



Corrosion inhibition study of mild steel in hydrochloric acid using *Citrus sinensis* and *Mangifera indica* peel extracts

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Abstract The effects of corrosion and the inhibitive effects of plants extract were investigated on samples of mild steel immersed in Hydrochloric acid. Findings have shown that inorganic chemicals used to inhibit corrosion of some organic material, are also suitable for corrosion inhibition of metals and their alloys. Extracts of mango and sweet orange were investigated for their inhibitive effects. In this study, corrosion inhibition of mild steel coupons was carried out on 1.0M solution of hydrochloric acid media through the application of mango peel extract (*Mangifera indica*) and orange peels extract (*Citrus sinensis*) which are organic materials. The method of mass loss test experiment was employed for ten days, at room temperature. Energy dispersed x-ray spectrometer (EDX 3600B) was used to analyze a coupon of the mild steel used before the commencement of the experiment. The results confirm that mango (*Mangifera indica*) is capable of inhibiting corrosion of steel in inorganic acids. The results further show that inhibition by the inhibitors of steel in inorganic acid environment depends on the relative concentration of the inhibitors applied. For example, 1.0 g per litre of each of the inhibitors inhibits better than 0.2 g per litre of same. Mango peel extract has proved to be slightly more effective in HCl solution for mild steel inhibition as revealed by the results.

Keywords Inhibition, Orange peels, Corrosion, Mass loss, X-ray Spectrometer, Inorganic.

Introduction

Inhibitors are frequently used for controlling corrosion of metals and alloys in acidic media for removing scales and rust in metals finishing industries, cleaning of boilers and heat exchangers. Acid solutions of hydrochloric and sulphuric acids are widely used in industries to remove mill scale from metallic surface. However, most acid media cause metal corrosion. Use of inhibitors is one of the most practical methods for protecting against corrosion especially in acid solutions, to prevent unexpected metal dissolution and acid consumption [1]. Organic compounds containing hetero-atoms are commonly used to reduce the corrosion attack on steel in acidic media. The use of non-toxic inhibitors called green or eco-friendly environmental inhibitors is one of the possible solutions to prevent the corrosion of the metallic materials [2]. Metals are the pre-eminent important materials used in structural and decorative applications. The corrosion, deterioration or destruction of metals has significant impact on the development of a country, which can be compared to any natural disaster like earthquake, flood, etc. For example, the direct metallic corrosion cost in the US was established as approximately \$276 million on an annual basis, which is several times greater than the normalized loss incurred due to the natural disaster (\$17 billion per annum). It was also suggested by Standards Organization that about 25 - 30% of annual corrosion cost be saved by means of optimum corrosion management practices [3]. Corrosion affects most of the industrial sectors and may cost billions of dollars each year for prevention and replacement maintenance. Thus, the modern world has made investigations to overcome this problem by



conducting enrichment studies of corrosion inhibitors. Corrosion inhibitors will reduce the rate of either anodic oxidation or cathode reduction or both. Most of the potential corrosion inhibitors possess an active functional group, such as a nitro (-NO₂) or a hydroxyl (-OH) group. In an attempt to find corrosion inhibitors that are environmentally safe and readily available, there has been a growing trend in the use of natural products such as leaves or plant extracts as corrosion inhibitors for metals in acid cleaning processes.

The known hazardous effect of most synthetic corrosion inhibitors have motivated scientists to use naturally occurring corrosion inhibitors since they are inexpensive, readily available and renewable; environment-friendly and ecologically acceptable. Use of some inhibitors such as chromates, has been banned because of the toxicity and the environmental hazards they create. Hence, there is a trend to make use of environmentally-friendly, non-toxic extracts of naturally occurring materials as corrosion inhibitors. Extracts of plant materials contain a wide variety of organic compounds. Most of them contain hetero-atoms such as Phosphorus, Nitrogen, Sulphur, and Oxygen. These atoms coordinate with the corroding metal atom (their ions), through their electrons. Hence, protective films formed on the surface and hence corrosion is prevented [4]. Several different methods can be employed to slow down or prevent corrosion of metallic structures. The most commonly used methods are protective coating on metals using organic molecules, plastics, polymers, and cathode and or anodic protection using organic and inorganic inhibitors [5]. A large number of organic compounds, particularly those containing nitrogen, oxygen or sulphur in a conjugated system, are known to be applied as inhibitors to control acid corrosion of iron and steel. Some investigations have in recent times been made into the corrosion inhibiting properties of natural products of plant origin, and have been found to generally exhibit good inhibition efficiencies. This area of research is primarily due to the fact that natural products are environmentally friendly and ecologically acceptable. Corrosion reactions are thermodynamically favourable on less noble metals and alloys when exposed to a corrosive environment such as acids. The inhibition of these reactions can be controlled by many types of organic and inorganic compounds, but organic compounds are the more common type of corrosion inhibitors. Most organic compounds which are efficient corrosion inhibitors contain functional groups which incorporate phosphorus, oxygen, nitrogen, sulfur atoms and multiple bonds. The action of these inhibitors are closely related to factors such as: the types of functional groups, the number and type of adsorption sites, the charge distribution in the molecules and the type of interaction between the inhibitors and the metal surface. A large number of organic compounds have been investigated as corrosion inhibitors for different types of metals. With increased awareness towards environmental pollution and control, the search for less toxic and environment friendly corrosion inhibitors are becoming increasingly important.

