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RESEARCH ARTICLE

Eggshell waste extract as potential natural corrosion inhibitor for AISI 1020 steel in acidic environment

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ABSTRACT - Using natural corrosion inhibitors from calcium carbonate has gained attention in corrosion prevention approaches as it offers comparable and significant benefits compared to other corrosion inhibitors. Consequently, eggshells with a high amount of calcium carbonate were proposed as a corrosion inhibitor to evaluate the effect on the corrosion behaviour of AISI 1020 steel. In this study, the eggshell waste was extracted in ethanol solution using a Soxhlet extractor and thickened through the rotary evaporator to produce the proposed natural corrosion inhibitor with 10%, 20%, and 30%. The characteristics of the inhibitor were then examined and verified through FTIR and XRD analysis. The corrosion performance was then evaluated through the weight loss method in 1.0 molar hydrochloric acid in different durations, which are 7, 14, and 21 days. The corrosion rate and inhibiting efficiency were also performed to analyse the effect of eggshell concentration on the AISI 1020 steel. In addition, macrostructure observations were executed to assess the physical appearances of the samples. The results show that the proposed eggshell inhibitor successfully helped improve the inhibiting efficiency of AISI 1020 steel by 88.37%. Additionally, increasing the eggshell concentration decreases the corrosion rate and increases the inhibitor efficiency. This is due to $CaCO_3$ in eggshells, a barrier to metal surfaces. Results indicate that selecting eggshell as a natural corrosion inhibitor successfully and confirmably protected the surface. Thus, this study is a viable utilisation of sustainable use from eggshell waste in reducing the corrosion occurrence of AISI 1020 steel in an acidic environment.

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1. INTRODUCTION

Nowadays, the development of natural corrosion inhibitors as a corrosion prevention method is widely considered in the petroleum industry and construction [1 - 4]. Generally, corrosion inhibitors can be categorised as green organic and inorganic. Both categories were superior in preventing corrosion, but the result shows that green and natural corrosion inhibitors are more environmentally friendly, low cost, non-toxic, and harmless to humans [5 - 7]. Most of the green and organic corrosion inhibitors are from plants and minerals. Examples of this include plant extract [8 - 10], vegetable oil [11], calcium carbonate [12, 13], amino acid [14, 15], tannins [16], salicylic acid [17], and many more. Many green and natural organic compounds have been studied as potential natural corrosion inhibitors, such as Biebersteinia Mulfida [4], Bee Wax Propolis [18], Citrus Limonum Peels [19], Mikania Micrantha Extract [20], Equisetum Arvense Extract [21], Terminalia Arjuna Leaves Extract [22], Cabbage Extract [23], Tomato Pomace Extract [24], Tetradenia Riparia Leaves Aqueous Extract [25], Eucheuma Seaweed Algae [26], Daucus Carota L Essential Oil [27] and Fucus Spiralis Extract [28]. These organics are chosen because they are highly effective and pose no threat to humans and the environment [29]. At the same time, the inhibitor also needs to fulfil the important requirements of a good inhibitor, such as inhibiting the corrosion process, sustaining the barrier properties, and avoiding unnecessary interaction with the host matrix [30]. Therefore, calcium carbonate ($CaCO_3$) fulfilled these requirements and reduced the corrosion issues. The main advantages of $CaCO_3$ are cheap production, ease of management, and the capability to sense local acidification. According to previous work, the capacity of $CaCO_3$ to reduce corrosion and use it as a pH-sensitive additive in epoxy coating with different organic or inorganic corrosion inhibitors improves the corrosion resistance of coating formulation [31]. Roma Raj et al. [32] also demonstrated that $CaCO_3$ was loaded with triethanolamine and polyethyleneimine as corrosion inhibitors, which is why this addition of $CaCO_3$ did not damage the barrier properties of the coatings. Meanwhile, this inhibitor was also previously explored by Gandi et al. [33]for corrosion protection for aluminium alloys, and the result mentioned that $CaCO_3$ presented excellent protection in terms of corrosion rate.

