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The inhibition of *Carica papaya* leaves extract on the corrosion of cold worked and annealed mild steel in HCl and NaOH solutions using a weight loss technique

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Abstract

The current work investigates the corrosion inhibition of cold worked and annealed mild steel in 0.5 M HCl and 0.5 M NaOH solutions with *Carica papaya* leaf extract as an inhibitor. The as-received diameter of the mild steel rods was 4.42 mm before some of them were cold drawn to 3.35 mm wire bars. Rods that were 30 mm in length were cut from the as-received, cold worked and annealed samples. The cut samples were thoroughly pickled, dried and weighed before they were suspended in an aggressive media that contained the inhibitor as well as in the media without inhibitor. The samples were examined on the 3rd, 5th, 7th, 10th, 12th, 14th and 17th days, and then, pickled, dried and reweighed. In the 0.5 M HCl solution without inhibitor, maximum corrosion rates of the as-received and cold worked samples were reported on the 5th day, and their values were $1.0x10^{-4}$ and $1.3x10^{-4}$ g/cm^{2}h, respectively. The maximum corrosion rate of the annealed sample was reported on the 12th day and its value was $5.9x10^{-5}$ g/cm^{2}h. The extract was able to reduce the maximum corrosion rates of the as-received, cold worked and annealed samples in 0.5 M HCl solution by 54.1 %, 42 %, and 23.1 %, respectively. Similarly, in a 0.5 M NaOH solution without inhibitor, maximum corrosion rates of the as-received and cold worked samples were reported on the 5th day. Their values were $7.0x10^{-5}$ and $8.8x10^{-5}$ g/cm^{2}h, respectively. The maximum corrosion rate of the annealed sample was reported on the 12th day and its value was $4.1x10^{-5}$ g/cm^{2}h. The inhibitor reduced the maximum corrosion rates in a 0.5 M NaOH solution by 53.8 %, 51.4 % and 33.3 % for the as-received, cold worked and annealed samples respectively. The corrosion rates of all the samples were reduced in the media that contained the inhibitor.

Keywords: Mild steel, *Carica papaya*, Leaf extract, Corrosion, Inhibition

1. Introduction

Mild steel has found use in diverse engineering applications such as steel tanks, concrete reinforcement, machine parts and numerous engineering applications due to its low cost, weldability, availability, and ease of fabrication [1]. Corrosion of mild steel is encountered in service due to its interaction with aqueous media, highly concentrated solutions, as well as an acidic and alkaline solutions. This can lead to failure and economic losses [2]. Corrosion study, its prevention, and control are very active research areas that seek solutions to industrial problems. Corrosion of metals can be controlled through proper material selection, design, cathodic and anodic protection, surface treatments and coatings, as well as with inhibitors. The use of inhibitors is a straightforward and effective method to minimize the corrosion of metals in harsh environments, even when the inhibitors are used in small quantities [3]. Inhibitors synthesized from inexpensive raw materials are highly desired [4]. Chemical inhibitors can be expensive and environmentally unfriendly. Hence, there is need to find corrosion inhibitors from green sources [5]. Plant extracts have been reported as corrosion inhibitors. They are renewable, inexpensive, environmentally friendly, readily available and less toxic [6]. Some investigations on the use of green inhibitors to control the corrosion of metals have been reported [2-14]. There has been interest in *Carica papaya* leaf extract as a corrosion inhibitor. Acid extract from the leaves (LV), seeds (SD), heartwood (HW) and bark (BK) of *Carica papaya* has been reported to inhibit the corrosion of mild steel in H_2SO_4 with an order of effectiveness of LV>SD>HW>BK [15]. *Carica papaya* leaf extract also been reported to inhibit the corrosion of aluminum in hydrochloric acid [16-17]. Other reports on the inhibition of metal corrosion with *Carica papaya* leaf extract

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Table 1 Composition of mild steel

Element	Fe	C	Si	Mn	P	S	Cr	Ni	Cn
%composition	98.67	0.200	0.192	0.451	0.040	0.140	0.100	0.100	0.250

Table 2 Hardness values of the mild steel

Specimen	Cold worked	Annealed	As- received
Hardness (BHN)	155	127	140

indicate that it inhibits corrosion of brass in 0.1 M nitric acid [18] and of aluminum in sulphuric acid [19]. This work evaluates the inhibition properties of *Carica papaya* leaf extracts on the corrosion of cold worked and annealed mild steel in 0.5 M HCl and 0.5 M NaOH, respectively.

