum exudate (Eddy *et al*.,2014d), *Commiphora pedunculata* gum (Ameh and Eddy, 2014a), *Gloriosa superba* (GS) gum (Eddy *et al*., 2014), *Ficus thonningii* gum (Eddy *et al*., 2014b), by *Commiphora africana g*um (Eddy *et al*., 2014c), *Acasia sieberiana* gum exudate (Ameh and Eddy, 2014b), *Anacardium occidentale* gum exudates (Eddy

et al., 2014d), *Anogeissus leiocarpus g*um (Eddy *et al*., 2013a), *Albiziaz ygia* gum (Eddy *et al*., 2013b), *Trichilia roka* (Eddy *et al*., 2016). In these and other studies, gums are excellent corrosion inhibitors and their inhibition potentials are linked to the presence of some compounds in the gum that have hetero atoms, suitable functional groups, pi-electron, aromatic systems and the provision of large surface area for adsorption (Eddy *et al*., 2015).

The use of gum exudates as corrosion inhibitors has been widely reported. It requires little or no cost to process these naturally occurring substances which are ecologically friendly and possess less threat to the environment are good green inhibitors for metals. Stainless steel arch bar (a metallic implant used in dentistry) is used for maxilla-mandibular fixation; following accident or fracture. Also, The release of cobalt, iron, manganese, nickel and chromium ions from new and reused stainless steel arch bar have been reported (Lori *et al*., 2009). This study is therefore aimed at studying the functional groups associated with the corrosion inhibition of stainless steel arch bar in acidic medium by *Khaya grandifolia gum* exudate.

2.0   Materials and Methods

Crude *Khaya grandiforlia* gum was obtained as dried exudates from the parent trees grown at Tsanni in Batagarawa Local Government Area of Katsina State, Nigeria in June 2017. The plant material was identified and authenticated in the Department of Biology of Umaru Musa Yar'adua University, Katsina State, Nigeria. The gum was collected from the plant species by tapping in the daytime. The stainless steel arch bar (metallic implant) used for the corrosion inhibition study was obtained from the Dental and Maxillofacial Department of Ahmadu Bello University Teaching Hospital,Zaria.

2.1   Purification of the gum

The crude sample of *Khaya grandiforlia* gum collected was hand sorted to remove

fragments of bark and other visible impurities and then the gum particles were spread out in the sun to dry for two weeks. The dried crude gum was then dissolved in cold distilled water and the solution was strained through muslin and was centrifuged, depositing a small quantity of dense gel. The straw-colored supernatant liquor was separated and acidified to a pH of 2 with dilute hydrochloric acid. Ethanol solution was then added until it becomes 80 percent. The gum that precipitated out was removed by centrifugation at 2000 r/minutes, washed with alcohol followed by ether and finally dried in a desiccator. The dried flakes were pulverized using a blender and stored in an air-tight container.

2.2   Corrosion study

The implant bar was mechanically press-cut into different coupons, each dimension 3.0 cm. Each coupon of the arch bar used was then degreased by washing with ethanol, cleaned with acetone and allowed to dry in the air before preservation in a desiccator. All reagents used for the study are of Analar grade and double-distilled water was used for their preparation. The study of the metallic composition of the implant was carried out, by acid digestion, and measurement was taken using graphite furnace atomic absorption spectrophotometry (Model TAS990, Intec Co. Ltd., Rome) as reported by Lori *et al.,* (2009); and gave 60.05 % Fe, 18.35 % Cr, 18.62 % Ni, 2.94 % Mn and 0.03 % Co. Indicating that some of the metals are of health concern.

2.2.1   Weight loss experiment

In the gravimetric experiment, each of the 3 x 2cm dimension stainless steel arch bar coupon of mass 0.3202g was completely immersed in 40 cm^3 solution of accurately prepared HCl of pH 4.0 in a 50 cm^3 beaker (in triplicate); this served as the control experiment. For the corrosion inhibition experiment, the corrodent contained 1.0 g/L or 5.0 g/L treated *Khaya grandiforlia* gum exudate. The beaker of each setup was covered with aluminum foil and then inserted into a water bath maintained at

37°C (310K). After every 7 days, the corrosion product (in terms of the concentration of iron) was determined by washing each coupon (taken from the test solution in the water bath) in a solution containing 50% of NaOH and $100g^{-1}$ of zinc dust. The washed material was rinsed in acetone and dried in the air before re-weighing to determine weight loss in the triplicate experiment. The experimental procedure was repeated every week, up to the sixth week.

