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Protection of Mild Steel Structures against Microbiologically Induced Corrosion in Fresh-Water Environment using Carica Papaya Leaf Extract

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Abstract

Mild steel structures in fresh-water environments such as rivers and rain-water harvest facilities suffer corrosion induced by microbiological agents. Continual study to minimize or possibly eliminate the microbiological agents of corrosion is essential. This study investigates the use of Carica papaya leaf extract in the protection of differently treated mild steel against microbiologically induced corrosion (MIC) in a fresh-water environment. The investigations were carried out using the gravimetric technique. The tested mild steel consists of untreated and treated samples. Also, the bio-corrosion medium consists of the uninhibited and inhibited conditions. All mild steel samples were exposed to MIC attack for specific incubation periods in the uninhibited and inhibited media. The results of the cold-worked and annealed specimens indicated the maximum alkalinity with a pH value of 9.84 on the 49th day for the cold-worked sample and a pH value of 10.01 for that of the annealed sample on the 49th day, respectively. In contrast to that of the as-received sample, which recorded a maximum pH value of 8.60 on the 42nd day. Therefore by implication, the results of this study have shown that Carica papaya leaf extract is an efficient inhibitor of mild steel in fresh-water environment and can also be extended to other environments where metallic corrosion is a problem.

1. Introduction

Mild steel has broad applications, including the manufacture of reactors [1, 2], gathering pipelines [3, 4], storage vessels [5], automobile chassis, and parts [6-8], petrochemical and chemical plants [9]. Mild steel has these broad applications because it has excellent mechanical properties [10, 11], ease of fabrication [12], and affordability [13]. Also, a significant percentage of these facilities made of mild steel operating in a fresh-water environment. However, mild steel has weak resistance to corrosion, especially in the water environment [14, 15]. The implication of corrosion on mild steel is a grave industrial problem.

In particular, mild steel structures in fresh-water environments such as rivers and rain-water harvest facilities suffer corrosion induced by microbiological agents [16, 17]. Studies showed that microbiologically induced corrosion (MIC) causes about 20 % of the total damages in various facilities worldwide [18]. Therefore, a continual study to minimize or possibly eliminate the microbiological agents of corrosion is essential. That is because they constitute a significant threat to mild steel structures, especially in fresh-water environments.

Studies showed that the destroying of MIC causative agents is a viable means of prevention or control of MIC [19, 20]. Also, [20] identified the chemical method (biocides and corrosion inhibitors principle) as the most effective MIC prevention or control methods, especially in the water environment. However, several studies showed that the chemical method is toxic, expensive, and challenging to degrade [20-26]. Chemical inhibitors may cause temporary or permanent damage to the human organs and systems such as the kidneys or liver, disturb biochemical processes, and enzyme at some site in the body [27, 28].

Hence, it is essential to search for a new class of biocides and corrosion inhibitors that are human and environmental friendly for the protection of mild steel against MIC. Different studies showed that different plants extract including Carica papaya peel and leaf, Gossypium hirsutum leaf, Theobroma cacao peel, Mango and Orange peel, Pseudomonas marginalis, Acacia tortilis, Musa paradisiaca peels, and Moringa oleifera leaf contain the biocides and corrosion inhibitors that are human and environmental friendly for the protection of different metals against MIC [14, 29-34]. A particular study showed that the bioactive metabolites defend plants against micro-organisms [32]. These bioactive metabolites can defend plants against the attack of yeast, filamentous fungi, and bacteria [35]. Also, some studies showed that bioactive metabolites could control or prevent bio-corrosion in different metals [36, 37]. Moreover, the report of a particular study on the bio-corrosion inhibition of mild steel in the crude oil-water environment asserted that it is challenging to eliminate MIC [34]. In that report [34], Carica papaya peel extract showed a superior attack on the microbial growth among biocidal-adsorption inhibitors understudied. Also, it was reported in [34] that the adsorption of Carica papaya peel extracts biomolecules onto the surface of the mild steel is spontaneous. Hence, the physical adsorption phenomenon of the Carica papaya extracts biomolecules on the surface of mild steel implies; it could control MIC actively.

However, recent valuable studies showed that the activeness of Carica papaya extracts biomolecules for the protection of mild steel against MIC varies with the environment and treatment of the mild steel [14, 38]. Also, in those reports [14, 38], for the specific bio-corrosion medium (marine, acidic, and alkaline environments), the trend of the inhibition efficiency varies with the incubation period for all samples. In the report of [14], the as-received samples had the highest inhibition efficiency compared with the cold-worked and annealed samples at the end of the incubation period in the marine environment. Also, the heat treatment of mild steel alters its mechanical and chemical properties. On the other hand, in the acidic and alkaline environment, the cold-worked and annealed samples had the highest inhibition efficiency, respectively, at the end of the incubation periods [38]. Thus, it is essential to test the activeness of the Carica papaya extracts for the protection of mild steel structures against MIC in a different environment. It is because the different environments would consist of different microbes and elements, thereby experience the different phenomenon of MIC attack on the mild steel structures. An excellent understanding of the activeness of the Carica papaya extracts biomolecules on differently treated mild steel samples in a specific environment would guaranty the exact process for the protection of mild steel structures against MIC using Carica papaya derivatives.

To the authors' knowledge, investigations on the use of Carica papaya derivatives in the protection of mild steel structures against microbiologically induced corrosion (MIC) in a fresh-water environment still lack in the literature. Hence, this study investigates the use of Carica papaya leaf extract in the protection of differently treated mild steel against microbiologically induced corrosion (MIC) in a fresh-water environment.

2. Materials and Methods

2.1 Collection of samples

The authors collected a fresh-water sample at Otamiri river of degrees, minutes, seconds (DMS) latitude: 4° 54' 14.00" N and longitude: 7° 08' 30.00" E in Imo State, Nigeria. Also, the authors collected mild steel samples from Trident Steel Limited at Port Harcourt City of DMS latitude: 4° 49′ 27.0012″ N and longitude 7° 2′ 0.9996″ E in Rivers State, Nigeria. Finally, the authors plucked fresh Carica papaya leaf from its tree in a Farm Garden at Imo State University, Owerri of DMS latitude: 5° 30′ 13.4208″ N and longitude: 7° 2′ 37.662″ E in Imo State, Nigeria.

2.2 Preparation of samples

2.2.1 The fresh-water sample

First, the collected fresh-water sample was filtered through a 0.1 mm stainless steel wire sieve. Then, the physio-chemical analysis of the filtrate was carried out according to a standard method (APHA, 2005) [39]. Based on the APHA 2005 techniques, the authors measured the pH, dissolved oxygen (DO), conductivity, turbidity, halogen gas, and salt ions for hardness (SO_4^{2-}) of the filtrate.