2. Materials and methods

The mild steel used in this study had the composition shown in Table 1. It was obtained from Trident Steel Limited, Port Harcourt, Rivers State, Nigeria. It was in the form of 4.42 mm diameter drawn bars.

Some of the supplied mild steel bars were subjected to cold drawing, and the diameter of the cold drawn wire was reduced to 3.35 mm. The percentage of cold work was calculated from equation (1). A_0 and A_f are the cross-sectional areas of the undrawn and drawn wires respectively.

$$\text{Percentage of cold work} = \frac{A_o - A_f}{A_o} \; x\ 100\% \qquad (1)$$

Some portions of the as-received wires were subjected to an annealing process by raising their temperature to 870 ^{0}C in a furnace and holding them at that temperature for one hour before the furnace was switched off to allow slow cooling of the annealed steel in the furnace.

The hardness of the as-received, cold drawn and annealed samples were measured using a Digital Brinell Hardness Testing Machine. 0.5 M HCl and 0.5 M NaOH solutions for the corrosion study were prepared using a serial dilution method.

A liquid was extracted from *Carica papaya* green leaves. This leaf extract served as an inhibitor in the experiment. The leaves were harvested from a tree and ground in a laboratory mortar and pestle. A liquid extract was expressed from the resulting ground matter with addition of no water. The extract was used immediately after preparation to ensure optimum performance and to reduce the risk of contamination.

30 mm length specimens for corrosion study were cut from the as-received, cold drawn and annealed mild steel samples. A thorough surface preparation to remove all mill-scales, rough edges due to cutting, dust, grease oil, and dirt, was done. The steel bars were pickled in 0.5 M HCl by dipping the samples in the acid and bringing them out after 60 seconds. This was followed by dipping in ethanol to remove all oxides and to stop further oxidation before they were immersed into the media for corrosion measurements.

The experimental setup is shown in Figure 1. A total of twenty-four containers were prepared, twelve containing one liter of 0.5 M HCl while the other twelve contained one liter of 0.5 M NaOH, as the corrosion media. 10 ml of *Carica papaya* leaf extract was added to six containers containing HCl and into another six containers containing NaOH using a clinical syringe. The inhibitor concentration was 1 vol% in each of the HCl and NaOH media. The other containers had no inhibitor. Seven rods of as-received mild steel were weighed using a polymer thread and suspended in a vessel containing corrosive media, as shown in Figure 1. The same process was repeated using cold worked and annealed samples in different containers. There were two containers for each set samples and the average weight lost from each sample was reported to ensure reproducibility. Samples were immersed in corrosive media that contained inhibitors while other were exposed to solutions that contained no inhibitor. They were allowed stand for seventeen days during which time, one rod was removed on the 3rd, 5th, 7th, 10th, 12th, 14th and 17th days. The removed rods were pickled by dipping them in another vessel containing of 0.5 M HCl, then in ethanol to stop further surface oxidation. They were dried and reweighed and the final masses recorded. The experiment was carried out at an ambient temperature of 26 $\pm$ 2 ^{o}C and atmospheric pressure.

