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Evaluation of *Matricaria aurea* Extracts as Effective Anti-Corrosive Agent for Mild Steel in 1.0 M HCl and Isolation of Their Active Ingredients

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Abstract: Plant extracts have shown promising corrosion inhibitive actions for different metals in diverse corrosive climate. In numerous studies, it has been demonstrated that corrosion inhibitive features of plant extracts are due to the presence of complex mixtures of phytomolecules in their composition. However, rare efforts have been made to identify those phytomolecules accountable for the activity of the extracts. Therefore, in this paper, several *Matricaria aurea* extracts were prepared and assessed for their anticorrosive actions for mild steel (MS) in corrosive media (1.0 M HCl). Among the tested extracts, the methanolic extract showing the utmost anticorrosive activity was selected and processed further to identify its active phytomolecules, which led to the identification of a novel green corrosion inhibitor, **MAB** (Apigetrin). Furthermore, the anticorrosive properties of **MAB** on MS were evaluated comprehensively involving gravimetric, linear polarization, Tafel plots, EIS, and techniques like SEM and EDS. These findings expose that **MAB** performs like a mixed-type inhibitor and conforms the isotherm of Langmuir adsorption model. Moreover, the MS surface via SEM techniques exhibits a remarkable advanced surface of the MS plate in the company of **MAB**. The outcome of results through electrochemical analysis and weight loss methods were in good consonance, which depicts remarkable inhibition properties of the novel green inhibitor **MAB**.

Keywords: *Matricaria aurea*; corrosion inhibitor; phytomolecules; natural products

1. Introduction

Plants have been an excellent, cheap, and renewable source of natural products either in the form of extracts or pure organic compounds (phytomolecules). Plant extracts and their phytomolecules have been extensively employed in food, cosmetic, perfumery, textile, and pharmaceutical industries. One of the most important areas where natural plant products have shown astonishing success is cancer therapy. Corrosion is another area where plants have demonstrated significant promising results. Natural products from plants have been successfully applied as green corrosion inhibitors for varieties of metals in diverse corrosive media [1–3]. For example, tomato peel waste collected from canning industries was successfully utilized for the protection of tin corrosion in sodium chloride, acetic acid, and citric acid corrosive media [4]. Elgahawi et al. reported the effects of *Linum usitatissimum* seeds extracts as a potential source for the inhibition of aluminum alloy corrosion in sodium chloride solution [5]. In another study, water extract of henna leaves has been successfully employed for the protection of metals like C-steel, Zinc, and nickel in HCl, NaCl, and NaOH corrosive environment [6].

Similarly, Finsgar and Jackson has described the importance of natural products as effective corrosion inhibitors against various concentrations of hydrochloric acid solution for low grade steel samples useful in oil and gas industries [7].

Generally, plant extracts-based corrosion inhibitors are considered to be economical, renewable, non-toxic, biodegradable, and environmentally friendly compared to synthetic corrosion inhibitors [2,3,8,9]. Plant extracts are composed of highly complex mixtures of phytomolecules belonging to various chemical classes such as flavonoids, terpenoids, alkaloids, anthocyanins, tannins, and saponins. These phytomolecules are rich in π electrons (benzene ring, double/triple bonds) and contain electronegative functional groups and heteroatoms such as oxygen, sulfur, and nitrogen in their chemical structure. Adsorption of these phytomolecules on metal surface through: (1) electrostatic attraction of charged phytomolecules and charged metals, (2) metals vacant d-orbital and π electrons or lone pair electrons of phytomolecules, and (3) a combination of these two described processes tend to protect metals from corrosion [10].

Many extracts of plants have been proven to be remarkable candidates for the novel corrosion inhibitor development for different metals in numerous aggressive mediums. For instance, *Ginkgo* leaf extract [11], date palm leaves and seed [12], *Holoptelea integrifolia* leaf [2], *Thymus vulgaris* leaves [13], *Rhus verniciflua* [8], *Cymbopogon citratus* [14], *Pimenta dioica* leaf [15], *Guatteria ouregou* and *Simira tinctoria* alkaloid extracts [16], and *Michelia alba* leaves extract [17] were discovered to be commendable, environmentally friendly corrosion inhibitors for different metals in several aggressive solutions.

