Enhanced corrosion resistance of stainless steel type 316 in sulphuric acid solution using eco-friendly waste product

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A R T I C L E   I N F O

A B S T R A C T

Literature has shown that different organic compounds are effective corrosion inhibitors for metal in acidic environments. Such compounds usually contain oxygen, nitrogen or sulphur and function through adsorption on the metal surface, thereby creating a barrier for corrosion attack. Unfortunately, these organic compounds are toxic, scarce and expensive. Therefore, plants, natural product and natural oils have been posed as cheap, environmentally acceptable, abundant, readily available and effective molecules having low environmental impact. The corrosion resistance of austenitic stainless steel Type 316 in the presence of eco-friendly waste product was studied using weight loss and potentiodynamic polarization techniques in 0.5 M H_2SO_4. The corrosion rate and corrosion potential of the steel was significantly altered by the studied inhibitor. Results show that increase in concentration of the inhibitor hinders the formation of the passive film. Experimental observation shows that its pitting potential depends on the concentration of the inhibitor in the acid solution due to adsorption of anions at the metal film interface. The presence of egg shell powder had a strong influence on the corrosion resistance of stainless steel Type 316 with highest inhibition efficiency of 94.74% from weight loss analysis, this is as a result of electrochemical action and inhibition of the steel by the ionized molecules of the inhibiting compound which influenced the mechanism of the redox reactions responsible for corrosion and surface deterioration. Inhibitor adsorption fits the Langmuir isotherm model. The two methods employed for the corrosion assessment were in good agreement.

Introduction

The exceptionality of stainless steel among other metallic materials can be associated with its broad application and usefulness in industries. These steels are generally corrosion resistant and do perform optimally; but, the limit of their corrosion resistance depends on the composition of operating environment and strength of their passive protective films [5,6]. The significance of this metal protection process in different areas of applications has necessitated the keen interest in research of corrosion inhibition by various corrosion scientists [1–4]. Calcium and magnesium-based deposits in desalination plants face unavoidable problems, and acids used to remove such deposits include HCl, H_2SO_4 and HSO_3NH_2. The application of acid corrosion inhibitors in the treatment of scale parts in multistage flash desalination plants is widely used to prevent or minimize material loss during contact with the acid. Inhibitors are practical and cheap means to minimize the corrosive attack of acids on metals. In order to minimize these problems, many inhibitors have been used both inorganic and organic compounds containing hetro atoms in their chemical structures [7–13]. The inhibition efficiency of the studied inhibitors was found to reduce the rate of corrosion. The inhibiting effect of these compounds was due to its adsorption on the metal surface and isolates the metal from the aggressive ions. Nevertheless, the use of chemical inhibitors has been limited because of environmental threat. The hazardous effects of most synthetic inhibitors are the motivation for the use of natural products. Recently, plant extracts have again become important as an environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. Various natural products were used as scale inhibitors in different applications. The obtained data showed that plant extracts could serve as environmentally friendly scale inhibitors; palm leaves, Fig leaf extracts [14–16]. Sulphuric acid used as the test medium in this work is highly corrosive, strong mineral acid with many industrial uses. Its complete dissociation enhances more reactive

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corrosion reactions. In dilute solution, sulphuric acid is a strong dibasic acid forming two series of salts. Its diverse use in industry accounts for its selection in this work. The egg shell powder (ES) is expected to give an appreciable amount of electrochemical activities of corrosion inhibition for the stainless steel Type 316 in sulphuric acid environment. Besides, ES is regarded as a waste product and readily available. It is anticipated that the results emanating from this research work will be of technological and economic benefits.

Experimental studies

Materials preparation

The rectangular stainless steel sample of 10 mm diameter was each cut into average size of 2 mm × 2 mm × 1 mm coupons for weight loss and potentiodynamic polarization measurements. Test samples used for the weight loss experiments were de-scaled with a wire brush, ground with various grades of emery paper and then polished to 6 μm. The samples were further rinsed in distilled water to remove any corrosion products and further cleaned with acetone to degrease. The samples were fully immersed thereafter preventing further exposure to moisture in the atmosphere. Another set of samples for the corrosion polarization experiments were cleaned in the same way as those for the weight loss experiment. The samples for polarization tests were mounted with resin to ensure that only the tested surface of the sample was exposed to the corrosive medium. Before mounting, copper wire was spot-welded to each of the samples. The surface of the samples were thoroughly cleaned and prepared for experimental use with silicon carbide papers up to 1000 grades before being cleansed in distilled water and dried with acetone.

