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Evaluation of Inhibitive Performance of Some Plants Extracts on Low Carbon Steel Corrosion

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Abstract

The corrosion inhibitive potential of Plumeria Alba, Blighia Sapida and Secamone Afezeli plants extracts on heat-treated and non-heat-treated mild steel samples immersed in different concentrations of hydrochloric acid (HCl) were investigated using weight loss technique. The mild steel samples were cut and prepared for the corrosion test in the acid media mixed with the plant extracts obtained by natural drying, grinding and chemical extraction using hexane. The plants were collected from the botanical garden of University of Lagos, Nigeria. Samples of the mild steel were weighed before immersion and at regular interval of 7 days for a period of 56 days after immersion. The experiment was repeated using 0.1 M and 0.2 M of an inorganic inhibitor. Results obtained showed that the extract of Blighia Sapida exhibited the highest inhibitive power, while annealed samples have the least corrosion rate in the Hcl solution.

Keywords: plant extract, corrosion, weight loss, inhibitor

1. Introduction

Today, steel is one of the most common materials in the world, and it is a major component in buildings, infrastructure, pipeline transport, offshore construction tools, ships, automobiles, machines, appliances, and weapons. Modern steel is generally identified by various grades defined by assorted standards organizations. The corrosion resistance of carbon steels is poor because they rust easily, and so they should not be used in a corrosive environment unless some form of corrosion protection is used.

Inhibitors are used internally with carbon steel pipes and vessels as an economic corrosion control alternative to stainless steels and alloys, coatings, or non-metallic composites, and can often be implemented without disrupting a process. The major industries using corrosion inhibitors are oil and gas exploration and production, petroleum refining, chemical manufacturing, heavy manufacturing, water treatment, and the product additive industries. Some chemical inhibitors such as oxidizers and the adsorption inhibitors such as amines, thiourea, antimony trichloride, benzoate, are used quite widely in many proprietary mixtures which are marketed to control corrosion. Ashby et al (1992)

Organic inhibitors observe the presence of both anodic and cathodic effects sometimes, but as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors usually designated as 'film-forming', protect the metal by forming a hydrophobic film on the metal surface. An inhibitor prevents and reduces the ions from diffusing with the metallic surface by causing an increase in the anodic and the cathodic polarization behaviour. In considering an inhibitor factors like toxicity, environmental friendliness, and availability should be considered (Benjamin, 2005).

Several types of corrosion inhibitors were evaluated using active ingredients of those inhibitors which included long chain amines, fatty amides, imidazolines, fatty acids and their salts. Inhibitors were tested at the concentration range of 50 - 200 ppm in the electrolyte and electrolyte/hydrocarbon mixture in the presence of CO2 and H2S in static and dynamic conditions (Badiea et al, 2009). Several evaluations were performed when corrosion inhibitors were added into electrolyte containing flow modifiers. The results, which include the corrosion and electrochemical testing data, show that generally tested corrosion inhibitors are effective in studied range of flow rates and compatible with flow modifiers. (Corrosion Doctor.Org, 2010). Sedricks (1996) used impedance method to study the effect of inhibitor adsorption on metal surface. The study clearly reveals that the addition of inhibitor moves the corrosion potential towards positive values and reduces the corrosion rate. Changes in impedance parameters (R_{ct} and C_{dl}) are indicative of adsorption of inhibitor on the metal surface leading to the formation of protective films.

Wang and Neville (2008) investigated the effect of oil soluble commercial corrosion inhibitors (OSCI) on the growth of bacteria and its corrosion inhibition efficiency. In this work the Corrosion inhibition efficiency was studied by rotating cage test and the nature of biodegradation of corrosion inhibitor was also analyzed by using FTIR, NMR and GC-MS. This isolate has the capacity to degrade the aromatic and aliphatic hydrocarbon present in the Corrosion inhibitors. The degraded products of corrosion inhibitors and bacterial activity determined the electrochemical behaviour of API 5LX steel. The influence of bacterial activity on degradation of corrosion inhibitor and its influence on corrosion of API 5LX were evaluated by employing weight loss techniques and electrochemical studies.

The effectiveness of these inhibitors depends on the chemical composition, their molecular structure, and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are important factors.

Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the surface. Cationic inhibitors, such as amines, or anionic inhibitors, such as sulfonates, will be adsorbed preferentially depending on whether the metal is charged negatively or positively. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors. Most pure synthetic chemicals (inhibitors) are costly, some of them are not easily biodegradable and their disposal creates pollution and health problems. Plant extracts are environment friendly, bio-degradable, non-toxic, easily available and of potentially low cost. Most of the naturally occurring substances are safe and can be extracted by simple procedures .This is why it is being used in this study.