Moreover, natural products from plants as green corrosion inhibitors have been reviewed in several papers [1–3,18,19]. From all these studies, it has been revealed that a large number of phytomolecules that present in the extract composition are responsible for their corrosion inhibitive properties. However, in the majority of the studies, it has been found that very rare efforts have been made to identify active phytomolecules of plant extracts accountable for the corrosion inhibitive activity. Therefore, in order to proceed with our work on medicinal plants [20–23] in this paper, various extracts of *Matricaria aurea* were examined for their corrosion inhibitive actions for mild steel (MS) in corrosive solution (1.0 M HCl). In addition, active phytomolecules accountable for corrosion inhibitive properties were identified from the highly active extract of *M. aurea* through activity-assay guided isolation approach.

M. aurea is an important medicinal plant which belongs to Asteraceae family. In Saudi Arabia and in different parts of the world, it is popularly used in traditional medicines for various ailments such as asthma, cough, spasmodic, common cold, flatulence, and influenza [24]. Moreover, *M. aurea* has also been reported to possess anti-inflammatory and analgesic activity [25]. Varieties of chemical compounds such as quercetin, coumarins: umbelliferone, caffeic acid, apigenin-7-O-glucoside, and naringenin have been isolated from *Matricaria* species. However, chemical investigation of *M. aurea* are very scarce and only few phytomolecules have been reported from it [25]. Furthermore, corrosion inhibitive properties of *M. aurea* are being investigated here for the first time.

2. Experimental Section

2.1. Materials

2.1.1. Collection and Identification of Plant Material

The flowers of *M. aurea* produced in Saudi Arabia central province were obtained from an herbal market, Batha, Riyadh, in February 2011. A taxonomist from the King Saud University (Riyadh, Saudi Arabia) performed the identification of this tested plant. A sample of the identified plant is upheld with a voucher sample no. KSUHZK-303.

2.1.2. Test Specimen Preparation

The MS working electrode was procured from Goodfellow, England, with the following composition (wt%): C-0.2%, Si-0.3%, Mn-0.94%, and iron (an uncovered region of 0.9498 cm²).

This uncovered region was instinctively polished with numerous sandpapers of multi-grades, ranging from rough (600) to the flushest (1000) quality. The MS electrode was subsequently cleaned thoroughly with distilled water (DW) and finally with acetone to instantly take out all oily substances before incorporation in to the cell. With analytical grade chemicals and reagents, the *M. aurea* dried extracts and purified isolated compound were used for the inhibitor assay solution preparation.

2.2. Methods

2.2.1. Purification of the Active Phytomolecule

Purification of the active phytomolecules from *M. aurea* was achieved using activity-guided isolation approach as shown in the flow diagram in Figure 1. In short, dried and grinded *M. aurea* flowers were initially defatted with *n*-hexane and the marc was then extracted with methanol (MeOH), water (H₂O), and finally with a mixture of MeOH: H₂O (80:20) at room temperature. The resultant extracts were individually dried under vacuum at 50 °C. Evaluation of corrosion inhibitive properties of these three extracts revealed that MeOH extract was more active than those of aqueous and aqueous methanolic extracts. Therefore, methanolic extract was selected for the isolation of active compound. MeOH extract was dissolved in water and fractionated with solvents of different polarity like *n*-hexane, chloroform (CHCl₃), ethyl acetate (EtOAc), and finally with *n*-butanol (*n*-BuOH). Testing of corrosion inhibitive properties of EtOAc and *n*-BuOH fractions showed that butanol fraction had the highest activity. Thus, in order to identify its active phytomolecules, *n*-BuOH fraction was loaded on a silica gel column applying different ratios of *n*-hexane, chloroform, and methanol as eluting solvents to produce an active compound **MAB**.

Figure 1. Activity-guided isolation of anticorrosive agent **MAB**.

2.2.2. 1D and 2D Nuclear Magnetic Resonance (NMR) Analysis

The NMR spectra 1D (¹H, ¹³C, DEPT) and 2D (COSY, HMQC and HMBC) of the purified compound **MAB** were recorded on a 500 MHz spectrometer (JEOL, ECP) by dissolving the sample in deuterated dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) and taking tetramethylsilane (TMS) as an internal standard. The coupling constants (*J*) and chemical shifts are represented in Hz and δ (ppm), respectively.

2.2.3. UV-Visible Spectroscopy

UV spectra $\lambda_{\max}$ ($\log \epsilon$, nm) of the purified compound **MAB** were documented by a Shimadzu-UV-260 spectrophotometer using a quartz cell.

2.2.4. Mass Spectrometry (MS) Analysis

MS spectra of the purified compound **MAB** were documented through UPLC-MS/MS (Waters Acquity) attached with a TQD detector. The test compounds were imparted as a MeOH-H₂O suspension through API-ESI ionization with a positive or negative mode.

