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Corrosion Protection Effectiveness and Adsorption Performance of Whey Inhibitor with Cocoa for Mild Steel in Hydrochloric Acid Environment

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A weight loss technique was used to stabilize whey protein (97%) with a small percentage of cocoa (3%) and bond it to a mild steel surface in hydrochloric acid at temperatures ranging from 303 K to 333 K. Results of analyzing whey inhibitor's effectiveness showed the highest percentage (90%) at a temperature ranging from 30 ºC to 60 ºC and an amount of 15 grams, leading to outstanding corrosion resistance properties. The efficiency of the inhibitor increased with increasing concentration but decreased with increasing temperature. To evaluate corrosion areas, samples were subjected to cross-section analysis before and after adding the inhibitor. The contact angle test conducted on steel alloys indicated that the angle decreases with increasing inhibitor concentration. Adhesion of the samples was also examined after adding the inhibitor. Results showed that the best area removal was 11.692%. When examining the inhibitor using FTIR spectroscopy, the whey protein with cocoa showed a great efficiency. Thus, whey inhibitor can be used as a corrosion inhibitor for mild steel alloys immersed in acidic conditions.

Keywords: *Corrosion inhibition, Whey Protein, Weight loss, Mild steel*

1. Introduction

Corrosion is a significant challenge for industries today, with costs comparable to those of natural disasters. It is crucial for industrial designs to consider the impact of corrosion on equipment lifespan, as failure to do so can lead to substantial financial losses. Corrosion occurs when metals interact with their environment, causing detrimental effects on their properties [1]. The treatment of corrosion is important for economic and safety reasons. Direct losses include expenses related to replacing corroded structures, while indirect losses encompass decreased efficiency, product and environmental contamination, business interruption, and other economic factors [2]. These factors provide strong incentives for corrosion research. Carbon steel is widely used in various industries due to its availability, favorable physical and chemical properties, and cost-effectiveness [3]. Mild steel finds applications in sectors such as chemical processing, piping, automotive components, and food can production. On the other hand, mild steel, with its exceptional strength, toughness, and malleability, holds great value in many applications [4]. It exhibits remarkable resistance to stress corrosion cracking, making it suitable for high-temperature or corrosive acidic environments. Heterocyclic organic compounds like HCL and H_2SO_4 act as corrosion inhibitors by forming a protective barrier layer on the metal surface, a process known as passivation [5,6]. Corrosion inhibitors play a vital role in reducing the corrosion rate and protecting metals from degradation by creating a shielding layer that isolates the metal from its surroundings [7]. They can be classified as organic or inorganic coatings based on their chemical nature [8]. The inhibition mechanism involves strong interactions such as orbital adsorption, chemisorption, and hydrostatic adsorption, leading to the formation of a protective layer that hinders the access of corrosive materials to the metal surface [9]. The effectiveness of an organic inhibitor in inhibiting corrosion depends on its adsorption capacity and the structural, mechanical, and chemical properties of the adsorbed layer formed in the specific environment [10]. Heterocyclic organic molecules with coordination sites, especially those containing heteroatoms like S, N, O, and pi electrons, can act as corrosion inhibitors in mild steel [11]. In a study, 97% whey protein with a trace amount of 3% cocoa was used as a corrosion inhibitor.