In the oil and gas industries, mild steel found many applications such as in pipelines, pressure vessels, storage tanks, well heads, and so on. It is also extensively used in the form of flat and rolled plate in the construction of offshore production platforms, steel jackets and drilling rigs along with piping systems that are subjected to rigorous grit blasting(Li,2006 and Benjamin,2006). Plant extracts have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. They are the rich sources of ingredients which have very high inhibition efficiency.

The effect of Solanum melongena L. leaf extract on the corrosion of aluminium in 0.5 M H_2SO_4 was investigated by Niktan et al (2010) using the gravimetric technique. It was shown that the presence of S. melongena L. leaf extract inhibited the corrosion of aluminium in the test solutions and that the inhibition efficiency depended on the concentration of the plant extract as well as on the time of exposure of the aluminium samples in 0.5M H_2SO_4 solutions containing the extract. The experimental data complied with modified form of the Langmuir adsorption isotherm and the value and sign of the Gibb's free energy of adsorption obtained suggested that inhibitor molecules have been spontaneously adsorbed onto the aluminium surface through a physical adsorption mechanism.

The extract from Annona squamosa plant was studied as possible corrosion inhibitor for C38 steel in molar hydrochloric acid (1 M HCl) by Afidah et al (2008). Potentiodynamic polarization and AC impedance methods were used. The corrosion inhibition efficiency was found to increase on increasing plant extract concentration. Polarisation studies showed that Annona squamosa extract was mixed-type inhibitor in 1 M HCl. The inhibition efficiency of Annona squamosa extract was temperature dependent and its addition led to an increase of the activation corrosion energy revealing a physical adsorption between the extract and the metal surface. The adsorption of the Annona squamosa extract followed Langmuir's adsorption isotherm. The inhibitive effect of Annona squamosa is ascribed to the presence of organic compounds in the extract. The examined extract is considered as non-cytotoxic substance.

Inhibitors are employed predominantly for corrosion control in closed systems, as a cost-efficiently alternative to the use of high corrosion-resistant materials. Due to the environmental requirements that are currently imposed on the development of cleaner inhibitors, vegetal tannins, a class of natural, non-toxic, biodegradable organic compounds that can be obtained at reduced cost was proposed by Afidah et al (2008) . They relate recent uses of several vegetal tannins in corrosion protection, particularly as corrosion inhibitors of iron and steel in acidic and near neutral media. Several methods of inhibition efficiency evaluations along with their action mechanisms are discussed. They presented some important patents in the development of vegetal tannins in corrosion protection of iron and steel.

The effect of extracts of Chamomile (*Chamaemelum mixtum* L.), Halfabar (*Cymbopogon proximus*), Black cumin (*Nigella sativa* L.), and Kidney bean (*Phaseolus vulgaris*L.) plants on the corrosion of steel in aqueous 1 M sulphuric acid were investigated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. EIS measurements showed that the dissolution process of steel occurs under activation control. Potentiodynamic polarization curves indicated that the plant extracts behave as mixed-type inhibitors. The corrosion rates of steel and the inhibition efficiencies of the extracts were calculated. The results obtained show that the extract solution of the plant could serve as an effective inhibitor for the corrosion of steel in sulphuric acid media. Inhibition was found to increase with increasing concentration of the plant extract up to a critical concentration. The inhibitive actions of plant extracts are discussed on the basis of adsorption of stable complex at the steel surface. Theoretical fitting of different isotherms, Langmuir, Flory–Huggins, and the kinetic–thermodynamic model, were tested to clarify the nature of adsorption Badiea and Mohana (2010).

The role of seed extract of Cyamopsis tetragonaloba on corrosion mitigation of mild steel in 1 M HCl was investigated by weight loss method and potentiodynamic polarization technique. Maximum inhibition efficiency of Cyamopsis tetragonaloba in 1 M HCl was found to be 92%. Experimental results were fitted into Langmuir and Temkin adsorption isotherm to study the process of inhibition. The potentiodynamic polarization results reveal that the seed extract behaved like mixed type inhibitor.