Due to the presence of $CaCO_3$ in eggshells, it is selected as a natural corrosion inhibitor in this study, as $CaCO_3$ was found to have a positive impact on the properties of steel and iron [29], [34], as proven by past literature. Eggshells, which contained 95% to 97% of $CaCO_3$, were successfully used to improve steel's mechanical properties, thermal stability,

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biodegradability, and biocompatibility [12], [35]. From the previous study [36], eggshell has a good adsorptive property, including pore-structure, neutralizing agent to any aqueous solution, to bind heavy metal deposits on eggshell particles [35]. According to Abu Bakar et al.[34], the eggshell can be formed as a coating using electrophoretic deposition (EPD) on grey cast iron. In addition, a study by Jafar et al. [37] has shown that eggshells successfully protect mild steel and have the ability as a coating [37]. This also proved that eggshells served as an excellent inhibitor for Type 9045 stainless steel in chloride medium with a maximum inhibition efficiency value of 92.45% from the weight loss technique [38]. Technically, when eggshells are mixed with an acid solution, calcium carbonate is transformed into calcium oxide, carbon dioxide, and water. Furthermore, the extract is generous of minerals such as $CaCO_3$, calcium, crude fat, lysine, methionine, tryptophan, threonine, arginine, isoleucine, leucine, histidine, phenylalanine and valine water, and many more from animal and suitable as corrosion inhibitor [39]. However, there are limited studies on the effectiveness of $CaCO_3$ in eggshells on the corrosion behaviour of steel and cast iron [34, 37, 40]. Thus, this research investigated eggshells' inhibiting efficiency and corrosion rate as a natural corrosion inhibitor for AISI1020 steel in a 1.0 M hydrochloric acid (HCl) medium. Other than that, the abundance of eggshells, often considered waste, will introduce a potential usage of eggshells as natural corrosion inhibitors.

2. MATERIALS AND METHODS

2.1 Samples and Solution Preparation

The samples used in these studies are metal samples of AISI 1020 steel. The samples were first cut into pieces with dimensions of 50 mm (length) x 25 mm (width) x 4 mm (thickness). The chemical composition of the samples was then checked through an arc spark optical emission spectrometer machine. The results revealed that the metal acquired the composition (wt%) of 92.8 Iron, 0.316 Carbon, 0.168 Silicon, 0.56 Manganese, 0.022, Phosphorus, 0.012, Sulfur, 0.193 Chromium, 0.081 Nickel, 0.0228 Copper, which is in accordance the AISI 1020 steel standard chemical compositions. The experiment was then continued with the preparation of natural corrosion inhibitors. The natural corrosion inhibitor was prepared by collecting the waste eggshell. Then, the waste eggshell was washed with water, boiled for half an hour, and dried in direct sunlight and oven to remove the moisture and contamination. Next, the eggshell was fine-grained using a grinding machine with a speed of 36000 r.p.m until it became an eggshell powder. After that, the 100 grams of eggshell powder was then sieved through a vibrating sieve with an average of 45 µm until a fine eggshell powder was obtained. This sieve parameter enables the eggshell powder (shown in Figure 1) to be suitable with ethanol as a dispersion medium. It has the effect of absorbing the surface of the samples [34]. The eggshell powder was mixed with an ethanol solution (approximately 99% concentration) for 6 to 8 hours using a Soxhlet extractor, according to EPA Method 3540C standard [41], as shown in Figure 2. The solution then undergoes an evaporation process using a rotary vacuum evaporator at 200 bars and under 50 °C temperature to obtain the highly concentrated eggshell solution or extraction. Finally, the eggshell extracts varied at three different concentrations: 8g (10%), 16g (20%), and 24g (30%). This is to comply with the size of the thimble used in the Soxhlet extraction apparatus (maximum 30g).