The corrosion rate (CR) in g/cm^{2}h was estimated using equation (2), while the inhibitor efficiency over the exposure time was estimated from equation (3) [15, 20]. ΔW is the weight loss in g, A is the surface area of the steel bar in cm^2 and t is the exposure time in hours. “UI” is the medium without inhibitor while “I” is the medium with inhibitor, as represented in equation (3).

$$\text{Corrosion rate (CR) (g/cm}^2\text{h)} = \frac{\Delta W}{At} \qquad (2)$$

$$\text{Inhibition Efficiency} = \frac{CR\ in\ UI - CR\ in\ I}{CR\ in\ UI} \; x\ 100\ \% \qquad (3)$$

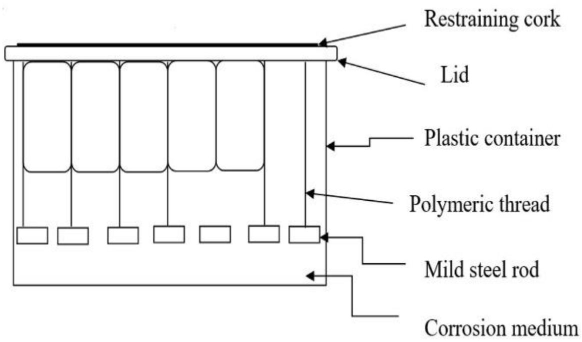

Figure 1 Experimental set up

3. Results and discussion

The estimated percentage of work on the cold worked samples was 45.56 %. This is a measure of the plastic deformation of mild steel from its original to its final diameter. The hardness values of the samples are shown in Table 2.

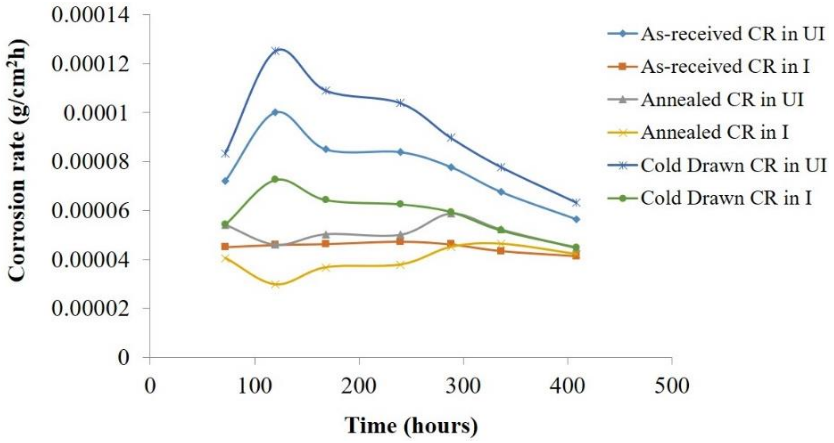

Figure 2 Corrosion rates of the samples in a 0.5 M HCl medium

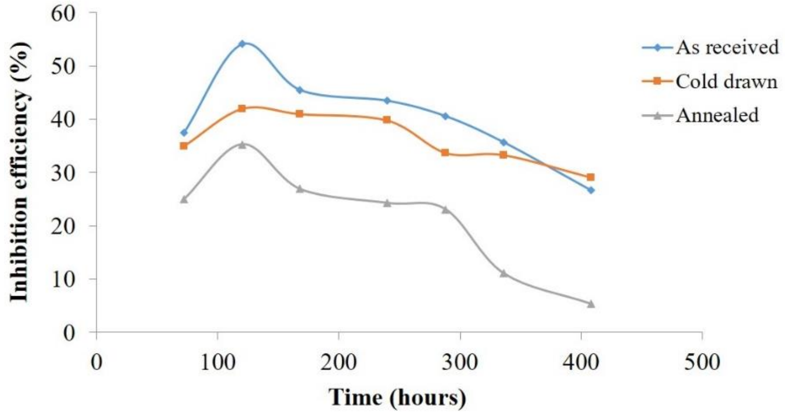

Figure 3 Inhibition efficiency of *Carica papaya* leaf extract in 0.5 M HCl

The higher hardness observed in the cold worked samples is in agreement with the literature [21-23]. Cold working increases the hardness of steel due to strain hardening resulting from plastic deformation as a result of movements of dislocations and the generation of other dislocations in the material structure [21, 23]. The lower hardness observed in the annealed sample is also in agreement with the literature [21, 24-25]. Annealing processes remove distortion and homogenizes the microstructure. They are used to relieve stress, induce ductility and soften the material due to the formation of a soft ferrite matrix in the microstructure [25].