Experimental setup

The experiments were set up in six different environments, one control experiment and five other experiments with different concentrations of the inhibitor (egg shell powder) in 0.5 M sulphuric acid solutions. The egg shell inhibitor concentrations used were: 2, 4, 6, 8 and 10 g respectively. The chemical composition of the stainless steel and structural formula of egg shell powder are shown in Table 1 and Fig. 1 respectively.

Weight loss tests

The non-electrochemical method of weight loss was done in order to determine the corrosion rate and inhibition percentage. This physical measurement will provide direct result on how the corrosive environments affect the test samples. In each experiment, stainless steel samples of dimension 2 × 2 × 1 mm was drilled at the centre with hole 0.3 mm polished with different grades of emery paper. Then, the specimens were washed several
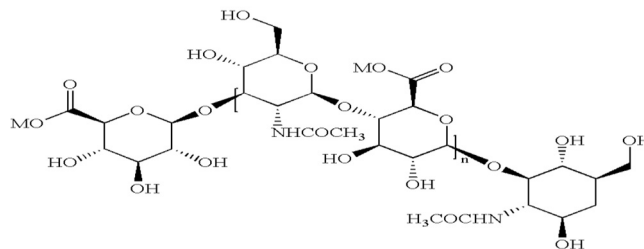
Table 1
Chemical composition of stainless steel (%wt).

Element	Composition
C	0.030
S	0.030
P	0.045
Mn	2.000
Si	0.750
Cr	18.000
Ni	14.000
Mo	3.000
N	0.100

Fig. 1. Chemical structure of egg shell powder.

times with deionized water, dried and stored in desiccators. The cleaned and weighed samples in duplicate were suspended in beakers using glass hooks and rods containing the test solutions of different concentrations of 2, 4, 6, 8 and 10 g egg shell. The pre-weighed samples were retrieved from the test solutions after every 24 h, appropriately cleaned, dried and reweighed. The difference between the weight at a given time and the initial weight of the coupons was taken as the weight loss which was used to calculate the corrosion rate [17,22].

$$\text{Corrosion rate } CR = \frac{87.6W}{DAT} \qquad (1)$$

where W is the weight loss in milligrams, D is the density in g/cm^2, A is the area in cm^2 and T is the time of exposure in hours. The surface coverage and inhibition efficiency was calculated from the relationship [21]:

$$\theta = 1 - \frac{W1}{W2} \qquad (2)$$

where θ is the degree of surface coverage. W1 and W2 are the weight loss of stainless steel samples in absence and presence of egg shell (ES) in acid solution respectively.

$$IE\ (\%) = \frac{W1 - W2}{W1} \times 100 \qquad (3)$$

where W1 and W2 are the weight loss in the absence and presence of ES. The %IE was calculated for all the inhibitors every 24 h during the course of the experiment.

Electrochemical polarization method

The electrochemical polarization techniques were performed on the prepared test specimens immersed in sulphuric acid solution in the absence and presence of different inhibitor concentrations. A three electrode system was used in the potentiodynamic polarization measurements. The working electrode was made of stainless steel Type 316 plate which was embedded in resin with an exposed area of 1.0 cm^2. Platinum rod was used as the counter electrode and silver chloride electrode (Ag/AgCl) as reference electrode, which was connected to the cell through a Luggin capillary. Nova software was used with linear polarization resistance (LPR) and the current was set to 10 mA (maximum) and 10nA (minimum). LSV staircase parameter start potential −1.5 v, step potential 0.001 m/s and stop potential of +1.5 v set was used in this study. The solution was stirred with a magnetic stirring bar and maintained at a constant temperature of 301 K. Before the experiment, the electrode was polished, degreased in acetone and rinsed thoroughly with distilled water. Applied potential versus current density was plotted. Extrapolation of linear part to the corrosion potential gives the corrosion current. In anodic and cathodic plots, the slope of the linear part gives Tafel anodic and cathodic constants (ba and bc) respectively according to the Stern-Geary

equation, the steps of the linear polarization plot are substituted to get corrosion current.

$$Icorr = \frac{baXbc}{2.303(baXbc)XRp} \qquad (4)$$

where Rp is the polarization resistance. The values were calculated from the intersection of the anodic and cathodic Tafel lines. Potentiostat/Galvanostat with NOVA software, Version 1.8 was used in this study.