Methodology

Materials

The materials used in this work were mild steel, Sulphuric acid of 95 – 97% conc. Ethanol of 99.7 – 100% conc. (absolute), Hydrochloric acid of 36% conc., Acetone of 95.5% conc, Sweet orange (*Citrus sinensis*) peels and Mango (*Mangifera indica*) peels.

Apparatus

The apparatus used in this work were beakers, grinder, measuring cylinder, electronic weighing balance (AR2 140, maximum capacity 210g; readability of 0.0001g), sand paper, and sieve and water bath.

Materials collection

Mild steel bar was obtained from the workshop. Standard grades of Sulphuric acid, Hydrochloric acid, Ethanol and Acetone were obtained from the Analytical Laboratory. Freshly removed peels of orange and mango were collected from local fruit vendors.

Preparation of Corrosion Inhibitors

Fresh peels of fairly ripe orange (*Citrus sinensis*) and of mango (*Mangifera indica*) were separately gathered into different pre-cleaned plastic containers. Orange peels of the same parent and mango peels of the same parent were targeted. This was done in order to avoid unnecessary complications which may arise from their respective phyto-chemical content. A sizeable collection of both orange and mango peels were carefully rinsed



severally under a clean tap water to remove possible unwanted inclusions. The peels were allowed to drain for about one hour separately, before drying commenced. 2.0 kg of orange peels and an equal amount of mango peels were measured apart into pre-washed and dried Aluminium containers labelled C₁ and C₂ for orange and mango respectively. They were exposed to sunlight for 26 days to dry. The materials were properly subjected to weighing each day while drying until a constant mass was noted in each case.

Each of these materials was ground using Corona Grinder. Both CS and MI were separately sieved (Figs. 3.3 and 3.4) and a measured amount of fine product of each sample was soaked apart in a 500 mL beaker 1.0 M ethanol solution. This was done to prevent contamination which may arise from the previously prepared ethanol solution (already available in the Analytical Laboratory). The beaker of Ethanol that contained CS was labelled C.I₁ while the other one was labelled C.I₂, (For corrosion inhibitors 1 and 2 respectively). The top of each of these beakers was properly covered with clean white filter papers and left on standing for 48 hours.

Preparation of Mild Steel Coupons Used

Twelve mild steel coupons, having the same composition were carefully cut by means of arc saw with the mild steel firmly fastened to jig-and-fixture equipment. The thickness of the steel bar was 5 mm and the average dimension of each coupon was 5 by 5 by 0.5 cm³.

The 24 mild steel coupons were labelled 1, 2, 3, ..., 24. They were divided into two groups (A and B) of 12 per group. Group A had coupons labelled 1, 2, ..., 12, while group B had 13 to 24 labels. All these objects were carefully polished on both sides with the aid of sand paper. They were outwardly degreased with the aid of absolute ethanol and completely dried using acetone. Their respective masses were then noted.

Experimental procedure: Mass loss test measurement technique

Twenty four glass beakers of 250 mL were washed with detergent solution and brush, and then rinsed with distilled water. They were then dried with Acetone. Each of these was filled up to 200 mL mark with 1.0 M Hydrochloric acid. These 12 coupons in group A were attached to the first 12 beakers, labelled A₁ – A₁₂. They were subdivided into two groups of six. A₁ – A₆ and attached to coupons 1 to 6 respectively. Into A₂ – A₆, 0.2, 0.4, 0.6, 0.8 and 1.0 g per litre of C.I₁ were added in that order. A₁ served as control (having no C.I₁ in it at all). Again, A₇ – A₁₂ were attached to coupons 7 to 12 respectively. Into A₈ to A₁₂, 0.2, 0.4, 0.6, 0.8 and 1.0 g per litre of MI were added in that order, with A₇ serving as control.