Six weeks was considered because stainless steel arch bar is removed from a patient's mandible or maxilla after six weeks of implantation through surgery. Weekly weight loss for 6 weeks was taken as the total weight loss. From the average weight loss (Mean of three replicate results), inhibition efficiency (I%), corrosion rate(CR) and degree of surface coverage(ɵ) were calculated using the following equations:

$$\%I = \left(1 - \frac{W_1}{W_2}\right) \times 100 \qquad (1)$$

$$\theta = \left(1 - \frac{W_1}{W_2}\right) \qquad (2)$$

$$CR = \frac{\Delta W}{At} \qquad (3)$$

where W_1 and W_2 are the weight losses (g) for stainless steel arch bar in the presence and absence of the inhibitor, θ is the degree of surface coverage of the inhibitor, $\Delta W = W_2 - W_1$, A is the area of the stainless steel arch bar coupon (in cm^2), t is the period of immersion (in days).

Each coupon of stainless steel arch bar used for the corrosion studies is 3cm in length and 2cm in width, thus its area (A) is 3cm x 2cm = 6 cm^2.

2.3 Fourier Transform Infrared (FTIR) analysis

FTIR analysis of the *Khaya grandiforlia* gum and that of the corrosion products (in the absence and presence of the gum) was carried out using SCIMADZU (Model: FTIR-8400S) Fourier transform infra-red spectrophotometer at the Ahmadu Bello University, Multi-user Laboratory, Zaria in October 2017. Samples were prepared in a solution of KBr and the analysis was carried out by scanning the samples through a wave number range of 400 to $4000cm^{-1}$.

2.4 Scanning Electron microscope (SEM) analysis

The structure and surface morphology of the fresh and immersed stainless steel arch bar in a high concentration of the inhibitor was carried out at the Central Research laboratory of Umaru Musa Yar'adua University Katsina, Katsina State, Nigeria,

The energy of the acceleration beam employed was 30 kV. The analysis by SEM was carried out on the surface of gum exudates samples before immersion and after immersion in the acidic solutions with and without the optimal concentration of inhibitor.

3.0 Results and Discussion

3.1 Weight loss measurement

Weight loss of the stainless steel was observed to increase with time (Fig. 1), which means that the corrosion rate of the metal in HCl also increases with time.

The results aligned with the observed trend of an increase in inhibition efficiency with an increase in the concentration of the exudate gum. A simultaneous decrease in inhibition efficiency with time was observed at both concentrations. This suggests that at both concentrations, the exudate gum behaves as an adsorption inhibitor. The observed increase in inhibition efficiency with an increase in the concentration of the gum is evidence of an increase in the surface area of coverage as the concentration of the inhibitor molecules diffusing from the bulk solution to the surface of the metal increases.

A close comparison of the inhibition efficiency of the gum exudate show that at any given time, the higher concentration (5 g/L) gave better inhibition efficiency compared to the 1 g/L concentration as shown in Fig. 1.