Extract of *Bridelia retusa* leaves was investigated as corrosion inhibitor of mild steel in 1 NH2SO4 using conventional weight loss, electrochemical polarizations, electrochemical l impedance spectroscopy and scanning electron microscopic studies. The weight loss results showed that the extract of *Bridelia retusa* leaves is excellent corrosion inhibitor and electrochemical polarizations data revealed the mixed mode of inhibition. While the results of electrochemical impedance spectroscopy have shown that the change in the impedance parameters, charge transfer resistance and double layer capacitance, with the change in concentration of the extract is due to the adsorption of active molecules leading to the formation of a protective layer on the surface of mild steel. Scanning electron microscopic studies provided the confirmatory evidence of improved surface.

Also ,the effects of radish leaves and black cumin as plant extracts on the corrosion behaviour of low-carbon steer in industrial water in the temperature range of 30 to 80 degrees centigrade and velocity range of 1.44 to 2.02m/s using potentiodynamic polarization, electrochemical impedance spectroscopy, and mass loss measurement have been investigated by Badiae and Mohana (2009). Brill and Beggs (1981) noted that generally the inhibition efficiency increased with increasing concentration of the plant extracts up to a critical value but it slightly decreased with increasing temperature. Inhibition efficiency values obtained from mass loss and potentiodynamic data were in reasonable agreement. Potentiodynamic polarization clearly indicated that radish leaves and black cumin extracts acted as anodic inhibitors. The adsorption behaviour was found to obey the Flory-huggins isothermal model. The associated activation parameters and thermodynamic data of adsorption were evaluated and discussed. The results show that radish leaves and black cumin could serve as effective inhibitors for low carbon steel in industrial water media, with black cumin providing better protection than radish leaves. Plumeria Alba has beautiful white flowers with yellow centers, and the flower looks fully opened unlike plumera rubra. It is well-known for its intensely fragrant, lovely, spiral-shaped blooms which appear at branch tips. Blighia Sapida which is also called *Cupania sapida is a* Native to tropical West Africa, and is cultivated sporadically throughout the tropics.

Much work has been done using different plant extracts as organic inhibitors in different environments, mostly in different acidic media, and in industrial water. Various investigations have shown that the inhibition efficiency increased with increasing concentration of the different plant extracts, but decreased with increasing temperature(Smith,1999), showing that plant extracts are good organic inhibitors.

The major aim of this research work is to assess and compare the corrosion inhibitive powers of Plumeria Alba, Blighia Sapida and Secamone Afezeli plant extracts on mild steel samples in different concentrations of HCl solution and also to study the effect of annealing and quenching heat treatment on the corrosion response of the mild steel in the acid solution. This is with a view to replacing carcinogenic (toxic) and environmentally damaging chromate based chemical inhibitors used in the oil and gas transportation pipeline and storage facilities with alternatives or plant extract inhibitors, with little burden on the environment.

2. Materials and Methods

The mild steel sample, 6mm thick, used for this study was obtained from a popular metal market in Lagos, Nigeria. The steel was cut into 54 pieces of 75mm X 75mm each. The surfaces of the samples were ground using emery papers 140micron to emery to 320micron grade after which they were polished and etched with sodium hydroxide (NaOH) and kept in a desiccator to prevent atmospheric corrosion before experimentation.

The chemical analysis of the mild steel was conducted using a spectrometer. The result is shown in the table 1.0 below.

Table 1. Chemical analysis of mild steel

Elements	**C**	**Si**	**S**	**p**	**Mn**	**Ni**	**Cr**	**Fe**
Composition (%)	0.24	0.21	0.006	0.022	0.51	0.02	0.07	98.92

36 of the 54 samples were subjected to heat treatment at austenitizing temperature of 900^{o}C and soaked for 6 hours. 18 of the austenitized samples were cooled to room temperature in the furnace (annealed) while the others were quenched in water.

The remaining 18 samples were left untreated. All the samples were cleaned and their initial weights taken, using an electronic weighing balance.

The stems of the various plants: plumeria alba, secamone afzelii, and blighia sapida were collected from the botanical garden, University of Lagos and allowed to dry naturally. They were ground and extracted using hexane .The solutions were prepared up to 300ml. each. Also the acid solutions (Corrodant) were prepared by diluting concentrated hydrochloric acid into proportions of 0.1M, 0.3M, and 0.5M respectively.

Samples of the mild steel were immersed in a glass jars containing 300ml of the acid and 100ml of inhibitor .The samples were left in the solutions for 7 days and weighed at seven days interval for 7 weeks. Weight loss measurements were made and later converted to corrosion rates. Metallographic examination was also carried out using optical microscope to observe the microstructures of the samples.

