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Investigation of Eggshell Agro-Industrial Waste as a Potential Corrosion Inhibitor for Mild Steel in Oil and Gas Industry

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Abstract: Corrosion inhibitors are generally used in reducing metallic corrosive effects. Nevertheless, most inhibitory compounds have harmful effects on the environment, as well as being expensive and toxic. Therefore, there is growing awareness of the need to replace petroleum inhibitors with eco-friendly inhibitors. Eggshell agro-industrial waste (ESAW) is a compound with high inhibitive activity and its utilization is desirable to minimize the quantity of agricultural waste generated. Hence, this study aims to demonstrate the inhibition efficiency of eggshell extract, a waste compound, on mild steel (material frequently utilized in the oil and gas sector) in one molar hydrochloric acid solution accessed via weight loss and electrochemical methods. Potentiodynamic polarization results shows that the current densities of mild steel corrosion significantly decreased using eggshell agro-industrial waste. Similarly, electrochemical impedance spectroscopy results suggest that eggshell agro-industrial waste enhances the mild steel polarization resistance significantly. The inhibitor performance increases with increasing eggshell agro-industrial waste concentration, with optimum efficiency of 97.17%. The inhibition was due to the adsorption and adhesion of the eggshell agro-industrial waste constituents on the surface of the mild steel; the adsorption obeys the Langmuir adsorption isotherm model. Compared with various reported corrosion inhibitors in the literature, eggshell agro-industrial waste is very effective. Therefore, eggshell agro-industrial waste can be recommended as a potential inhibitor in the oil and gas sector.

Keywords: oil and gas industry; mild steel; corrosion; sustainable inhibitors; agro-waste

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1. Introduction

Mild steel has been extensively utilized for numerous years in the oil and gas sector owing to its low cost and outstanding mechanical properties. However, in this industry, the materials are susceptible to localized and general corrosion on exposure to aggressive media [1]. Nevertheless, mild steel is prone to corrosion process, mostly in acid environments [2,3]. Several acids, such as acetic, hydrochloric, and hydrofluoric acid, are typically utilized for descaling, pickling, industrial acid cleaning, and oil well acidizing in the industry. The costs owing to corrosion in oil refining plants and natural gas sweetening is estimated to be 25% of the total maintenance budget [4]. Corrosion inhibitor is added to the electrolytic solution to reduce the corrosion effects in acidic environments. One of the most practical means of mitigating the corrosion process and extending mild steel's useful life is the use of organic inhibitors—that is, substances that are directly applied to the corrosive solutions and interact with the material surface, thus forming defensive layers. Generally, the challenges of corrosion mitigation are that the reagents or synthesis methods used are hazardous to the environment and/or human health and very expensive. As a result, in the last few years researchers have investigated feasible alternative green options with good corrosion inhibition efficiency that are also safe for the ecosystem [5–9].

Corrosion inhibitor is generally utilized to decrease the aggressive attack on mixing tanks, coil tubing, well tubular, and other metal surface in acid media. The application of inhibitor is one of the most practical techniques (typically performed in acid environments) where prevention of metallic dissolution and acid consumption is crucial. The use of corrosion inhibitor is a cost-effective and realistic means of protecting metal against corrosion in the oil and gas sector. Indeed, the largest consumer of corrosion inhibitors is the petroleum industry [10,11]. It should be pointed out that replacing this material with a high-grade corrosion-resistant alloy could be costly compared to the application of inhibitors. In the last few years, several acids, such as arsenic or arsenate acid, and inorganic salts were utilized as inhibitors; these compounds have been substituted by organic inhibitors as they are environmentally friendly with higher efficiency. Therefore, substituting this toxic compound with biodegradable and ecological alternatives is now of great interest. The technological use of food and agro-industrial waste has been studied extensively to reduce waste disposal and increase the agro-industry's value. Different organic inhibitors are available in controlling the steel corrosion in acidic environments. Most effective organic inhibitors have been reported to contain aromatic character that facilitates the inhibitor adsorption on the metal surface and/or heteroatoms (nitrogen, oxygen, and sulfur) [12,13]. The physicochemical properties, such as the inhibitor's electronic structure, π-orbital character, and electron densities at the donor atoms, play significant roles in the inhibitors adsorption propensity on the surface of the metals. Interestingly, many agricultural waste products contain substances that can serve as effectual corrosion inhibitors. Waste management is one of the most complex concerns worldwide [14–16]. It is expected that waste is properly disposed without pollution danger. To achieve this aim, the European Environment Agency has suggested that appropriate guidelines should be given to policymakers and the public on waste management [17]. In the US alone, the Associated Press Report (2008) estimated that about 115 million kg (250 million pounds) of waste is generated annually. An increase in food waste generation is expected since increasing food consumption is an emerging trend. Therefore, the utilization of agricultural wastes as inhibitors in the petroleum industry could have economic benefits and offer more green approach for creating a sustainable environment.

The inhibition tendencies of different agricultural waste types have been examined [18–24]. Shahmoradi et al. [19] investigated the corrosion inhibition behavior of pistachio shell on steel in hydrochloric acid solution and the adsorption that was owing to the adsorbed molecular species on the metal surface. Shahmoradi et al. [20] investigated the inhibiting performance of walnut fruit containing aromatic rings on mild steel in acid solution. Pal and Das [24] examined the effect of tea solid waste in HCl solution on mild steel corrosion and reported its physisorption inhibition mechanism. The authors clarified that tea solid waste influences the kinetics of hydrogen evolution. Odewunm et al. [21] investigated the inhibition performance of water melon extract on mild steel in H_2SO_4 and HCl solutions. The authors found that water melon is an effective inhibitor. Kaban et al. [23] examined the effects of rice husk in acid solution. They proposed that rice husk is a good inhibitor and the adsorption occurs through heterocyclic and aromatic rings. Mohammed et al. [25] studied date palm seed's inhibition propensity on steel in HCl solution. The authors reported that date palm seed inhibition takes place through the adsorption mechanism. Globally, agro-industrial activity generates huge waste. Most of the generated waste is utilized as animal feed [26]. This waste contains huge amount of antioxidant compounds and nutrients, which can be utilized in obtaining substances with inhibitory tendencies, improving the agro-industrial waste economy, and adding value to the waste. Many tons of eggshell waste is been generated per annum; its composition includes high content of natural antioxidants. In addition, it is rich in calcium, protein, and other minerals, and is incorporated into many diets and food products [27]. However, there is no literature on the performance of ESAW for mild steel in a 1 M hydrochloric acid solution. Hence, this research aims to examine the application of eggshell from agricultural waste as inhibitors in HCl solution. Consideration of agricultural waste (eggshells) for application as a corrosion inhibitor is of interest owing to fact that consumption of egg is increasing. Such increases in its consumption will inevitably lead to increases in its disposal. Exploring the idea of proposing waste management, with economic value, coupled with the search for sustainable inhibitors, the eggshell used in this research was generated in South Africa. Therefore, the objective of this research is to investigate the potential of eggshell extract as a corrosion inhibitor that will proffer a solution to corrosion deterioration of mild steel used in the oil and gas industry. Using eggshells as corrosion inhibitor tends to minimize the amount of waste generated.

2. Experimental Section

2.1. Materials and Methods

1 M hydrochloric acid was used as the corrosive solution in this experiment was prepared from 37% purity concentrated HCl (Sigma Aldrich, St. Louis, MO, USA) and was used without further purification. The stock ESAW inhibitor (100, 200, 300, 400, and 500 ppm) solution was prepared by diluting 1 M HCl solution with double-distilled water and then diluted to the concentration of hydrochloric acid suitable for pickling and descaling mild steel. Table 1 shows the material composition used in this study. The experiments were conducted in aerated stagnant solution and reproduced three times in similar conditions to ensure reproducibility at a temperature of 302 K.

Table 1. The mild steel composition.