2.2.5. Chemical Structure Identification of **MAB**

Apigenin-7-O- β -D-glucoside (**MAB**): [26] C₂₁H₂₀O₁₁; Yellow amorphous powder, m.p. 235–239 °C. ESI-MS (negative mode) m/z : 431 [M – H][−]. UV ($\lambda_{\max}$, MeOH): furnishes bands at 267 and 333 nm, adding NaOMe; 266 and 389, NaOAc; 267 and 335, NaOAc-H₃BO₃; 266 and 336, AlCl₃; 273, 384 while AlCl₃-HCl; 274, 384. ¹H-NMR (500 MHz, DMSO-*d*₆) δ (ppm): δ 7.94 (2H, d, J = 8.4 Hz, H-2' and H-6'), 6.93 (2H, d, J = 8.4 Hz, H-3' and H-5'), 6.83 (1H, s, J H-3), 6.80 (1H, d, J = 2.0 Hz, H-8), 6.42 (1H, d, J = 2.0 Hz, H-6), 5.06 (1H, d, J = 6.9 Hz, H-1''), 3.16–3.89 (5H, m, H-2'', H-3'', H-4'', H-5'', H-6''). ¹³C-NMR (100 MHz, DMSO-*d*₆) δ (ppm): δ 182.8 (C-4), 164.9 (C-2), 163.5 (C-7), 161.9 (C-5), 161.8 (C-4'), 157.5 (C-9), 129.8 (C-2' and C-6'), 121.8 (C-1'), 116.7 (C-3' and C-5'), 105.8 (C-10), 103.9 (C-3), 100.7 (C-1''), 100.0 (C-6), 95.3 (C-8), 77.9 (C-5''), 76.9 (C-3''), 73.6 (C-2''), 70.3 (C-4''), 61.2 (C-6'').

2.2.6. Weight Loss Experiments

Firstly, the varieties of MS samples were abraded using various grades of sandpapers (grade 600, 800, and 1000). Subsequently, the drying with an air blower was done right after the water washing and acetone degreasing. After precisely weighing with an accurateness of 0.1 mg, these samples were fully submersed in a beaker containing 1.0 M HCl solution (100 mL) in the absence and presence of various quantities of inhibitors (0.116–0.580 mM) at altered temperatures (298, 313, and 328 ± 1 K) for 3 h. Finally, the MS specimens were collected, cleaned, desiccated, and precisely weighed. All experiments were repeated thrice, and results are mentioned in three runs. The inhibition efficiency (IE %) and the surface coverage degree (θ) were determined using the following equations:

$$IE \% = \frac{W_0 - W_i}{W_0} \times 100 \quad (1)$$

$$\theta = \frac{IE \%}{100} \quad (2)$$

where W_0 and W_i are the weight loss of the MS samples in the absence and presence of the inhibitors, respectively.

The MS corrosion rate (C_R) was measured using Equation (3):

$$C_R (\text{mm year}^{-1}) = \frac{87.6 W}{AtD} \quad (3)$$

where A is the specimen area, W is the MS weight loss (mg), D is the MS density (gcm^{−3}) and t is the exposure time (h).

2.2.7. Electrochemical Studies

For the electrochemical study, a traditional 3-electrode cell assembly was used at 25 °C, having a typical potentiostat fitted through an impedance spectra analyzer. A platinum sheet acts as the counter electrode (CE) and a saturated calomel electrode (SCE) attached to a fine Luggin capillary acts as the reference electrode. Initially, to attain a steady open-circuit potential (OCP), the working electrode was dipped in the standard solution for 30 min. The Tafel plots were recorded for the test samples on MS

corrosion, from a cathodic potential (−250 mV) to an anodic potential (+250 mV) at a constant sweep rate of 1 mV/s. The anodic and cathodic linear Tafel segments were inferred to the corrosion potential to get the corrosion current densities (I_{corr}). The IE % was determined through the measured corrosion current density (I_{corr}) values using Equation (4):

$$IE \% = \frac{I_{corr}^0 - I_{corr}^i}{I_{corr}^0} \times 100 \quad (4)$$

where I_{corr}^i and I_{corr}^0 are the corrosion current densities with and without the inhibitor, respectively.

The linear polarization resistance (LPR) R_p was calculated through polarizing the test specimen from −25 to +25 mV as compared to the corrosion potential (E_{corr}) at a scanning frequency of 0.125 mV/s. From this computed value of polarization resistance, the IE % was determined using the following equation:

$$IE \% = \frac{R_p^i - R_p^0}{R_p^i} \times 100 \quad (5)$$

where R_p^i and R_p^0 are the polarization resistances in the presence and absence of the inhibitor, respectively.