3.2   FTIR studies

The FTIR spectra of the crude and purified *Khaya grandiforlia* gum are presented in Figs. 3 and 4 respectively. The FTIR spectrum of the crude gum (Fig 3) shows weak broadband at around 3400 cm^{-1} which is the characteristic absorption of OH stretch in phenol due to stretching, moving on in the spectrum at the range of 1500 – 1600cm^{-1}. A weak but sharp peak that is typical for the presence of C=C, C=N, or C=O functional groups was seen. At the fingerprint region (600 – 1400cm^{-1}) a sharp and strong band was evident at around 1000 cm^{-1} which suggests the presence of C-C, C-N, and C-O due to carboxylic acid stretching or alcohol bonds in the gum.
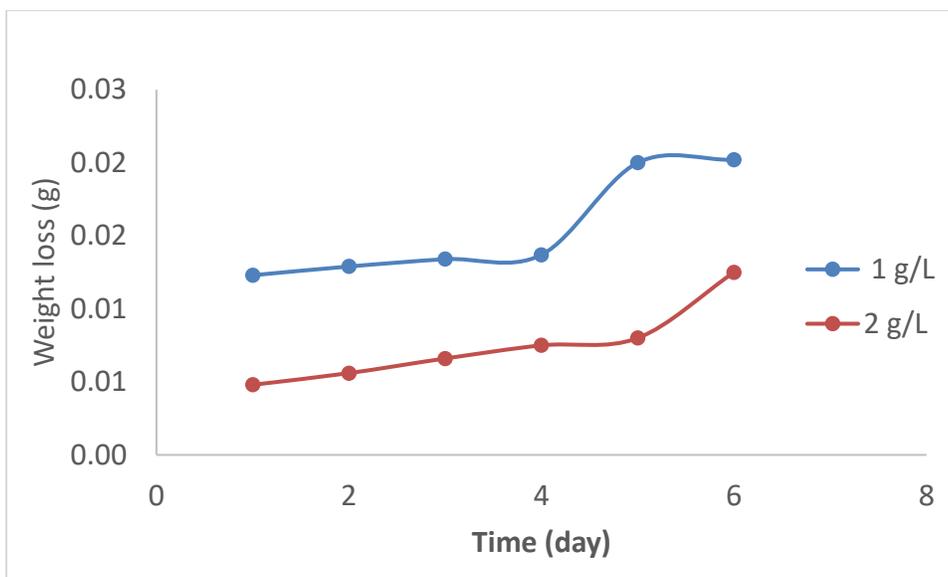

Fig, 1: Variation of weight loss with time for the corrosion of arch bar in solutions of HCl
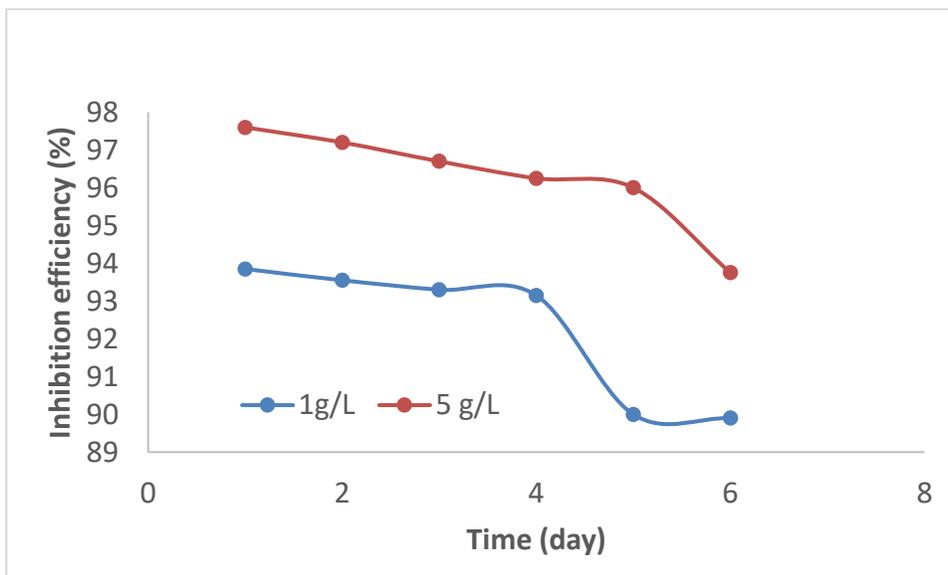

Fig. 2: Variation of inhibition efficiency of *Khaya grandifolia gum exudates* with the period of immersion in different concentrations of HCl

On comparing the two spectra (i.e. Fig 3 and 4), it can be observed that the results are similar and almost the same, which signifies that the pre-treatment (purification) of the gum did not

impact significantly on the functional groups of the organic compound in the gum (Such as albeitic acid, n-hexadecanoic acid, d-glucose and sucrose) (Eddy *et al*., 2015).