Furthermore, the authors carried out the metal analysis of the filtrate and sediments (air-dried). Metallic ions extracted are calcium (Ca^+), Iron (Fe^+), manganese (Mn^+), Crinum (Cr^+), aluminium (Al^{3+}). The authors used a microwave accelerated reaction system (CEM MARS 6^{TM} -microwave digester) to extract the metals. The microwave digester was set at 1500 W, and 175 ^{0}C held for 4.5 minutes. Then, it was allowed to cool down for one hour in the digester environment [40]. The authors filtered the cold digest solution through the Whatman 42 filter paper. Next, the authors added deionized water in a volumetric flask up to 60 mL. Finally, the metal concentrations were analyzed by inductively coupled plasma mass spectrometry (PerkinElmer NexION 2000B ICP-MS). Table 1 and 2 shows the elements and properties of the fresh-water sample, respectively.

Table 1 The elements of the fresh-water sample

Element	Ca	Fe	Mn	Cr	Al	Cl	DO	CO_2^-	SO_4^{2-}
Composition(mg/l)	2.6	0.1	0.12	-	-	-	5.5	3.1	0.004

Table 2 The properties of the fresh-water sample

Properties	pH	Turbidity (cm)	Conductivity (µS/cm)	Hardness (mg/L)
Amount	6.8	52.1	375.4	30.1

2.2.2. The mild steel samples

The authors received several mild steel wire samples from Trident Steel Limited. The dimension of the original samples is approximate 1 m length and 4.42 mm in diameter. According to Trident Steel limited, table 3 shows the chemical composition of the mild steel samples [14]. The authors prepared three sets of samples for the bio-corrosion tests as detailed below [14]. Some samples were initially press-cut into 30 mm length by a Convectional Hydraulic Cable Cutter (CG25-XCG25) (i.e., to get as-received samples). In contrast, some samples were first drawn to a diameter of 3.35 mm by a cold-work method with Small Drawing Machine for thin steel wires (KGT 12). They were press-cut into 30 mm length by a Convectional Hydraulic Cable Cutter (CG25-XCG25) (i.e., to get cold-worked samples). Also, some of the cold-worked samples were annealed at 860 ^{0}C for one hour by a high-temperature electric furnace (SG-XS1200) after cutting (i.e., to get annealed samples).

Table 3 Elements of the mild steel sample in wt. % composition [14]

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

Moreover, the authors polished all samples to a mirror finish with different grades of emery paper. Also, the polished samples were de-greased in absolute ethanol, rinsed with double-distilled water, and dried in acetone. Polishing and de-greasing of samples are essential because it helps to remove all mill-scales, rough edges due to cutting, flush out all oxides, and stop further oxidation, which might introduce significant error in the measured data. Finally, the polished and de-greases samples were labeled appropriately and stored in a moisture free and dry desiccator ready for the bio-corrosion tests.

2.2.3 The Carica papaya leaf extract sample

First, the authors used distilled water to wash the plucked Carica papaya leaves. After washing, the leaves were carefully sliced into smaller sizes with a table knife on the plastic chop board. Then, the authors sun-dried the sliced leaves for seven days before oven-drying at 40 ^{0}C for 1hour. After that, the oven-dried leaves were ground to fine particles using an electric blender (1960s General Electric chrome 2-speed blender). Next, 1000 g of the pulverized leaves were carefully poured into a Soxhlet apparatus and extracted with methanol solvent diluted with 25 % distilled water at a temperature equal to the boiling point of the solvent. Afterward, the authors decanted and filtered the extracts. Then, the filtrate was transferred into a vacuum evaporator placed on a temperature-controlled water bath at 60 ^{0}C. The temperature controlled-bath enables one to obtain the solid residue of the Carica papaya leaf extract devoid of methanol solvent. The solid residue of the extract was stored in a cork-tight bottle.

Furthermore, the authors relied on the tests for phytochemical constituents of the Carica papaya extract recently carried out by [34]. In the reports of [34], it was shown that the Carica papaya extract contains a reasonable concentration of flavonoids, tannins, anthraquinones, triterpenes, alkaloids, polyphenols, sterols, and saponins. Particular studies showed that these metabolites display both biological and physiological attributes [41] and active bio-corrosion inhibitors [42].

2.2.4 *The bio-corrosion medium*

The authors prepared two kinds of bio-corrosion medium. First, the uninhibited bio-corrosion medium consists of only the filtrate of the fresh-water sample described in sub-section 2.2.1 above. Secondly, the inhibited bio-corrosion medium consists of the mixture of the fresh-water sample and the Carica papaya leaf extract. For the inhibited bio-corrosion medium, the authors dissolved the solid residue of the Carica papaya leaf extract (described in subsection 2.2.3 above) in the fresh-water filtrate solvent at a concentration of 10 grams per liter in four-liter glass bottles at room temperature [14]. The measured pH of the inhibited bio-corrosion medium was 5.31.

2.3 *The setup of experiments and gravimetric technique*

The authors used the same setup of experiments and the procedure of measurement of the bio-corrosion data developed in the previous study [14]. In the design by [14], six bowls were used for the tests. Three bowls for each of the uninhibited and inhibited conditions. In each case, the authors tied seven specific samples with the help of a polymeric thread. Before the samples are tied, the initial weight was taken one by one using the digital balance with a sensitivity of ± 1 mg. Then, the tied samples were submerged entirely into the bowl containing the bio-corrosion medium. The authors ensured sufficient anaerobic conditions by the tightly close of the bowl with a restraining cork. The same concentration of bio-corrosion medium was used throughout the tests. That was because the primary aim of this study is to determine the capacity of Carica papaya leaf metabolites for the protection of differently treated mild steel against MIC in a fresh-water environment.

Based on the gravimetric technique, materials under the attack of MIC would lose weight with time. Hence, in this study, the authors incubated the setup described earlier for 49 days at room temperature of 25 ^{0}C to allow for the attack of the samples by MIC. In determining the weight loss as a function of time, the submerged samples were withdrawn at seven days' intervals. The withdrawal of the submerged samples was carried out progressively for the entire incubation periods (i.e., 49 days). After each withdrawal of the submerged samples, they were washed in distilled water, cleaned with ethanol, dried in a desiccator, and re-weighed. The weight loss was taken as the difference between the weights of the MIC attacked samples at a specific time and their initial weights. The authors used several samples to ensure adequate reproducibility. The experiment was reproduced up to a range from 94 to 97 %.

All the tests were carried out in duplicate and the average values of the weight loss used for the calculations of the MIC rate. The MIC rate (MIC_R) in mils per year (mpy) was calculated by [43]

$$MIC_R = \frac{\beta \Delta W}{\rho T A}, \qquad \textbf{Eqn. 1}$$

where MIC_R is the MIC rate (mpy), β is the MIC rate constant (3.45×10^6 mpy), ΔW is the difference in weight between the free and MIC attacked samples (g), ρ is the density of the mild steel sample (g/cm^3), T is the progressive time interval of incubation (hours), A is the area of exposure of a mild steel sample (cm^2) defined as

$$A = 2\pi r(l + r), \qquad \textbf{Eqn. 2}$$

r is the radius of a Mild steel sample, π is constant (~3.142) and l is the length of a mild steel sample.