3. Results and Discussion

The chemical analysis of the three plant extracts used as inhibitors are show in the tables 2.0, 3.0 and 4.0 below:

Table 2. Composition of Plumeria Alba (Organic Inhibitor A)

Elements	Mn	Fe	Ca	Na	K	Mg
Stem extracts(mg/l)	0.909	1.697	784.364	11.173	6.989	4.312

Table 3. Composition of Blighia Sapida(Organic Inhibitor B)

Elements	Mn	Fe	Ca	Na	K	Mg
Stem extracts(mg/l)	0.320	0.767	838.663	70.759	7.214	4.688

Table 4. Composition of Secamone Afzelii (Organic Inhibitor C)

Elements	Mn	Fe	Ca	Na	K	Mg
Stem extracts(mg/l)	0.785	1.411	648.131	10.833	8.991	5.111

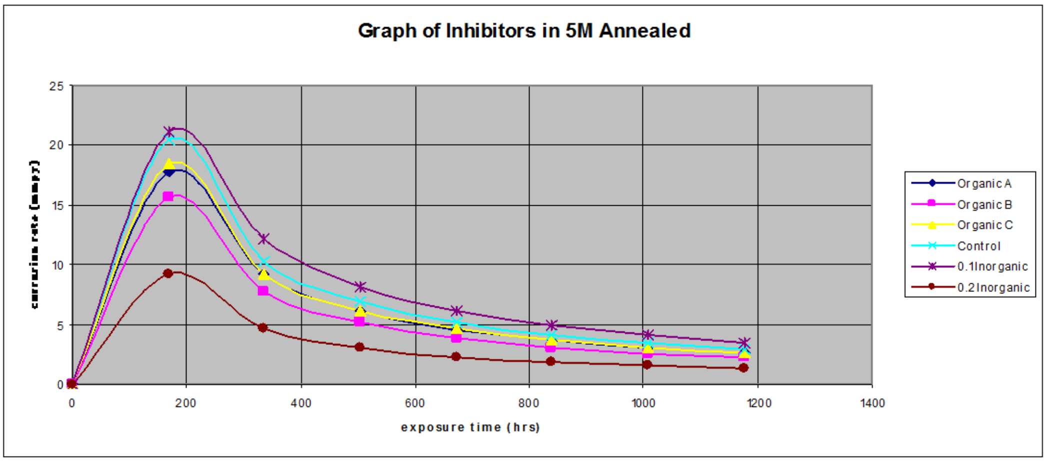


Figure 1. Graph of corrosion rate (mmpy) against time (hrs) of annealed samples in 5M HCl with different inhibitors.

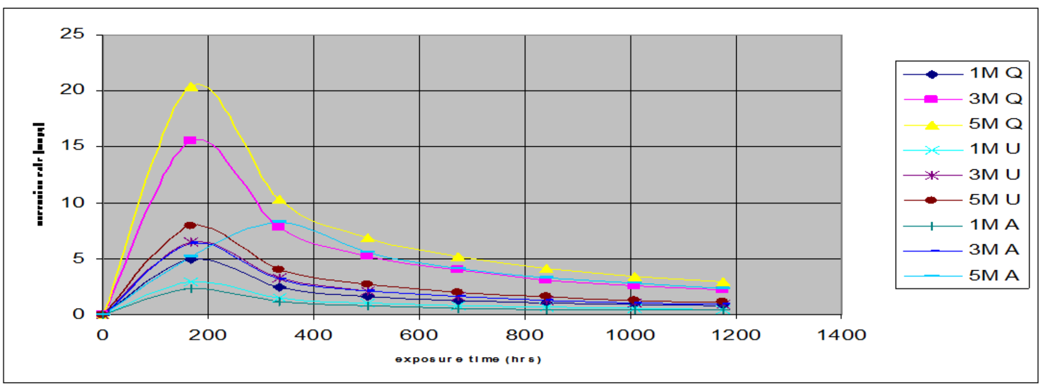


Figure 2. Graph of corrosion rate (mmpy) against time (hrs) of annealed, quenched and un-heat-treated samples in 1M, 3M and 5M HCl (without inhibitor).