Fourier transform infrared spectroscopy analysis (FTIR) of the test solution (containing the inhibitor in HCl solution) used for the corrosion study is shown in Fig. 5 while Fig. 6 shows the FTIR of the scratched corrosion product of the stainless steel after seven days of immersion.
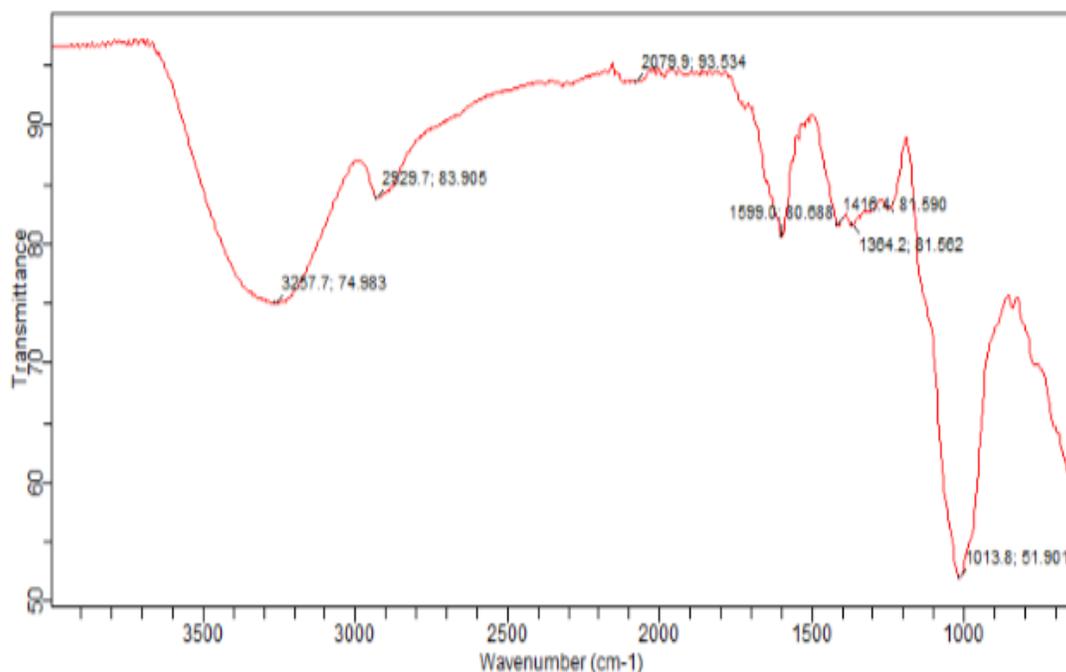
Fig. 3: FTIR spectrum of crude K*haya grandiforlia gum*