The corrosion rates of the samples in 0.5 M HCl are shown in Figure 2. The corrosion rate of the cold worked sample was the highest, followed by that of the as-received sample. The annealed sample showed the least corrosion throughout the experiment. The higher corrosion rate of the cold drawn sample was due to the accumulation of dislocations during cold working and a lower H_2 overvoltage of the dislocations sites [26]. A higher corrosion rate of the cold drawn sample was reported in similar work [27]. The corrosion rate of the cold drawn and as-received samples initially increased before they decreased. The annealed sample showed the lowest corrosion rate at all times. This was as a result of coarser grains in the microstructure obtained as a result of annealing, making it more resistant to corrosion [28-29].

Corrosion rates of the samples in 0.5 M HCl that contained *Carica papaya* leaf extract are depicted in Figure 2. The annealed sample also showed the lowest corrosion rate, while the cold drawn sample yielded the highest corrosion rate at times less than 320 hours per the earlier discussed mechanism. All samples showed lower corrosion rates in media with an inhibitor. In the 0.5 M HCl solution without inhibitor, maximum corrosion rates of the as-received and cold worked samples were measured on the 5th day. Their values were $1.0\text{x}10^{-4}$ and $1.3\text{x}10^{-4}$ g/cm^2 h, respectively. The maximum corrosion rate of the annealed sample was reported on the 12th day. Its value was $5.9\text{x}10^{-5}$ g/cm^{2}h. *Carica papaya* leaf extract used as an inhibitor reduced the maximum corrosion rates of the as-received, cold worked and annealed samples in 0.5 M HCl by 54.1%, 42%, and 23.1% respectively. *Carica papaya* leaf extract contains tannins and phytic acid, among other chemicals, which are non-toxic corrosion inhibitors in various media [16]. Omotioma and Onukwuli [17] reported that a shifting mechanism of the stretched C-O functional groups in some components of the extract is responsible for corrosion inhibition. Okafor and Ebenso [15] reported that corrosion inhibition involves physical adsorption of the phytochemical components of the *Carica papaya* leaf extract onto the surfaces of the metal. Dar [30] further highlighted that an inhibitor is a mixture of various types of compounds that are adsorbed onto metal surfaces through heteroatoms and their pi-orbitals.