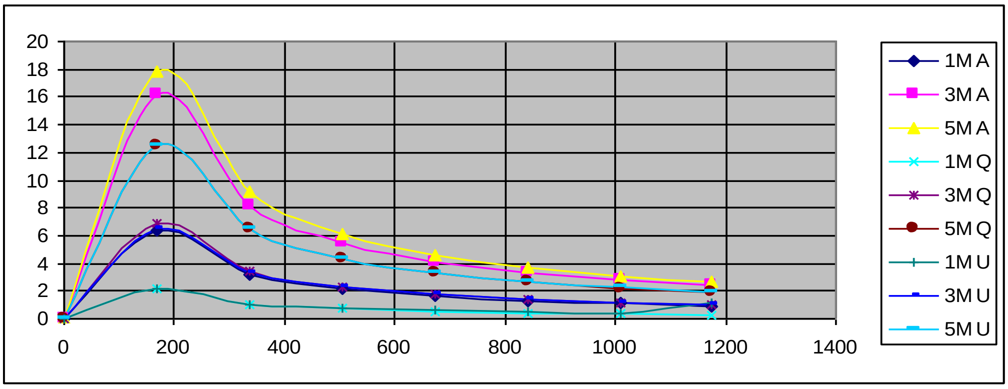


Figure 3. Graph of corrosion rate (mmpy) against time (hrs) of annealed, quenched and un-heat-treated samples in1M, 3M and 5MHCl with Organic inhibitor A.

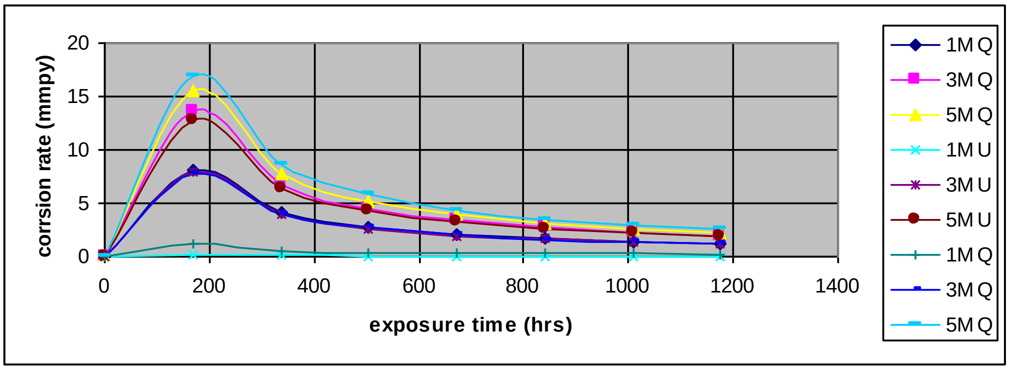


Figure 4. Graph of corrosion rate (mmpy) against time (hrs) of annealed, quenched and un-heat-treated samples in1M, 3M and 5MHCl with Organic inhibitor B.

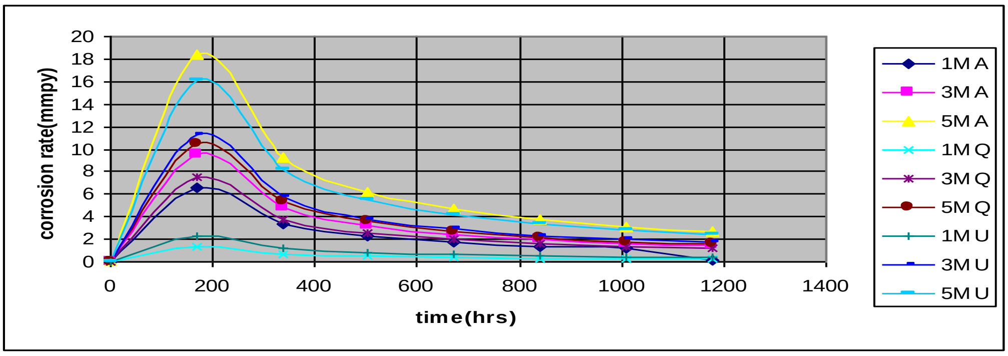


Figure 5. Graph of corrosion rate (mmpy) against time (hrs) of annealed, quenched and un-heat-treated samples1M, 3M and 5MHCl with Organic inhibitor C