Element	Si	P	S	Mn	Al	C	Fe
Composition, weight %	0.38	0.09	0.05	0.05	0.01	0.21	Balance

2.2. Electrochemical Measurements

Electrochemical and gravimetric tests were performed to evaluate ESAW's anticorrosive properties. Specifically, electrochemical methods, including linear polarization resistance, potentiodynamic polarization, and electrochemical impedance spectroscopy, were utilized to assess the inhibition performance of ESAW. A potentiostat and frequency response analyzer driven by NOVA 2.1 software were used for the electrochemical corrosion tests. The test was conducted in an Autolab Potentiostat/Galvanostat (Metrohm, Utrecht, The Netherlands) with three-electrode cells: mild steel sample as working electrodes, platinum rod as counter electrodes, and silver/silver-chloride (Ag/AgCl) as reference electrodes. The three-electrode flat cell electrochemical compartment was designed with a 1 cm^2 surface area of mild steel exposed to the aggressive media. The specimens were ground with different grades of emery papers (400, 600, 800, 1000, and 1200 grits), polished, and washed; the electrochemical tests were then conducted. The NOVA 2.1.5 software was utilized to estimate the electrochemical data. The impedance measurement (EIS) was recorded at 10 mV amplitude. The EIS result was modeled using ZSimpWin 3.20 software. The potentiodynamic polarization experiment was conducted at 0.5 mV/s scan rate before the electrochemical experiment; the specimen was dipped in the solution for two hour to attain free corrosion potential. The impedance measurement was calculated by using the inductance resistance (RL), charge transfer resistance (Rct), and film resistance (Rfm) to estimate the total impedance resistance. Equations (1)–(3) were utilized to calculate the inhibition efficiencies (IE) [28]:

$$IE = \frac{Rp_{inhibitor} - Rp_{blank}}{Rp_{inhibitor}} \times 100 \tag{1}$$

$$IE = \frac{Rct_{inhibitor} - Rct_{blank}}{Rct_{inhibitor}} \times 100 \tag{2}$$

$$IE = \frac{icorr_{blank} - icorr_{inhibitor}}{icorr_{blank}} \times 100 \tag{3}$$

where *Icorr* is the corrosion current density (from LPR study), *Rct* is the charge transfer resistance (from EIS study), and *Rp* is the polarization resistance (from PP study).

2.3. Weight Loss Tests

The weight loss was carried out in agreement with the ASTM G1-03 (American Society for Testing Material, West Conshohocken, PA, USA). Weight loss tests were conducted to establish the long-term inhibitive performance of ESAW on mild steel in addition to the electrochemical tests. The corrosion inhibitor test should be at least 100 h for practical application of inhibitor in the petroleum industry [29]; therefore, in this research the weight loss assessment was carried out in a 250 mL corrosive solution in the absence and presence of diverse ESAW concentrations for 336 h. The cleaning of the samples was the same to the electrochemical corrosion test specimens. A digital balance was used to measure the weight loss before and after the corrosion test. The test was performed three times to confirm reproducibility. The sample was cut with a drilled hole (2 mm drilling beat) at the center of the specimen to enable the coupon suspension in the corrosive media. The specimen was ground with emery papers (400 to 1200), polished, and cleaned prior to the weight loss tests. The specimen dimension was 3.00 cm × 2.92 cm × 0.50 cm after being abraded with silicon carbide of different sizes. We freed the coupons of polished residue and moisture by following these steps: rinsing and cleaning the coupons with acetone and ethanol, drying them in air, and then storing them in the desiccators before use. The corrosion product was mechanically and chemically loosened following the ASTM cleaning standard procedure; this occurred after the complete immersion of the samples every 24 h. Equation (4) was used to calculate the corrosion rate, while the efficiency was estimated by Equation (5) [30]:

$$Corrosion\ rate = \frac{87.6\ W}{density(g/cm^3)xarea(cm^2)xtime(hours)} \tag{4}$$

$$Inhibition\ efficiency = \frac{Corrosionrate_{blank} - Corrosionrate_{inhibitor}}{Corrosionrate_{inhibitor}} \tag{5}$$

where W is the difference between the initial and final weight of the mild steel immersed in the HCl media.

2.4. Surface Characterization

The coupons immersed in 1 M HCl media in the presence and absence of ESAW were investigated via scanning electron microscopy to examine the morphology of corrosion attack, and by energy-dispersive X-ray spectroscopy to determine elemental composition (EDX).

3. Results and Discussion

3.1. Characterization of the Egg-Shell Agro-Industrial Waste

The ESAW morphology shown in Figure 1 is characteristically alveolar and fibrous, with the irregular rod resulting from the milling process. Figure 2 shows the EDX mapping.

It is observed in Figure 2 and Table 2 that the ESAW presents intensities of calcium, oxygen, and carbon. The proportion of these constituents is 37.3%, 35.7%, and 25.0%, respectively. High carbon quantities are present in the ESAW as shown in Figure 2. From the data given in Figures 1 and 2, the main constituents in the eggshell are shown to be O, C, Ca, K, and Cl—which are all organic compound features—and S, Mg, Na, P, and Si. The O and C present in the eggshell compound are potential sources of electron pairs available for adsorption on the surface of the metal; this supports the inhibition of corrosion in the acid solution and consequent partial blockage of the metal [31]. The eggshell has a high level of protein, which in turn presents O, and C atoms; therefore, this compound can be proposed for use as an inhibitor. The extraction of the rich constituents present in the eggshell could be achieved by diverse means before being utilized as inhibitors in other aggressive media/metal. The molecular structure of ESAW (Figure 3) was confirmed by O-H, and C-O groups, indicating that the ESAW has functional groups containing heteroatoms. This functional group is capable of aiding the inhibitor's adsorption on the metal. FTIR test of the ESAW was conducted to affirm the existence of heteroatoms that have different aromatic systems and functional groups. FTIR test of the ESAW (Figure 4) was conducted in the range of 400–5000 cm^{-1}.

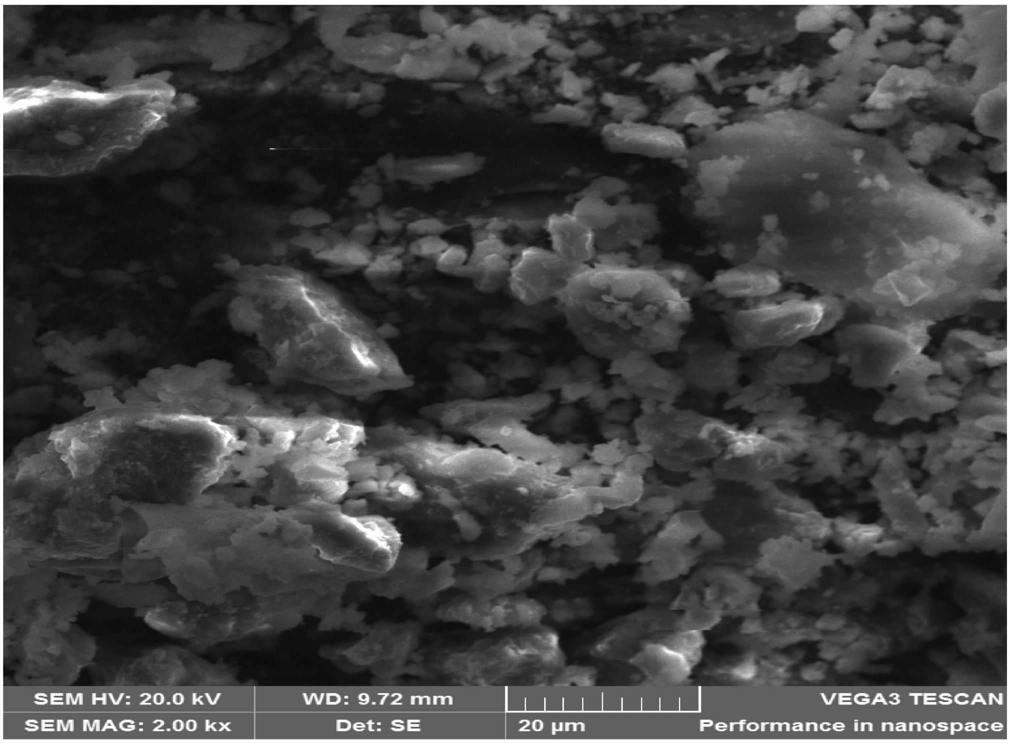

Figure 1. SEM image of the eggshell agro-industrial waste (500× zoom).

