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An evaluation of wood ashes as an eco-friendly environmentally corrosion inhibitor for low carbon steel in acidic solution at different temperatures

ABSTRACT

Corrosion is an unavoidable fact in everyday life but always receive attention to control due to its technical, economical, and esthetical importance. Carbon steel (CS) is the most commonly used material for equipment and pipes in the oil production processes. However, presence of water/salts and carbon dioxide, among other gases, in the oil is a serious problem due to increased corrosion rate of the material. The most common way of mitigating this problem is by using corrosion inhibitors. However, many common corrosion inhibitors that are in use today are health hazards. Corrosion inhibitors are one of the most widely used and economically viable methods protect-ing metals and alloys against corrosion. In this work the inhibitory effect of wood ash (olive and palm) on mild carbon steel was studied in a solution of 0.00001 M or pH around 5 of hydrochloric acid. The corrosion rate and inhibitor efficiency were calculated by conducting the inhibition efficiency test for 10% aqueous wood ash solutions for both (olive and palm) using (weight loss method). The effect of temperature on the corrosion behavior of mild carbon steel was studied at 0.00001 M and pH = 5 hydrochloride with the addition of 10% aqueous wood ash solutions (olive and palm) in the temperature range 25-50 degrees Celsius. An inhibition efficiency of up to 54.16 % for Palm Ash Solution and 48.18 % for Olive Ash Solution can be obtained.

The interaction between the corrosion rate of mild steel and the inhibitor is affected by temperature and the protection mechanism of wood ash solution is more efficient at higher temperatures. This is due to corrosion of the metal or damage that occurs on its surface due to high temperatures. It occurs at non-adsorbed sites of inhibitory elements. As for the adsorbed sites, the interaction between the active substance of the inhibitor and the surface occurs gradually with increasing temperatures, which leads to an increase in the efficiency of the inhibitor.

Keywords: Corrosion inhibitors; carbon steel; palm ash; olive ash; hydrochloric acid; inhibition efficiency

1. INTRODUCTION

Currently, steel alloys, including mild steel, are used extensively in various industrial applications due to their remarkable mechanical qualities. Unwanted steel corrosion is brought on by the aqueous acidic fluids used in many industrial processes, such as descaling, pickling, cleaning, and oil acidification [1–3]. Money and material waste are caused by corrosion, one of the main issues facing industries. When it comes to preventing steel corrosion, using inhibitors is the most effective preventative strategy [4,5]. Generally speaking, the coordination bonds formed by the inhibitor molecules' free lone electron pairs with the unoccupied orbitals of steel ions allow them to form an adequate inhibitive film against the attacks of hostile molecules [6,7].

Therefore, a barrier between corrosive media and the active portions of the steel surface could be created by the adsorption of inhibitor molecules. The high toxicity level of synthetic and chrome-based inhibitors makes them environmentally unacceptable despite their great protective capability, as they have ineffective negative impacts on human health and the environment [8–10]. Due to their low cost and less toxic nature, green inhibitors have been used in various applications in recent years, and extensive research has been done in this area [11]. Plant leaf extracts, fruit peels, seeds, and fruit shells are potent, affordable, renewable, and biocompatible sources of green inhibitors that can significantly reduce metal corrosion [12,13].

The breakdown of a metal as a result of its contact with its environment is known as corrosion [14]. Metal corrosion occurs as a result of its interaction with specific elements in the environment, resulting in the deterioration of metal's characteristics. This is a natural and

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unavoidable process [15]. Metal corrosion has several negative effects on human society's progress [16]. Alloys and metals, in particular, had shown a significant proclivity to corrode in the presence of acid. Certainly, metals are vulnerable to corrosion in acid solutions because the acid can target the metal's surface, dissolving it into its ions [17]. In addition, weldments also corrode in the presence of degrading environments [18,19].

Corrosion inhibition is one of the strategies used to reduce the impact of corrosion. In general, corrosion inhibition is one of the strategies used to reduce the impact of corrosion. In general, corrosion inhibitors are divided into two types: inorganic and organic [20]. Organic corrosion inhibitors (such as chromium-based inhibitors) can successfully prevent metal corrosion, but they also have drawbacks. Many chemical compounds, for example, are very poisonous and will cause significant environmental harm when used [21]. The use of aqueous extracts is favoured over organic extracts in theory because aqueous extracts, being inorganic inhibitors, include comparatively polar phytochemicals that allow stronger bonding with the metallic surface than the non-polar phytochemicals of organic extracts [22].