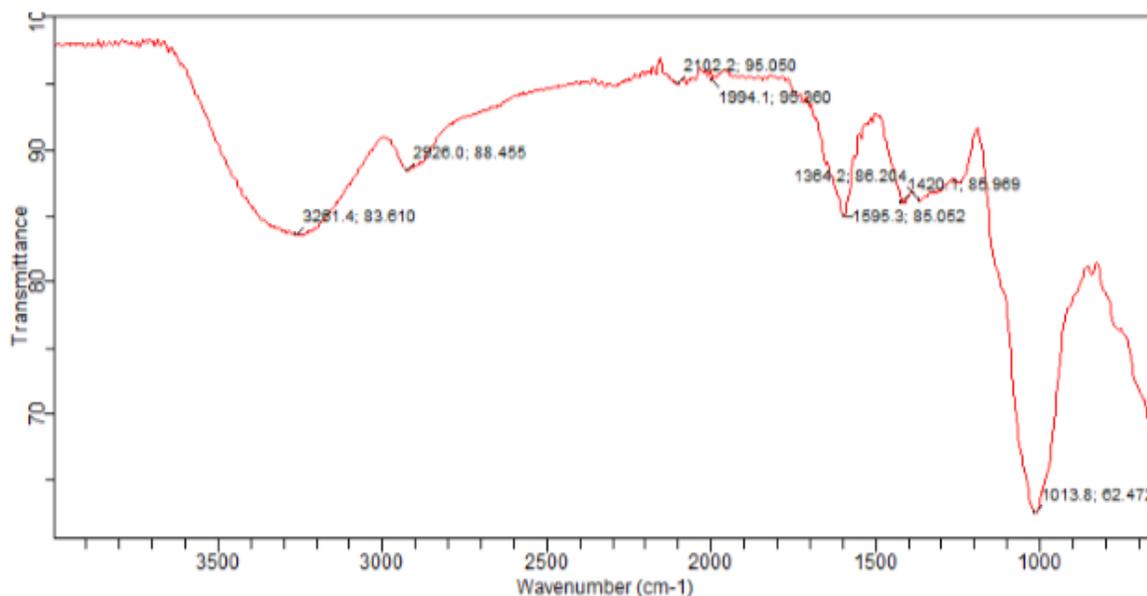
Fig 4: FTIR Spectrum of purified (treated) *Khaya grandiforlia gum*
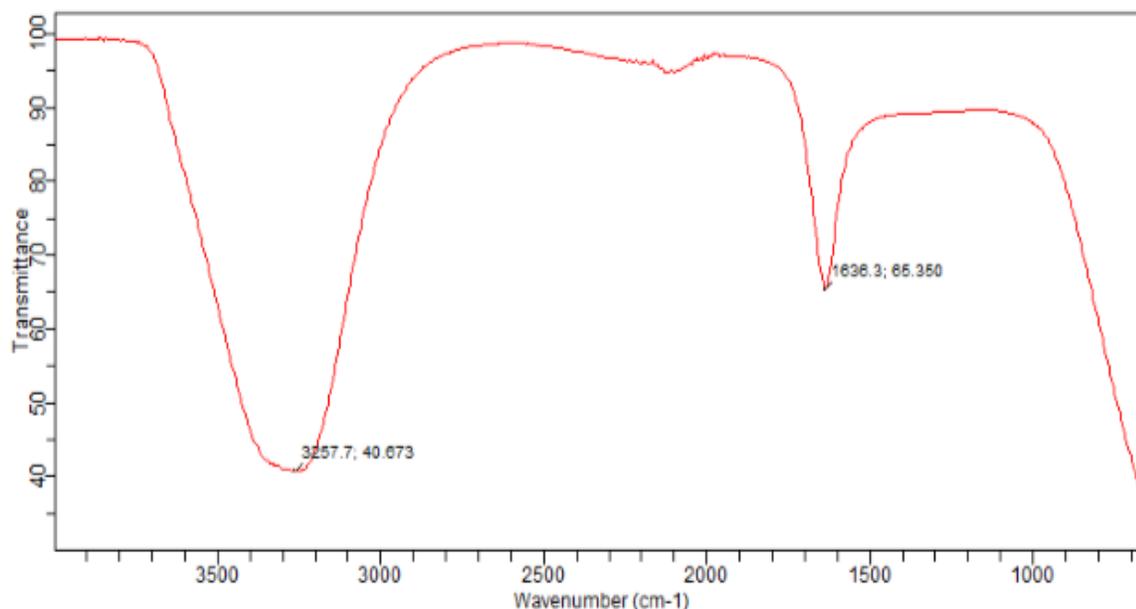
Fig. 5: FTIR spectrum of the test solution before the immersion of the stainless steel arch bar
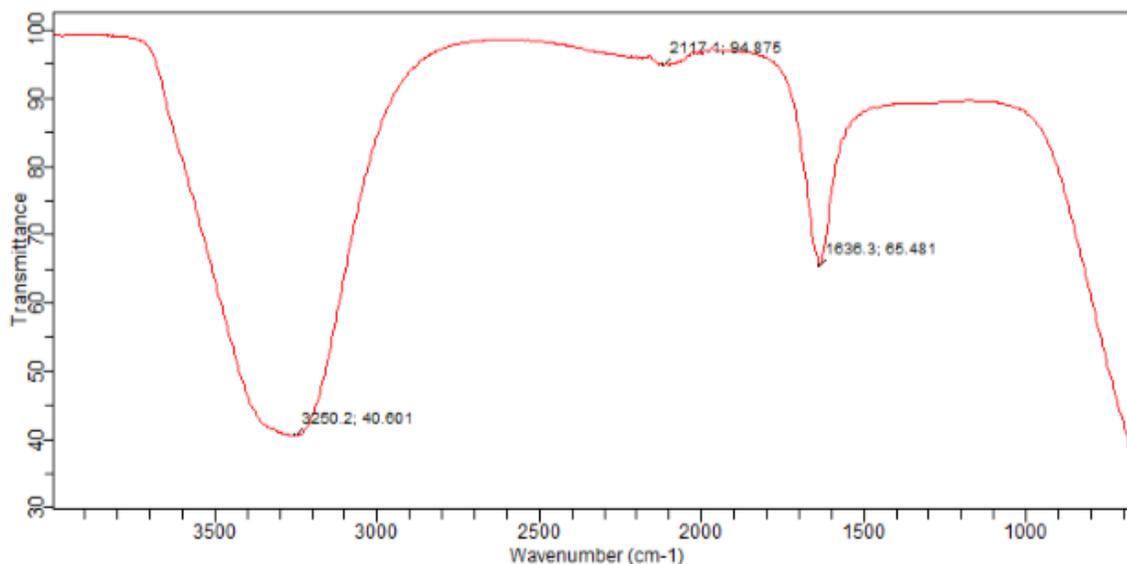
Fig. 6: FTIR spectrum of the corrosion product (test solution containing 5g/L of the gum after the immersion of the arch bar)

