Study on tea leaves extract as green corrosion inhibitor of mild steel in hydrochloric acid solution

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Abstract. Corrosion inhibitor from extraction of plant has been considered as the most preferable and most chosen technique to prevent corrosion of metal in acidic medium because of the environmental friendly factor. In this study, black tea leaves extraction was tested as corrosion inhibitor for mild steel in 0.1M of hydrochloric acid (HCl) with the absence and presence of corrosion inhibitor. The efficiency and effectiveness of black tea as corrosion inhibitor was tested by using corrosion weight loss measurement experiment was carried out with varies parameters which with different concentration of black tea extract solution. The extraction of black tea solution was done by using aqueous solvent method. The FT-IR result shows that black tea extract containing compounds such as catechin, caffeine and tannins that act as anti-corrosive reagents and responsible to enhance the effectiveness of black tea extract as corrosion inhibitor by forming the hydrophobic thin film through absorption process. As a result of weight loss measurement, it shows that loss in weight of mild steel reduces as the concentration of inhibitor increases. The surface analysis was done on the mild steel samples by using SEM.

1. Introduction
Corrosion can be defined as degradation of materials when being in contact with corrosive environment as stated by Fontana [1]. Despite of many definitions provide by scholars, corrosion basically can be defined as interaction material with the environment. Corrosion of metal in engineering field has produced undesirable environment in industry. In which, the degradation of metal that happened in pipeline, tank and cooling system has brought many issues and problems. As a result there will be wastage of money, time, materials and manpower. Pourmarazi [2] has stated that one of the important and useful techniques to protect metal from the deterioration due to corrosion is by using corrosion inhibitors. According to Otaibi [3], corrosion inhibitor is known to be the most preferable method to avoid or prevent the destruction of metal because it is low cost and it has excellent anti-corrosive properties especially when it used in acidic environment. Although corrosion inhibitors have a great anti-corrosive properties but it is proven to bring secondary effect to the environment and human health.

Thus, there are tremendous studies and researches have been carried out to develop environmental friendly inhibitors. Research done by Bribri [4] and Loto [5] have found out that the use of environmental friendly corrosion inhibitors or known as “green inhibitors”. The intensive study of green inhibitors is provoked by properties of green inhibitor which are known as environmental friendly, non-toxic, biodegradable and low cost. Considering the cost and the availability of the raw
materials, the natural plant extraction are commonly used. Research done by Fouda [6] has stated that black tea leaves extraction contains many compounds such as polyphenols, caffeine, flavonoids, tannins, volatile oil and alkaloids that will act as anti-reagents for corrosion in acidic environment.

Thus in this study, the effectiveness of black tea leaves extraction as corrosion inhibitors was studied for mild steel in Hydrochloric acid solution by using weight loss measurement technique to determine the corrosion rate and the inhibitor efficiency percentage. The mild steel specimen will be further characterized by using Scanning Electron Microscope for the surface analysis.

2. Experimental procedures

2.1 Preparation of Black Tea solution extract
The black tea powder was obtained directly from the tea bag packets. The extraction process was done using the aqueous solvent method. The solution of inhibitor was prepared by boiling the 4.5 grams of black tea bag in 750ml of distilled water for 90 minutes. Then, the extract solution was left for 24 hours at room condition and filtered. Next, the solution extract of black tea was further concentrated by using Rotary Vacuum Evaporator for 4 hours. The 30 ml of extract left was collected kept in the chiller at 4°C to keep it fresh and avoid from it denatured.

2.2 Preparation of mild steel specimens
The mild steel was cut into average dimension of 30 x 20 x 2mm. The specimens were grinded with different grade from 120 grits to 420 grits of silicon carbide abrasive paper to remove the oxide film. Then it was polished and degreased with acetone, cleaned and dried for the corrosion weight loss measurement experiment.

2.3 Preparation of test media and solution extract
The 37% AR of Hydrochloric acid (HCl) is diluted with distilled water to get specific concentration of 0.1M, 0.5M and 1M. With ratio 1:10, 25 ml of HCl was added slowly in the 250 ml of distilled water in 7 different beakers. Then tea extract of inhibitor was added by using dropper with difference amount of drops of 2, 4, 6, 8, 10 and 12 drops for the first 6 beakers. There is no tea extract added in the seventh beaker as it will use for sample reference.

