Electrochemical Analysis of Austenitic Stainless Steel (Type 904) Corrosion Using Egg Shell Powder in Sulphuric Acid Solution

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Abstract

Stainless steel is one of the most widely used metals in many industries resulting from the formation of protective film layer on their surface which prevents the metal to react with corrosive environments such as, sulphuric acid. This acid contains various impurities, including aggressive agents which increase the risk of corrosion damage depending on the type of stainless steel used. In addition, it has been shown that corrosion causes acceleration in electrochemical process leading to decrease in the resistance of materials. This research objective is to investigate egg shell powder as corrosion inhibitor on (Type 904) stainless steel in 0.5M H_2SO_4 environment. This research utilized weight loss and potentiodynamic polarization measurements. Egg shell powder was found adequate to reduce corrosion rate of stainless steel Type 904 by 99.45% efficiency. The optimum concentration of inhibitor was 8g/250 ml 0.5% H_2SO_4. From polarization study, egg shell powder was indicated as mixed type inhibitor with predominant cathodic effect. In addition, the egg shell powder completely adsorbed onto the stainless steel surface following Langmuir isotherm.

Keywords: corrosion; inhibitor; egg shell; sulphuric acid

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1. Introduction

Corrosion of metal has attracted attention globally due to huge losses of finances sustained annually all over the world due to metallic degradation. The main vital feature of stainless steel is its high resistance to corrosion as a result of adherent passive and invisible oxide film on the stainless steel surface which consists of iron rich outer deposited salt or hydroxide layer and chromium (III) oxide inner barrier [1-4]. Because of these advantages, stainless steels are widely used in many industries; waste water treatment plants, petrochemical plants, chemical processing etc due to high corrosion resistance. Nevertheless, stainless steel still undergoes localized corrosion when in aggressive medium. One of the methods used in preventing metals against corrosion is to develop new corrosion resistant alloys with improved metallurgical structure that can withstand corrosive anions effect [3], but unfortunately this method is costly compared with conventional stainless steels, therefore, the use of chemical compound for corrosion inhibition is cheaper and effective. Different organic compounds have performed excellently in inhibiting stainless steels surface through film formation [5-8]. From material point of view, corrosion inhibitor is divided into two types: organic inhibitor and inorganic inhibitor. Organic inhibitors have many atoms including O (oxygen), N (nitrogen), and S (sulfur). O, N and S is the center absorption activation process on the metal surface. The performance of an organic inhibitor can be related to physicochemical properties and chemical structure of the compound as a functional group, p-orbital characters, electron structure of the molecule and electron density in the atom donor. Inhibition can be caused by absorption of molecules or ions on anodic or cathodic sites. Egg shell powder (ES) can be considered as environmental friendly corrosion inhibitor on stainless steel in acidic solution containing 0.5M H_2SO_4. The purpose of this study is to determine the inhibitive effect of the egg shell powder as corrosion inhibitor in 0.5 M H_2SO_4 solution, and determine the optimum concentration of egg shell inhibiting corrosion rate of stainless steel, and to understand the mechanism of egg shell inhibition on stainless steel surface.

2. EXPERIMENTAL METHODS

2.1. Materials and Solution

Metal samples of stainless steel grade 904 with composition (%) 0.011 C, 0.33 Si, 1.35 Mn, 0.021 P, 0.001 S, 19.66 Cr, 24.22 Ni, 4.32 Mo, 0.015 Nb and the remaining Fe was used in this study. The inhibitor used in this study was prepared by mixing egg shell powder with methanol for minimum 7 days, then the initial extract result continued by evaporation to remove methanol and water contents. The evaporation was done using equipment rotary vacuum evaporator with pressure parameters of 185 bar at room temperature. While H_2SO_4 solution was prepared by mixing H_2SO_4 and distilled water to obtain 0.5M H_2SO_4 solution.