Results and discussion

The results of the experiment are presented in this session. Based on the data obtained from the experiment, tables were drawn and graphs were plotted.

Weight loss method

The results obtained for weight loss of the stainless steel immersed in 0.5 M H_2SO_4 in the absence and presence of egg shell (ES) in different concentrations were presented in Fig. 2 and the corresponding corrosion rate in Fig. 3. The test in the absence of ES showed highest amount of weight loss value during the duration of the experiment. The weight loss decreased with the increase in the egg shell concentration from 2 to 10 g. The lowest weight loss values were achieved by the 10 g of ES in 250 mL-0.5 M H_2SO_4. On the whole, the ES inhibitor could be said to be effective corrosion inhibitor for stainless steel in the 0.5 M sulphuric acid solution studied. The curves in Fig. 3 show that corrosion rate decreased with exposure time for all the tested specimens at all the concentrations used similar results have been reported [18,22]. The observed phenomenon could be associated with the slower corrosion reactions emanating from the weak test environment due to contamination by the corroding test metal in solution. The graph further shows that the sample with the highest inhibitor concentration had the lowest corrosion rate. Also corrosion deposit from the corroding electrode could cause passivation on the electrode surface. Fig. 4 shows the inhibition efficiency plots with exposure time. The results of inhibitor efficiency reveal that after 24 h, 10 g of ES in 250 mL H_2SO_4 showed the highest inhibition efficiency which was 94.74%. After 168 h of exposure time in sulphuric acid, 8 g and 10 g of ES in 250 mL H_2SO_4 still showed a good performance achieving inhibition efficiency of 73.03 %and 87.64%, respectively. At the end of the experiment a recorded 86.73% inhibitive performance was seen with 10 g concentration of ES sample. This implies that firstly adsorption take place but impede over time based on inhibitor concentration. Also, it is good to state that the studied inhibitor affects the redox process, thereby influencing the cathodic regions of the stainless steel surface through physio-
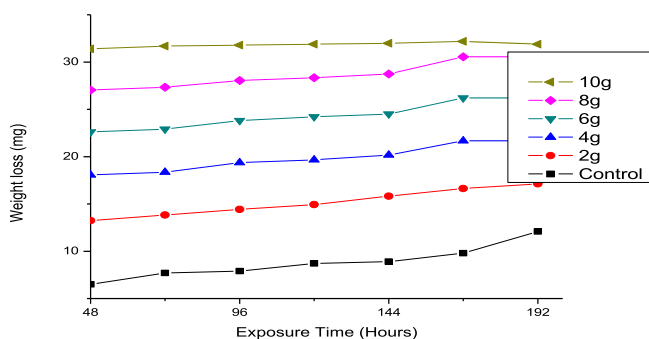

Fig. 3. Corrosion rate against time for stainless steel specimen immersed in H_2SO_4 in the absence and presence of different concentrations of ES.

Fig. 4. Variation of inhibition efficiency of stainless steel with different concentration of ES in 0.5 M H_2SO_4 solutions.

chemical interaction between the molecules of the inhibitor and the acid solutions.

Potentiodynamic polarization method

Anodic and cathodic polarized potentials were measured in the absence and presence of ES. Fig. 5 shows the anodic and cathodic polarization curves for ES in 0.5 M H_2SO_4 solution at different concentrations. The electrochemical variables such as corrosion potential (Ecorr), corrosion current (icorr), cathodic Tafel constant (bc), anodic Tafel constant (ba), corrosion rate (mm/yr[1]) and polarization resistance (PR) with their values are presented in Table 2. The curves generated for different concentrations of ES used in the test medium as inhibitor of stainless steel are presented in Fig. 5. In Table 2, 10 g concentration of ES in 250 mL–0.5 M H_2SO_4 with the lowest current density of 1.24E−05 (A/cm^2)