Also, the inhibitor's efficiency, η (%) was calculated by

$$\eta = \frac{MIC_{R(uninhibited)} - MIC_{R(inhibited)}}{MIC_{R(uninhibited)}} \times 100, \qquad \textbf{Eqn. 3}$$

Moreover, the authors relied on the essential studies of bio-corrosion attributes of Carica papaya extract on mild steel in the water environment carried out elsewhere [34]. In that report, it determined the surface morphology of the bio-corroded mild steel and active functional groups of the Carica papaya extracts that attacks the microbiological agents of corrosion. Also, they reported the chemical kinetics, adsorption attributes, and microbial activities of the Carica papaya metabolites on the mild steel sample.

3. Results and Discussion

3.1 The analysis of the fresh-water sample

Table 1 above shows the results of the fresh-water analysis. As shown in Table 1, it can be observed that the dissolved oxygen content is the highest among the gas ions in the fresh-water analyzed. The dissolved oxygen content is 5.5 mg/L. Also, the carbon (IV) oxide ion content is significant. The carbon (IV) oxide ion content is 3.3 mg/L. The significant dissolved oxygen and carbon (IV) oxide contents imply that the fresh-water would support sufficient MIC. Still, in Table 1, it can be observed that the SO_4^{2-} salt ions concentration is 0.004 mg/L. SO_4^{2-} salt ion concentration of 0.004 mg/L is small compared with that of an earlier study in the southern region of Nigeria, which had a range from 10 – 762 mg/L [26]. The authors could not determine the cause of the wide disparity of the SO_4^{2-} salt ion concentration of water around this region during this study. Also, there are zero traces of Cl^- gas in the fresh-water sample. Moreover, as shown in Table 1, the fresh-water has a significant concentration of Ca^+, Fe^+ and Mn^+, metallic ions, whereas, there are zero traces of the Al^+ and Cr^+ metallic ion. As shown in Table 2, the pH of the fresh-water is 6.8. The pH of 6.8 is a little alkaline based on the pH scale. The authors attributed the little alkalinity to the little concentration of the SO_4^{2-} ions and zero concentration of Cl^- an ion in the fresh-water sample, as indicated in Table 1. Still, in Table 2, the turbidity of the fresh-water sample is 52.1 cm. The turbidity of 52.1 cm is at the optimum turbidity of fresh-water. Also, in table 2, it can be observed that the conductivity and hardness of the fresh-water sample are 375 µS/cm and 30.1 mg/L, respectively.

3.2 The influence of the MIC on the pH of the corrosion media

Figure 1 shows the influence of the MIC on the pH of the corrosion media for the as-received samples. As indicated earlier in Table 2, also, in Figure 1, it can be seen that the initial pH value of the uninhibited medium is 6.8. In contrast, still, in Figure 1, it can be seen that the initial pH value of the inhibited medium is 5.4. The relatively smaller pH value of the inhibited medium compared with that of the uninhibited medium is attributed to the influence of the concentration of some metabolites in the Carica papaya extract. It had been shown that the Carica papaya extract contains a reasonable concentration of flavonoids, tannins, anthraquinones, triterpenes, alkaloids, polyphenols, sterols, and

saponins [34]. These metabolites can have a significant influence on the bio-corrosion medium. As shown in Figure 1, for the as-received samples, the inhibited and uninhibited medium shows several coinciding pH values, as indicated with the polygon dotted-lines enclosed points. The coinciding pH values occurred on the 7th day, 14th day, 21st day, and 35th day. Also, it can be seen that, for the entire incubation periods, the pH value for both media is higher compared with the initial values. Excluding the initial pH value, both media experienced the lowest pH value on the 7th day, as indicated with circle dotted-lines enclosed point. On the other hand, both media experienced the highest pH value on the 42nd day, as indicated with the rectangle short-dash enclosed points. Still, in Figure 1, one can observe that the uninhibited medium indicates relatively higher pH values compared with the inhibited medium from the 7th day to the 28th day. In contrast, the inhibited medium indicates relatively higher pH values compared with the uninhibited medium from the 28th day to the end of the incubation periods. The authors could not determine precisely why the uninhibited medium exhibited relatively higher pH values compared with the inhibited medium between the 14th and 21st days. In contrast, the inhibited medium exhibited higher pH values compared with the uninhibited medium between the 28th and 49th day.

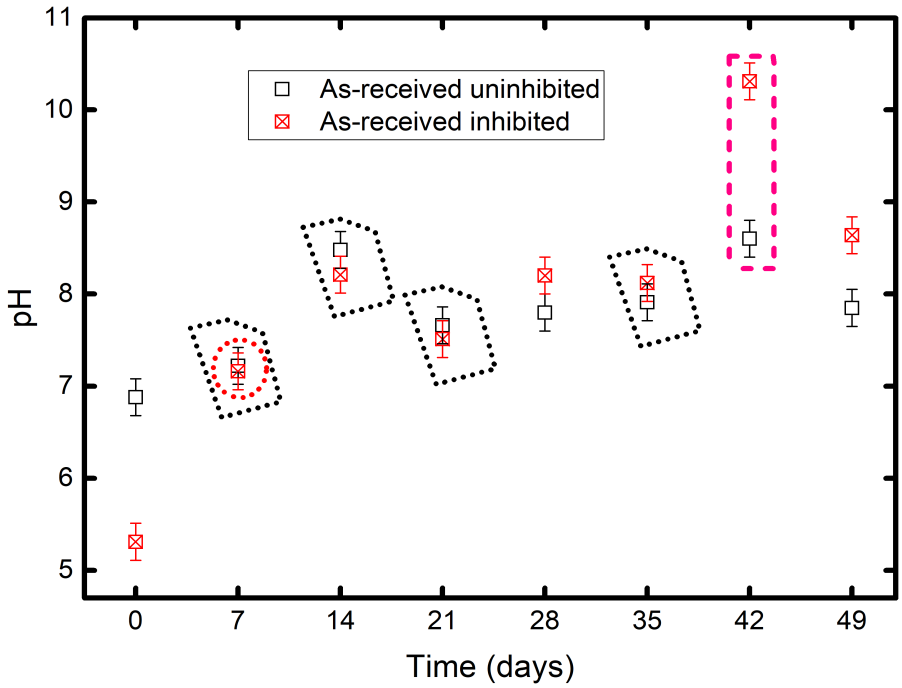

Figure 1 The influence of MIC on the pH of bio-corrosion media for the as-received mild steel samples

Notwithstanding, the authors are hypothesizing that the varied trend of the pH values with time for the uninhibited and inhibited medium could be related to the different chemical kinetics of MIC in the media as a function of time. The spontaneous adsorption of the Carica papaya extract metabolites on the MIC attacked mild steel could change with time. Thus, there are different release, adsorption, and a combination of ions in both media.

Figure 2 shows the influence of the MIC on the pH of the corrosion media for the cold-worked samples. As shown in Figure 2, for the cold-worked samples, the inhibited and uninhibited medium has three coinciding pH values, as indicated with the triangle dotted-lines enclosed points. The coinciding pH values occurred on the 21st day, 35th day, and 42nd day. Also, it can be seen that, for the entire incubation periods, the pH value for both media is higher compared with the initial values.