2.2. Weight Loss Determination

Specimens of previously weighed stainless steel coupons of 2 x 2 x 1 mm with holes in them were suspended in 250 ml beakers of the test solution in the absence and presence of ES. The weight loss was monitored by retrieving the coupons from the test medium at 24 hours intervals progressively for 168 hours. Weight loss was calculated by finding the difference in the coupons weight before and after immersion in the test medium as shown in Equation 1. The procedure for weight loss determination was similar to that reported by [8].

$$W = W_O - W_F \tag{1}$$

Where W is weight loss (mg), W_O is initial weight (mg) and W_F is final weight (mg)

From the weight loss test corrosion rate (CR), surface coverage (θ) and the percentage inhibition efficiency (%IE) were calculated.

$$Corrosion\,rate\,(CR) = \left(\frac{87.6W}{DAT} \right) \tag{2}$$

Where W is the weight loss (mg), A is specimen area (cm^2), D is specimen density (g/cm^3) and T is time of exposure (hour)

The surface degree of coverage (θ) at each inhibitor concentration, which is defined as the fraction of surface material covered by the inhibitor was calculated from the equation below:

$$\theta = \frac{CR_o - CR}{CR_o} \qquad (3)$$

Where CR and CR_O are corrosion rates of the material in the presence and absence of egg shell powder respectively in the corrosive environment. The percentage inhibition efficiency $(\% IE)$ of egg shell powder used as inhibitor in the solution was calculated using the relationship:

$$IE\,(\%) = \frac{CR_o - CR}{CR_o} \quad x \quad \frac{100}{1} \qquad (4)$$

2.3. Linear Polarization Measurements

The stainless steel Type 904 samples were machined and grinded using different grades of emery paper (80, 320, 600, 800 and 1000) prior to washing with distilled water and dried using acetone for corrosion measurement according to ASTM [9]. ES was prepared in different concentrations of 2g, 4g, 6g, 8g and 10g per 250ml of 0.5 molar sulphuric acid was prepared from (98%) analar grade with distilled water. This technique was carried out using three electrode system in an aerated glass cell containing 250ml of the sulphuric acid solution prepared at different ES concentrations and 904 stainless steel cylindrical electrodes with a Potentiostat/Galvanostat (PGSTAT 30 computer controlled) with a NOVA software version 1.8. Polarization curves were achieved with a scan rate of 0.0015V/s.

3. RESULTS AND DISCUSSION

3.1. The effect of egg shell powder on stainless steel corrosion in H_2SO_4 medium (Weight Loss)

The variations of weight losses with time for stainless steel in 0.5 molar sulphuric acid containing different concentrations of egg shell powder are presented in Figure 1. From the plot, weight losses for systems with egg shell (ES) were found to be lower compared to the systems without the inhibitor. The figure also reveals the tendency of weight losses to decrease with increase in concentration of the ES. These results suggest significantly the inhibitive effect of ES on stainless steel in 0.5M H_2SO_4 medium and the degree of inhibition increases with an increase in concentration of the inhibitor. Similar results on the adsorption of Gossipium hirsutum Leaves extract as inhibitor have been obtained [10].

3.2. The effect of egg shell concentration on inhibition efficiency

The corrosion rate and inhibition efficiency (IE %) of stainless steel in different concentrations of ES in 0.5 M H_2SO_4 is shown in Figures 2 and 3. The plots show that inhibition efficiency increases as concentration increases but decrease slightly with increase in time of exposure. Maximum inhibition efficiency of 99.45% was observed at optimum concentration of 8g. Hence, increase in the concentrations of the inhibitor increased the adsorption of the inhibitor molecules on the metal surface thus retarding weight loss of stainless steel coupons. The same trend was also observed by [11] in the study of adsorption behaviour and corrosion inhibitive properties of Piper guinensis extract obtained from ethanol.
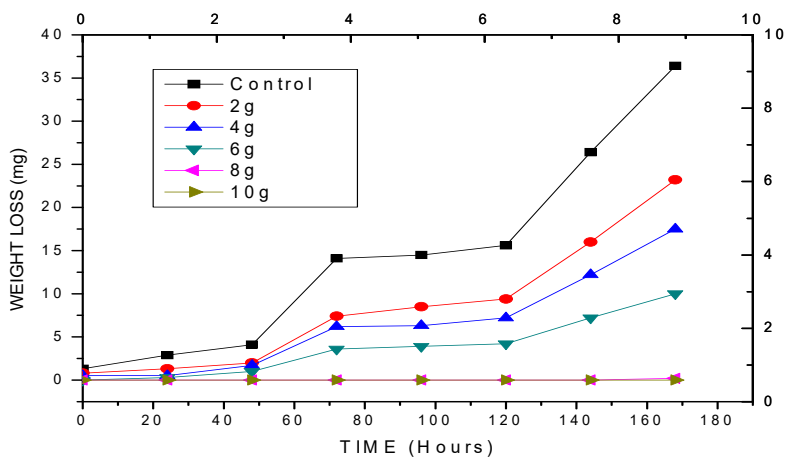
Fig. 1. Variation of weight loss (mg) with exposure time for stainless steel in 0.5 M H_2SO_4 solution at different concentrations of ES