Fig. 2. Weight loss against exposure time for stainless steel specimen immersed in H_2SO_4 in the absence and presence of different concentrations of ES.
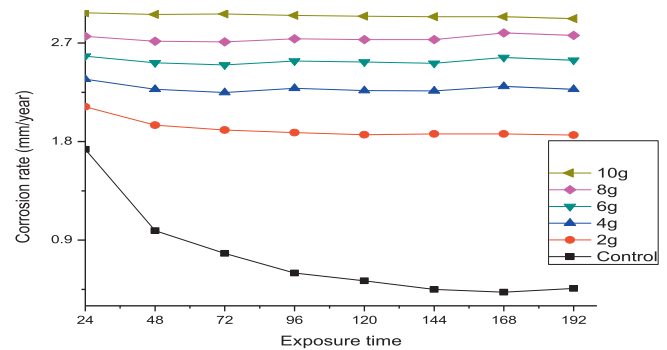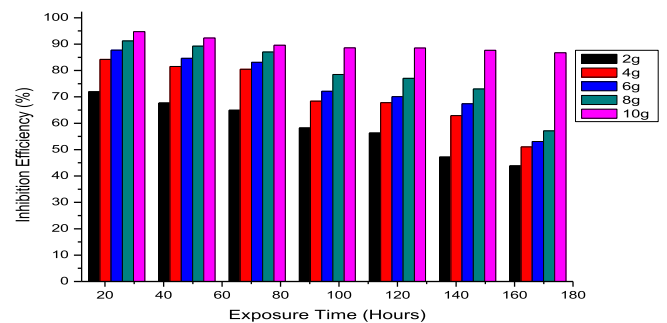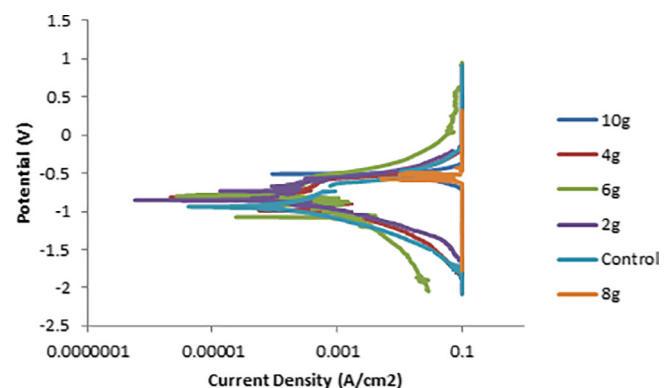

Fig. 5. Cathodic and anodic polarization curve of stainless steel in 0.5 M H_2SO_4 solution at different concentration of ES.

Table 2
Polarization data for stainless steel in the absence and presence of ES 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	0.040886	0.033505	0.000332	24.091	−0.93929	2.8163
2 g	0.059611	1.946	0.000207	121.44	−0.82755	1.5054
4 g	0.23691	0.016319	0.000157	42.121	−0.88251	0.94759
6 g	0.054014	0.32332	5.39E−05	373.18	−0.80269	0.43181
8 g	0.055633	0.12403	5.46E−05	305.65	−0.58957	0.37724
10 g	0.008625	0.038164	1.24E−05	246.08	−0.53561	0.091971
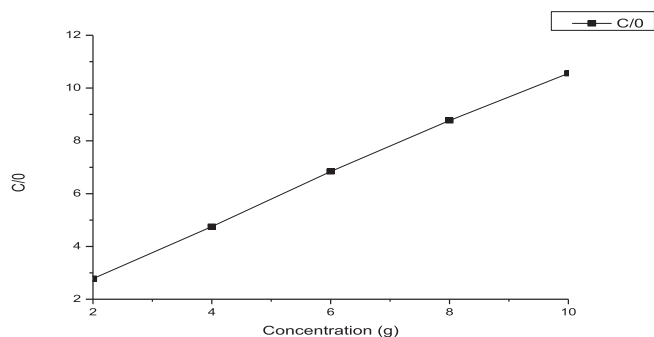
Fig. 6. Langmuir adsorption isotherm of the inhibitor (ES).

SUMMARY

	Intercept		Slope		Statistics
	Value	Error	Value	Error	Adj. R-Square
B	0.86824	0.10144	0.97847	0.01529	0.99902
Interpolate Y1	0.85275	0.0157	0.98386	0.00244	0.99939

Fig. 7. Frumkin isotherms for adsorption of ES inhibitor against concentration.