The contents of A₁ to A₁₂ made the test solutions. Ohaus Electronic balance of maximum capacity 210 g; readability of 0.0001g was used for measuring the masses of the coupons throughout the period of experimentation. It was also used to measure C.I₁ and C.I₂ added to test solutions. A mild steel coupon of known mass was then suspended and absolutely immersed to each of the test solutions and left for a period of ten days. However, at an interval of 24 hours within the ten-day period, each coupon was removed, immediately rinsed several times in dilute solution of NaOH and dried using acetone, to obtain a clean and constant mass in each case. This procedure was used to determine the “mass loss” on each coupon.

The corrosion rates were then computed from the equation 3.3, stating the relationship for the mass loss data:

$$CR = \frac{M}{A_{sx} t} L$$

Where CR is corrosion rate (g/cm².h); “A_s” is average surface area in cm² and “t” is immersion period in hour.

Prior to the commencement of the experiment, a sample of the mild steel was subjected to analysis using Energy Dispersed X-Ray Spectrometer (EDX 3600B) shown in the figure below.



Figure 1: Energy Dispersed X-Ray Spectrometer (EDX 3600B)



Results

The result of the chemical analysis (i.e. Chemical composition) of the mild steel (carried out at Nigerian Foundry Limited, located at 1, Adeyemi Bero Crescent, Ilupeju, Lagos) is shown in Table.1. From the result of the chemical analysis of a sample of the mild steel used in this work It is obvious that Iron (Fe) dominated the mild steel, having 99.3552% by weight. Apart from Carbon (0.1325%) and Manganese (0.3325%), the remaining fourteen (14) mineral elements in this mild steel were insignificant in proportions. According to standard texts in Mechanical Engineering, a mild steel of this nature is regarded as low Carbon steel, which is easily attacked by mineral acids, especially Sulphuric acid and Hydrochloric acid.

Table 1: Chemical Analysis showing Chemical Composition of the Mild Steel used for the Work

Atom	Average	Sd	Sd%
C	0.1325	0.0063	4.76245
Si	0.0087	0.0007	8.2775
S	0.0118	0.0024	19.3981
P	0.0023	0.0024	32.8787
Mn	0.3323	0.1013	3.101
Ni	0.0248	0.0012	4.9759
Cr	0.0324	0.0007	2.1405
Mo	0.0015	0.0002	16.3634
V	0.0026	0.0004	13.626
Cu	0.0582	0.0017	2.9707
W	0.002	0.0003	13.1551
Ti	0.0015	0.0005	34.1946
Sn	0.0028	0.0001	2.8665
Co	0.0061	0.00001	0.1603
Al	0.0186	0.0026	14.2149
Nb	0.0016	0.0004	24.3678
Fe	99.3552	0.0066	0.0067

Table 1 shows that Iron with average composition of 99.35 % dominated other mineral elements in the mild steel used for the work. Apart from carbon (average composition of 0.1325 %) and Manganese (average composition of 0.3325 %), no other mineral element had up to 0.1000 % in the mild steel. The composition of carbon makes it clear that the mild steel was a low carbon type. Mechanical Engineering Standard texts have confirmed that low carbon steels are easily attacked (corroded) by the solutions of the common mineral acids especially Sulphuric acid and Hydrochloric acid. Upon introduction of each of the inhibitors, it was observed that a yellow coloration occurred which depended on the concentration of the inhibitor introduced. The higher the concentration of the inhibitor introduced into a test solution, the higher the intensity of the yellow coloration observed. This phenomenon is attributable to the formation of protective films on the surface of the test piece, which increases in intensity as the concentration of the inhibitors increases [4]. This was commonly observed while dipping each coupon into the test solution. While introducing a mild steel coupon for immersion, a slightly reactive sound was heard with clear bubbling sensation, especially all around the just immersed coupon. Figure 2 indicates that mass loss occurred progressively from the first to the tenth day. The lowest mass loss as shown in this table was 2.90 g on the first day and 7.24 g on the tenth day. It is also observed that mass loss increased without any inhibitor in HCl test solution.

Figure 2 reveals a sharp loss in mass of Mild Steel with time when there was no inhibitor in HCl Solution. However, mass losses with exposure time are drastically reduced according to this figure at higher concentrations of C.I₁ in HCl Solution. With different concentrations of orange peel extract in HCl solutions, it was observed from this figure that the curves of mass losses with time are almost parallel.