Environmentally friendly inhibitor as a replacement for chromate-based inhibitors is a long-standing endeavour by researchers to solve environmental challenges [23]. A lot of plant extracts have previously been reported as effective for inhibiting the corrosion of carbon steel in some corrosive media [24-34].

Rebars are used in concrete technology to fortify the concrete's structure. Electrochemical studies, such as polarization studies and AC impedance spectroscopy, have been used to assess the corrosion resistance of mild steel rebars in a simulated concrete pore solution. The rebars made of mild steel have been coated with SUMO XTRA, a durable exterior emulsion from Nippon Paint. Electrochemical studies have yielded corrosion parameters such as phase angle, impedance value, charge transfer resistance (R_t), double layer capacitance (C_{dl}), Tafel slopes, corrosion current density, corrosion potential, and linear polarization resistance (LPR) [35]. The weight loss method was used to assess the effectiveness of an aqueous extract of apple juice in preventing mild steel from corroding while it was submerged in simulated concrete pore solution (SCPS) made with seawater. The SCPS technology provides mild steel submerged in seawater with an inhibition efficiency of 60%. The efficiency of inhibition rises with increasing extract concentration when apple juice extract is present. An addition of 10 ml of extract results in an 85% inhibitory efficiency [36].

The effect of thermal cycling was carried out on steel bars (0.4 C %). A single run was performed at a lower temperature of 32°C and an upper temperature of 500°C cooled in oil [37], water [38] and seawater [39]. For several numbers of cycles up to 30 cycles for an accurate determination of heating and cooling times. The effect of thermal cycling on the corrosion rate was evaluated. The effect of thermal cycling on the following properties was evaluated the corrosion rate. The comparison between the effect of thermal cycling on carbon steel (0.4 C %) seawater and water-cooled (previous results as shown in references [38, 39] and the effect of thermal cycling on carbon steel (0.4 C %) water-cooled (new results) has been studied. From the obtained test results (previous and in this paper, it was found that: the type of corrosion is uniform attack; corrosion rate of the first stage gradually increases with the number of thermal cycling up to 15 cycles, then it takes steady-state up to 30 cycles. It was found that the rate of corrosion (previous results, seawater and water-cooled) is more than the rate of corrosion of the new results, oil-cooled respectively.

According to Nofrizal et al., by regulating the rates of both anodic and cathodic processes, green tea extract was able to regulate steel corrosion in 1 M HCl with 90% inhibitory efficiency [40]. Mild steel corrosion has been managed by using an aqueous extract of Hibiscus rosa-sinensis flower (HRF) as a corrosion inhibitor in simulated oil well water (SOWW). According to the weight loss method, 10% v/v of the extract provides mild steel (MS) immersed SOWW with 82% inhibitory efficiency (IE) [41].

To precisely determine the heating and cooling times, repeat the process up to thirty times. The effects of thermal cycling on microstructures, microhardness, and corrosion rate were assessed. Based on the results, it was discovered that: for all carbon steel types, the number of thermal cycles increased the grain size; uniform attack was the type of corrosion; and the number of cycles increased the corrosion rate significantly, especially at low cycles. When thermal cycling annealed samples, the rate of corrosion rises with increasing carbon content; while decreases for the thermal cycling of (tempered martensite samples) [42, 43].

2-D MM of axisymmetric transient industrial quenched low carbon steel bar, to examine the influence of process history on metallurgical and material characteristics, a water-cooled model based on the finite element technique was adopted. A 2-dimensional axisymmetric mathematical model was utilized to predict temperature history and, as a result, the hardness of quenched steel bar at any node (point). The LHP (lowest hardness point) is evaluated. In the work, specimen points

hardness was evaluated by the transformation of determined characteristic cooling time for phase conversion $8/5$ to hardness. The model can be used as a guideline to design cooling approach to attain the desired microstructure and mechanical properties, for example, hardness. It will be more necessary to understand LHP on the radius of the quenched steel specimen is high because LHP will be low, that is, lower than the hardness on the surface, implying that increasing the radius of the bar is inversely proportional to LHP. Experimentally, LHP value is almost impossible to determine and previous methods only calculate hardness at the surface. This surface hardness value is normally higher than (LHP) which can cause deformation and failure of the component [44-47].