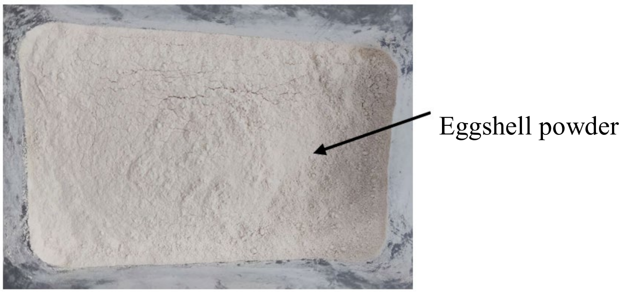

Figure 1. Eggshell powder produced using Vibratory Sieve Shaker Analysette 3 Pro

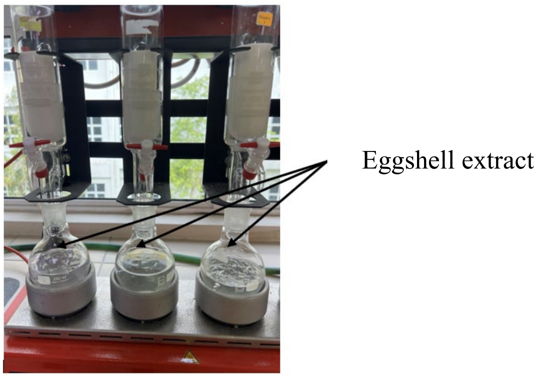

Figure 2. Soxhlet extraction set-up

2.2 Characterization of the Eggshell Powder

The eggshell extraction was characterized by two types of testing: X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) testing. The characteristics of the crystalline eggshell using XRD Bruker D8 Advance Series II and the range of 10 to 90 degrees with the temperature of 25 °C were studied to determine whether the eggshell contained $CaCO_3$. In this study, eggshell powder was placed in the sample holder using a spatula. Then, the powder was deposited on the slide and spread out to cover the entire surface. The data obtained from the XRD was compared with the catalogue from the Joint Committee on Powder Diffraction Standards (JCPDS) by the International Centre for Diffraction Data [42]database to determine the structural properties of the samples. For FTIR, a small amount of eggshell powder was placed into the sample holder, ensuring the sample was covered and aligned with the infrared spectroscopy source. FTIR was used to determine the band value and presence of heteroatoms, which is the main element required to prove the effectiveness of the natural corrosion inhibitor's inhibiting efficiency. In this study, the range 4000-400 cm^{-3} with a resolution of 4 cm^{-1} was used to analyse the main functional group using VERTEX 70 equipment.

2.3 Weight Loss Determination

Static weight loss was measured according to standard ASTM G1-03 [43]. This measurement determined the inhibitor efficiency and corrosion rate. To investigate the effect of eggshell corrosion inhibitors on the corrosion behaviors of AISI 1020 steel under an acidic environment, hydrochloric acid (HCl) was used as the immersion medium. The acidic solution used in this study was 1.0 M (molar) HCl. The acidic solution was placed inside a 100 ml beaker capacity. The corrosion rate was calculated by using the weight loss method. This study polished all samples with varying sandpaper grades: 240, 360, 600, 800, and 1200. After that process, the sample was rinsed, dried, and wiped with a small amount of acetone to eliminate other organic impurities. For the weight loss experiment, pre-weighted rectangular samples with 50 mm x 25 mm and a thickness of 4 mm dimensions, having a 10 mm hole, were immersed in 100 ml HCl solution for 7, 14, and 21 days with and without the presence of eggshell natural corrosion inhibitor extract. After the immersion, the samples were washed, dried, and reweighted. The corrosion rate (CR) and inhibition efficiency were then measured by obtaining the difference in the sample's weight before and after immersion using the Equations. (1) and (2), respectively.

$$CR = \frac{W_0 - W_t}{S.t} \tag{1}$$

$$\eta\ (\%) = \frac{CR_{inh,0} - CR_{inh}}{CR_{inh,0}} \times 100 \tag{2}$$

where, W_0 is the mass (in mg) before immersion and W_t is the mass (in mg) after immersion in corrosive solution. S is the AISI1020 surface area (in cm^2), t is the corrosion time in hours, CR_{inh} is the corrosion rate with inhibitors, and $CR_{inh,0}$ is the corrosion rate without inhibitors (in mm/y). All testing was conducted with a minimum of three successful attempts to obtain the average values of all the testing results.

2.4 Macrostructure Observations

The sample for macrostructure observation was first cut and ground to a surface roughness of 1200 µm. Then, the samples were polished with DIAMAT polycrystalline diamond until a mirror-like surface was obtained. This was to ensure that all samples inhibited the same surface roughness and that the corrosion mechanism was not affected by the surface roughness of the samples. The macrostructure of AISI 1020 steel before and after immersion in the 1.0 M HCl solutions with and without eggshell extract was observed. After 7, 14, and 21 days of immersion, AISI 1020 steel was scrubbed with absorbent cotton with acetone. The surface corrosion products were rinsed off with distilled water and dried using an oven at 30°C or a hand dryer. The macrostructure image was taken using macro mode iPhone 13 Pro Max 12MP Ultrawide Camera at an overall image of the samples.

3. RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectroscopy

FTIR spectra of eggshell powder detect hetero atoms and functional groups of inhibitor molecules on the metal surface. The information on spectra characteristics is shown in Table 1. Figure 3 shows the composite extraction of eggshell extract for 8g, 16g, and 24g had a broad band at 3230 to 3500 cm^{-1}, clearly indicated as O-H stretching. This band may be assigned to the presence of the alcohol hydroxyl group [13]. The extraction was assigned to the C-H stretching group at 2968 cm^{-1} [44]. Meanwhile, bands at 1411 cm^{-1} nearly indicated a stretching carbonate group strongly associated with carbonate within the eggshell powder. This result is also observable –the C=O bending group at 875 $cm^{-1,}$ which is in and out of plane deformation, confirms the presence of a carbonate group. This result confirmed the existence of hetero atoms, sulfur, phosphorus, and oxygen in $CaCO_3$ [29], one of the most crucial elements in natural corrosion inhibitors. The presence of hetero atom in the eggshell extract was expected to facilitate the adsorption energy of the inhibitor onto the surface, thus protecting the AISI 1020 steel surface from corrosion [40].

Table 1. Information of functional groups in eggshell

Wavelength Band (cm^{-1})	Possible Functional Group
875	–C=O inorganic carbonate
1411	Stretching carbonate group
2968	C-H stretching
3230 to 3500	O-H stretching