SUMMARY

	Intercept		Slope		Statistics
	Value	Error	Value	Error	Adj. R-Square
B	−2.09476	2.06476	1.79708	0.31127	0.8899

exhibits the best inhibitive characteristics. It also has the lowest corrosion rate and the highest polarization resistance which show it to be the most effective concentration. From anodic and cathodic Tafel constant for all the inhibitor concentrations recorded in Table 2, this indicates that ES is a mixed type inhibitor. In the absence of inhibitor, highest corrosion magnitude was recorded

as indicated by the overall polarization results. This polarization test revealed that ES significantly alters the electrochemical process responsible for corrosion. In addition, the inhibitive action of the inhibitor is related to its adsorption and formation of a compact barrier film on the metal electrode surface. This was further indicated by the values of the corrosion potential of the tests in the presence of inhibitor when compared to corrosion potential test values of the tests in the absence of inhibitor. It is evident from Fig. 5 that anodic and cathodic curves were both polarized. The adsorption of the inhibitor molecules on the metallic surface blocks the active sites thereby retarding the rate of corrosion. Ecorr values do not show any signification change suggesting ES is mixed type inhibitor. The results obtained from the polarization technique were in good agreement with those obtained from the weight-loss method.

Adsorption studies

Molecular adsorption can further be used to explain corrosion inhibition. The chemical structures of organic compounds, distribution of charge in the molecule, nature and surface charge of metal and the type of aggressive media are known to influence the adsorption process. This is achieved by putting to test the
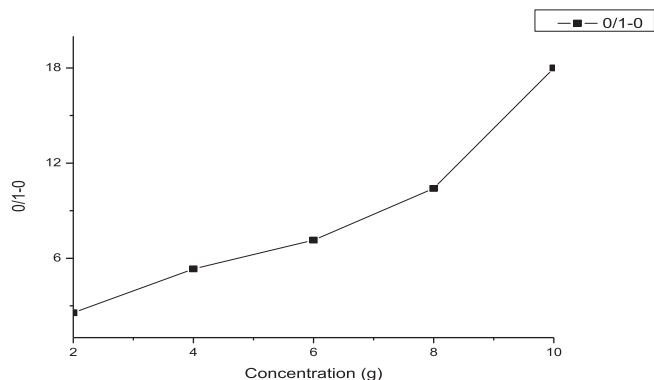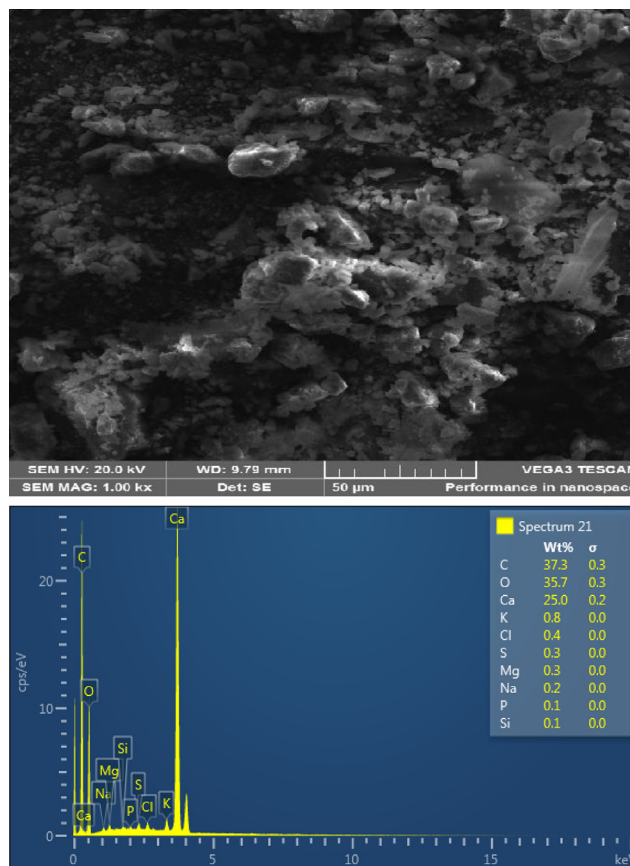