3.3. The effect of time on corrosion rate (CR) and inhibition efficiency (IE)

The effect of exposure time on the corrosion rate of stainless steel in the absence and presence of different concentrations of ES (inhibitor) is shown in Figures 2 and 3. The plots indicate that corrosion rate increase with increase in exposure time but decrease with increasing concentrations of the inhibitor. However, throughout the exposure period, corrosion rate is higher for uninhibited stainless steel than the inhibited ones. The decrease in corrosion rate for inhibited acid solutions compared to the uninhibited suggests retarding effect of ES on the corrosion of stainless steel. The figure also shows the dependence of inhibition efficiency on the concentration of inhibitor and time of exposure. While % IE generally decreased with exposure time, it increases with increasing concentration of the inhibitor. The decrease in inhibition efficiency with time could be attributed to desorption of the molecules of ES from stainless steel surface. Similar observations have also been reported by [12]. The plots also show a good correlation between surface coverage and percentage inhibition efficiency and both decreased with increase in time of exposure.
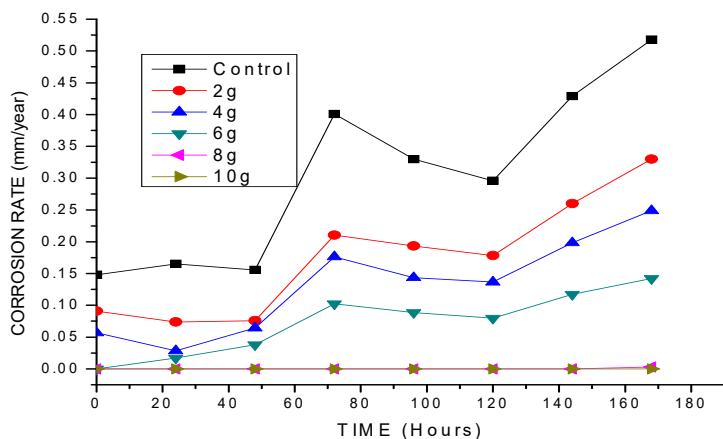

Fig. 2. Variation of corrosion rate (mm/year) with exposure time for stainless steel in 0.5 M H_2SO_4 solution at different concentrations of ES
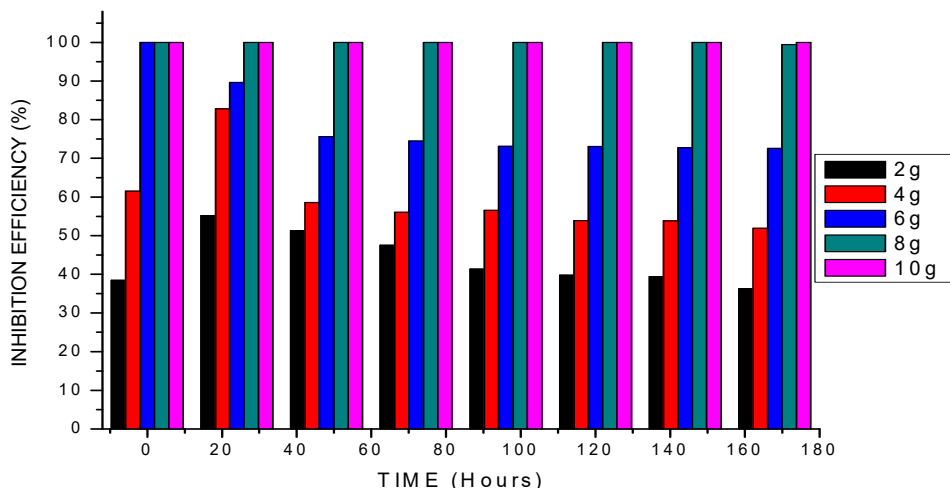
Fig. 3. Variation of inhibition efficiency (%) with exposure time for stainless steel in 0.5 M H2SO4 solution at different concentrations of ES