The spectrum of the test solution before the corrosion studies (Fig. 5) shows a broad and strong band at between 3200 – 3400 cm^{-1} which suggests the presence of alcohol OH stretch. A medium peak was also observed around 1600 cm^{-1}, evident of C=C and C=O vibrations due to aldehyde or ketone. A C=N bond functional group was also seen in the solution. Similar functional groups but slightly modified intensity were observed in the FTIR spectrum of the corrosion product.

3.3   Characterization   of   surface morphology

The surface of the stainless steel arch bar was examined to obtain an insight into the morphological changes that occurred on the

surface before and after the immersion in the inhibitor using scanning electron microscope (SEM) at the Central Research Laboratory of Umaru Musa Yar'adua University, Katsina and the resulting images are depicted in Figure 3.0, 4.0 and 5.0 corresponding to the image of fresh arch bar, one in 5g/L of the inhibitor and the absence of the inhibitor respectively.
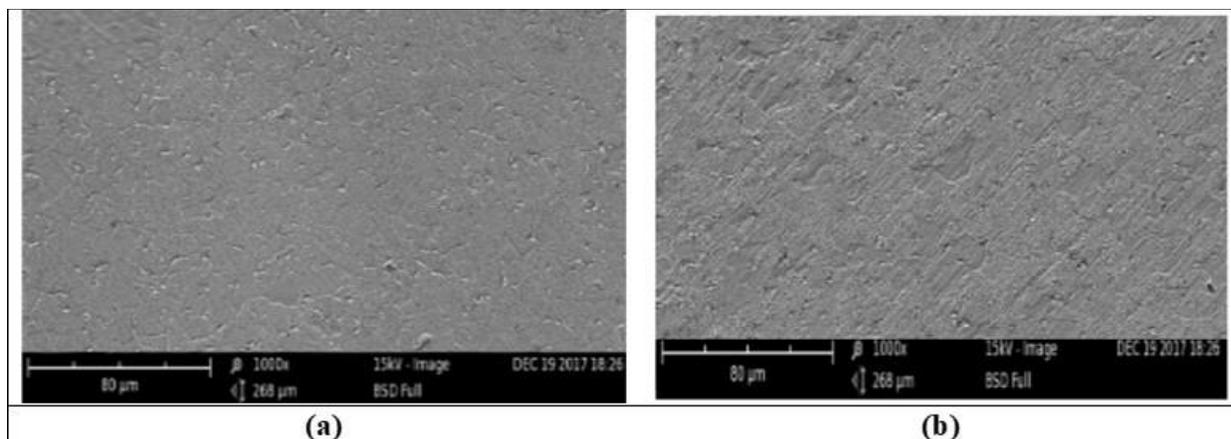
Fig. 7: Scanning electron micrographs of (a) arch bar.   (b) arch bar in a solution of HCl
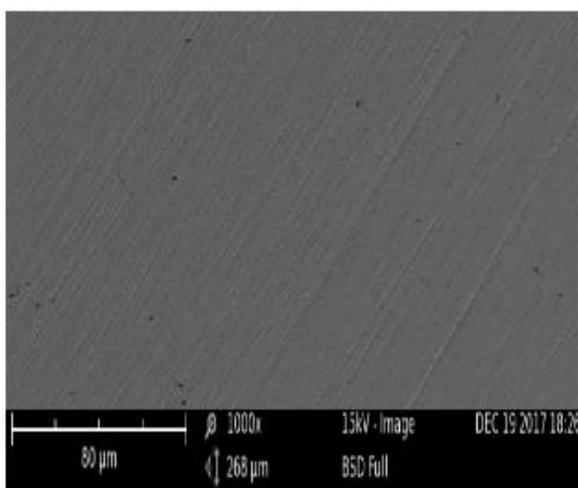
Fig. 8: Scanning electron micrograph of the arch bar in the presence of the inhibitor