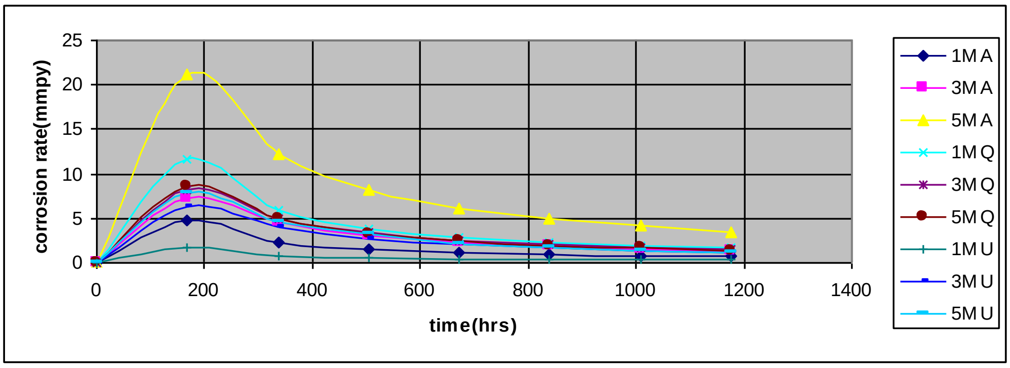


Figure 6. Graph of corrosion rate (mmpy) against time (hrs) of annealed, quenched and un-heat-treated samples in1M, 3M and 5M HCl with 0.1M inorganic inhibitor

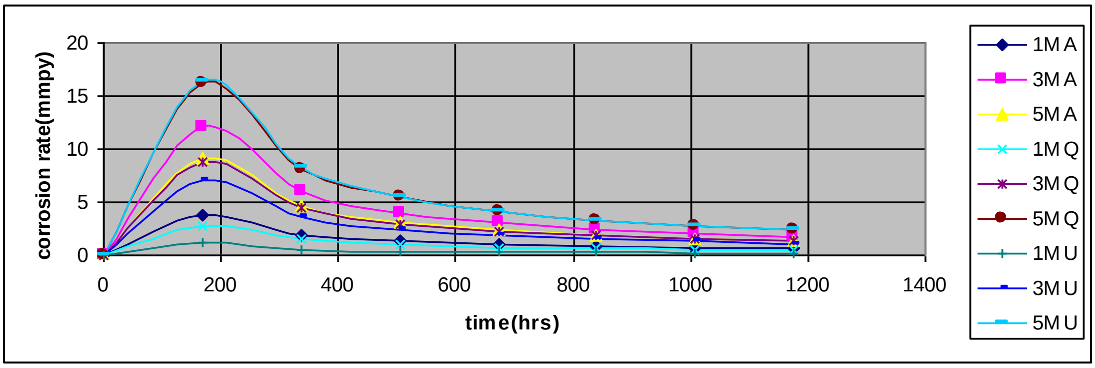
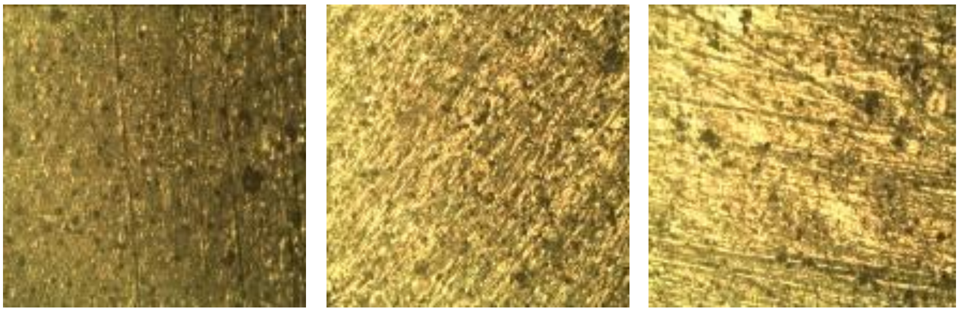


Figure 7. Graph of corrosion rate (mmpy) against time (hrs) of annealed, quenched and un-heat-treated samples in1M, 3M and 5M HCl with 0.2M inorganic inhibitor



A B C

Plate 1. Micrographs of (a) un-heat-treated (b) quenched and (c) annealed mild steels before corrosion test