2.4 Weight loss experiment
Mild steel specimens were immersed in 0.1M HCl solutions with various concentration of inhibitor which 2, 4, 6, 8, 10 and 12 drops for 3 hours at room temperature. The test specimens were immersed in the acid medium that contains different amount of tea extract concentration and without the tea extract as sample reference. For every 1 hour, the test specimens were removed, rinsed with distilled water and dried for the weight measurement. The weight loss of the test specimens were calculated by using equation in (1).

\[
\text{Weight loss} = W_o - W_i
\]  
Eq (1)

Where Wo is the initial weight of mild steel specimen in gram and Wi is the final weight of mild steel specimens in gram after every 1 hour interval. The inhibitor efficiency (IE %) can be measured and calculated by using the equation shows in equation (2). Where, IE% is the inhibitor efficiency, R0 and R1 (in g) are the values of the weight loss observed of mild steel in the absence and presence of inhibitor respectively.

\[
IE = \frac{R_0 - R_1}{R_0} \times 100
\]  
Eq (2)

\[
R = \frac{86.7 \times \Delta w}{A \times T \times \rho} \times 100
\]  
Eq (3)
Where $R = \text{Corrosion rate (mpy)}$, $\Delta w = \text{Weight loss (mg)}$, $A = \text{Area of metal exposed to corrosive media (cm}^2)$, $\rho = \text{Density of mild steel (g/cm}^3) = 7.86 \text{g/cm}^3$, $T = \text{Time of immersion (h)}$

2.5 Surface analysis
Surface morphology of the mild steel specimen was examined by using SEM and EDX. For the surface analysis, mild steel specimens were immersed in the 0.1M HCl solution with condition of the presence and absence of black tea extract solution. The mild steel was cleaned and dried after 24 hours and 7 days immersion for the surface analysis.

3. Results and Discussion

3.1 Characterization of black tea extract
The black tea extract solution was characterized by using FT-IR to determine the presence of certain functional group in a molecule of organic and inorganic compounds. Figure 1 shows the FT-IR spectrum peaks of the tea extract solution. In this spectrum, the peak appeared at 3307 cm$^{-1}$ corresponds to stretching mode of hydroxyl (O-H) and (N-H) amide group. While at peak 1633 cm$^{-1}$ corresponds to the stretching mode of carbonyl group (C=O).

Therefore based on the presence of these two peaks, it indicates that the tea extract solution contains the functional group of molecular structure of main constituent of tea leaves which are catechin, caffeine and tannins which responsible as anti-corrosion reagent in black tea extract. Besides, the presence of tannin in black tea extract is proved to be an effective corrosion inhibitor. While the presence of catechin and caffeine provide high complexation affinity to metals which responsible for effective corrosion inhibitor performance .In other words, the presence of catechin and caffeine will provide strong adsorption molecules of the tea extract film on the mild steel surface. To conclude with, presence of these compounds are really important to make black tea as effective corrosion inhibitors.

3.2 Weight loss measurement
To start with, one drop of tea extract solution is approximately equal with ±0.005ml. As shown in figure 2, the effectiveness of black tea extract solution as corrosion inhibitor of mild steel in 0.1M HCl can be proven by increasing the concentration of black tea extract. It appears that, the loss in weight of mild steel reduced as the concentration of black tea inhibitor increased. Basically, the concentration of the black tea extract can be varies by increasing or reducing the number of black tea droplets in the HCl medium.
Thus, mild steel immersed in HCl with the absence of tea extract solution has the highest weight loss of mild steel which the values ranging between 13.8 mg at the beginning to 27.3 mg at the end of experiment in 3 hours. While the lowest of weight loss change was achieved with the presence of 12 drops of tea extract solution with values ranging between 4.8 mg at the beginning and 10.3 mg after 3 hours of immersion as shown in figure 2.