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Although not traditionally recognized as corrosion inhibitors, whey protein and cocoa may possess inhibitive properties in acidic environments. Proteins have the ability to create protective layers on metal surfaces, which can impede corrosive reactions. Cocoa may contain polyphenolic compounds that contribute to inhibition by adhering to the metal. However, the effectiveness of these substances depends on various factors, and it is crucial to conduct thorough testing to assess their potential for corrosion inhibition under specific conditions. Professional studies and experimental data would provide more precise insights into how well they perform as inhibitors in acidic corrosion environments [12,13]. Amino acids have been acknowledged for their ability to control harmful reactions in various metals when exposed to acidic conditions. Fourier transform infrared spectroscopy (FTIR) was employed to determine the protein, and the inhibitory effect of whey protein as a corrosion inhibitor for low carbon steel in hydrochloric acid solution (1 M concentration) was evaluated using weight loss techniques [14].The primary goal of this research is to leverage regionally accessible natural materials and convert them into nanoparticles for the purpose of studying their efficacy as corrosion inhibitors on mild steel. The investigation will center on evaluating the impact of these nanoparticles on corrosion rates, employing weight loss and polarization techniques across a spectrum of temperatures (30, 40, 50, and 60 ºC) and concentrations (10, 15, and 20 g) of the inhibitors. The materials subjected to scrutiny in this study encompass mild steels sheet metal. The scope of experimentation will be delineated by three primary variables: temperature, types of inhibitors, and concentrations. Initial trials will be conducted in corrosive water devoid of any inhibitors, encapsulating all pertinent variables. The overarching objective is to discern and meticulously analyze the nuanced influence of temperature, inhibitor types, and their concentrations on the corrosion rates exhibited by the steel samples.

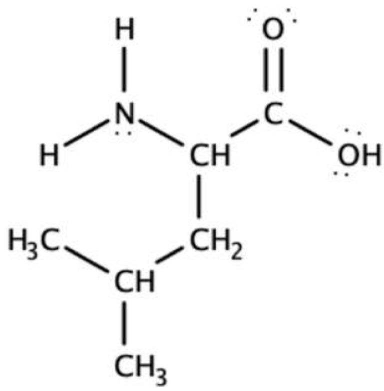


Fig. 1. Partial formula of whey protein

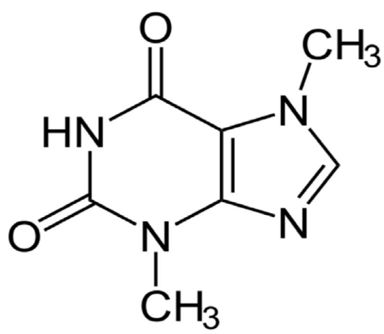


Fig. 2. Partial formula of cocoa

2. Experimental Methods

2.1 Sample preparation

The initial step in the experimental phase is sample preparation, involving the use of carbon steel sheets measuring (2 × 4) cm. At Al Nabaa Engineering Services Company in Iraq, optical emission spectroscopy (OES) was employed to assess the materials for weight loss procedures. Table 1 presents the chemical composition of the mild steel obtained.

2.2 Weight loss

The weight loss method was used for gravimetric measurements. The investigated mild steel tools were placed in reaction bottles in the presence and absence of different inhibitor concentrations in 1M hydrochloric acid solution. The sample was weighed before it was immersed in the solution using a high-precision four-decimal digital scale, and then the solid (2 × 4) cm was suspended with a small hole of 3 mm in diameter. Immersion in a corrosive environment for extended periods of time (from 2 to 24

Table 1. Chemical Composition of mild steel (wt%)

elements	Percent
Fe	99.6%
C	0.114%
Other elements	0.0277%

hours). Experiments were carried out at different temperatures (30, 40, 50, and 60 ºC). The concentrations of the inhibitors used were (10 g, 15 g, and 20 g). The mineral sample is weighed again after cleaning the samples with acetone and distilled water, then drying them, removing the corrosion medium, and removing all corrosion products. The weight loss process was calculated by the equation (1) [17]:

$$MPY = \frac{87.6 \times W}{Pat} \quad (1)$$

Where: (mpy) is a mill per year, (W) is a weight loss (gm), d is the Density (gm/cm^3), A is the surface area (cm^2), t is the time (hr)

3. Result

3.1 Weight loss measurements

Fig. 3 shows the corrosion rates and inhibition efficiencies observed in mild steel. These measurements were performed in a 1 M HCl solution without any inhibitor present. Our findings indicate significant wear on metal surfaces across different temperatures and immersion periods [15,16]. In Fig. 4, the effect of adding