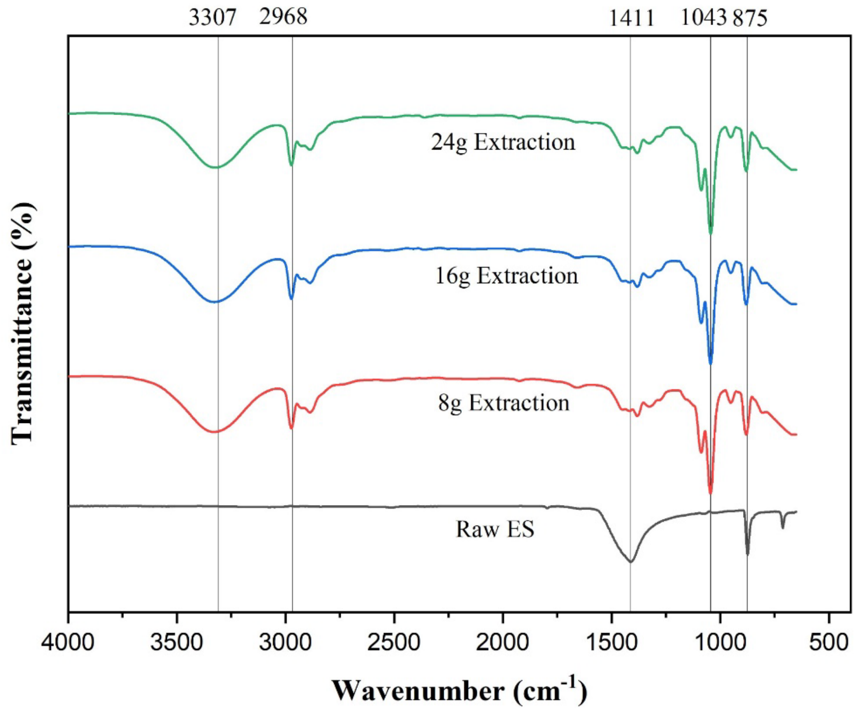

Figure 3. FTIR spectrum of eggshell extract

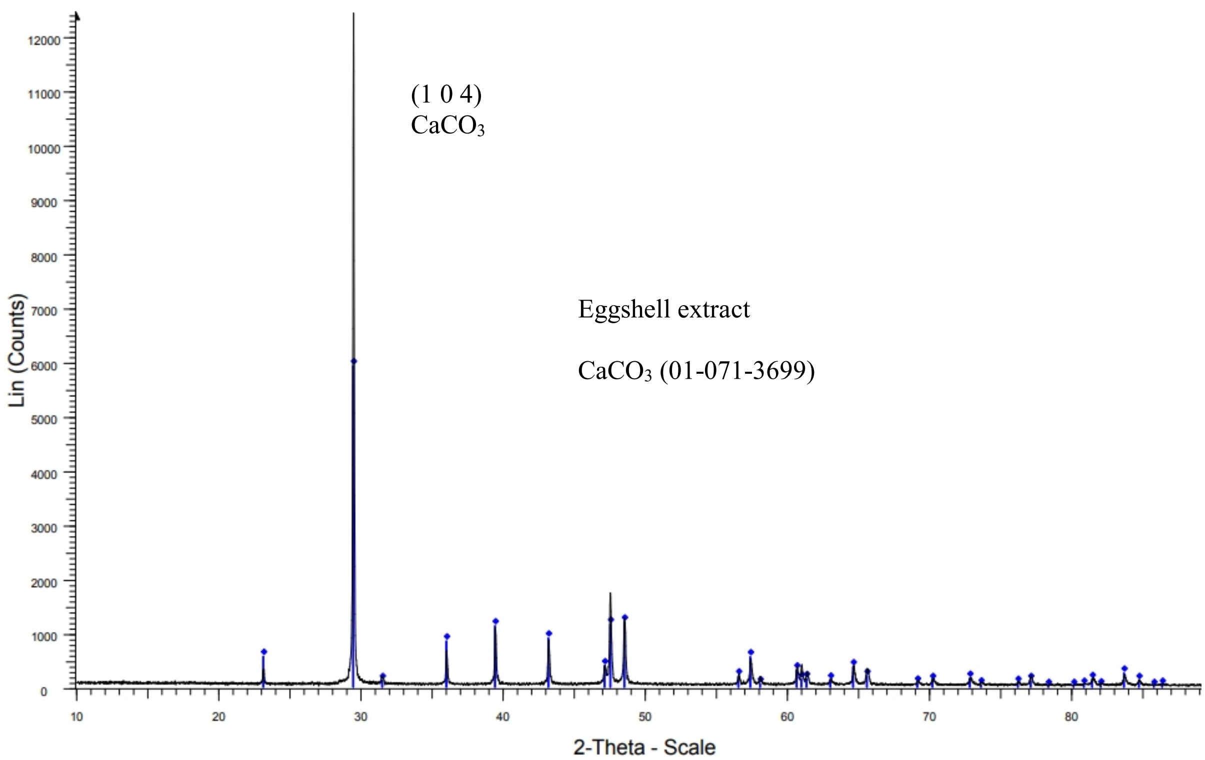

Figure 4. XRD pattern of the eggshell extract

3.2 X-ray Diffraction Results

The XRD pattern of the eggshell powder is shown in Figure 4. From the result, the distinctive characteristics of the crystalline mineral of calcium carbonate matched with the Joint Committee on Powder Diffraction Standards (JCPDS) by the International Centre for Diffraction Data database: pattern number is 01-071-3699 [42]. This crystalline mineral is present in calcium carbonate, an essential element for preventing corrosion in metal. It was shown that the major peak at 2θ was observed at 29.5° with hkl miller indices of 104, indicating that the calcite is a major phase of the eggshell [45]. The other diffraction peaks of calcium carbonate are at 23.0°, 35.9°, 39.3°, 43.5° and 48.5°. The XRD lines are intercepted among theoretical and experimental values. Thus, the eggshells exhibited a high amount of calcium carbonate [34]. According to the study by Raj et al. [46], elements such as calcium carbonate will modify the electrochemistry of the steel surface and help reinforce the oxidation passive film, thus protecting the surface from corrosion. This is because the calcium carbonate will react with ferrous ions in the local acid media formed at the anodic site, and the subsequent release of corrosion inhibitors will form a protective film on the steel surface [46].

3.3 Corrosion Rate and Inhibitor Efficiency Result

The weight loss method was used to compare the concentrations of eggshells (8g, 16g, and 24g) with different immersion times (7 days, 14 days, and 21 days). Table 2 shows the results of corrosion rate and percentage of inhibition efficiency for AISI 1020 steel in 1.0 M HCl solution with specific eggshell concentrations at 7, 14, and 21 days. Figure 5 shows the corrosion rate of all samples versus eggshell concentration. The sample with 0% eggshell suffered the most corrosion damage compared to samples with eggshell corrosion inhibitors with a corrosion rate of 0.27611 mm/y in 7 days. Adding 8 grams of eggshell with an average of 0.07705 mm/y corrosion rate reduced the corrosion rate by over 70% compared to a 0% eggshell sample. The corrosion rate was further decreased with the increment in eggshell concentration up to 24 grams.