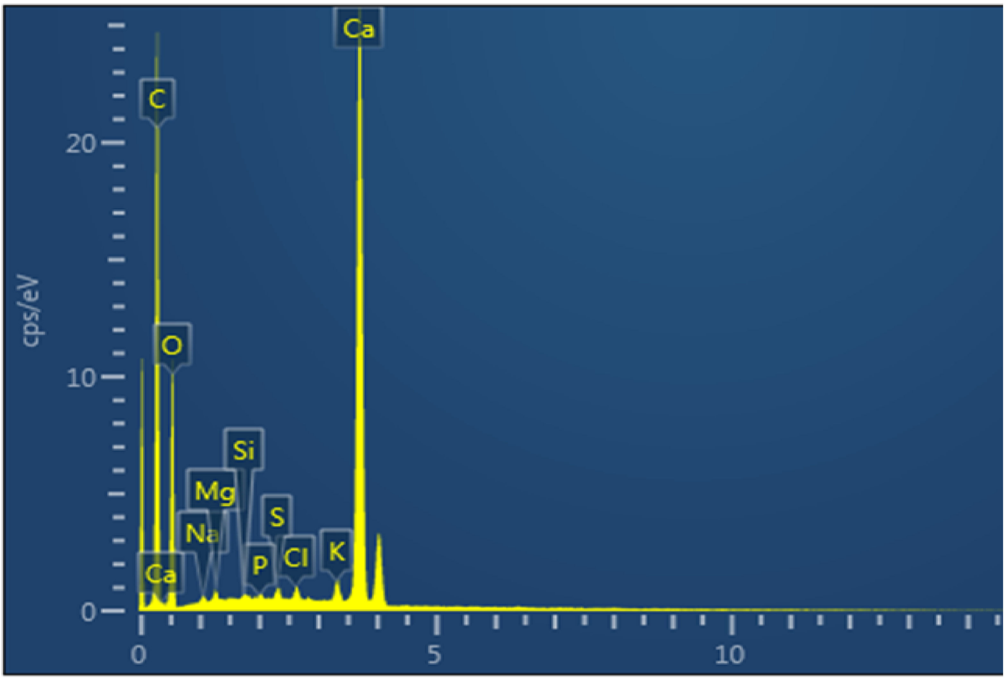

Figure 2. EDX mapping of eggshell agro-industrial waste.

Table 2. Elemental analysis of the eggshell agro-industrial waste.

Element	Eggshell (Wt %)
C	37.3
O	35.7
Ca	25.0
K	0.8
Cl	0.4
S	0.3
Mg	0.3
Na	0.2
P	0.1
Si	0.1

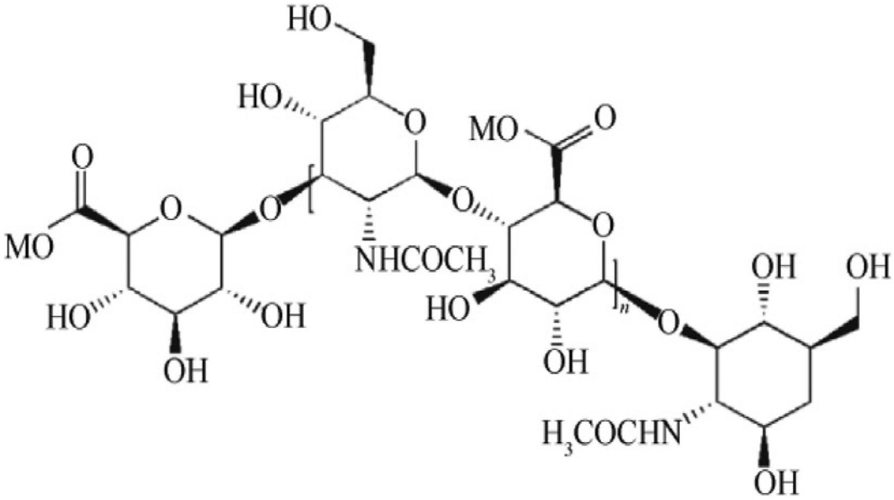

Figure 3. Molecular structure of the eggshell agro-industrial waste.

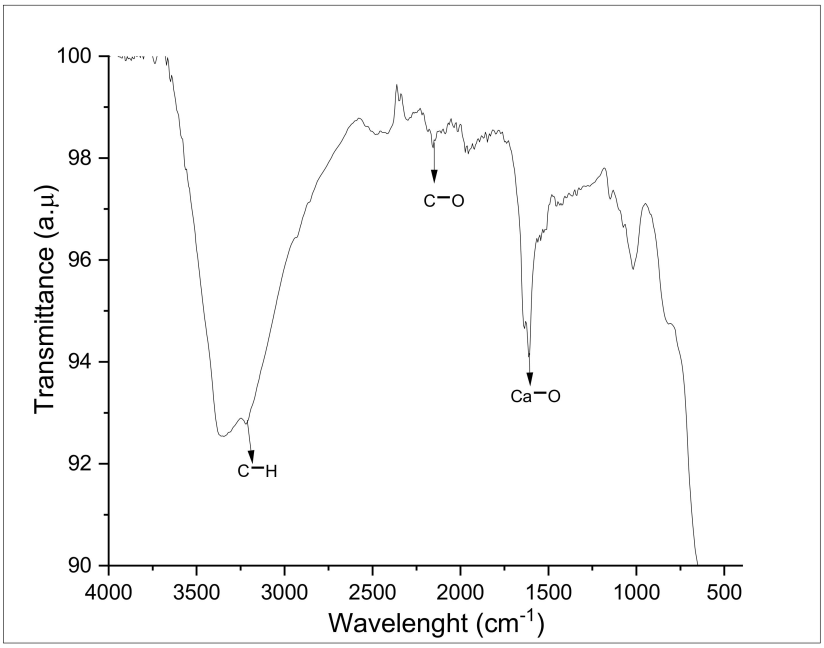

Figure 4. FTIR spectroscopy of the eggshell agro-industrial waste.

3.2. Corrosion Inhibition Evaluation

3.2.1. Electrochemical Impedance Spectroscopy (EIS) Analysis

Shown in Figure 5 is the Nyquist plot in the acidic electrolyte with and without ESAW. Figure 6 represents the equivalent circuit model used in this study, and Figure 7 shows the Bode plots in the acidic electrolyte with and without ESAW. The phase angle, Nyquist impedance spectra, and Bode's modulus were obtained to examine the ESAW capacitive behavior of mild steel and the 1 M HCl solutions interface in the presence and absence of different inhibitor concentrations. As presented in Figure 6, the basic equivalent circuits model was utilized for the uninhibited mild steel in the electrolyte, which consists of Rs (solution resistance), CPE (constant phase element), and Rct (charge transfer resistance). However, with ESAW, Cf (film capacitance) and Rf (film resistance, formed due to the material passivation layer) was included in the basic equivalent circuit. CPE is defined by n and $Y_0$and was used instead of a pure capacitance due to itsnon-homogenous metallic surface.