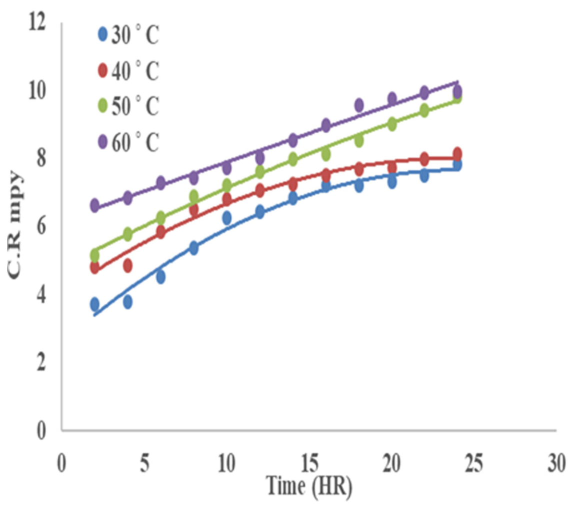


Fig. 3. The relationship between corrosion rate and time before adding the inhibitor

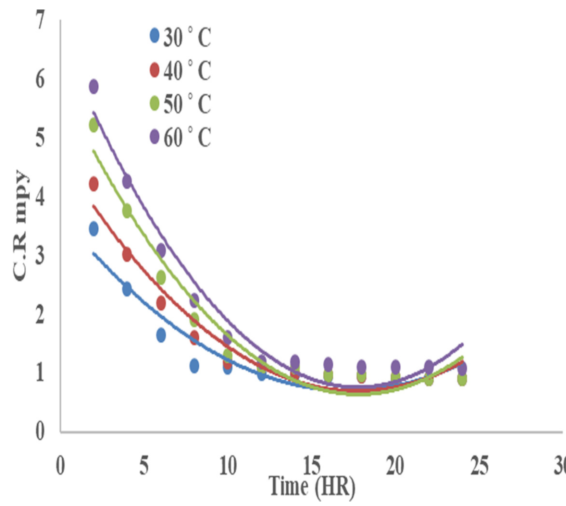


Fig. 4. The relationship between corrosion rate and time after adding the inhibitor 10 g

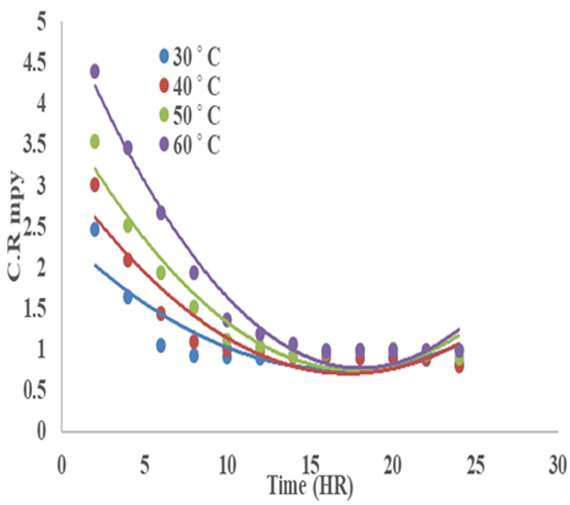


Fig. 5. The relationship between corrosion rate and time after adding the inhibitor 15 g

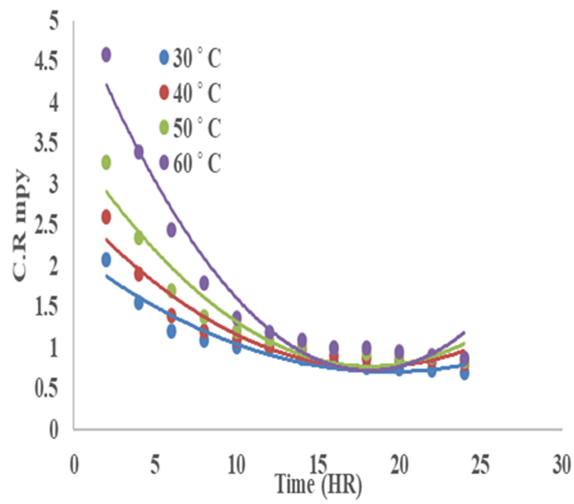


Fig. 6. The relationship between corrosion rate and time after adding the inhibitor 20 g