4.0   Conclusion

The findings obtained from this study show that *Khaya grandiforlia gum* is effective in controlling the rate of corrosion of the stainless steel arch bar and it is environmentally friendly as there is no observed hazard to the analyst or the environment due to its green nature. The major functional groups observed are OH, C=O, C=N, C=C, and C-C, C-O, C-N which justifies that the gum contained alcohols, acids and sugar as shown by previous literature/researches. Additionally, the morphology of the stainless steel arch bar may be maintained because there is little observable change in the SEM images, thus the material can be reused after being subjected to corrosion studies since the adsorption is not chemisorptions. The inhibitor is locally available and its application in corrosion inhibition will solve the problem of high cost and importation of substances used as inhibitors for corrosion of metals in the industrial sectors, thereby boosting the economy of our country.

5.0   Acknowledgement

6.0   References

Aloysious A., Ramanathan R., Christy A., Baskaran S., and Antony N., (2017). Experimental and theoretical studies on the corrosion inhibition of vitamins – Thiamine hydrochloride or biotin in corrosion of mild steel in aqueous chloride environment. *Egyptian Journal of Petroleum*, 3, pp. :1 -11.

Ameh, P. O. & Eddy, N. O. (201)4b. Characterization of *Acacia sieberiana*(AS) gum and their corrosion inhibition potentials for zinc in sulphuric acid medium. *International Journal of Novel Research in Physics, Chemistry and Mathematics*, 1, 1, pp. 25-36.

Ameh, P. O. & Eddy, N. O. (2014a). *Commiphora pedunculata* gum as a green inhibitor for the corrosion of aluminium alloy in 0.1 M HCl. *Research in Chemical Intermediates* 40, 8, pp. 2641-2649.

Ameh, P. O., Odiongenyi, A. O. & Eddy, N. O. (2012). Joint effect of *Anogessius leocarpus* gum (AL gum) exudate and halide ions on the corrosion of mild steel in 0.1 M HCl. *Portugaliae Electrochimica Acta,* 30, 4, pp. 235-245.

Eddy, N. O., Abechi, S. E., Ameh, P. & Ebenso, E. E. (2013b). GCMS, FTIR, SEM, physicochemical and rheological studies on *Albiziaz ygia* gum. *Walailak Journal,* 10, pp. 247-265.

Eddy, N. O., Ameh, P. O. Victor, E. & Odiongenyi, A. O. (2014b). Chemical information from GCMS and FTIR studies on *Ficus thonningii* gum and its potential as a corrosion inhibitor for aluminum in acidic medium. International *Journal of Chemical, Materials and Environmental Research*, 1, 1, pp. 3-15.

Eddy, N. O., Ameh, P. O., Danclementino, O. & Odiongenyi, A. O. (2014c). Adsorption and chemical studies on the inhibition of the corrosion of aluminum in hydrochloric acid by *Commiphora africana g*um. International *Journal of Chemical, Materials and Environmental Research*, 1, 1, pp. 15-28.

Eddy, N. O., Ameh, P. O., Gimba, C. E. & Ebenso, E. E. (2013). Rheological Modeling, surface morphology and physicochemical properties of *Anogeissus leiocarpus g*um. *Asian Journal of chemistry,* 25, 3, pp. 1666-167283.