Fig. 8a. SEM/EDS images of the egg shell powder used as inhibitor.
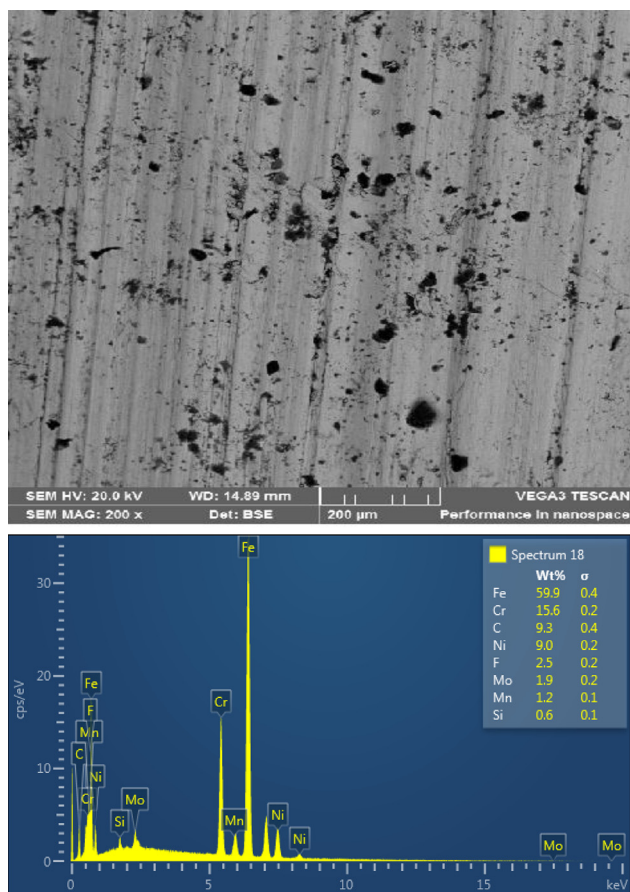
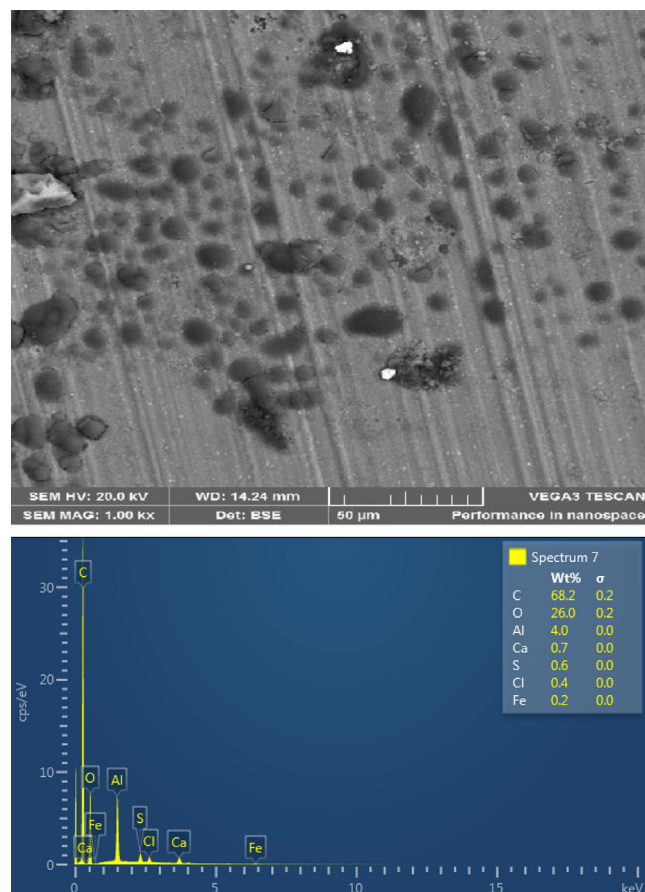**Fig. 8b.** SEM/EDS images of as received stainless steel sample.

Fig. 8c. SEM/EDS images of stainless steel immersed in 0.5 M H$_2$SO$_4$ solution in the absence of inhibitor.

experimental data obtained with different adsorption isotherms. Egg shell consists among others, nitrogen (N) and oxygen (O) which are heteroatom, present in the structure of ES chemical constituents. These constituents are believed to have remarkable inhibitory effect which facilitates their adsorption on the metal surface. The inhibition efficiency of an inhibitor may therefore, depend on the structure of the inhibitor, number of adsorption active centres in the molecule, charge density, molecular size, mode of adsorption and formation of metallic complexes [19]. From this work, ES can be considered as environmentally friendly and cheap compounds with very appreciable corrosion inhibition in 0.5 M sulphuric acid solution as obtained in this investigation. The results of the inhibitor concentrations affected both the anodic and cathodic reactions according to the Tafel slope (ba and bc) values presented in Table 2 thereby confirms the ES inhibitor to be a mixed type inhibitor in 0.5 M H$_2$SO$_4$ medium. Obtained data for degree of surface coverage (θ) were applied for different adsorption isotherm equations including Langmuir, El-Awady, Frumkin, Freundlich, Bockris-Swinkel, Temkin and Florry - Huggins. The results showed that the isotherm that fits the adsorption characteristics of ES on stainless steel surface is Langmuir adsorption (Figs. 6 and 7). According to Langmuir adsorption isotherm degree of surface coverage (θ) and the concentration of the inhibitor in the bulk electrolyte are related to following equation reported elsewhere [20].