The inhibited medium experienced the lowest pH value on the 28th day, as indicated with the circle dotted-lines enclosed point. On the other hand, the uninhibited medium experienced the highest pH value on the 49th day, as indicated with the square short-dash enclosed point. Still, from Figure 2, one can observe that the uninhibited medium indicates relatively higher pH values compared with the inhibited medium on the 7th day, 14th day, 28th, and 49th day. In contrast, the inhibited medium indicates relatively higher pH values compared with the uninhibited medium on the 42nd and 49th day. The authors inferred from the variation of the pH values for the cold-worked samples compared with those of the as-received samples that the chemical kinetics of the MIC vary as a function of time depending on the nature of the samples irrespective of the bio-corrosion medium. That could be because the spontaneous adsorption of the Carica papaya extract metabolites and the combination of ions in the distinct samples, and bio-corrosion medium, respectively, would vary during the specific incubation period. Thus, the various chemical reactions and other processes like oxidation and corrosion products dissolution in the bio-corrosion media changes as a function of time.

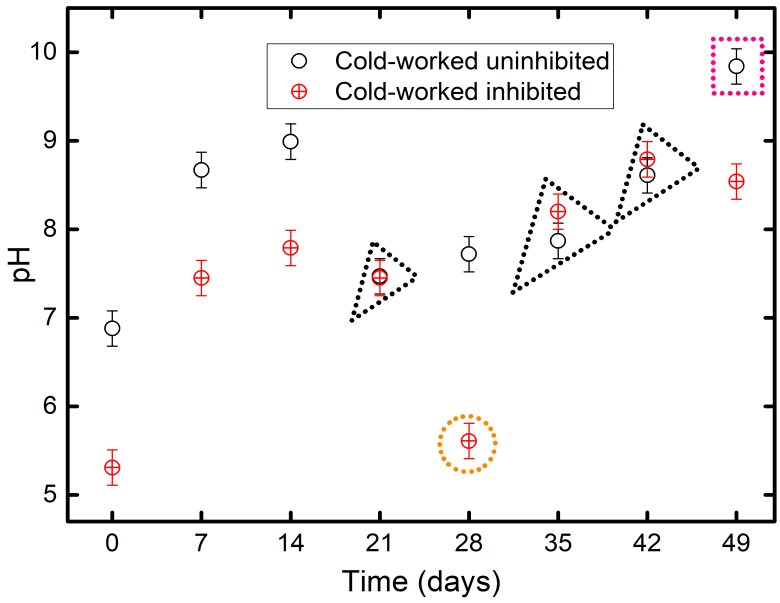

Figure 2 The influence of MIC on the pH of bio-corrosion media for the cold-worked mild steel samples

Figure 3 shows the influence of the MIC on the pH of the corrosion media for the annealed samples. As shown in Figure 3, for the annealed samples, the inhibited and uninhibited medium has no coinciding pH value. Also, it can be seen that, for the entire incubation periods, the pH value for both media is higher compared with the initial values. The inhibited medium experienced the lowest pH value on the 7th day. In contrast, the uninhibited medium experienced the lowest pH value on the 21st day, as indicated with the circle dotted-lines enclosed point. On the other hand, both media experienced the highest pH value on the 49th day, as indicated with the rectangle short-dash enclosed point. Still, in Figure 3, one can observe that the inhibited medium indicates relatively higher pH values compared with the uninhibited medium on the 7th day, 21st day, 28th, 35th day, 42nd day, and 49th day. In contrast, the uninhibited medium indicates relatively higher pH values compared with the inhibited medium only on the 14th day. The authors inferred from the variation of the pH values for the annealed samples compared with those of the as-received and cold-worked samples that the annealed samples experienced the most significant difference in chemical kinetics of MIC for the uninhibited and inhibited medium.

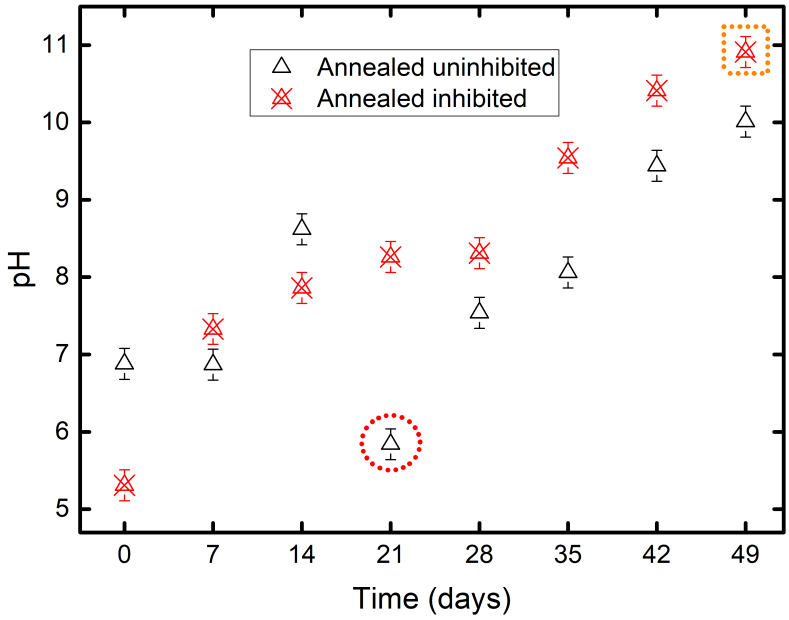

Figure 3 The influence of MIC on the pH of bio-corrosion media for the annealed mild steel samples

Figure 4 shows the comparison of the influence of MIC on the pH of uninhibited conditions for all samples. As shown in Figure 4, for the uninhibited condition, the values of pH as a function of time in all samples indicates that each of the samples was able to release different ions at an unequal rate. However, the bio-corrosion medium increased the amount of its alkalinity because of the bio-corrosion activities within the medium. However, the media for the cold-worked and annealed specimens indicated the maximum alkalinity with a pH value of 9.84 on the 49th day for the cold-worked sample and a pH value of 10.01 for that of the annealed sample on the 49th day, respectively. In contrast to that of the as-received sample, which recorded a maximum pH value of 8.60 on the 42nd day. Still, in Figure 4, one can observe that all samples in the uninhibited condition had coinciding pH values on the 28th and 35th days, as indicated with the polygon dotted-lines enclosed points.