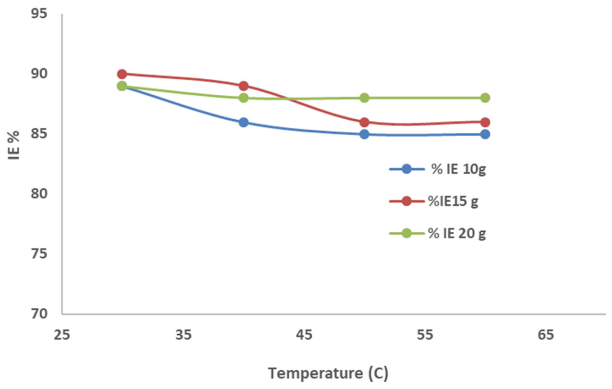


Fig. 7. Relation between temperatures and IE % for mild steel

10 g of inhibitor concentration to the alloy is shown. These graphical representations reveal the effect of the inhibitor under different conditions. Furthermore, Fig. 5 and Fig. 6 display significant reductions in corrosion rates and simultaneous improvements in protection efficiency when introducing a concentration of 15 and 20 g of inhibitor respectively under equivalent changes in temperature and duration [17,18]. To expand on these weight loss measurements, we performed an in-depth analysis of wear rate and inhibition efficiency data. The following subsections provide a detailed examination of the results obtained for mild steel under different experimental conditions.

Upon evaluating each concentration in relation to the observed inhibition strength, it is discerned that the protective efficacy diminishes with the temperature escalation within the range of 303 to 333 K. The elevation in temperature facilitates the heightened adsorption of inhibitor molecules onto the steel substrate, thereby forestalling the development of resistance through the adsorption of the inhibitor on the surface, as elucidated in previous research [19] Fig. 5 the intricate interplay among temperature, corrosion rate for mild steel, adding inhibitory activity in a 1 M HCL solution, encompassing temperatures ranging from 303 to 333 K, both in the with and without adding the inhibitor, the efficacy of the inhibitor experiences a decrement with the rise in temperature. The outcomes reveal that the optimal efficiency reached 87% at a concentration of 10 grams at a temperature of 30 ℃ for mild steel. Furthermore, the addition of 15 grams at the same temperature resulted in an increased efficiency of the inhibitor to 90%. At a concentration of 20 grams, also at the same temperature, the efficiency further elevated to 87%., an increase in the concentration of the inhibitor leads to an increase in the efficiency.

4. Discussion

4.1 Analysis using contact angle

Demonstrates that the hydrophobic/hydrophilic properties of steel surface in the absence and presence of inhibitor. The contact angle increased first and then decreased with the increase of whey protein inhibitor concentration, reaching the maximum of (108.651) without inhibitor concentration and while adding a concentration is 10 g reaching the maximum of (90), the concentration is 15 g reaching the maximum of (68.735) and at 20 g reaching the maximum of (59.585) as shown in Fig. 8. This indicates that the hydrophobicity of the metal surface first increased and then decreased with the increase in concentration of inhibitor, the BCAA molecules that have formed metal coordination compounds with iron ions continue to oxidative addition reaction with HCL. The product has a weaker adsorption capacity on the metal surface than the substance before the oxidative addition, resulting in desorption. The exposed metal surface is more hydrophilic. Therefore, the concentration of whey protein continues to increase and the hydrophobicity of the metal surface decreases [21,22]. The adhesion force between the water molecule and corrosion inhibitor molecule on the metal surface is less than the cohesive forces of water molecules themselves, and water molecules cannot spread on the surface at which the inhibitor is adsorbed [23-26]. The adsorption of corrosion inhibitors on the metal surface improves the solid-liquid interfacial tension. Thus, the spreading coefficient is reduced which makes the spreading of water on the metal surface with adsorbed inhibitor relatively difficult. Thus, the hydrophobicity of the metal surface is enhanced. Whey protein coordinates with iron ions and absorbs instead of Cl, H^+, of the metal. The hydrophilic corrosive ions are difficult to absorb on the film of polymer, thus, The higher contact angle is, the better hydrophobicity is, thus enhance the corrosion inhibition.