Eddy, N. O., Ameh, P., Gimba, C. E. & Ebenso, E. E. (2011). Eddy, N. O., Ameh, P. O. and Odiongenyi, A. O. (2014d). Physicochemical characterization and corrosion inhibition potential of *Ficus benjamina (FB)* for aluminum in 0.1 M H2SO4. *Portugaliae Electrochimica Acta* 32(3): 183-197*International Journal of Electrochemical Sciences,* 6, pp. 5815-5829

Eddy, N. O., Ameh, P., Gimba, E. C. & Ebenso, E. E. (2012). Chemical information from GCMS of *Ficus platyphylla* gum and its corrosion inhibition potential for mild steel in 0.1 M HCl. *International Journal of Electrochemical Sciences,* 7, pp. 5677 – 5691.

Eddy, N. O., Ja'O, A. M. & Usman, N. S. (2016). Rheological modeling, physicochemical, spectroscopicand rheological characterizations of *Trichilia roka* (*TR*) gum exudates. *Journal of Chemical, Biological and Chemical Sciences. Section A: Chemical Sciences*, 6, 3, pp. 1034-1055

Eddy, N. O., Odiongenyi, A. O., Ameh, P. O. & Ebenso, E, E, (2012a). Corrosion inhibition potential of *Daniella oliverri* gum exudate for mild steel in acidic medium. *International Journal of Electrochemical Sciences,* 7, pp. 7425-7439

Eddy, N. O., Paul O. A. & Ali I. (2015). Physicochemical characterization and corrosion inhibition potential of *Fiscus benjamina (FB)* gum for aluminum in 0.1M HCl. *Walailak Journal of Science and Technology*, 12, pp. 1121-1136.

Eddy, N. O., Udo, J. Ibok, Ameh, P. O., Nsor, O. Alobi & Musa M. Sambo (2014a). Adsorption and quantum chemical studies on the inhibition of the corrosion of aluminum in HCl by *Gloriosa superba* (GS) gum. *Chemical Engineering Communications*, 201, 10, pp. 1360-1383.

Eddy, N. O., Udofia, I. & Uzairu, A. (2014a). Physicochemical, spectroscopic and rheological characterization of *Albizia lebecck* gum exudates. *Pigment and Resin Technology*, 43, 4, pp. 228 – 244.

Eddy, N. O., Udofia, I., Abechi, S. E., Okey, E. & Odiongenyi, A. O. (2015). Rheological modeling, spectroscopic and physicochemical characterization of Raphia hookeri gum exudates. *Walialak Journal of Science and Technology*, 12, 5, pp. 407-429.

Eddy, N. O.,Udofia, I., Odiongenyi, A. O. & Obadimu, C. (2014). Physicochemical, spectroscopic and rheological characterization of *Anacardium occidentale* gum exudates. *Journal of Polymer and Biopolymer Physics Chemistry*, 2, 1, pp. 12-24.

Lori A. Joseph, Omoniyi K. Israel, Ekanem J. Edet & Patricia A. Ekwumemgbo (2009). Determination of metal ions released from stainless steel arch bar into biofluids. *Bulletin of Chemical Society of Ethiopia*, 23, 1, pp. 37-46.

Loto, C.A., Loto, T.R., & Popoola, I. P. A. (2011). Corrosion and plant extract inhibition of mild steel in HCl. *International Journal of Physical Science*, 6, 15, pp. 3616-3626.

Namrata, C., Savita, V., Kumar, S. &Quraish, M.A. (2017). Corrosion inhibition in performance of different bark extracts on aluminum in alkaline solution. *Journals of the Association of Arab Universities for Basic and Applied Sciences,* 22, pp. 38-44.

Umuren, A.S. (2009). Polymers as corrosion inhibitors for metals in different media-A reviews. *The Open Corrosion Journal*, 2: 175-188.

Zakari, K., Hamdy, A., Abbas, M.A., and Abo-Etenin, O.M. (2016). New organic compounds based on siloxane moiety as corrosion inhibitors for carbon steel in HCl solution; Weight loss, electrochemical and surface studies. *Journal of Taiwan Institute of Chemical Engineers*, 000(2016): 11-14.

Conflict of Interest

The authors declared no conflict of interest