Table 2. Corrosion rate and inhibitor efficiency at several concentrations

Concentration	Corrosion Rate (mm/y)	Inhibitor Efficiency (%)	Corrosion Rate (mm/y)	Inhibitor Efficiency (%)	Corrosion Rate (mm/y)	Inhibitor Efficiency (%)
	7 Days	7 Days	14 Days	14 Days	21 Days	21 Days
Raw	0.27611	0	0.37885	0	0.41123	0
8 grams	0.07705	72.09	0.15128	60.07	0.16985	58.70
16 grams	0.05522	80.00	0.09795	74.14	0.11352	72.39
24 grams	0.03211	88.37	0.07834	79.32	0.09175	77.67

A similar trend was observed in samples that were immersed for 14 days, as the 0% eggshell sample experienced tremendous corrosion damage with a corrosion rate of 0.37885 mm/y compared to other types of samples. This is followed by adding 8 grams of eggshell at an average of 0.15128 mm/y, 16 grams at an average of 0.09795 mm/y, and 24 grams at an average of 0.07834 mm/y of corrosion rate. It was observed at 21 days that 0% of eggshells were highly in corrosion damage (0.41123 mm/y) compared to the other days. When adding 8 grams of concentration, the corrosion rate decreased to 0.16985 mm/y, followed by 16 grams of 0.11352 mm/y, and continued decreasing at 24 grams with a corrosion rate of 0.09175 mm/y. It was concluded that longer immersion times resulted in a higher corrosion rate. This matter confirms that corrosion damage has been caused by the active anion HCl on the metal surface of the control sample due to the unavailability of eggshell extract.

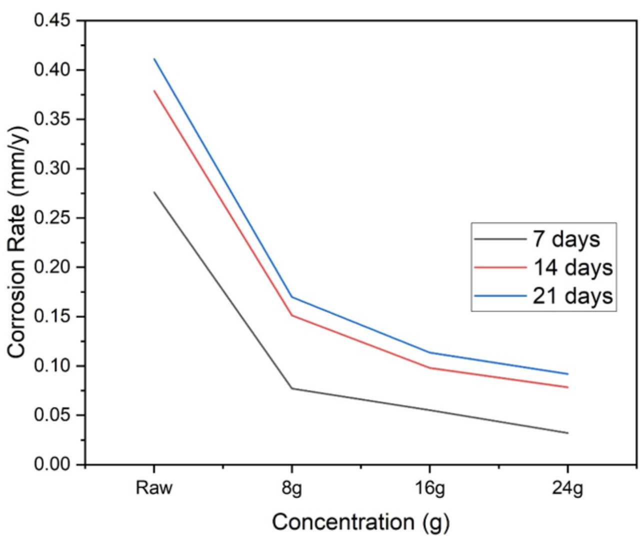

Figure 5. Corrosion rate against difference concentration

Figure 6 shows the inhibiting efficiency of the samples concerning different eggshell concentrations. In contrast to the corrosion rate, the inhibition efficiencies increased with the eggshell concentration. The maximum eggshell concentration of 88.37% and the lowest corrosion rate of an average of 0.03211 mm/y were achieved at 7 days. For 14 days, inhibition efficiency was achieved with the highest eggshell concentration at 79.32%, corresponding to the lowest corrosion rate of 0.07834 mm/y of average value. Meanwhile, at 21 days, inhibition efficiency was slightly reduced by 77.67% at 24 grams of concentration compared to 7 and 14 days. This result showed that increasing the immersion time also increased the inhibiting efficiency of the AISI 1020 steel. The surface was exposed to more hydroxyl cation (OH+) elements. This shows strong inhibitory adsorption of eggshell in a 1.0 M HCl solution for 7, 14, and 21 days. Meanwhile, the higher amount of $CaCO_3$ helps develop the surface's barrier properties [32]. Kamaruzzaman et al. [47] found that the effect of $CaCO_3$ in mild steel influences the corrosion rate at 7.99×10^{10} $mgcm^{-2}s^{-1}$ and maximum inhibition efficiency at 99.27% [47]. This has proven that $CaCO_3$ in eggshell waste was an important element in reducing corrosion occurrence [40].