3.4. Potentiodynamic polarization technique

The polarization measurements result as shown in Figure 4 shows the inhibition effect of ES on stainless steel in 0.5M H_2SO_4 environment, while Table 1 is the polarization parameters of inhibitor concentration variations. Parameter results in Table 1 show a decrease in current density (Icorr) with corresponding addition of inhibitor concentrations from 2g to concentration of 10g with a noticeable shift in Ecorr values. The same pattern also applied in corrosion rate (CR) values; the inhibitor concentration addition reduced the corrosion rate values from 1.0522mm/year at 2g inhibitor concentration then the corrosion rate values reduced drastically to 0.000651mm/year at concentration of 10g.
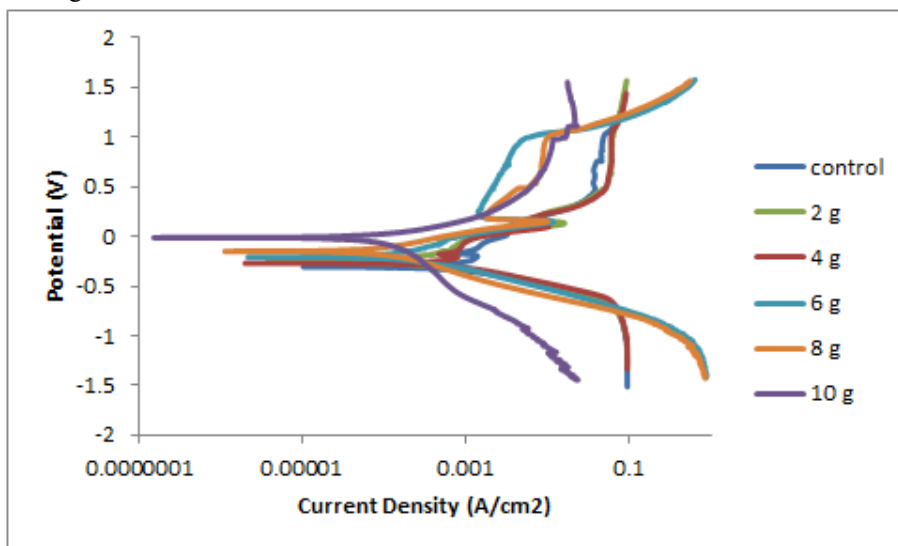

**Fig. 4.** Polarization curve for stainless steel in 0.5M H_2SO_4 solution with inhibitor concentration variation

Table 1. Polarization parameters of inhibitor concentration in 0.5 M H_2SO_4 solution

Sample	ba (V/dec)	bc (V/dec)	icorr (A/cm^2)	Polarization resistance (Ω)	Ecorr (V)	Corrosion rate (mm/year)
control	1.3155	0.060592	0.000172	146.45	-0.85302	1.999
2g	0.25627	0.045953	9.05E-05	186.89	-0.78412	1.0522
4g	1.9453	0.13924	7.93E-05	711.93	-0.61731	0.92105
6g	1.3941	0.013097	7.43E-06	758.75	-0.29964	0.086297
8g	0.33748	0.11481	6.17E-08	602520	-0.20843	0.000718
10g	0.17012	0.30125	5.60E-08	842690	-0.16043	0.000651