The steel corrosion mitigation in 0.5 M HCl using 500 ppm alkaline oil Palm was investigated by Hussin et al. [48]. The electrochemical results demonstrated that utilizing this green inhibitor 81% effectiveness in both anodic and cathodic reactions retardation was obtained. In a similar study, Ji et al. found 92% inhibition level for the steel subjected to 1 M HCl solution containing 500 ppm *Argemone mexicana* plant extract [49]. The polarization assessments of this investigation clarified the combined influence of green inhibitor upon cathodic and anodic reactions. Murthy et al. explored the inhibition effect of *Hibiscus sabdariffa* leaves extract by EIS and polarization techniques and understood that 1500 ppm extract dissolved in H_2SO_4 electrolyte resulted in 73% efficiency with mixed type inhibition mechanism [50]. In another effort reported by Sharma et al. it was proved that the leaves extract of *Azadirachta indica* mature considerably mitigated the steel corrosion against HNO_3 medium [51]. Znini et al. evaluated the inhibitory action of another green inhibitor based on *Asteriscus graveolens* essential oil leaves for MS corrosion in H_2SO_4 environment (0.5 M). According to electrochemical analyses, it was observed that 3000 ppm extract showed 81% effectiveness by preventing the anodic and cathodic corrosion reactions [52]. Bourazmi et al. reported 87% protection performance for 1800 ppm *Salvia officinalis* plant extract in 1 M HCl corrosive solution [53]. Recently, Qiang et al. examined the inhibition characteristics of green inhibitor based on Ginkgo leaf extract (GLE) for controlling the corrosion of X70 steel in 1 M HCl and observed inhibition level of 90% applying 200 mg/L extract [54]. Clove plant grows in various geological parts of Asia and South America. The Clove oils, dried flower buds, leaves, and stems can be used for the preparation of useful medicines. Clove is mainly employed directly to the gums for toothache, pain control, and other related issues. Generally, eugenol composes 72–90% of the oil extracted

from Clove plant and is the compound mainly available for the plant aroma [55].

2. EXPERIMENTAL WORK

Corrosion of carbon steel poses a significant challenge in various industries, leading to material degradation, infrastructure damage, and financial losses. While traditional synthetic corrosion inhibitors are effective, their toxicity and environmental concerns have spurred the need for sustainable alternatives. This study explores the potential of naturally occurring materials like olive and palm wood ash to act as eco-friendly inhibitors for carbon steel in acidic environment. Previous research has highlighted the promising role of wood ash in corrosion inhibition due to its rich composition of alkali and alkaline earth metal oxides, particularly calcium, potassium, and magnesium. These oxides react with the acidic environment, forming protective surface layers on the steel that hinder metal dissolution and impede corrosion. Notably, olive and palm wood ashes have received particular attention due to their readily available sources and potentially advantageous chemical composition.

This experiment aims to systematically evaluate the corrosion inhibition properties of 10% aqueous solutions of olive and palm wood ash against carbon steel exposed to an acidic environment. By comparing the corrosion rates of steel immersed in an acidic aqueous solution (pH = 5) with different dosage rates of the ash solutions, the effectiveness of these natural alternatives can be determined. The key parameters influencing the inhibition, such as ash type, dosage rate, and temperature, will be investigated.

2.1. Materials

This section explains all the details of the experiment, including the materials and work methods that were used in this experiment. This experiment was conducted in the laboratories of the Corrosion Protection Department of the Sirte Oil and Gas Production and Manufacturing Company.

2.1.1. Wood ash

Wood Ash of (Olive and Palm): Collected from a fireplace and sieved to obtain fine particles, (As in Fig.1).



Figure 1. Wood ash

2.1.2. Mild Steel Coupon

The steel coupons used for the study were 12 specimens of COSASCO Coupon model CI and 8 specimens of CAPROCO Coupon, both are made of 1018 mild steel alloy. The COSASCO coupons has a dimension $7.3 \times 2.2 \times 0.32$ cm (As in Fig.2. a) while the CAPROCO coupon dimension is $7.6 \times 19 \times 1.6$ cm (As in Fig. 2. b).

All weighing of the coupons was done with a digital analytical balance.