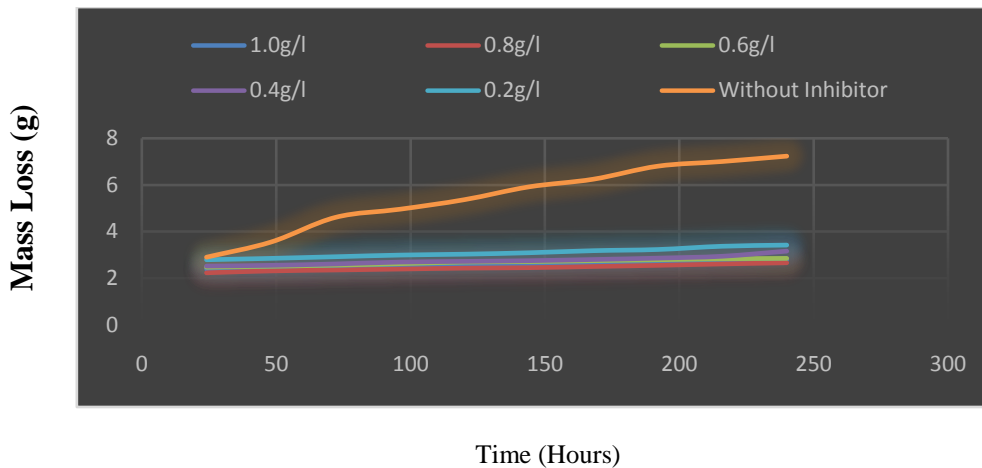


Figure 2: Graph of Mass Loss against Time for C.I₁ in HCl Solution

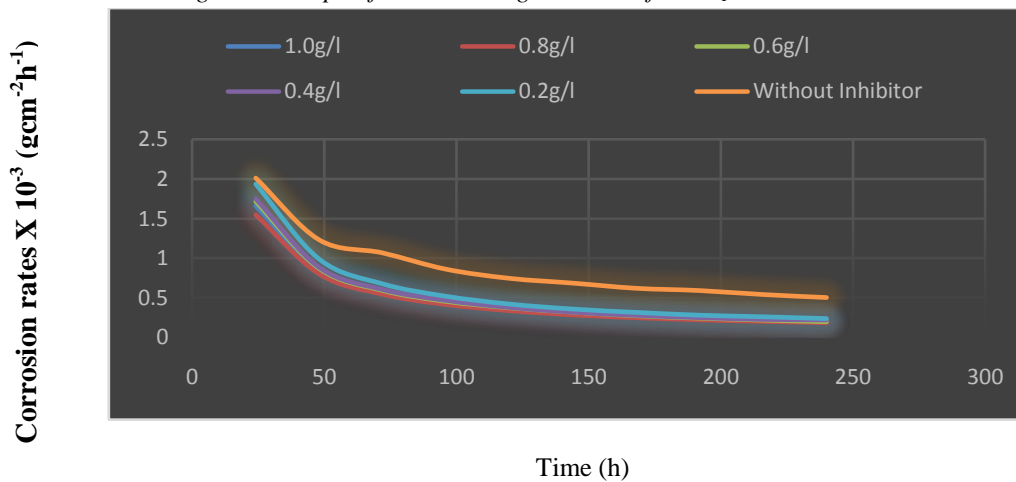


Figure 3: Graph of Corrosion Rates versus Time for C.I₁ in 1.0 M HCl Solution

Figure 3 shows a high corrosion rate without mango (*Mangifera indica*) peel extract in HCl solution. The lowest corrosion rate in this figure was provided by 1.0 g/L of C.I₁ in HCl Solution, while the highest corrosion rate in this medium was given by the topmost curve (without C.I₁ as inhibitor). Corrosion rates are observed in this figure to be very high in the first 24 hours of experimentation.

Figure 3 reveals loss in mass of Mild Steel with time when there was no inhibitor in HCl Solution. However, mass losses with exposure time are slightly high according to this figure at higher concentrations of C.I₂ in HCl Solutions. With different concentrations of mango peel extract in HCl Solutions, it was observed from this figure that the curves of mass losses with time are almost parallel.