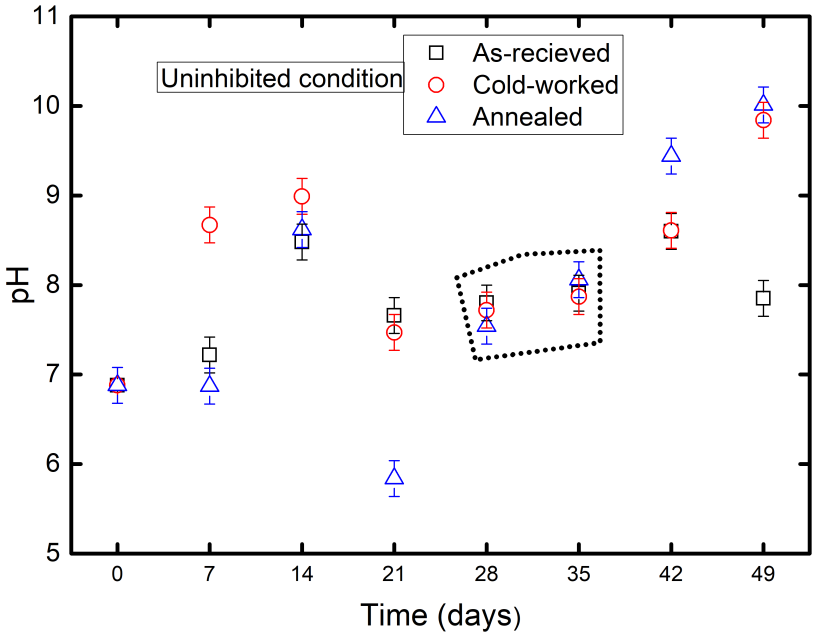

Figure 4 The comparison of the influence of MIC on the pH of uninhibited condition for all samples

Figure 5 shows the comparison of the influence of MIC on the pH of inhibited condition for all samples. As shown in Figure 5, it can be seen that the bio-corrosion media of as-received and cold-worked samples had a maximum pH value of 8.79 and 10.51, respectively, both on the 42nd day. In contrast, the bio-corrosion medium of the annealed sample had a maximum pH value of 10.91 on the 49th day. Still, in Figure 5, it can be observed that the bio-corrosion medium of the annealed samples has a relatively higher pH value compared with other media from the 21st day to the end of the incubation period, as indicated by the polygon dotted-lines enclosed points. It can be inferred from this that the annealed samples had superior spontaneous adsorption of Carica papaya extract metabolites in the later period of the incubation period. Also, it can be seen that all bio-corrosion media have coinciding pH values on the 7th day for the inhibited condition.

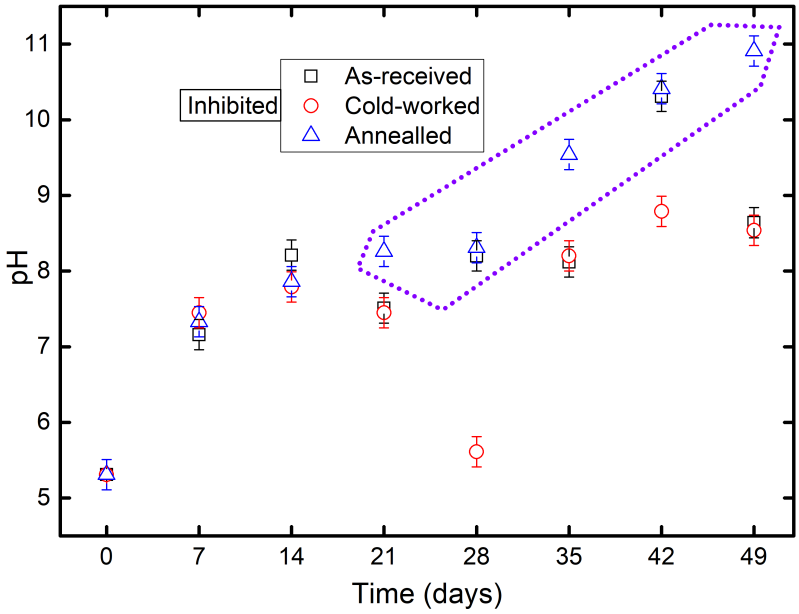

Figure 5 The comparison of the influence of MIC on the pH of inhibited bio-corrosion media for all samples

3.3 The rate of MIC in the samples

Figure 6 shows the rate of MIC in the as-received samples for uninhibited and inhibited conditions in a fresh-water environment. As can be seen in Figure 6, for the as-received samples, the inhibitor is active in a fresh-water environment. That is because the rate of MIC is relatively higher in the uninhibited condition compared with the inhibited condition. The calculated average rate of MIC in the uninhibited condition is roughly 0.065 mm/year. In contrast, the calculated average rate of MIC in the inhibited condition is about 0.043 mm/year. Still, in Figure 6, it can be seen that the rate of MIC decreased progressively as a function of time in the entire incubation periods for the uninhibited condition. In contrast, as can be seen in Figure 6, for the inhibited condition, the rate of MIC is constant for the first 21 days; then, it increased slightly between the 21st and 35th days. Finally, it decreased slightly between the 35th and 49th day.

Figure 7 shows the rate of MIC in the cold-worked samples for uninhibited and inhibited conditions. The calculated average rate of MIC in the uninhibited condition is roughly 0.075 mm/year. In contrast, the calculated average rate of MIC in the inhibited condition is about 0.053 mm/year. Thus, it can be inferred that, for the cold-worked samples, the rate of MIC is relatively higher in the

uninhibited condition compared with the inhibited condition. Still, in Figure 7, it can be seen that the rate of MIC is highly non-linear as a function of time in both conditions.

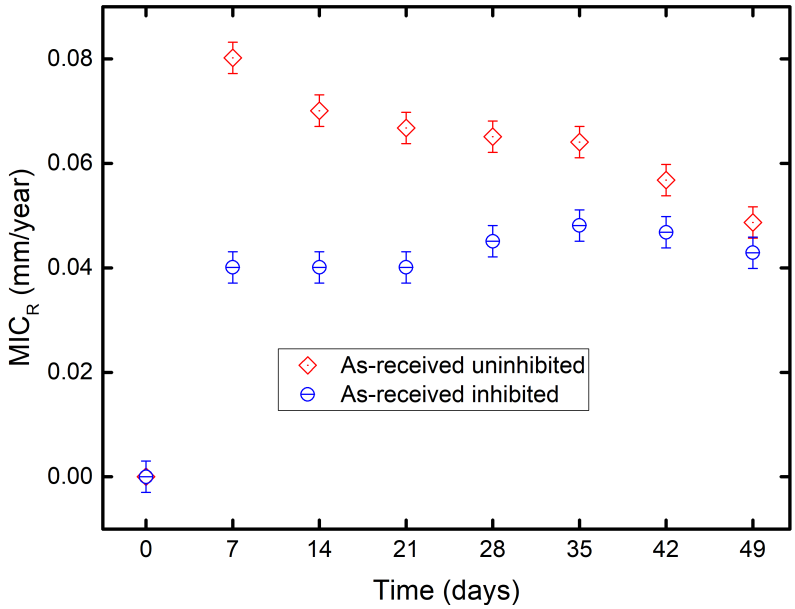

Figure 6 The rate of MIC in the as-received samples for uninhibited and inhibited conditions

On the 7th and 14th day, both conditions had an increase in the rate of MIC compared with the previous. On the other hand, on the 21st day, both conditions had a decrease in the rate of MIC compared with the previous. In contrast, on the 28th day, the rate of MIC remains constant concerning the uninhibited condition, then decreased compared with the previous for the inhibited condition. The non-linear trend of the rate of MIC for both conditions continued until the end of the incubation periods.