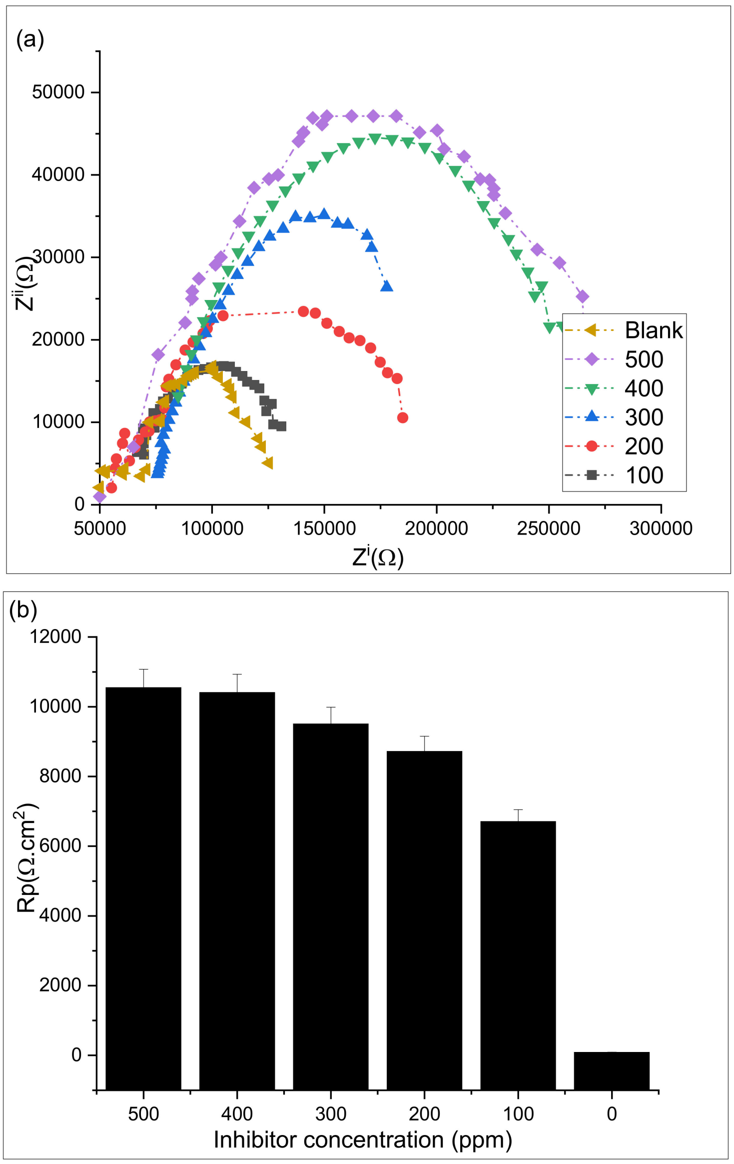

Figure 5. (**a**,**b**) Mild steel Nyquist plots obtained in the presence and absence of the eggshell agro-industrial waste for Rp with diverse eggshell agro-industrial waste concentrations (0, 100, 200, 300, 400, and 500 ppm).

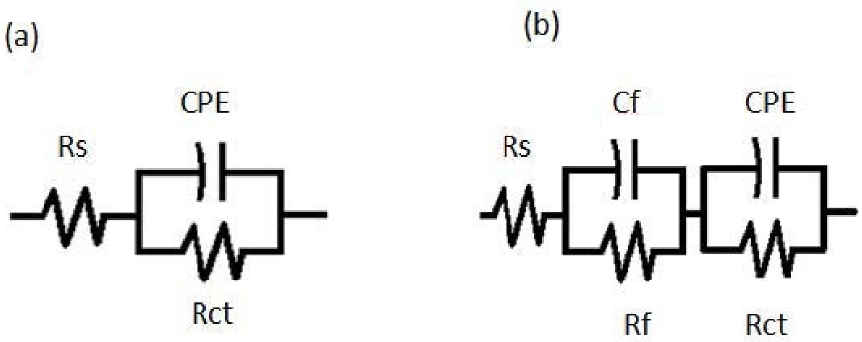

Figure 6. Equivalent circuits (**a**) blank and (**b**) with Eggshell agro-industrial waste used to fit EIS data. (CPE: constant phase element; Rct: charge transfer resistance; Cf: film capacitance; Rf: film resistance).

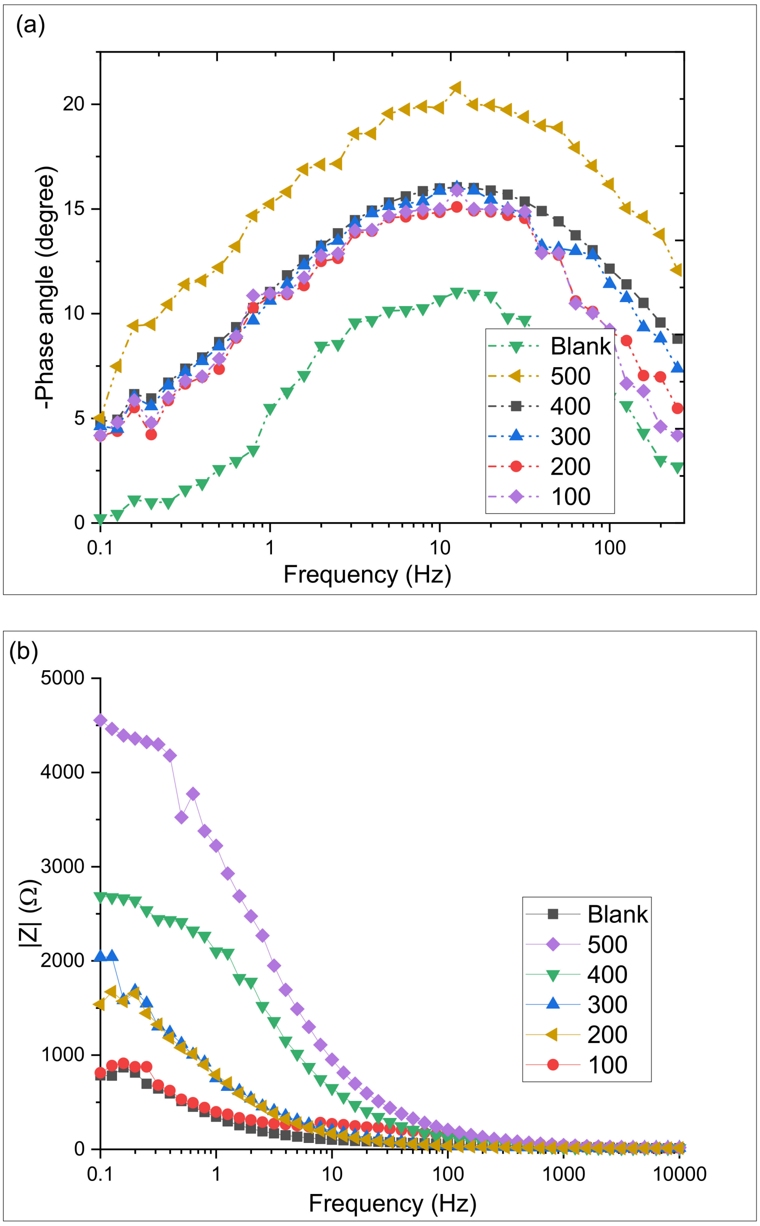

Figure 7. Bode phase (**a**) and Bode modulus (**b**) in the absence (blank) and presence of the eggshell agro-industrial waste (100 to 500 ppm).

The mild steel Rp (polarization resistance) was estimated by adding Rf and Rct values [32]. The metal shows an Rp value of 87.18 Ω cm^2 in the uninhibited solution. The presence of 100 ppm ESAW in the solution increased the polarization value. A further raise in the ESAW dosage increased the metal Rp:Rp = 8718 (200 ppm); 9510 (300 ppm); 1041 (400 ppm); 1055 Ω cm^2 (500 ppm). The obtained results show that as the concentration of ESAW increases, the Rct value also increases, showing that the ESAW is adsorbed successfully on the metal as the Cdl values drop. The Cdl drop could be related to a decrease in the dielectric constant surrounding, denoting the possibly that ESAW performs via adsorption at the interface region. This could also be ascribed to the relaxation of intermediate adsorbed elements such as the H^+ads with negative potentials due to the interface coverage for H^+ads adsorbed [33]. This decline in Cdl can possibly be ascribed to the inhibitor molecules limiting the charged species' access to the mild steel surface. The observed trend can be ascribed to the ESAW adsorbed onto the metal, promoting corrosion inhibition. A similar trend was reported by Odewunmi et al. [34]. When Barley is used as an inhibitor in 1.5 mol L^{-1} H_2SO_4, a similar trend was also recorded [35]. The ESAW present increased the Rct of the metal; the eggshell can also be utilized as a replacement for synthetic organic compounds for protecting mild steel against corrosion. The high frequency section of the Nyquist plots and polarization resistance (Figure 5a,b) was observed to display capacitive loops with increased depressed semi-circle diameters and Bode's modulus impedances (Figure 7a,b); these increases were proportional to the ESAW concentrations in the acidic solution. This observation can be ascribed to the formation of protective films that obstructed the process of corrosion by displacing the corroding ions on the mild steel surface [36].