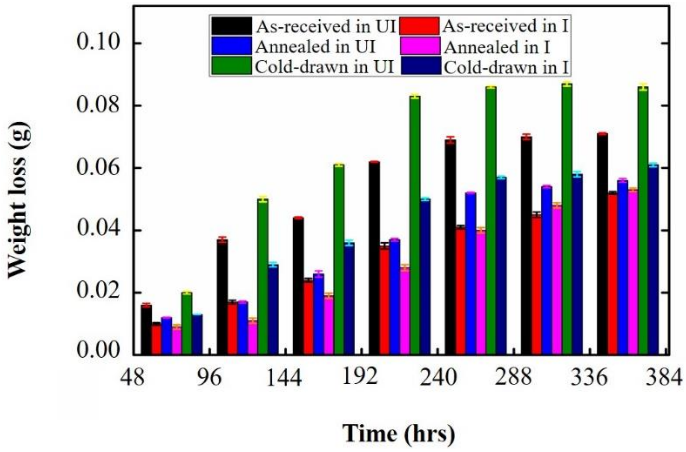

Figure 4 Weight loss of the samples in a 0.5 M HCl medium

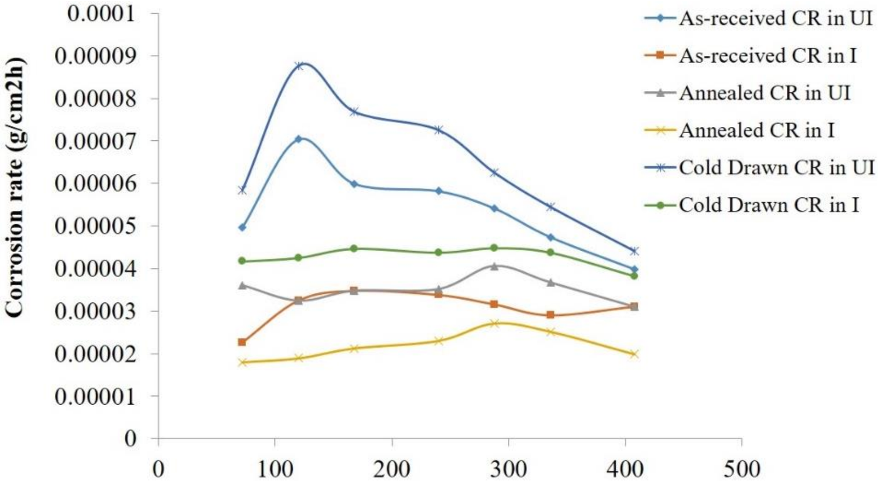

Figure 5 Corrosion rates of the samples in a 0.5 M NaOH medium

The inhibition efficiency of the leaf extract in 0.5 M HCl is shown in Figure 3. It was reduced with time for all the samples and its value depended on the treatment given to the metal. The inhibition efficiency on the as-received sample was the highest, except for very long times. This efficiency on the annealed sample was very minimal after 320 hours, yielding similar corrosion rates as those of the as-received and cold drawn samples.

The weight loss of the metals in the 0.5 M HCl solution is shown in Figure 4. It can be seen that the weight loss increased with time as the metal corroded. The rate of metal loss was initially faster and reduced over time. Weight loss of the metals in a solution containing the inhibitor were lower than in solutions with no inhibitor. The cold drawn sample showed the highest weight loss due to its greater corrosion rate. However, with an inhibitor, the inhibition efficiency exhibited by the annealed sample was very minimal after about 320 hours. This resulted in higher weight losses compared to the cold drawn sample. Figure 2 shows the average weight loss for each sample in 0.5 M HCl. The standard deviation for each data set was quite small, validating the results.

Corrosion rates of the samples in 0.5 M NaOH are shown in Figure 5. The cold rolled sample showed the highest corrosion, while the annealed sample had the least. Comparing Figures 5 and 2, it can be seen that the corrosion rates of all samples in NaOH were less than those in HCl. HCl is a more severe environment for mild steel than NaOH. Also, in the 0.5 M NaOH solution with no inhibitor, maximum corrosion rates of the as-received and cold worked samples were reported on the 5th day. Their values were 7.0×10^{-5} and 8.8×10^{-5} g/cm^{2}h, respectively. The maximum corrosion rate of the annealed sample was reported on the 12th day and its value was 4.1×10^{-5} g/cm^{2}h. The inhibitor reduced the maximum corrosion rates in 0.5 M NaOH solution by 53.8%, 51.4% and 33.3% for the as-received, cold worked and annealed samples, respectively. *Carica papaya* leaf extract also inhibited corrosion of mild steel in a NaOH solution. Essential ingredients for corrosion inhibition in the extract were active in both the HCl and NaOH solutions.

The inhibition efficiency of the leaf extract in 0.5 M NaOH is shown in Figure 6. Compared to the values shown in Figure 3, the inhibition efficiency of *Carica papaya* leaf extract on the corrosion of annealed mild steel was higher in NaOH than in HCl, and it increased after 320 hours in NaOH, unlike in HCl, where it decreased. Corrosion inhibition on the cold drawn sample started diminishing after 220 hours in NaOH.