4.2 Optical microscopic analysis

In an effort to understand the effect of whey protein inhibitors with cocoa on the surface properties of mild

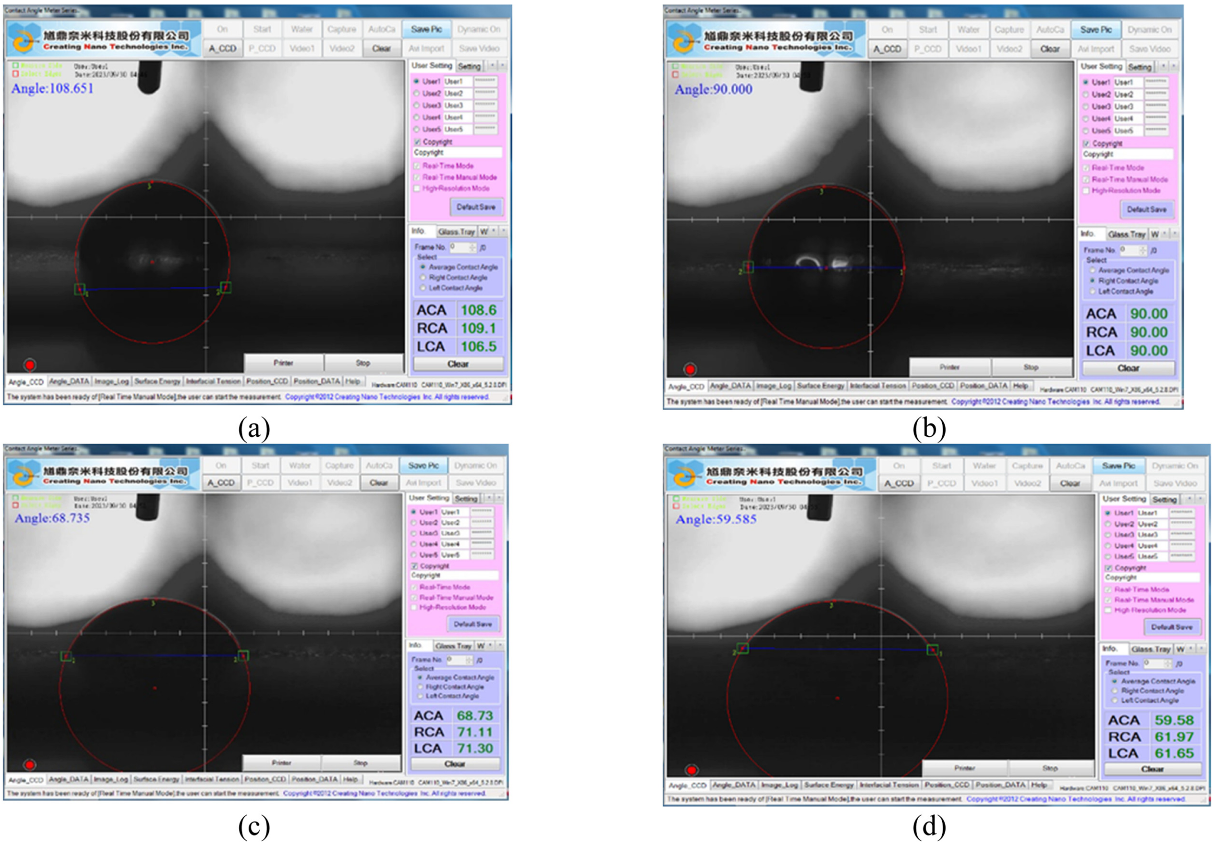


Fig. 8. Examination of contact angle, (a): Before adding inhibitor (b, c, d): After adding inhibitor