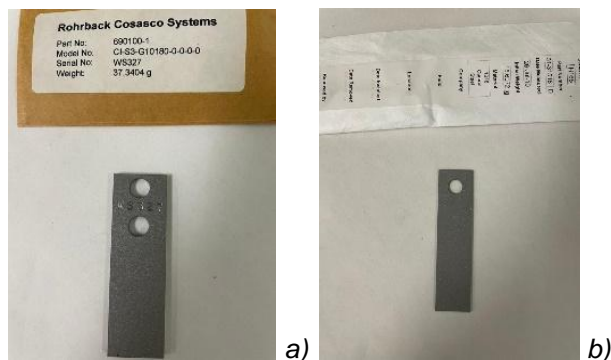


Figure 2. Specimens of: a) COSASCO Coupon, b) CAPROCO Coupon

2.2. Method "Preparation of solutions"

This paragraph explains the preparation of all the solutions used in the experiment, which are three solutions described as follows:

2.2.1. Aqueous Hydrochloric Solution

The acidic environment where the steel coupons was immersed was prepared using 0.00001M hydrochloric acid to achieve a pH of 5. All the experimental solutions were prepared with distilled water. (As in Fig. 3).

2.2.2. Preparation of 10% Aqueous Olive Wood Ash Solution

The ash from the wood of Olive tree (*Olea europaea*) were obtained from a local garden in Benghazi, Libya. The olive wood was burned naturally in an open field and ashes were collected and filtered to obtain its most powdered form. 100 g of the filtered wood ash and 900g of distilled water were mixed continually for 1 hour and the mixture was left at room temperature overnight (24 hours). The resultant solution was filtered and stored. This stock solution (100 g/L) was used directly as the inhibitor that was added to the acid solution where the coupons were immersed. (As in Fig. 4).

2.2.3. Preparation of 10% Aqueous Palm Wood Ash Solution

Palm wood sourced from Benghazi, Libya was burned in an open field. The collected ash was filtered to a fine powder. 100 grams of this palm wood ash was mixed with 900 grams of distilled water for 1 hour and was left overnight at room

temperature. the solution was filtered and stored. This 10% solution was used directly as the inhibitor that was added to the acid solution where the coupons were immersed.



Figure 3. Preparation of Aqueous HCl Solution



Figure 4. Preparation of 10% Aqueous Olive (WA) "same of Palm (WA)"

2.3. Corrosion Test

2.3.1. Weight Loss Method

- Steel coupons were immersed in glass containers containing 300 ml aqueous hydrochloric solution as shown in (Fig. 5. a).
- Specific dosages of the 10% olive and palm solution was then added to the containers: 0 ppm (blank), 50 ppm, 100 ppm, 150 ppm, and 200 ppm As shown in (Fig.5. b).
- 2 sets of the containers (1 set for each ash type) were then stored in two different temperatures: 25°C and 50°C. After a period of 22 days the coupon were removed from the solution and was washed carefully with distilled water. Subsequently, it was rinsed with acetone, and then dried at room temperature. Finally, the weight of each sample after the corrosion test was measured by digital balance.

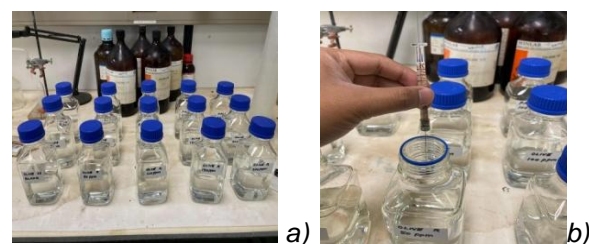


Figure 5. a) Immersing of coupons in glass containers, b) Adding the inhibitor in containers by ppm

The corrosion rate of each sample was then determined by using following (Eq. 1).

$$CR, \text{ mpy} = (W_1 - W_2) \times 365 \times 1000 / (A \times \rho \times t) \quad (1)$$

Where: W_1 = initial weight (prior to immersion), W_2 = final weight (after immersion), A = surface area of the sample, ρ = metal density, t = exposure time

Furthermore, the inhibition efficiency (IE) of each sample was calculated by using (Eq. 2).

$$IE = (V_0 - V_1) / V_0 \quad (2)$$

Where: V_0 = corrosion rate without inhibitor

V_1 = corrosion rate with the addition of inhibitor

3. RESULT AND DISCUSSION

3.1. Corrosion Rate Analysis

The resulting corrosion rates after the 22-days duration is shown in Table 1. It is observed that the corrosion rate of the coupons decreases with the addition of the 10% ash solution. This indicates that the wood ash mitigates the corrosion of mild steel in 0.00001 M HCl. Figs. 6, 7, 8 and 9. gives the trend of corrosion rate with concentration. There is a decrease in corrosion rate with increasing dosage rate of the inhibitor. This is an indication that the efficiency of the inhibitor increases with concentration as can be seen in Table 2.

Among the distinctive results obtained was the inhibition efficiency reaching 54.16% for palm ash solution and 48.18% for olive ash solution.