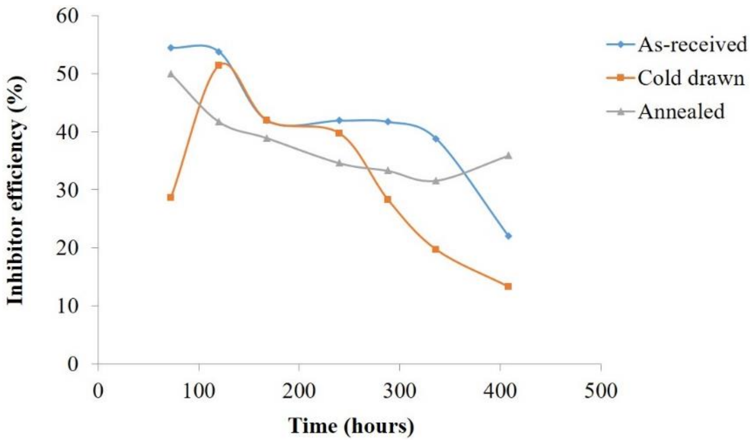

Figure 6 Inhibition efficiency of *Carica papaya* leaf extract in 0.5 M NaOH

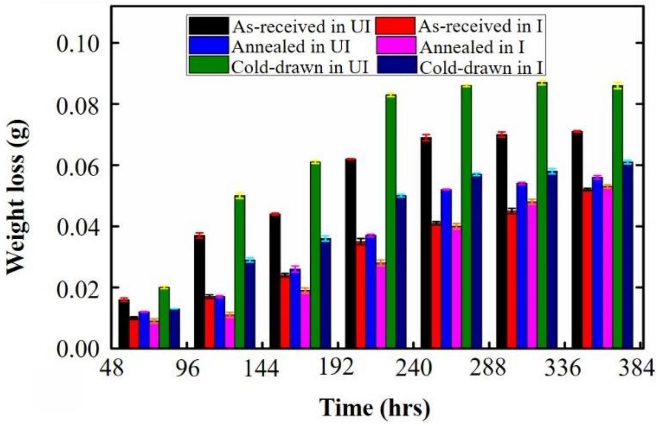

Figure 7 Weight loss in a 0.5 M NaOH medium

The weight loss of the metals in a 0.5 M NaOH solution is shown in Figure 7. It increased with time similar to observatons of the HCl solution. They were smaller compared to those in HCl due to lower corrosion of the metals in NaOH. The annealed sample showed the least weight loss while the cold drawn sample showed the most. The weight loss values in the media that contained inhibitor were smaller compared than in media with no inhibitor. Figure 5 shows the average weight loss for each sample in 0.5 M NaOH. The standard deviation was small enough to validate the results.

4. Conclusions

The corrosion rates of the as-received, cold drawn and annealed mild steel samples were reduced in both 0.5 M HCl and 0.5 M NaOH solutions by the addition of 10 ml of *Carica papaya* leaf extract into 1 liter of these acid and base solutions. In the 0.5 M HCl solution with no inhibitor, maximum corrosion rates of the as-received and cold worked samples were reported on the 5th day, and their values were 1.0x10^{-4} and 1.3x10^{-4} g/cm^{2}h, respectively. The maximum corrosion rate of the annealed sample was reported on the 12th day and its value was 5.9x10^{-5} g/cm^{2}h. The inhibitor reduced the maximum corrosion rates of the as-received, cold worked and annealed samples in 0.5 M HCl by 54.1%, 42%, and 23.1%, respectively. Inhibition in the HCl solution was highest at the 5th day, with values of 54.1%, 42% and 35.3% for the as-received, cold drawn and annealed samples, respectively. In 0.5 M NaOH with no inhibitor, the maximum corrosion rates of the as-received and cold worked samples were reported on the 5th day. Their values were 7.0x10^{-5} and 8.8x10^{-5} g/cm^{2}h, respectively. The maximum corrosion rate of the annealed sample, 4.1x10^{-5} g/cm^{2}h, was reported on the 12th day. The inhibitor reduced the corrosion in 0.5 M NaOH solution by 53.8%, 51.4% and 33.3% for the as-received, cold worked and annealed samples, respectively. The maximum inhibition in the NaOH solution for the as-received, cold drawn and annealed samples was 54.5% on the 3rd day, 51.4% on the 5th day and 50% on the 3rd day. Industries are called upon to effectively make use of *Carica papaya* leaf extract for corrosion inhibition of mild steel in both acidic and alkaline environments.

5. Acknowledgment

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