3.2.2. The Potentio-Dynamic Polarization

The polarization curve was obtained to improve understanding of the adsorption that takes place with the ESAW in the aggressive solutions and to qualitatively interpret its occurrence at the cathodic and anodic sites. The mild steel potentio-dynamic polarization plot in the electrolyte without/with ESAW is shown in Figure 8; the equivalent data is shown in Table 3. Table 3 shows high Rp values as the ESAW concentrations increase in the aggressive media. Moreover, the polarization resistance value was similar to the Rct value, verifying the anticorrosive efficiency of ESAW as a promising inhibitor. The graph illustrates that the inhibited solutions show lower reduction and oxidation values in current density, denoting that ESAW affects both hydrogen evolution (cathodic process) and iron dissolution (anodic process). The declined corrosion current observed is more prominent as the ESAW concentrations increase in the aggressive solution, supporting the previous results; the polarization curve shape is not altered, denoting that ESAW does not affect the corrosion mechanism [37]. The current density of the uninhibited solution was 0.00646 A/cm^2; this figure was significantly reduced to 3.761×10^{-5} A/cm^2 with 100 ppm of ESAW. An increase in the ESAW concentrations (100–500 ppm) denotes a marginal benefit in terms of resistance to corrosion, with current density values of: 3.761×10^{-5} A/cm^2 (100 ppm), 2.670×10^{-5} A/cm^2 (200 ppm), 2.150×10^{-5} A/cm^2 (300 ppm), 2.290×10^{-7} A/cm^2 (400 ppm), and 2.150×10^{-7} A/cm^2 (500 ppm). The corrosion rates estimated for mild steel from the Icorr measured by the Tafel measurements were 2.421, 1.222, 0.671, 0.537, 0.022, and 0.009 mm/year, respectively, with and without the different concentrations of ESAW presented in Table 3. This performance denotes the concentration dependence of ESAW on the mild steel surface in 1M HCl solutions. Addition of ESAW to the acid solution shifted the metal Ecorr in a negative direction. This observation could be ascribed to the reduced cathodic kinetics reaction with the ESAW. As a result, the anodic polarization curve exhibited breakdown and passivity potential for the inhibited mild steel sample; this phenomenon was not observed in the uninhibited sample. The potential breakdown can, however, be ascribed to the high chloride ions and polarization voltage present in the corrosive solution, which causes passivity breakdown. The Ecorr shift was in the range of ±85; therefore, the mixed-type nature of ESAW can be affirmed for mild steel in the HCl solution [38]. The LPR observed trend is in agreement with the electrochemical measurements (EIS).

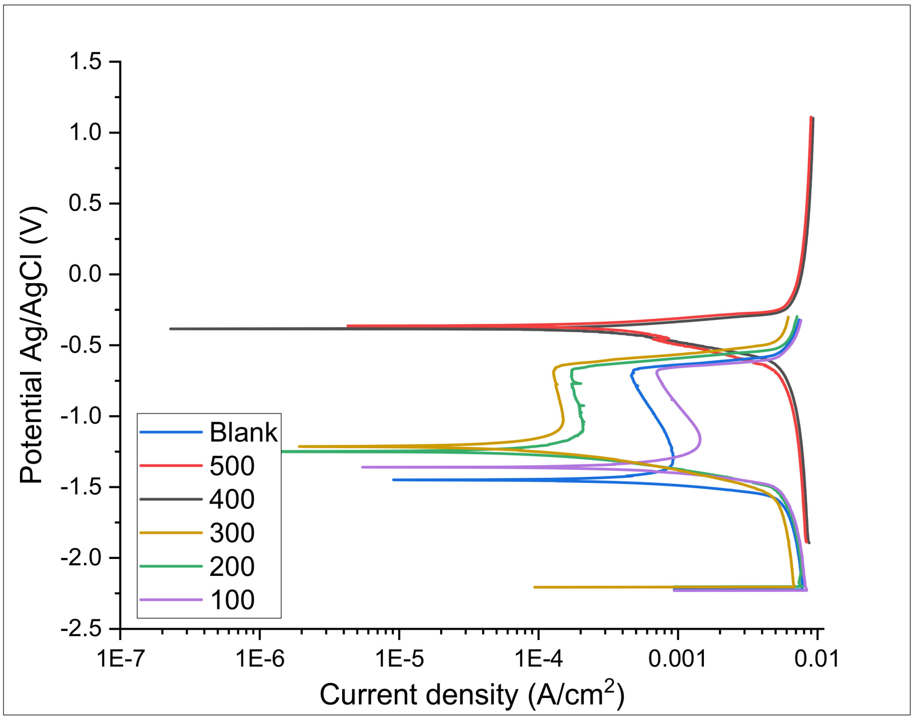

Figure 8. Tafel polarization curves of mild steel with different concentrations of the eggshell agro-industrial waste.

Table 3. Electrochemical parameters obtained by potentio-dynamic polarization for mild steel in 1 M HCl solution in the absence and presence of the eggshell agro-industrial waste.

Inhibitor Concentration (ppm)	Ecorr (V)	Icorr (A/cm^2)	Polarization Resistance (Ω)	Corrosion Rate (mm/Year)
0	−0.320	0.00646	39	2.421
100	−0.363	3.761×10^{-5}	108	1.222
200	−0.395	2.670×10^{-5}	114	0.671
300	−0.385	2.150×10^{-5}	339	0.537
400	−0.513	2.290×10^{-7}	899	0.022
500	−0.519	2.150×10^{-7}	1031	0.009

3.2.3. Weight Loss Measurements

The weight loss technique of examining the inhibition performance is useful due to its reliability and simplicity of application. Figure 9 presents the weight loss results for mild steel in 1 M HCl solution with/without ESAW exposed for 336 h. Without ESAW, the corrosion rate after 24 h was 0.83784 mm/year and increased to 0.60979 mm/year after 336 h. With 100 ppm ESAW, the weight loss value was 0.42477 mm/year and 0.16821 mm/year after 24 and 336 h, respectively. The effectiveness of the ESAW on mild steel in 1MHCl solution was apparent in Figure 9 as the inhibitor's effectiveness increased with increased ESAW concentration. The inhibitor's percentage efficiency rates of 62.75, 70.12, 76.31, 91.50, and 97.17 were achieved at 100, 200, 300, 400, and 500 ppm ESAW, respectively. This denotes that more molecule interacted with the surface of the metal and formed the protective film that delays the process of corrosion [39]. However, an increase in the exposure time displayed notable discrepancies in the ESAW performance at diverse concentrations, as presented in Figure 9a,b. The investigated compound shows satisfactory efficiency even at low concentrations, lowering the corrosion rate value. In weight loss tests, the inhibitor's performance is directly proportional to the metal surface's protection from contact with the corrosive media; thus, the degree of surface coverage indicates that with an increase in ESAW concentrations, there are better organic molecules available to interact with the mild steel surface, thereby forming protective films and protecting the surface of the metal [32]. Higher ESAW concentrations promote higher surface blocking, thereby leading to increase in the inhibitor's efficiency. The presence of the ESAW reduces the corrosion rate and, as a result, boosts inhibition efficiency; this behavior was enhanced by increasing the inhibitor dosage. It is obvious that as the inhibitor concentration rises, the inhibition efficiency increased to 97.17% at 500 ppm, demonstrating that the presence of this compound reduced iron dissolving in 1 M HCl solution and implying that it functions as an inhibitor. In both blank and inhibited solutions, the relationship between corrosion rate and exposure time is linear. In this situation, the ESAW is adsorbed on the metal and prevents corrosion by either changing the mechanism of the anodic and cathodic partial processes or blocking the reaction sites (anodic and cathodic) [40]. When compared to the efficiency obtained in prior works [18–25], the maximal inhibitor efficiency obtained utilizing 500 ppm of eggshell is higher (97.17%). This result can be linked to high organic molecules being adsorbed on the mild steel surface, signifying excellent surface protection due to the extensive compact films formed. This result could be due to the presence of functional groups in addition to the aromatic substituted benzene ring, which is an electron donating group. The investigated eggshell showed an optimum efficiency greater than 96%, denoting that agricultural waste can replace synthetic organic compounds as inhibitors in the oil and gas industry. The obtained result from the weight loss test is in good agreement with electrochemical tests.