Surface analysis

Scanning electron microscope/energy dispersive spectroscopy (SEM/ EDS)
    SEM/EDS surface analysis of stainless steel in sulphuric acid solution in the absence and presence of egg shell powder inhibitor has

been shown in Fig. 8. Fig. 8a is the SEM/EDS of the egg shell powder used as inhibitor in this study, Fig. 8b is the SEM/EDS of the as received sample, Fig. 8c is the SEM of stainless steel sample after 168 h immersion in sulphuric acid solution and a surface severely corroded was observed after immersion in the absence of egg shell as a result of corrosive attack of the sulphuric acid solution. The corrosion product layer on the surface of stainless steel in the absence of inhibitor (Fig. 8c was clearly porous and thus offers no corrosion protection. In the presence of egg shell (Fig. 8d, the corrosion damage was clearly reduced, and there was an evidence of the presence of egg shell on the surface of the metal.

Conclusions

The work presented in this paper is a contribution to study the possibilities of using new type of corrosion inhibitors called green inhibitors from waste products. From the experiments carried out and comparisons of the various test samples against the control experiment, the following conclusions are made:

- Egg shell is an excellent corrosion inhibitor for stainless steel Type 316 in 0.5 M sulphuric acid medium with inhibition efficiency of 94.74% at 10 g ES concentration.
- The results obtained from weight loss and potentiodynamic polarization methods are in good agreement at studied concentrations and temperature.
- Percentage inhibition efficiency increased with increase in the ES concentration.
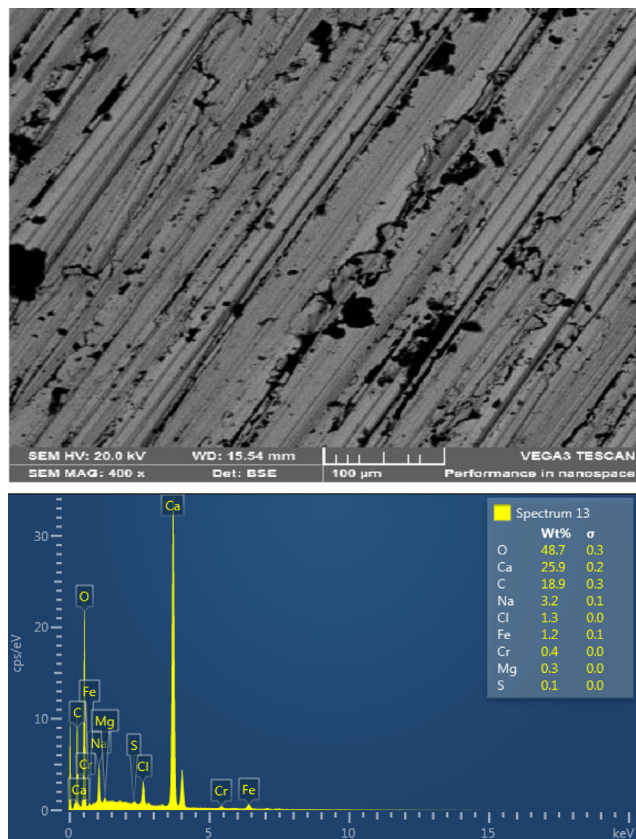
Fig. 8d. Stainless steel immersed in 0.5 M H$_2$SO$_4$ solution in the presence of inhibitor.

- The square correlation coefficient (R^2) was used to choose the adsorption isotherm that fits experimental data. The ES adsorption on the stainless steel surface in 0.5 M sulphuric acid solutions fits the Langmuir adsorption isotherms.
- The experimental data indicates that ES behaves as a mixed type inhibitor in the studied solution blocking both anodic and cathodic reaction.

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