From this study, concentration of 8g/250 ml H_2SO_4 is most effective inhibitor concentration with highest efficiency of 99.45% at the end of 168 hours of exposure time with the lowest current density (Icorr) and lowest corrosion rate (CR) values. In another words, the inhibitor concentration of 8g /250 ml is the most effective concentration inhibiting corrosion rate of stainless steel Type 904 in the 0.5 M H_2SO_4 solution. In accordance to Figure 4, polarization curves tend to shift to more negative potential values. From Table 1, corrosion potential (E_{Corr}) parameter at concentration of 10 g inhibitor shows shifting to anodic area with value of -0.16043 V, while other inhibitors concentration shifts toward cathodic area ranging from -0.20843 V up to -0.78412 V. According to [7, 13], ES is cathodic inhibitor type due to the shift in E_{Corr} values. From Table 1, value of the anodic Tafel constants (ba) and cathodic Tafel constants (bc) changes due to an increase in inhibitor concentration. Changes in bc and ba values indicate that absorption process of inhibitor was able to change cathodic solubility mechanism. According to [14], changes of bc and ba due to inhibitor concentration also indicate an absorption process on both anodic and cathodic areas. ES can be concluded as a mixed type inhibitor, with predominant cathodic effect.

3.5. Absorption Mechanism

Absorption process of the inhibitor molecule obeys the Langmuir adsorption isotherm based on Figures 5 because the correlation coefficient (degree of conformity) of modelling Langmuir has a value of 0.993. As investigated by [12], for organic molecules to be adsorbed as a monolayer on metal surfaces without any interaction with other absorbed molecules, there is only one site where the absorption of molecules takes place. Therefore, molecules of ES inhibitor in this study are strongly indicated to form a single layer (monolayer) on the stainless steel surface.

y = 0.7958x + 1.8551
R^2 = 0.9937
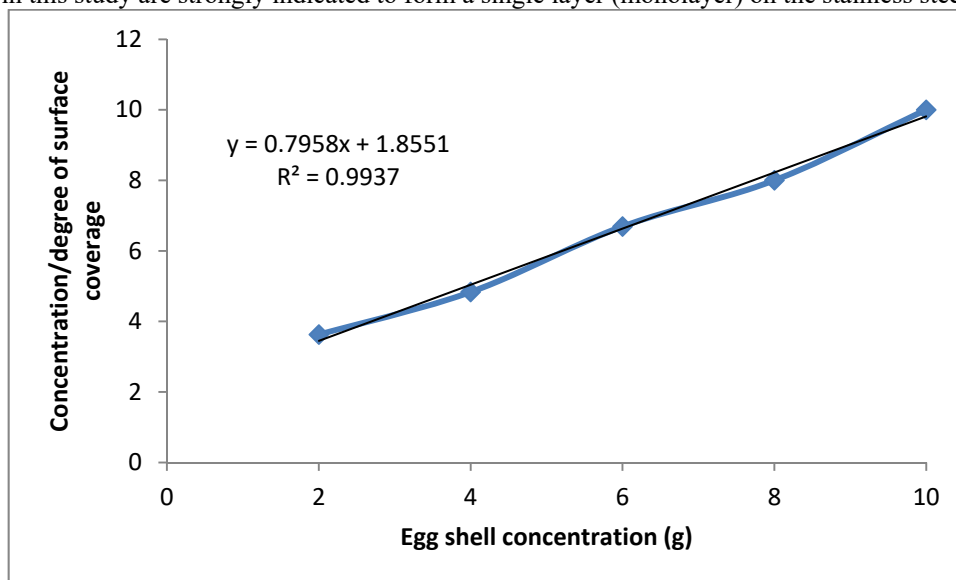
Fig. 5. Langmuir isotherm for ES inhibitor absorption on stainless steel surface in 0.5 M H_2SO_4 solution

4. Conclusion

Egg shell powder (ES) can be used as corrosion inhibitor because the waste product is proven to inhibit corrosion of stainless steel Type 904 in 0.5M H_2SO_4 environment; polarization study indicate ES as mixed type inhibitor with predominant cathodic effect. Inhibition efficiency is influenced by inhibitor concentration and time of exposure, the higher the inhibitor concentration the higher inhibition efficiency while conversely increase in exposure time leads to lower inhibition efficiency. The inhibitor concentration of 8g/ 250 ml 0.5 M H_2SO_4 gives the optimum inhibitor concentration reducing corrosion rate with inhibition efficiency of 99.45% after 168 hours based on weight loss result. The ES inhibitor obeys Langmuir isotherm model.

5. References

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