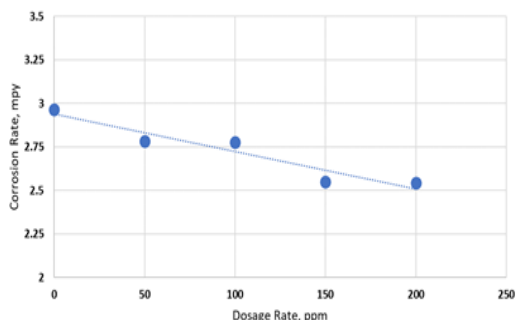


Figure 6. Corrosion rate of Mild Steel in Hydrochloric Solution with 10% Aqueous Olive Ash Solution, 25°C

3.2. Effect of Temperature

The corrosion rate increases with the increase of temperature as can be seen in Table 4.1 and from the data in Table 4.2 the inhibition efficiency was found to generally increase with rise in temperature. This suggests that the interaction between the corrosion rate mild steel and the inhibitor is affected by temperature and that the

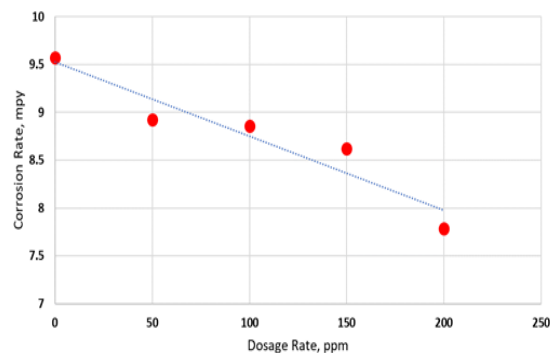


Figure 7. Corrosion rate of Mild Steel in Hydrochloric Solution with 10% Aqueous Olive Ash Solution, 50°C

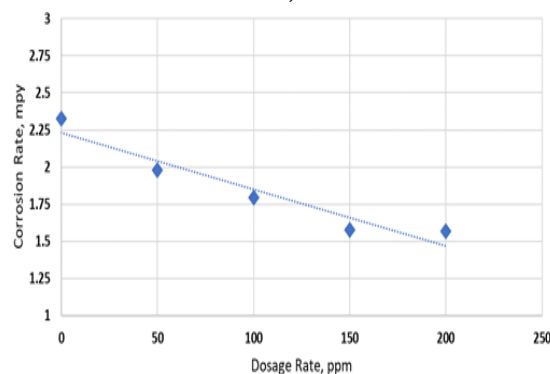


Figure 8. Corrosion rate of Mild Steel in Hydrochloric Solution with 10% Aqueous Palm Ash Solution, 25°C

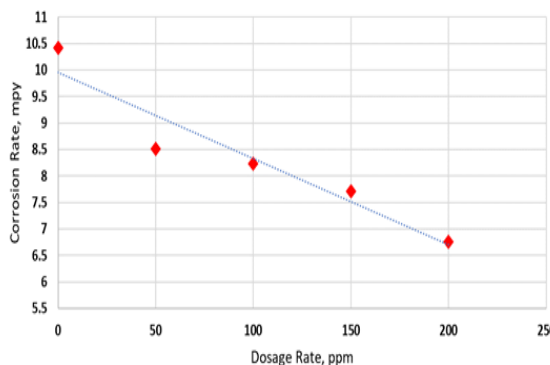


Figure 9. Corrosion rate of Mild Steel in Hydrochloric Solution with 10% Aqueous Palm Ash Solution, 50°C

protection mechanism of the wood ash solution is more efficient with higher temperatures.

This is due to the corrosion of the metal or the damage that occurs on its surface due to high temperatures. It occurs at the non-adsorbed sites of the inhibitory elements. As for the adsorbed sites, the interaction between the active ingredient of the inhibitor and the surface occurs incrementally with increasing temperatures, thus leading to an increase in the efficiency of the inhibitor.