Electrochemical impedance spectroscopy (EIS) calculations were carried out at an open circuit potential (OCP) with AC signals (10 mV amplitude with a frequency range (30 kHz to 10 mHz). The charge transfer resistance measurements were obtained from the semicircles diameter of the Nyquist plots. In the particular electrical equivalent circuit, R_{ct} is the charge transfer resistance, R_s is the solution resistance, and C_{dl} is the double-layer capacitance (Figure 2). The IE % of the inhibitors were obtained from the charge transfer resistance (R_{ct}) values using the following Equation (6):

$$IE \% = \frac{R_{ct}^i - R_{ct}^0}{R_{ct}^i} \times 100 \quad (6)$$

where R_{ct}^0 and R_{ct}^i are the charge transfer resistances in the absence and presence of the inhibitor.

Figure 2. The circuit (electrical equivalent) for AC impedance calculation.

2.2.8. SEM and EDS Measurements

The MS specimens were immersed in 1.0 M HCl for 3 h with or without **MAB** concentration of 0.464 mM. Next, they were recovered, washed with acetone, and kept at 25 °C to dry completely. The surface morphology of the recovered samples was scanned utilizing a JEOL-JSM-6380LA Scanning Electron Microscope.

3. Results and Discussion

3.1. Screening of *M. aurea* Extracts for Their Corrosion Inhibitive Properties

In order to study corrosion inhibitive properties of *M. aurea* and identify its active compound, various crude extracts such as water, aqueous methanolic (AqMeOH), and methanolic (MeOH) of *M. aurea* were screened for their corrosion inhibitive activities for MS in 1.0 M HCl utilizing Tafel plots, EIS methods, and LPR measurements.

The detailed potentiodynamic polarization curve of MS (in 1.0 M HCl) with 600 ppm of crude extracts and without crude extracts (Figure S1) and their various corrosion kinetic parameters for

example E_{corr} , I_{corr} , Tafel constants (β_a and β_c) and inhibition efficiency ($IE\%$) are provided in Table S1 (Supplementary Materials). Similarly, the EIS values (Figure S2) and the impedance parameters such as solution resistance (R_s), R_{ct} , C_{dl} and $IE\%$ achieved from the Nyquist plots are mentioned in Table S2 of the Supplementary Materials. The $IE\%$ attained from Tafel plots, LPR measurements, and EIS methods were determined using Equations (4)–(6), respectively. From these results, MeOH extracts were found to be the most active extracts, and thus, it was proceeded further to identify its active ingredients. Accordingly, the MeOH extract was dissolved in DW and fractionated with non-polar to polar solvents such as *n*-hexane, $CHCl_3$, EtOAc, and finally with *n*-BuOH. Due to poor solubility of *n*-hexane and $CHCl_3$ fractions in test solution, we have only tested two fractions (the EtOAc and *n*-BuOH) in order to study their anticorrosive activities.

Results from Tafel plots and EIS values for both fractions are expressed in Figures S3 and S4, whilst their particular electrochemical parameters are shown in Tables S3 and S4 (Supplementary Materials). The results clearly indicate that the *n*-BuOH fraction was significantly more active than the EtOAc fraction. Thus, it was further exploited for the isolation and identification of active phytochemicals.

Column chromatography of *n*-BuOH fraction (75.0 g) on silica gel column employing different ratios of $CHCl_3$ and MeOH as elutant, which yielded 97 fractions. Pooling of these fractions based on their TLC profile led to produce four major sub-fractions: Frs 11–13 (MA-1), Frs 15–19 (MA-2), Frs 28–34 (MA-3), and Frs 41–81 (MA-4) (Figure 1). These four sub-fractions were examined for their corrosion inhibitive properties. Results from potentiodynamic polarization and EIS methods are given in Figure S5, Table S5 and Figure S6, Table S6 respectively (Supplementary Materials). From the results, it was noticed that sub-fraction MA-3 eluted with $CHCl_3$: MeOH (80:20) possessed the highest activity and showed one major compound along with some small impurities on the TLC. Therefore, it was further purified through crystallization in MeOH to get pure compound **MAB**.

3.2. Identification of the Compound **MAB** Isolated from *M. aurea*

Figure 3 shows the mass spectrum, HMBC correlations, and chemical structure of **MAB**. The chemical structure of **MAB** was characterized as apigenin-7-O- β -D-glucoside exploiting numerous spectroscopic data (Figures 3 and 4, Supplementary Materials Figures S7a–S12c) and comparison of their spectroscopic data with literature values [26].

Figure 3. HMBC correlations, mass spectrum, and chemical structure of **MAB**.