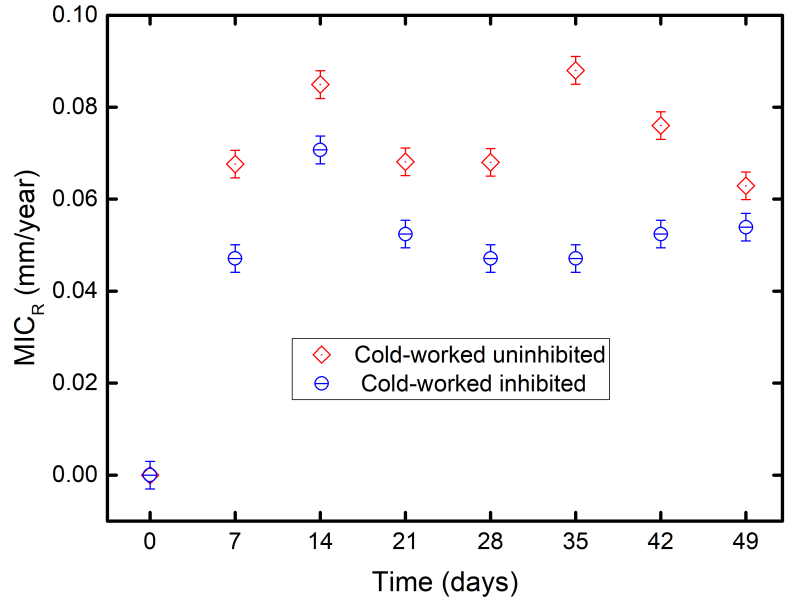

Figure 7 The rate of MIC in the cold-worked samples for uninhibited and inhibited conditions

Figure 8 shows the rate of MIC in the annealed samples for uninhibited and inhibited conditions. As can be seen in Figure 8, the trend of the rate of MIC is similar for both conditions. However, the rate of MIC concerning the uninhibited condition is relatively higher compared with that of the

inhibited condition for the entire incubation period. Still, in Figure 8, it can be seen that the rate of MIC decreased progressively from the 7th to the 49th day for both conditions. The authors believed this was because the medium begins to get saturated with the particles of the mild steel. Which consequently would make the corrosion rate to keep decreasing.

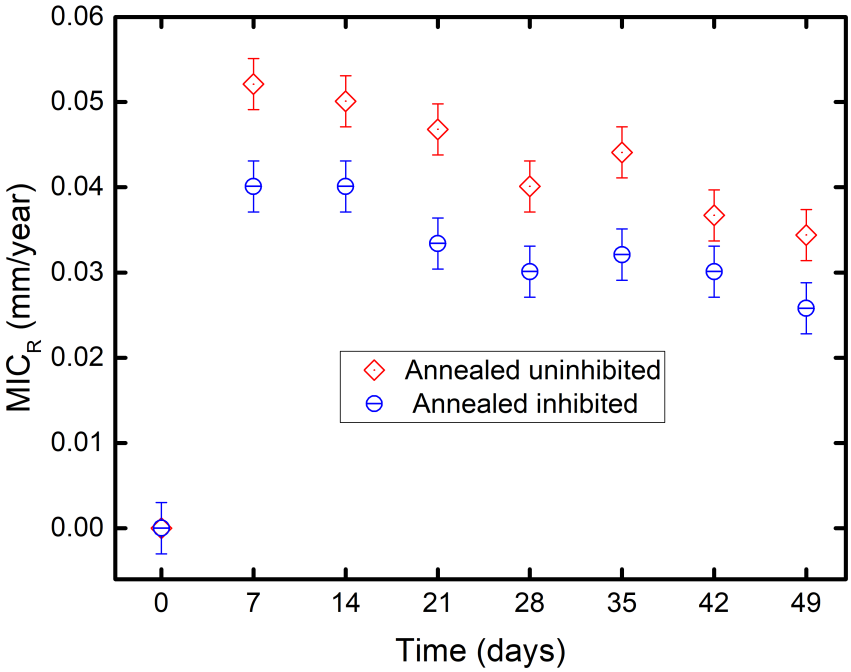

Figure 8 The rate of MIC in the annealed samples for uninhibited and inhibited conditions

3.4 The inhibition efficiency of the Carica papaya extract in different samples

Figure 9 shows the inhibition efficiency of the Carica papaya extract as a function of time for all samples. As shown in Figure 9, the as-received sample showed a progressive decrease in the inhibition efficiency as a function of time for the entire incubation period. The authors attributed the progressive decrease in the inhibition efficiency to the progressive depletion of the metabolites elements in the bio-corrosion media. Still, in Figure 9, it can be seen that the as-received sample showed relatively the highest value of the inhibition efficiency on the 7th, 14th, and 21st days. On those days, the as-received sample indicated inhibition efficiency values of above 35 %. In contrast, on those days, the cold-worked and annealed sample indicated an inhibition efficiency values of lower than 30 %. On the other hand, still, in Figure 9, the cold-worked and annealed samples have a coinciding value of inhibition efficiency on the 28th day. Also, on the 35th and 42nd day, the cold-worked samples had relatively the highest value of the inhibition efficiency. In contrast, the as-received sample that had the dominant inhibition efficiency on the 7th to the 21st day indicated relatively the lowest value of the inhibition efficiency on the 35th day. Moreover, in Figure 9, it can be seen that the annealed samples indicated relatively the highest value of inhibition efficiency on the 49th day only. As discussed in an earlier study [38], relatively high values of the inhibition efficiency of an inhibitor mean, it would suffer a relatively lesser rate of MIC. Here, in the fresh-water environment, the calculated average rate of inhibition efficiency is 31.16 % and 23.07 % for the as-received, and cold-worked samples, respectively. For the annealed samples, the calculated average value of the inhibition efficiency is 23.89 %. It can be inferred from these average values that the as-

received samples had relatively the lowest rate of MIC attach in the fresh-water environment under the Carica papaya extract bio-corrosion inhibitor. In contrast, the cold-worked sample had relatively the highest rate of MIC attack in the fresh-water environment under the Carica papaya leaf extract.

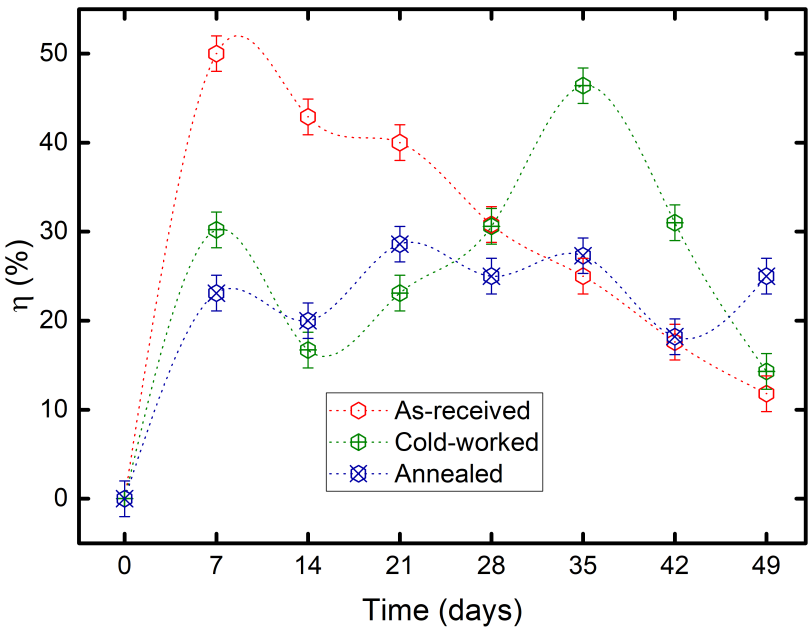

Figure 9 The inhibition efficiency of Carica papaya extract in all samples

3.5 Comparison of the protection of mild steel structures against MIC attach in the different environment using Carica papaya extract