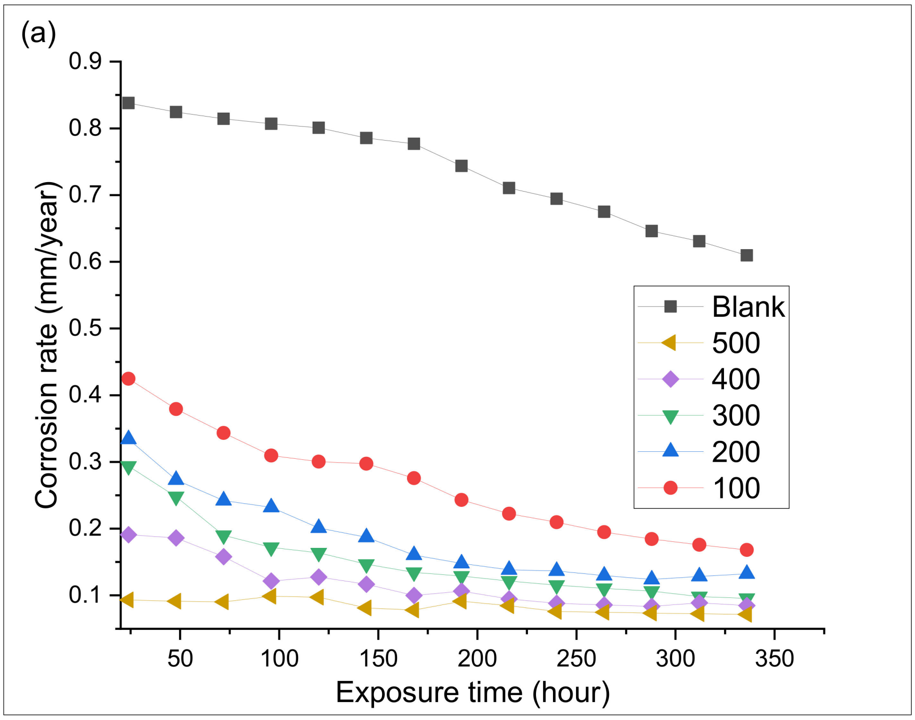

Figure 9. *Cont.*

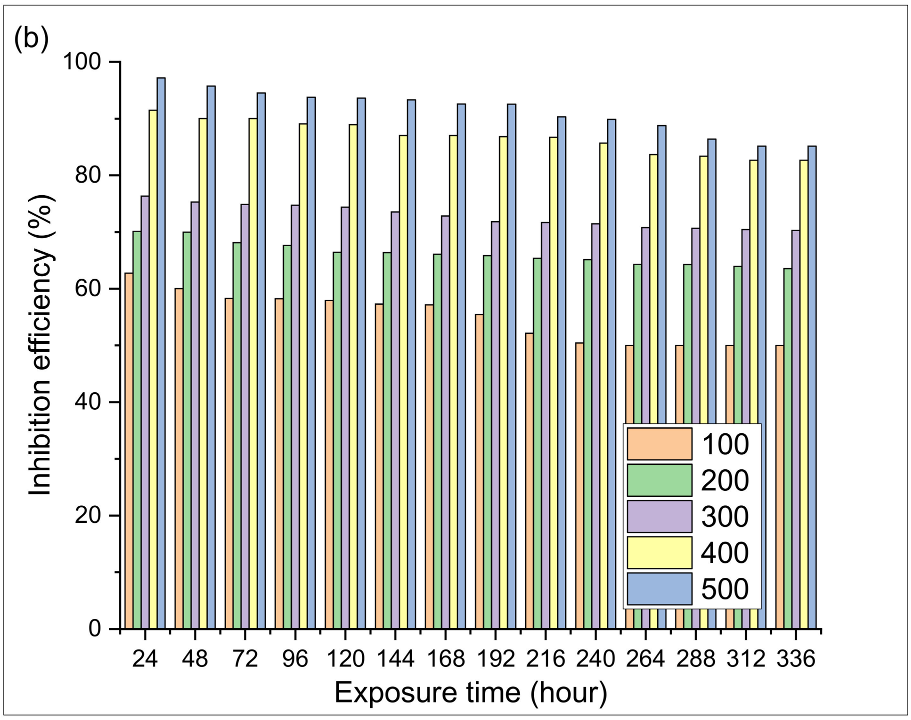

Figure 9. Corrosion rate (**a**) and inhibitory efficiency (**b**) as a function of exposure time in the absence (blank) and presence of the eggshell agro-industrial waste (100 to 500 ppm).

3.3. Adsorption Mechanism

Generally, it is established that corrosion inhibitors form a barrier or protective film on the metal surface, thereby reducing the corrosion rate of the metal. The process of adsorption in an aqueous solution can be considered as a substitution process between the water molecules at the electrode surface [$H_2O(ads)$] and organic compounds in the aqueous phase [*Org(sol)*] [35]:

$$Org(sol) + xH_2O(ads) \rightarrow Org(ads) + xH_2O(sol) \quad (6)$$

where x is the number of water molecules substituted by one organic inhibitor. The interface between the metal surface and the inhibitor could be explained by adsorption isotherm. The surface covered fraction (θ) by molecules adsorbed is directly proportional to the inhibitors performance. Therefore, higher inhibitor surface coverage is significant for excellent corrosion protection. The inhibitors' degree of surface coverage was calculated following the method of Matos et al. [35]. The adsorption isotherm model is generally used to understand the inhibition mechanisms. The isotherm adsorption models commonly used for corrosion inhibitors are: Langmuir, Tempkin, Freundlich, Flory-Huggins, and Frumkin. The surface coverage values were calculated using weight loss data in the presence of various inhibitor concentrations, and numerous adsorption isotherms were used to find the best fit from the data. Figure 9 shows a straight line shape as the graphic representation of C/θ against C; this approach is known for describing a monolayer assumption model which predicts the Langmuir adsorption isotherm where the inhibitor molecule interacts with the surface of the metal [41]. With Langmuir's mathematical equation, it is possible to estimate the Kads value through the linear coefficient shown in Figure 10. The high Kads value is similar to the values reported in the literature [42], indicating that the system is improved by the organic molecules adsorbed on the metal surface. This study proposes that ESAW is an excellent inhibitor for mild steel in acid environments. Even at low ESAW concentration, mild steel corrosion significantly decreases and the inhibitor efficiency increases with increased ESAW concentration. The comparison of different reported corrosion inhibitors in similar conditions with the same degree of protection of ESAW is given in Table 3. It is obvious that ESAW is highly effective, which can be ascribed to its exclusive structure that contains aromatic rings, nitrogen, and sulfur; thus, it could serve as an efficient corrosion inhibitor. Hence, ESAW can be regarded as a potential inhibitor for use in the oil and gas industry.