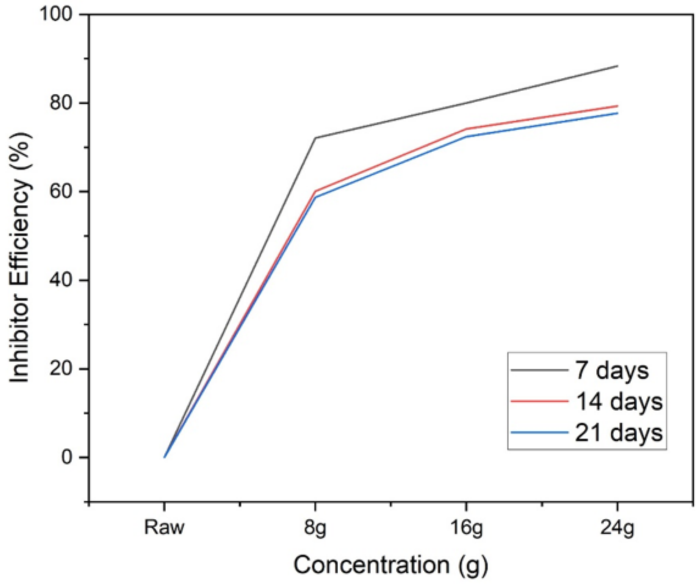

Figure 6. Inhibitor efficiency against difference concentration

In comparison, a study by P. Du et al. [20] reveal that the immersion times play an important role in determining the effectiveness of the corrosion inhibiting efficiency. In their study, cold rolled steel was immersed in an acidic environment with immersion times of up to two days. It was found that there is a uniform and dense saturated adsorption layer that will be formed on the steel surface with immersion times of 48 hours or two days. When the samples were immersed for more than two days, the effectiveness of the inhibiting efficiency increased to 93.6% compared to only 80% when immersed on the first day of immersion. It was also found that the extraction concentration also affects the samples' inhibiting efficiency and corrosion resistance. This is because the adsorption of the inhibitor molecules at the interface between the ferrous metal and the solution was increased to increment the extract concentration. It can be said that both the inhibitor extraction concentration and the immersion times largely influenced the effectiveness of the natural corrosion inhibitor inhibiting efficiency and, thus, the ability of the corrosion inhibitor to protect the surface from corrosion attack.

3.4 Macrostructure Results

Figure 7 shows the macrostructure of AISI 1020 steel concerning different corrosion inhibitor concentrations immersed in an HCl solution. AISI 1020 steel exposed in an acidic environment was observed to have severe chipping and spalling with a dark grey color. At the end of 7, 14, and 21 days, all the samples show uniformly formed corrosion at the surface. The appearance of corrosion is more severe when there are longer immersion times and less concentration of corrosion inhibitors, and the observations are comparable to those of previous studies [48]. Overall, regarding the eggshell concentration increment, the samples turned to dark grey, and the shine changed to light grey and silver, indicating less corrosion occurrence and better surface protection, especially in 7-day samples. When the concentration increased to 16g and 24g at 14 and 21 days immersion time, the sample converted to yellow and then had a dark brown as a particle on the surface of the AISI1020 steel. Yee et al.[49] stated in their study that corrosion severity might be due to a thick oxide film that breaks off and exposes the underlying metal. After the immersion, the sample exhibited a rough surface with irregularly shaped pits because the density of these pits grew with longer immersion times [49]. This result concludes that the corrosion substrate was more visible after 21 days of immersion, followed by 14 and 7-day samples.