Figure 10 shows the comparison of the protection of the as-received sample of the mild steel understudied against MIC attack in the different environments using the Carica papaya leaf extract. As can be seen in Figure 10, two previous studies consist of the test on the inhibition of MIC in acid (HCl) and alkaline (NaOH) [38], and sea-water [14] environments using the Carica papaya leaf extract. As shown in Fig. 10, the as-received sample indicated a similar trend of the inhibition efficiency as a function of time in all of the investigated bio-corrosion environments. One can observe that, for all of the investigated bio-corrosion environments, the as-received sample indicated a progressive decrease of the inhibition efficiency from the 7th day to the end of the incubation period. As shown in Figure 10, the sea-water environment indicated the highest value of the inhibition efficiency on the 7th day. It can be seen in Figure 10 that the sea-water environment indicated above 75 % inhibition efficiency on the 7th day. In contrast, on the 7th day, it can be observed in Figure 10 that the acid environment indicated below 40 % inhibition efficiency.

On the other hand, it can be observed in Figure 10 that the acid, alkaline, and sea-water environments had a coinciding value of the inhibition efficiency on the 14th day. Also, it can be seen in Figure 10 that the fresh-water environment had relatively the lowest value of the inhibition efficiency from the 14th to the 49th day. In contrast, the acid and alkaline environments had the dominant values of the inhibition efficiency from the 21st to the 49th day. On average, the alkaline environment indicated relatively the highest value of inhibition efficiency of 42.09 %, followed by the acid environment that has the inhibition efficiency of 40.51 %. In contrast, the fresh-water environment indicated relatively the lowest average value of the inhibition efficiency of 31.16 %.

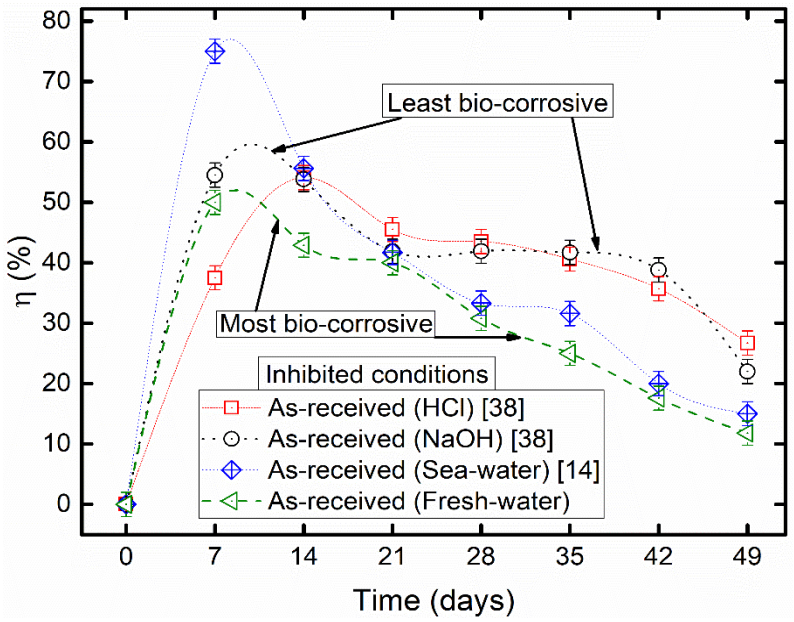

Figure 10 Comparison of the inhibition efficiency of the Carica papaya extract for as-received samples in a different environment

Based on these values of the inhibition efficiency, the as-received sample would have the least protection against MIC attack in a fresh-water environment under the Carica papaya leaf extract bio-corrosion inhibitor, as labeled most bio-corrosive in Figure 10. Also, the as-received sample would have maximum protection against MIC attack in an alkaline environment under the Carica papaya leaf extract bio-corrosion inhibitor, as labeled least bio-corrosive in Fig 10.

Figure 11 shows the comparison of the protection of the cold-worked sample of the mild steel against MIC attack in the different environments using the Carica papaya leaf extract. As shown in Figure 10, the cold-worked sample indicates a significantly different trend of the inhibition efficiency as a function of time in all of the investigated bio-corrosion environments. One can observe that, in Figure 11, for the acidic and alkaline environments, the cold-worked sample indicates a progressive increase of the inhibition efficiency from the 7th to 14th day, then decreased progressively from the 21st to the 49th day. In contrast to the sea-water, acidic and alkaline environments, it can be observed that the fresh-water environment indicates an increase in the inhibition efficiency on the 14th day compared with the 7th day; then, it increased progressively from the 14th to the 35th day. Finally, it decreased progressively from the 35th to the 49th day. As can be seen in Figure 11, the unique trend of the cold-worked sample is that it indicates the relatively highest value of the inhibition efficiency in all environments within a specific incubation interval. As can be seen in Figure 11, the sea-water environment indicates the highest value of the inhibition efficiency on the 7th day. Also, it can be seen in Figure 11 that the alkaline environment indicates relatively the highest value of the inhibition efficiency on the 14th day. In contrast, on the 35th day, it can be observed in Figure 10 that the fresh-water environment indicates relatively the highest value of the inhibition efficiency. Finally, it can be observed in Figure 11 that the acidic environment indicates relatively the highest value of the inhibition efficiency on the 49th day.

Moreover, on the average, for the cold-worked sample, the acidic environment indicated relatively the highest value of inhibition efficiency of about 36.12 %, followed by the acid environment that has the inhibition efficiency of about 31.84 %. In contrast, the sea-water environment indicated relatively the lowest average value of the inhibition efficiency of about 26.26 %.

Based on these values of the inhibition efficiency, it can be inferred that the cold-worked sample would have the least protection against MIC attack in a sea-water environment under the Carica papaya leaf extract bio-corrosion inhibitor, as labeled most bio-corrosive in Figure 11. Also, the cold-worked sample would have maximum protection against MIC attack in an acidic environment under the Carica papaya leaf extract bio-corrosion inhibitor, as labeled least bio-corrosive in Figure 11.