Table 1. Corrosion Rate of Mild Carbon Steel with 10% Wood Ash Solutions at 25°C and 50°C

Dosage rate, ppm	Corrosion Rate of Mild Carbon Steel with 10% Olive Ash Solution @ 25°C,(mpy)	Corrosion Rate of Mild Carbon Steel with 10% Palm Ash Solution @ 25°C,(mpy)	Corrosion Rate of Mild Carbon Steel with 10% Olive Ash Solution @ 50°C,(mpy)	Corrosion Rate of Mild Carbon Steel with 10% Palm Ash Solution @ 50°C,(mpy)
0 (Blank)	2.97	2.33	9.57	10.42
50	2.78	1.98	8.92	8.51
100	2.78	1.80	8.86	8.24
150	2.55	1.58	8.62	7.71
200	2.54	1.57	7.78	6.76

Table 2. Inhibition Efficiency of 10% Wood Ash Solutions at 25°C and 50°C

Dosage rate, ppm	Inhibition Efficiency of 10% Olive Ash Solution @ 25°C, (%)	Inhibition Efficiency of 10% Palm Ash Solution @ 25°C, (%)	Inhibition Efficiency of 10% Olive Ash Solution @ 50°C, (%)	Inhibition Efficiency of 10% Palm Ash Solution @ 50°C, (%)
50	6.60	7.29	17.54	22.41
100	6.79	8.07	29.56	26.46
150	16.25	11.05	47.48	35.14
200	16.59	22.98	48.18	54.16

4. CONCLUSION

Corrosion behavior of mild steel in 0.00001 M HCl solution with and without addition of 10% aqueous olive and palm wood ash solution for various concentrations and working temperatures have been investigated. This study concludes that:

- Olive and Palm wood ash can be a good corrosion inhibitor for mild steel in 0.00001 M HCl or around pH = 5.
- The inhibition efficiency of Olive and Palm wood ash solution increases with increase in concentration.
- Palm wood ash has better performance than Olive wood ash in inhibiting the corrosion rate of mild steel in HCl.
- Temperature does not decrease the inhibition efficiency of both wood ash solutions.

Recommendation

For future work, "Soxhlet" extraction method and electrochemical corrosion tests must be performed, namely voltage and galvanostat tests, and the experiment time must also be increased to see the efficiency differences over time.

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IZVOD

PROCENA PEPELA OD DRVETA KAO EKOLOŠKI PRIHVATLJIVOG INHIBITORA KOROZIJE ZA ŽIVOTNU SREDINU ZA ČELIK SA NISKIM SADRŽAJEM UGLJENIKA U KISELOM RASTVORU NA RAZLIČITIM TEMPERATURAMA

Korozija je nezaobilazna činjenica u svakodnevnom životu, ali se uvek vodi računa o kontroli zbog njenog tehničkog, ekonomskog i estetskog značaja. Ugljenični čelik (CS) je najčešće korišćeni materijal za opremu i cevi u procesima proizvodnje nafte. Međutim, prisustvo vode/soli i ugljen-dioksida, između ostalih gasova, u ulju predstavlja ozbiljan problem zbog povećane stope korozije materijala. Najčešći način za ublažavanje ovog problema je korišćenje inhibitora korozije. Međutim, mnogi uobičajeni inhibitori korozije koji su danas u upotrebi predstavljaju opasnost po zdravlje. Inhibitori korozije su jedna od najčešće korišćenih i ekonomski isplativih metoda zaštite metala i legura od korozije. U ovom radu proučavan je inhibitorski efekat drvenog pepela (masline i palme) na blagi ugljenični čelik u rastvoru 0,00001 M ili pH oko 5 hlorovodonične kiseline. Brzina korozije i efikasnost inhibitora su izračunati sprovođenjem testa efikasnosti inhibicije za 10% vodenih rastvora drvenog pepela za oba (maslina i palma) primenom (metoda gubitka težine). Uticaj temperature na koroziono ponašanje blagog ugljeničnog čelika proučavan je pri 0,00001 M i pH = 5 hidrohlorida uz dodatak 10% vodenih rastvora drvenog pepela (masline i palminog) u temperaturnom opsegu 25-50 stepeni Celzijusa. Može se postići efikasnost inhibicije do 54,16 % za rastvor palminog pepela i 48,18 % za rastvor maslinovog pepela.

Na interakciju između brzine korozije mekog čelika i inhibitora utiče temperatura i zaštitni mehanizam rastvora drvenog pepela je efikasniji na višim temperaturama. To je zbog korozije metala ili oštećenja koja se javljaju na njegovoj površini usled visokih temperatura. Javlja se na neadsorbovanim mestima inhibitorskih elemenata. Što se tiče adsorbovanih mesta, interakcija između aktivne supstance inhibitora i površine se odvija postepeno sa povećanjem temperature, što dovodi do povećanja efikasnosti inhibitora.

Ključne reči: Inhibitori korozije; ugljenični čelik; palm ash; olive ash; hlorovodonična kiselina; efikasnost inhibicije.

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