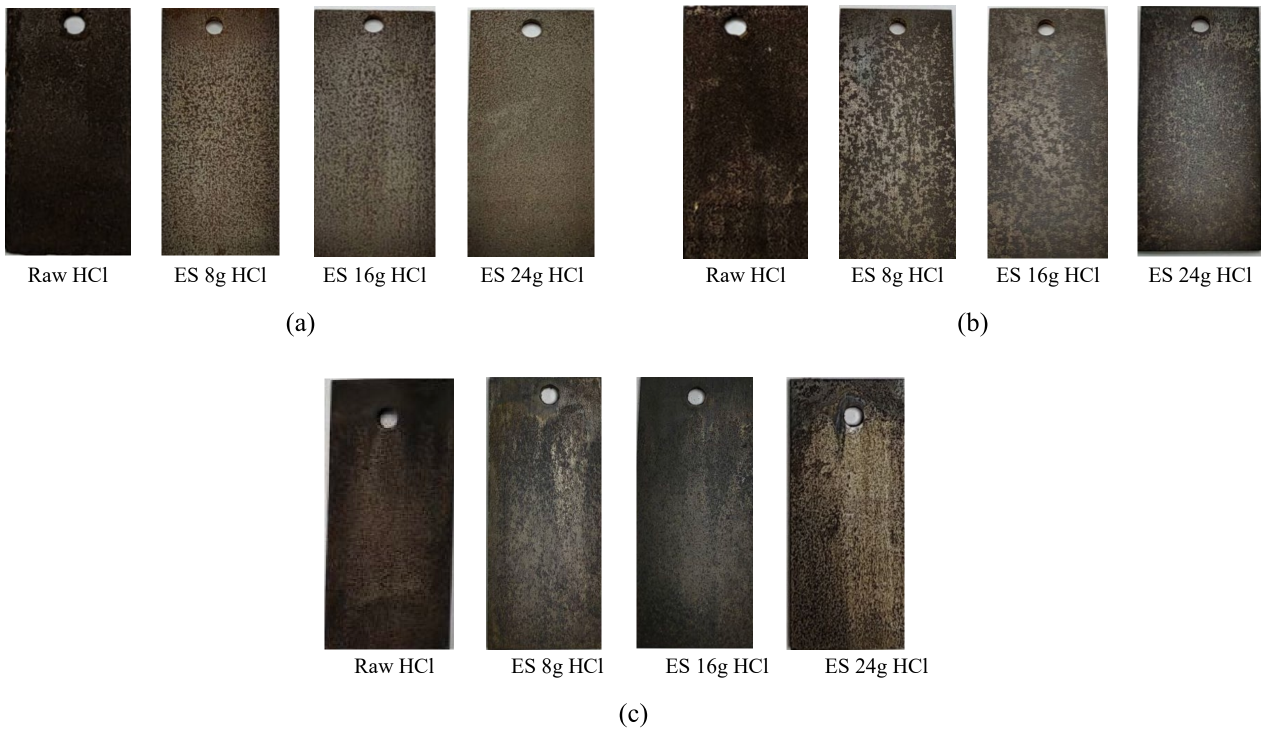

Figure 7. Macrostructure of AISI1020 steel at different concentrations in HCL solution: (a) 7 days, (b) 14 days and (c) 21 days

4. CONCLUSIONS

The current study strives to explore eggshell extract as a sustainable and potential natural corrosion inhibitor for AISI 1020 steel in an acid environment. The presence of an inhibitor was confirmed with FTIR and XRD, respectively. Each analysis shows eggshell powder contains high calcium carbonate content, crucial for reducing metal corrosion. A corrosion test of AISI1020 steel in 1.0 M HCl with varying concentrations of 7, 14, and 21 days found that higher eggshell concentration significantly reduced corrosion rates with the maximum concentration at 24 grams. Additionally, the longer immersion times increased the corrosion rates and improved the inhibition efficiency due to prolonged exposure to protect the surface of AISI1020 steel. Furthermore, macrostructural observation indicates severe corrosion with dark grey chipping and spalling under the lowest concentration and extended immersion but contradicts with higher concentration. The higher concentration obtains less corrosion and better surface protection. In conclusion, these results demonstrate the potential of eggshell waste as an eco-friendly, low-cost, harmless to humans, and efficient corrosion inhibitor for AISI 1020 steel in an HCl acid medium.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

AUTHORS CONTRIBUTION

H. F. Pahroraji (Conceptualisation; Formal analysis; Writing-original draft)
S. K. Alias (Methodology; Validation; Supervision)
M. M. Ali (Data curation; Investigation)
M. A. M Shah (Writing – review & editing)
B. Abdullah (Resources)
H. M. Hairi (Validation; Funding acquisition)

AVAILABILITY OF DATA AND MATERIALS

The data supporting this study's findings are available on request from the corresponding author.

ETHICS STATEMENT

Not applicable

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