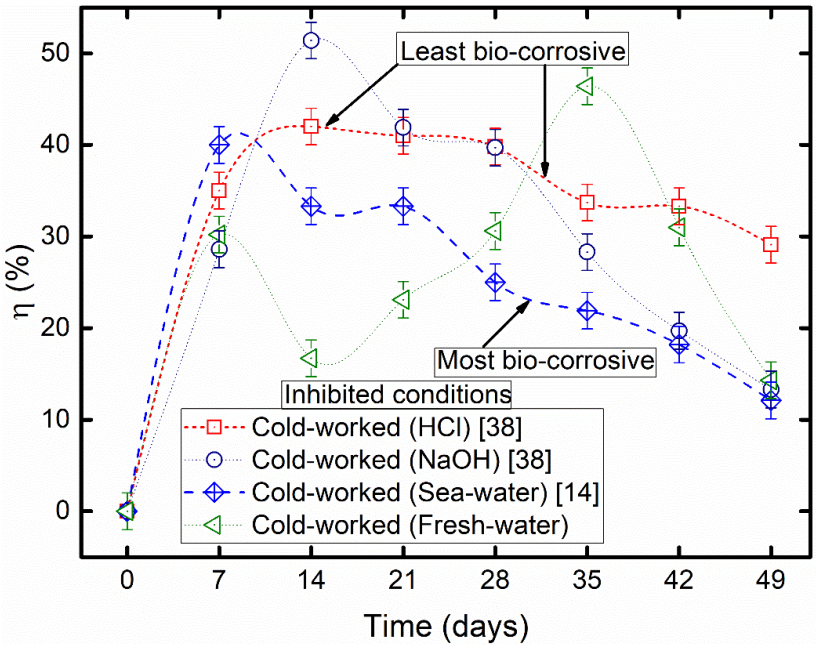

Figure 11 Comparison of the inhibition efficiency of the Carica papaya extract for cold-worked samples in a different environment

Figure 11 shows the comparison of the protection of the annealed sample of the mild steel against MIC attack in the different environments using the Carica papaya leaf extract. As can be seen in Figure 12, the annealed sample indicates a similar trend of the inhibition efficiency as a function of time in the alkaline and fresh-water bio-corrosion environments. One can observe, in Figure 12 that, for the alkaline and fresh-water bio-corrosion environment, the sample indicates a decrease of the inhibition efficiency on the 14th day compared with the 7th day. Then, there is an increase in the inhibition efficiency on the 49th day compared with the 42nd day.

On the other hand, also, one can observe, in Figure 12 that, for the acidic and sea-water bio-corrosion environments, the sample indicates a decrease of the inhibition efficiency from the 21st day to the end of the incubation period. On average, the alkaline environment indicates relatively the highest value of inhibition efficiency of 38.00 %, followed by the sea-water environment that has the inhibition efficiency of 27.60 %. In contrast, the acidic environment shows relatively the lowest average value of the inhibition efficiency of 21.56 %.

Based on these values of the inhibition efficiency, the annealed sample would have the least protection against MIC attack in an acidic environment under the Carica papaya leaf extract bio-corrosion inhibitor, as labeled most bio-corrosive in Figure 12. Also, the annealed sample would have maximum protection against MIC attack in an alkaline environment under the Carica papaya leaf extract bio-corrosion inhibitor, as labeled least bio-corrosive in Figure 12. It should be noted that the annealed sample relatively shows high bio-corrosiveness in the fresh-water environment. The annealed sample shows an average value of the inhibition efficiency of about 23.89 % in the fresh-water environment under the Carica papaya leaf extract inhibitor.

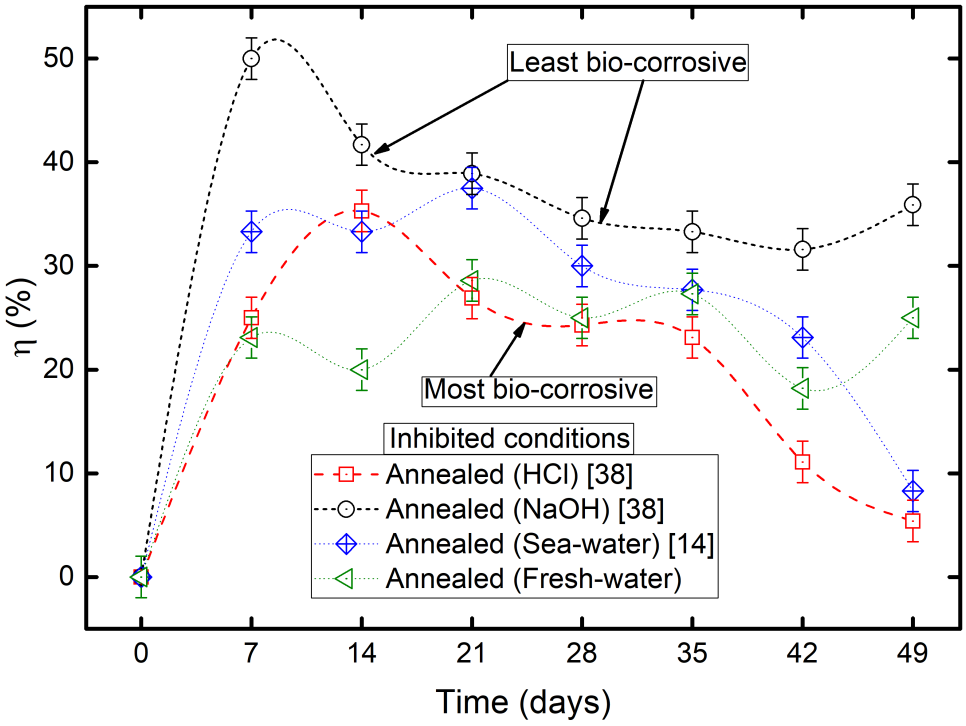

Figure 12 Comparison of the inhibition efficiency of the Carica papaya extract for annealed samples in a different environment.

Conclusion

From this study, it can be concluded that the Carica papaya extract can be used to effectively protect differently treated mild steel structures against MIC in fresh-water environments. Also, based on the results, it can be concluded from the average values of the inhibition efficiency that the as-received sample indicated relatively the highest protection against MIC attach in the fresh-water environment under the Carica papaya extract bio-corrosion inhibitor. In contrast, the cold-worked sample indicated relatively the lowest protection against MIC attack in the fresh-water environment under the Carica papaya leaf extract bio-corrosion inhibitor.

Moreover, based on the results of the comparison of the inhibition efficiency of the bio-corrosion inhibitor on the differently treated samples in different environments, it can be concluded that each of the samples experienced significantly distinct chemical kinetics and adsorption attributes of the inhibitor in the different environments. Thus, this study reveals the best treatment for mild steel structures under the protection of Carica papaya leaf extract bio-corrosion inhibitor against MIC in different environments. For instance, the as-received and annealed samples would have maximum protection against the MIC attack in an alkaline environment under the Carica papaya leaf extract bio-corrosion inhibitor. In contrast, the cold-worked sample would have maximum protection against the MIC attack in an acidic environment under the Carica papaya leaf extract bio-corrosion inhibitor.

However, it should be noted that this study did not determine precisely the chemical kinetics and adsorption attributes of the Carica papaya leaf extract metabolites concerning the different treated mild steel samples in the different environments. The authors hope to carry out these identified deficiencies in the nearest future.

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Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.
Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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