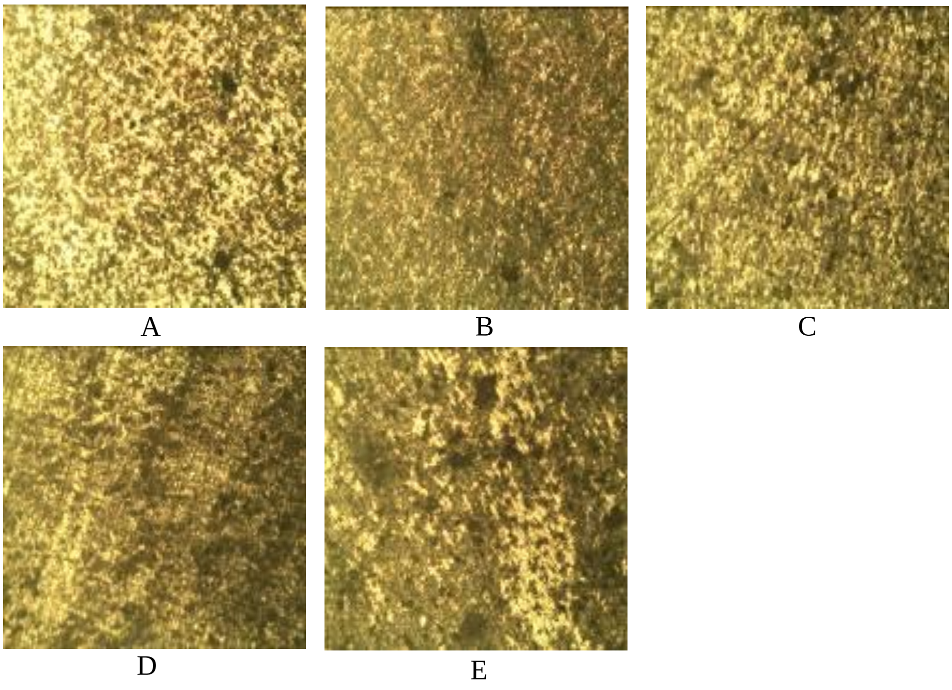


Plate 2. Micrographs of quenched Samples in 5M HCl with (a) 0.1 inorganic inhibitor, (b) 0.2 inorganic inhibitor, (c) organic inhibitor A, (d) organic inhibitor B, (e) organic inhibitor C, after corrosion tests

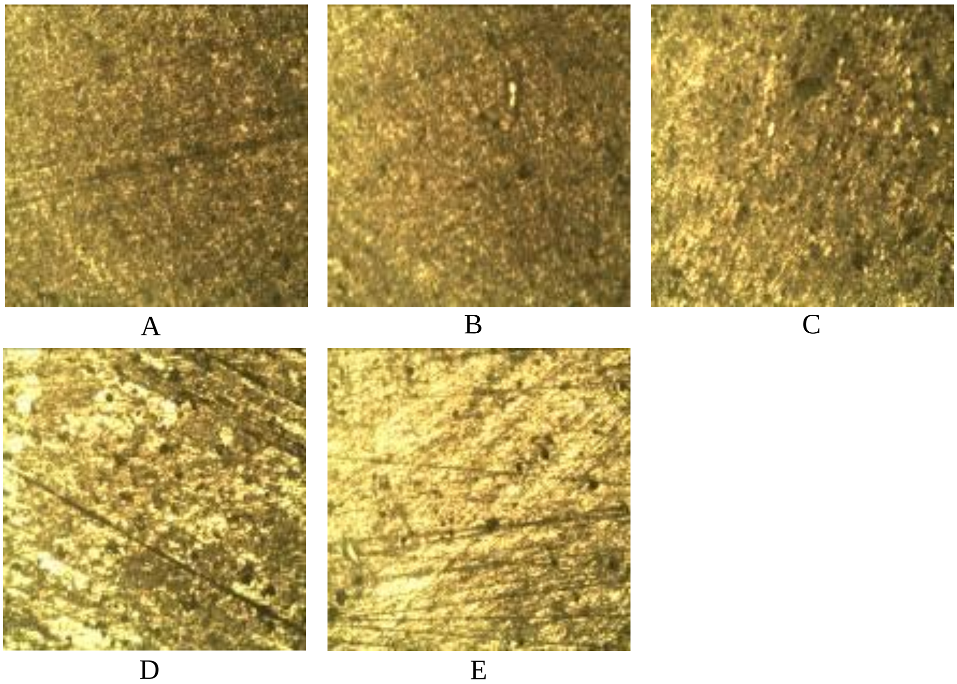


Plate 3. Micrographs of annealed samples in 5M HCl corrodant with (a) 0.1 inorganic inhibitor, (b) 0.2 inorganic inhibitor, (c) organic inhibitor A, (d) organic inhibitor B, (e) organic inhibitor C after corrosion tests.