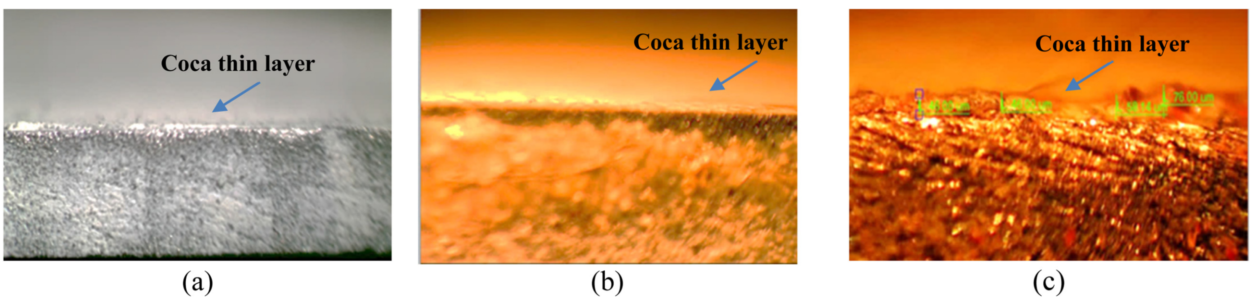
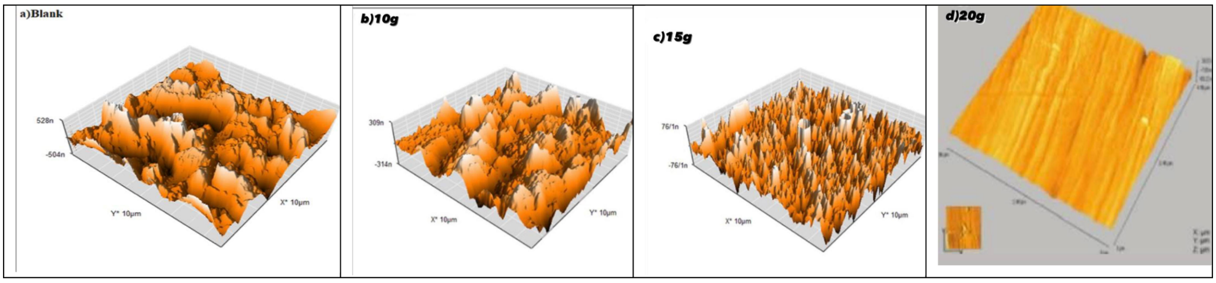


Fig. 9. Examination of microscope for (a, b, c, and d): mild steel

steel, cross-sectional analyzes were performed using a microscope. The primary goal was to reveal the protective layers that appear on metal surfaces after incorporating whey and cocoa protein inhibitors. Optical microscopic examinations allowed detailed exploration of changes in microstructure and formation of protective layers, highlighting the complex interaction between inhibitors and steel substrates. The findings from these analyzes greatly enhance our understanding of the effectiveness of inhibitors as protective agents in mitigating corrosion processes on these steel substrates. Dark areas indicate corrosion attacks on the sample under different environmental conditions. In an effort to understand the effect of whey protein inhibitors on the surface properties of mild steel, cross-sectional analyzes were performed using scanning microscopy. The primary goal was to reveal the protective layers that appear on metal surfaces after incorporation of inhibitors. Microscopic examinations allowed detailed exploration of microstructural changes and formation of protective layers, highlighting the complex