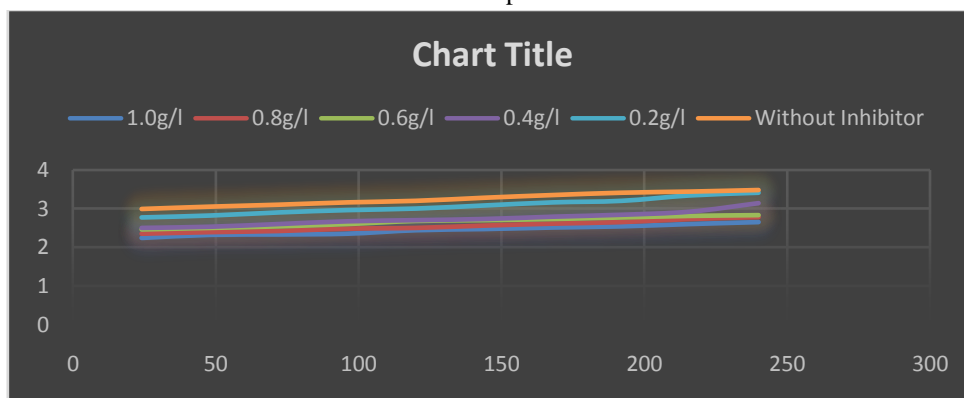


Figure 4: Mass loss versus Time for C.I₂ in HCl Solution

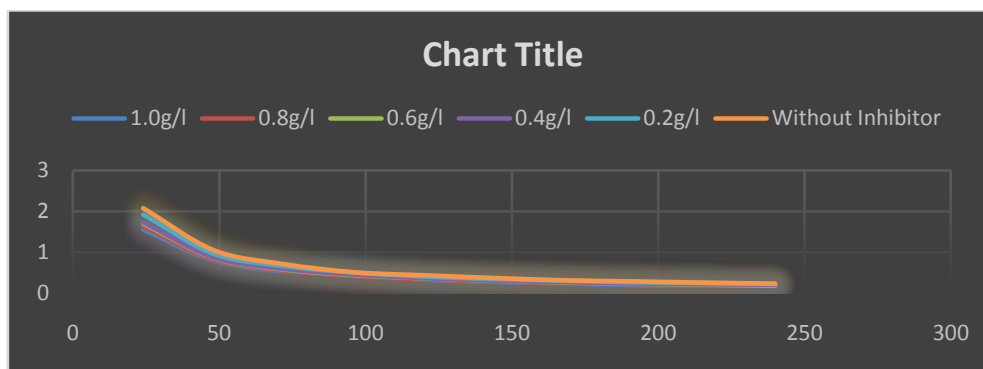


Figure 5: Corrosion Rates against Time for C.I₂ in HCl Solution

Figure 5 shows a slightly high corrosion rate without mango (*Mangifera indica*) peel extract in HCl Solution. The lowest corrosion rate in this figure was provided by 1.0 g/L of C.I₂ in HCl Solution, while the highest corrosion rate is given by the topmost curve (without C.I₂ as inhibitor). It is observed that the corrosion rates are very high with and without inhibitor in the first 24 hours of experimentation. The curves are almost parallel especially after the first 86 hours of experimentation.

Again with HCl test Solutions without any inhibitor, the mass loss is greater at the end of the ten days. The comparison here is that mango peel extracts has higher inhibition ability than orange peel extracts. This confirms the superiority of mango peel extract over that of orange peel extract in terms of inhibition ability. This agrees with the work of Dogan Ozdemir and Volkan Cicek [6].

However, corrosion rate of $2.6389 \times 10^{-3} \text{ g cm}^{-2} \text{ h}^{-1}$ at the end of the first day in the former is slightly higher than that of $2.3680 \times 10^{-3} \text{ g cm}^{-2} \text{ h}^{-1}$ within the same period. At the end of the tenth day, the least corrosion rate of the former ($0.6270 \times 10^{-3} \text{ g cm}^{-2} \text{ h}^{-1}$) is slightly higher than that of the latter ($0.4569 \times 10^{-3} \text{ g cm}^{-2} \text{ h}^{-1}$) in the same period. Again Figures 2 and 4 could be compared in terms of corrosion rates. The values of calculated corrosion rates for mango were all slightly higher than those of their orange counterparts. This also confirms that mango peel extract performs slightly better than orange peel extract in terms of inhibition strength in HCl solutions; this is in respect of corrosion rates, confirming that mango peel extract inhibits better than orange.

Conclusion

The results of this study have clearly revealed that both orange (*Citrus sinensis*) and mango (*Mangifera indica*) peel extracts are suitable for corrosion inhibition of mild steel (within the limit of Laboratory experimentation) in HCl solutions at room temperature. It should however be emphasised that since the peel extracts used in this work were from plant origin, their concentrations have the tendency of decreasing slightly with time, and their preparation is labour intensive. On the whole, mango (*Mangifera indica*) proved to be slightly more effective than orange (*Citrus sinensis*) for corrosion inhibition of mild steel in HCl.

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