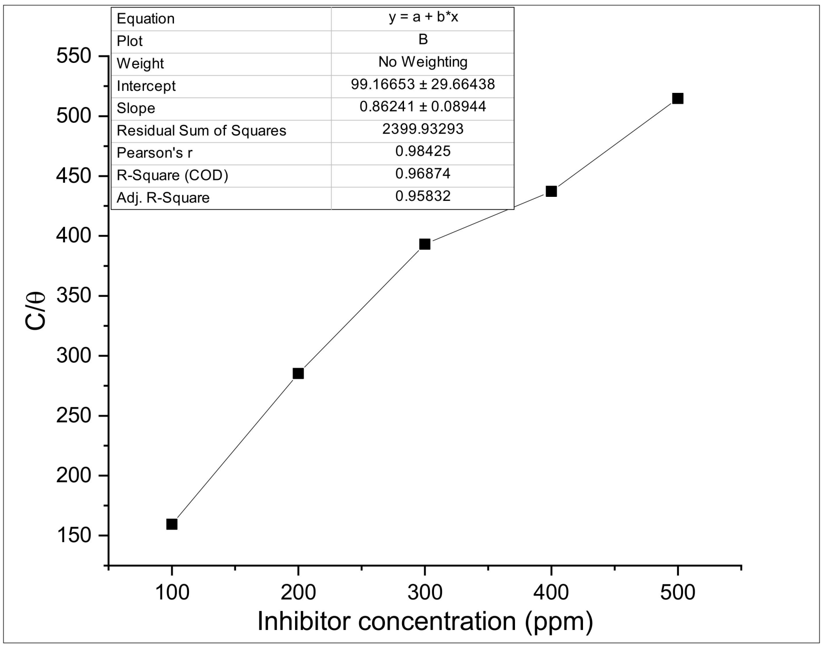

Figure 10. Langmuir adsorption isotherm of the eggshell agro-industrial waste.

3.4. Economic Considerations and Comparative Study of the Eggshell Extract

The use of corrosion inhibitors is considered as one of the most economical and effective means of protecting metals from corroding. Integrated valorization of waste is a progressive form of resource conservation due to its environmental and economic values. In almost every country in the world, the extraction of organic compounds from food waste has become a significant concern in the field of waste management. Searching for cost-effective, efficient, and environmentally friendly metal corrosion inhibitors in aggressive media is a continuous process. In the present work, we tried to propose eggshell extract as one of the inhibitors which satisfy the above-mentioned qualities. Eggshell extract showed a high inhibition efficiency of 97.17% in 1 M HCl solution; to confirm the inhibition performance of eggshell extract, its efficiency was compared with the results of other authors (Table 4). As can be seen in Table 4, the eggshell extract presented great inhibition efficiency on mild steel corrosion in 1M HCl solution. In contrast, inhibitorssuch as Ceratonia siliqua leaves' seed oil show higher inhibition but are not suitable for mass steel production due to their higher cost. Therefore, it is necessary to study the techno-economic aspect of using eggshell extract. The eggshell was collected at 0$ per kg. The total price of the eggshell extraction process, including the cost of water and ethanol, was less than 1$ per kg.

To achieve high inhibition efficiency, other inhibitors reported in Table 5 were added in higher amounts, while only 500 ppm of the eggshell extract was used for the present study. This makes eggshell extract a cost-effective alternative to other inhibitors reported in Tables 4 and 5. While most of the green inhibitor extraction required a high amount per kg, a spend of less than 1 $ was sufficient to develop 1 kg of eggshell extract, which is considerably less than the costs required for any of the inhibitors reported in Table 5. This makes eggshell extract a suitable inhibitor for large-scale production and industrial applications.

Table 4. Comparing the efficiency of eggshell agro-industrial waste against other inhibitors in similar conditions.

Compound	Average Efficiency	Reference
Pistachio shell	92%	[19]
Walnut fruits	95%	[20]
Tea solid waste	90%	[24]
Water melon	81.15%	[21]
Rice husk	97.73%	[23]
Date palm seed	95%	[25]
Licuri	91%	[28]
Barley waste	97%	[35]
Ircinastrobilina	82%	[43]
Spirogyra	88%	[44]
Tinosporavordifolia	87.18%	[45]
Wombolu extract	97.87%	[46]
Cotton seed	95.7%	[47]
Akebia trifoliate koiaz peels	90%	[48]
Zea mays hairs waste	87.92%	[49]
Pomegranate peels	96%	[50]
Sugar beet pectin	**93.9%**	[51]
Eggshell	**97.17%**	This work

Table 5. Comparison cost of some green and commercial corrosion inhibitors in aggressive solution.

Corrosion Inhibitor	Maximum Inhibitionefficiency (%)	Cost perkgOfinhibitor, ($)	Reference
Eggshell	97.17	Less than 1	Present study
Amorphophallus paeoniifolius leaves extract	93	1–2	[52]
2-Mercaptobenzimidazole	53.0	85–110	[53]
N-[1-(benzotriazol-1yl)methl]	~85.0	3400–4000	[54]
Ginkgo leaf extract	92	200–300	[55]
Konjac glucomannan	93	180–200	[56]
Ceratonia siliqua L Seed Oil	98	300–400	[57]
Polysaccharide	96	500–1000	[58]

3.5. Surface Analysis

The surface morphology of the samples after 336 h of immersion to the electrolyte without/with ESAW was conducted using scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy; the results are shown in Figure 11. The EDX results are also shown in Figure 12 and Table 6 representing the elemental analysis of the eggshell agro-industrial waste. The inhibited sample is smooth (Figure 11b) with small grooves resulting from the metal preparation. It is obvious from the morphology that ESAW greatly protected the mild steel surface from corroding. When the metal was immersed in the 1 MHCl solutions, the metal oxidation reactions occurred all over the metal surface, as presented in Figure 11a, where the rough surface was observed. The uninhibited mild steel sample was corroded severely, while with inhibited mild steel sample was smooth with no noticeable sign of corrosion. The SEM image is connected to the weight loss result, denoting that the inhibitor performs as excellent inhibitor for mild steel in HCl solution. The comparison of Figure 11a,b denotes the effectiveness of the ESAW as a corrosion inhibitor for mild steel in HCl solution. With the addition of 500 ppm ESAW, there is an increase in the accessibility of the constituents' element of the alloy. An adsorbed molecule layer is formed, protecting the mild steel surface and leading to a less severe corrosion process [59]; this result denotes that the organic molecule form a protective layer on the surface of the mild steel. After 336 h in contact with HCl solution (Figure 12a), it is obvious that the mild steel surface is attacked by the chloride ions. The oxygen atom detected by the EDX analysis pointed to the corrosion products formed on the metal. The oxygen and calcium percentages in Figure 12b are higher than the uninhibited sample, pointing to the protective layer that ESAW substituents formed on the metal surface. Moreover, the carbon substituent detected originated from the ESAW molecules in the presence of the corrosion inhibitor.

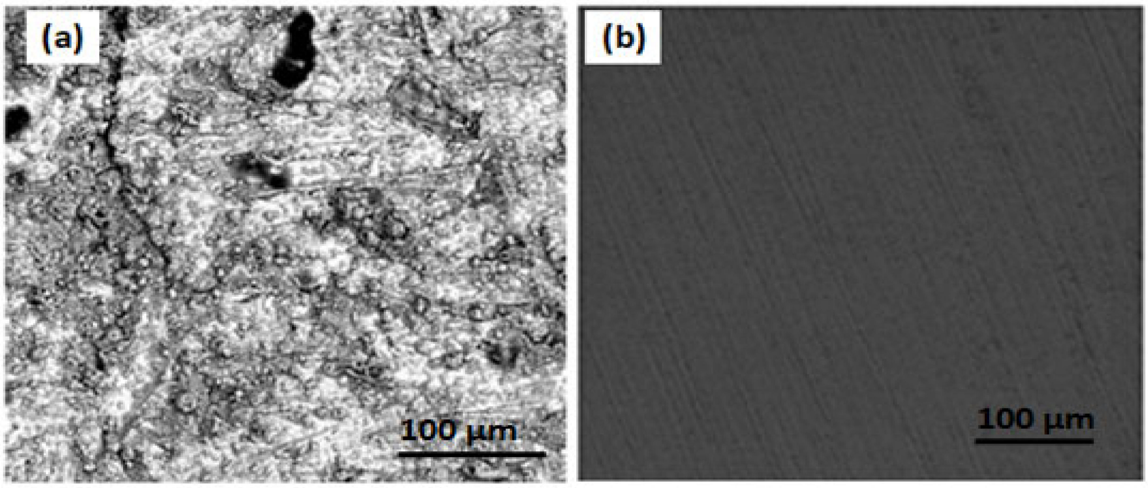

Figure 11. SEM images of mild steel after immersion in HCl (**a**) without, (**b**) with 500 ppm of eggshell agro-industrial waste.