Table 2. Data of roughness analysis

Inhibitor	Ra (μm)
Blank	2.682
10 g	1.186
15 g	0.969
20 g	0.419



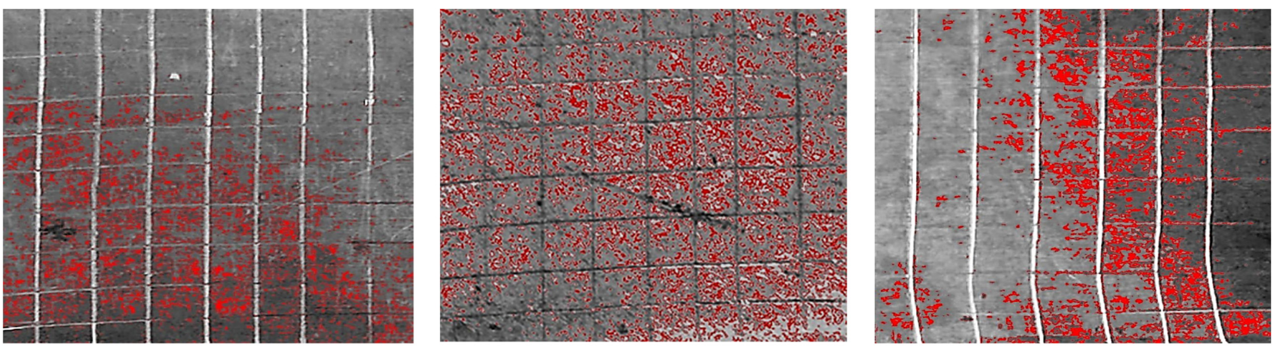
interaction between inhibitors and steel substrates. The findings from these analyzes significantly enhance our understanding of the effectiveness of the inhibitors Whey Protein 97% and Cocoa 3% as preventive agents in mitigating corrosion processes on these steel substrates. Dark areas indicate corrosion attacks on the sample under different environmental conditions.

4.3 Analysis using roughness

In the analysis of metal surface roughness during the experiment, four different samples were examined, each representing a different treatment condition. The results obtained consistently showed a reduction in surface roughness (Ra) as the quantity of inhibitor increased. The initial untreated sample had a surface roughness of 2.682 μm. However, when 10 grams of inhibitor was introduced, a noticeable decrease in roughness to 1.186 μm was observed. Subsequently, the samples treated with 15 grams and 20 grams of inhibitor exhibited further reductions in roughness, measuring 0.969 μm and 0.419 μm, respectively. The decreasing trend in surface roughness with increasing inhibitor quantities suggests a potential relationship between inhibitor concentration and the resulting surface quality. These findings indicate a promising opportunity to utilize inhibitors for improving the surface properties of metals, which can be beneficial in various applications where surface roughness is a critical factor.

4.4 Analysis using adhesion

To evaluate the quality of the bond between the protective layers and the mild steel substrate, we performed adhesion tape tests. After adding the inhibitor, we examined optical images of the different protective



(a) (b) (c)

Fig. 10. Examination of adhesion after adding inhibitor at a: 10 g, b: 15 g, c: 20 g

layers after adhesion tests. Fig. 10 shows these images, calculating the percentage of area removed from the protective layer on a 2 mm scale. The results showed that the delamination area ratio of the samples was (14.312%, 13.779%, and 11.692%) for the damping ratios of 10%, 15%, and 20%, respectively. Based on these results, it was found that the minimum layer removal area was 11.692%. This indicates strong adhesion and bonding between the protective layers and the metal substrate. Qualitative Tape Test for measure adhesion for the cross-hatch test area and removed quickly by pulling the tape back off of the test area to reveal the amount of coating lifted off as show the step of tape adhesion test then the removable area was calculated by Image J program.

5. Conclusion

Based on the findings derived from the experiments, the following conclusions can be established:

1. Optimal inhibition efficiency was observed in in the weight loss method (90%) when employing a whey-based inhibitor at a concentration of (15 g) at a temperature of 30 ºC.
2. Elevated temperatures, both in the presence and absence of corrosion inhibitors, correlated with escalated corrosion rates.
3. The inhibition mechanism predominantly involves adsorption on the metal surface, characterizing the whey inhibitor as a mixed type.
4. Overall, there is a discernible reduction in inhibition efficiency as the temperature of the corroded solution escalates.
5. The experimental outcomes unequivocally demonstrate the efficacy of whey as a corrosion inhibitor for mild steel in solution environments.

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