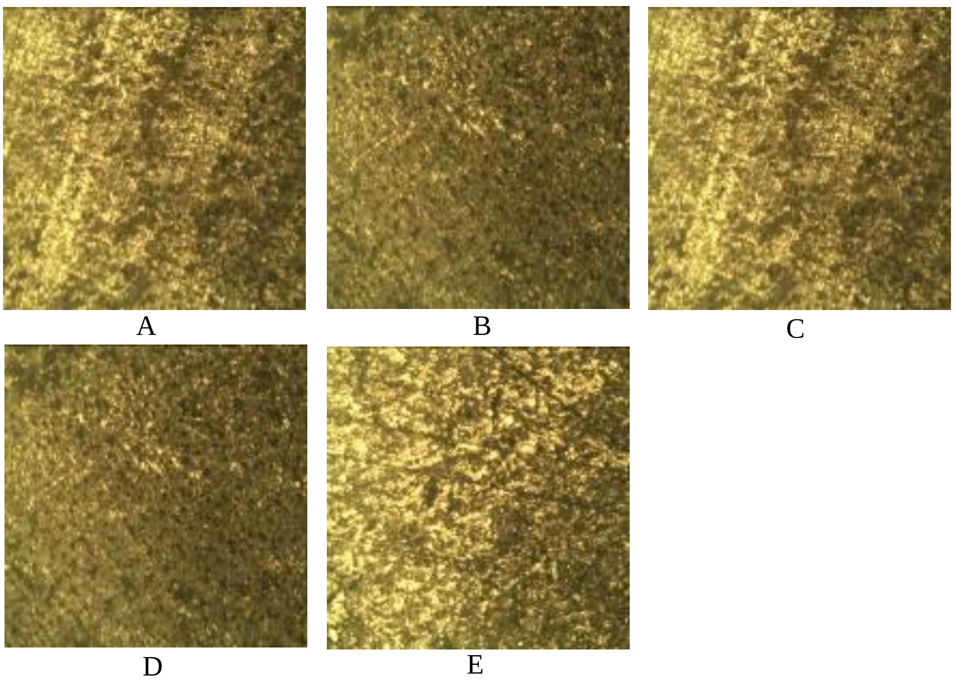


Plate 4. Micrographs of Un-heat- treated Samples in 5M HCl with (a) 0.1 inorganic inhibitor, (b) 0.2 inorganic inhibitor, (c) organic inhibitor A, (d) organic inhibitor B, (e) organic inhibitor C after corrosion tests

Figure 1 shows the corrosion rates of annealed samples in 5MHCl with the inhibitors. From this graph, although 0.2M inorganic inhibitor reduces the corrosion rate significantly; organic inhibitor B also has a considerable reduction in the corrosion rate compared to the control sample and other extracts inhibitors. Generally from the plots there is an increase in corrosion rates at initial stages with exposure time followed by a decrease with more exposure time. The steels experience passivation by forming a thin layer of oxide on the surface, as a result of which the corrosion rate became constant over a long period of time.

The same trend is observed in figure 2, where we have all the heat-treated, and non –heat-treated samples. From the graphs, the quenched samples have the highest corrosion rate in all the concentrations of acid. Figure 3, considers annealed, quenched and un-heat-treated samples in different concentrations of acid, containing organic inhibitor B, it is observed that the annealed samples were more corrosion resistant than that of the quenched samples which resulted in high corrosion rates in the different concentrations. Quenched samples suffer higher corrosion rates as a result of the coarse grain structure formed during the quenching operations. Consequently, coarse grains aides, high strength, but the accompanying corrosion could be taken care of using other heat treatment means.

Inhibitor A as observed in Figure 4 has little or no effect in the corrosion resistance of the mild steel in the various concentrations of acid.

In Figure 5, the annealed samples in 5M HCl solution as well as the quenched samples in 1M HCl solution corroded significantly, compared to the un-heat-treated samples in inhibitor C, which showed reduction in the corrosion rate. Figures 6 and 7 are the samples in the standard inorganic inhibitor at different concentration. The samples are better protected in this inhibitor, however

Inhibitor B has more inhibitive effect on the corrosion responses of the un-heat-treated and quenched mild steel, while annealed steel in 5M concentration of the acid when compared with A and C. And this protection is very close to those of the inorganic which is imported and not environmentally friendly. Plates 2-4 shows evidence of corrosion in the samples when compared to Plates 1 with different gradation. Least corrosion is observed in annealed samples in inhibitor B.

3. Conclusion

The development and testing of new corrosion inhibitors from three plants extracts namely: Plumeria Alba, Blighia Sapida and Secamone Afezeli have been carried out using heat-treated and un-heat-treated mild steel samples immersed in hydrochloric acid environment. These extracts are organic in nature and are environmentally friendly. From the tests results all the extracts effectively inhibit corrosion of the mild steel while Blighia Sapida extract has the most significant inhibition capability which is very comparable to the conventional inorganic inhibitor. The authors therefore recommend this plant extract for use as corrosion inhibitor in replacement for inorganic inhibitors.

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