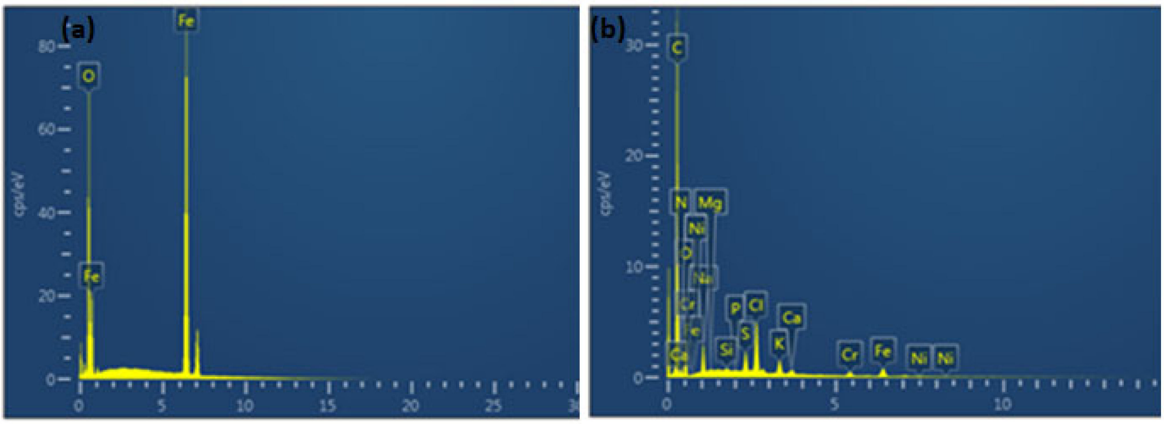

Figure 12. EDX mapping of mild steel after immersion in HCl (**a**) without, (**b**) with 500 ppm eggshell agro-industrial waste.

Table 6. Elemental analysis of the eggshell agro-industrial waste.

Element	Blank	With Inhibitor (500 ppm)
Fe	77.5	2.1
O	22.5	16.4
C	-	63.9
N	-	8.9
Cl	-	3.1
Na	-	1.9
K	-	1.1

Table 6. *Cont.*

Element	Blank	With Inhibitor (500 ppm)
S	-	1.0
Cr	-	0.8
Ca	-	0.4
Si	-	0.1
Mg	-	0.1
P	-	0.1

3.6. Inhibition Mechanisms

Organic molecules act as corrosion inhibitors via adsorption on the surface of the metal and form protective barriers. The phenomena that contribute to the barrier formation are as follows:

- Interaction amid the protonated organic compound with anion on the metal through cations from the compound oxidation process;
- Electrostatic attraction amid π-electron on the compound with vacant d orbital;
- π back interaction connecting the organic compound aromatic rings;
- A combination of the above.

Several organic corrosion inhibitors are heterocycles with unshared electron pairs on the heteroatoms of inhibitor molecules (P, N, O, and S); the presence of polar functional groups, such as Cl, OH, NO_2, CN, CH_3, CN, and others, along with double and triple bonds, enables them to donate the electrons and hence easily become protonated in strong corrosive electrolytic media such as HCl. Therefore, the inhibitor protects the outer layer of the metal from the uninterrupted influence of the aggressive ions, preventing deterioration of the metal. As a result, heteroatoms (Figure 3) are expected to play a significant role in inhibitor compound adsorption on the metal surface; the functional groups (CH_3, OH) are indicated in Figure 4. Since we are working with a complex molecule that forms ESAW and acts as an excellent corrosion inhibitor, one of these phenomena was selected to schematically represent what was discussed in the corrosion inhibition mechanism of ESAW, as shown in Figure 13.

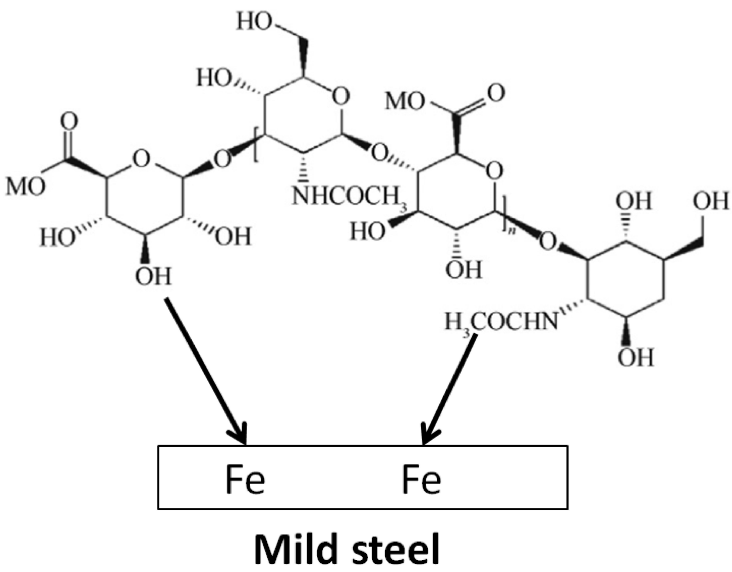

Figure 13. The proposed mechanism for the adsorption of eggshell agro-industrial waste on the surface of mild steel in 1 M HCl solutions.

4. Conclusions

Preventing mild steel corrosion is important for the environment because corrosion is a dreadful waste of money and natural resources. The eggshell is a sustainable alternative to recover agro-industrial wastes from a sector known for producing tons of waste on a daily basis. This process generates various products that can be used for a variety of purposes. Hence, this research work aimed to use eggshell extract as a corrosion inhibitor that will proffer solutions to corrosion deterioration of mild steel used in the oil and gas industry. The effectiveness of ESAW as an inhibitor was investigated on mild steel in 1 M HCl solutions via electrochemical and weight loss techniques, surface analysis by SEM, and EDX, with the following outcomes:

- By raising ESAW inhibitor concentrations to 500 ppm, the corrosion inhibition efficiency is increased to 97.17% as per the industrial application; this figure is comparatively better than that achieved in previous studies using tea solid waste, which had an efficiency of 90%, and Pomegranate peels extract, which had an efficiency of 96%. Consequently, the Fe^{+2} (ferrous ion) concentration is decreased in the corrosive solution;
- Electrochemical measurement shows that the presence of ESAW improves the mild steel surface with a noticeable increase in Rct with the ESAW and desorption of an intermediate species. Potentio-dynamic polarization tests demonstrate the effectiveness of ESAW, with an obvious decrease in the corrosion current densities. The tests show that the ESAW behaves as a mixed-type inhibitor;
- The obtained results from PDP and EIS measurements were in good agreement and both analyses are in favor of the increase in inhibition effectiveness of the ESAW with increasing concentration;
- The inhibition was due to the adhesion or adsorption of ESAW constituent on the mild steel surface without modifying the mechanism of corrosion; the adsorption follows the Langmuir isotherm model;
- The outcomes of the analytical methods are in good agreement with (±2%), demonstrating that the presence of ESAW inhibits mild steel corrosion in acidic conditions and slows the process of iron dissolution in these situations. Ultimately, this study proves that it is feasible to transform agro-industry wastes into sustainable inhibitors. Hence, this study proposes that there is ample scope for the application of eggshell as corrosion inhibitors in the oil and gas industry.

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