The curve obtained for the variation of weight loss of varies concentration of black tea extract with exposure time of 3 hours for mild steel specimen in 0.1M HCl with and without the tea extract solution. It seems that, the first highest curve represents the weight loss of mild steel specimen immersed throughout the hours with the absence of black tea inhibitor. However, mild steel immersed in 0.1M HCl with the presence of black tea extract solution shows lowest weight loss of mild steel which has the highest concentration (12 drops) of black tea solution.

It appears that, as the concentration of black tea extract is increased it will speed up the formation of thin film on the surface of mild steel as well as reduce the aggressiveness of HCl solution. Therefore undoubtedly, it is proved that the presence of black tea extract can reduce the weight loss of mild steel as the concentration of the black tea increased.

![Figure 2. Variation of weight loss with exposure time for mild steel specimens immersed in 0.1M HCl with various tea leaves extract concentrations.](image)

It appears that rate of corrosion of mild steel will drop drastically as the black tea extract solution is added in to the HCl solution as shown in figure 3. The rate of corrosion is reduced by range of 70%-90% with presence of black tea extract that act as corrosion inhibitor in HCl solution. The rate of corrosion is also reduced as the weight loss of mild steel reduced. To some extent, corrosion reagents that presence in black tea extract such as tannins, catechins and caffeine can form thin film through the adsorption process that act as barrier from the corrosive environment attack.
Figure 3. Corrosion rate of mild steel immersed in 0.1M HCl after 7 days with presence and absence of black tea extract solution in ( mpy).

On the other hand, the percentage of inhibitor efficiency is calculated by using equation (2) and the graph of percentages obtained is recorded in figure 4.10. The percentage of inhibitor efficiency for 0.1M, 0.5M and 1M of HCl solutions are at 97%, 92% and 87% respectively. The percentage of inhibitor efficiency reduced as the concentration of HCl solutions increased and as the days passed because of high aggressiveness of corrosive environment present. In which high concentration of acid solution can reduce the effectiveness of black tea extract to slow down the rate of corrosion. On the contrary, the corrosion inhibitor is classified as good inhibitor when the inhibitor efficiency percentage is greater than 90%. Therefore, black tea extract solution performed very well and effective as corrosion inhibitor for 0.1M and 0.5M of HCl solutions at which the percentage of inhibitor efficiency is 97% and 92% respectively.

Figure 4. Inhibitor efficiency of black tea extract in HCl solution.

3.3 Surface Analysis
The Scanning Electron Microscope (SEM) images were recorded in figure 5 to observe the changed of mild steel before and after the immersion in 1M of HCl solution with the absence and presence of
black tea extract. Figure 5(a) shows the scratches of mark that appeared from the grinding step before the mild steel is immersed in HCl solution. The surface of mild steel is observed to be free from any corrosion product. However, in figure 5(b) the surface of mild steel was observed with the production of corrosion product such as cavities and pits where it shows that mild steel that immersed in 0.1M HCl solution without the presence of black tea extract are exposed to corrosion activities which is degrading the metal surface.

On the other hand, the figure 5(c) shows the mild steel that immersed in 1M HCl solution with the presence of black tea extract. It is proved that, the smooth surface of mild steel can be seen because of the adsorption of black tea extract molecules that covered the surface of mild steel from the exposure of corrosion attack from the aggressiveness of the environment. Anti – corrosion reagents such as tannins, catechin and caffeine were absorbed on the surface of mild steel to form hydrophobic film to prevent from the corrosion attack. These compounds are said to be stable to form the thin even in high concentration acidic medium. This shows the effectiveness of black tea extract in HCl solution in order to slow down the corrosion process of the mild steel.

4. Conclusion

The efficiency of black tea extract solution of mild steel in 0.1M HCl solution increased by increasing the black tea extract concentration. By weight loss measurement, it proved that loss in weight of mild steel reduced as the concentration of inhibitor increased. While, inhibitor efficiency increased as the concentration of HCl solution decreased. It revealed that black tea extract has very good inhibitor efficiency for 0.1M where it achieved 97%. In other words, black tea extract solution is consider as a very good corrosion inhibitor in order to slow down the rate of corrosion of mild steel in HCl solution.

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