Figure 4. DEPT spectrum of MAB.

3.3. Detailed Study of Corrosion Inhibitive Properties of MAB

After isolation and complete chemical characterization of compound **MAB**, its corrosion inhibitive properties were assessed in detail through the weight loss, linear polarization, Tafel plots, and method like EIS, SEM, and EDS.

3.3.1. Weight Loss Study

The weight loss experiment for **MAB** was done at 298 ± 1 K for a 3 h immersion period in order to investigate the different concentrations effect on the MS inhibition efficiency in 1.0 M HCl. The percentage inhibition efficiency (*IE* %), surface coverage (θ), and corrosion rate attained from this experiment are expressed in Table 1. The inhibitor concentrations effect on the *IE* of MS in 1.0 M HCl solution is shown in Figure 5.

Table 1. The corrosive inhibitive properties of **MAB** for MS in 1.0 M HCl from weight loss measurements at 298 ± 1 K.

Concentration of Inhibitor (mM)	Weight Loss (g)	Surface Coverage (θ)	Corrosion Rate C_R (mm year ⁻¹)	<i>IE</i> %
0 (Blank)	0.2587	-	0.1354	-
0.116	0.0370	0.86	0.0194	85.70 ± 0.84
0.232	0.0304	0.88	0.0159	88.25 ± 0.98
0.348	0.0243	0.91	0.0127	90.61 ± 0.83
0.464	0.0161	0.94	0.0084	93.78 ± 0.91
0.580	0.0158	0.94	0.0083	93.89 ± 0.95

Figure 5. The inhibition efficiency variant vs. MAB concentration.

In both Table 1 and Figure 4, it is clearly shown that the *IE* is directly proportional to the inhibitor concentration, which suggests the rate increase in the MAB molecules absorbed over the MS surface. Therefore, the inhibitor molecules cover the MS active sites area and shield it against corrosion [27]. It was found that the highest *IE* was achieved at 0.464 mM concentration, and further increase in the MAB concentration does not significantly alter the green inhibitor protective effect. (Figure 5). Thus, 0.464 mM concentration for this green inhibitor MAB was considered to be the optimal. Subsequently, the effect of various temperatures (298 ± 1 – 328 ± 1 K) with or without the optimal inhibitor concentration (0.464 mM) was examined for 3 h of immersion time in aggressive solution. Results are given in Table 2 and Figure 6.

Table 2. The corrosive inhibitive properties of MAB (0.464 mM) at different temperatures for the MS corrosion in 1.0 M HCl.

Temperatures (K)	Weight Loss (g)	Surface Coverage (θ)	Corrosion Rate C_R (mm year ⁻¹)	IE %
298 $\pm$ 1	0.0161	0.94	0.0084	93.78 $\pm$ 0.91
313 $\pm$ 1	0.0174	0.93	0.0091	93.27 $\pm$ 0.85
328 $\pm$ 1	0.0258	0.93	0.0135	90.03 $\pm$ 1.02

Figure 6. The inhibition efficiency variant vs. solution temperature of MAB (0.464 mM).

From Table 2 and Figure 6, it is clearly shown that the inhibition efficiency of **MAB** (0.464 mM) is inversely proportional to the test solution temperature, which signifies that the physisorption may involve in the inhibitor adsorption mechanism rather than chemisorption. This is because of an electrostatic interaction in physisorption, which generally eludes its effect at raised temperatures [28].

3.3.2. Tafel Plots Measurements

The **MAB** inhibitive effect was also considered using potentiodynamic polarization experiments. Tafel plots of MS with or without different concentrations of **MAB** in 1.0 M HCl are presented in Figure 7.

Figure 7. Tafel plots with or without various concentrations of **MAB**.

Figure 7 manifestly demonstrates that the anodic and cathodic corrosion current density decreases when the green inhibitor **MAB** is used, and the decrease is more pronounced when compared with a blank solution, indicating corrosion mitigation of MS. Thus, this decrease triggers the increase in concentration of **MAB**, which clearly suggests that from enhancing the inhibitor concentration, the adsorption process of inhibitor constituents at the MS/acidic solution interface also increases. This affords enhanced shielding for the MS active sites to protect it from direct acid attack that results the corrosion mitigation [29]. The electrochemical factors acquired from the Tafel plots and LPR estimation are reported in Table 3.

Table 3. Potentiodynamic polarization parameters from Tafel plots with different concentrations of **MAB**.

MAB Concentration (mM)	E_{corr} (mV)	I_{corr} (μAcm^{-2})	β_a (mV/dec)	β_c (mV/dec)	R_p	IE % Tafel	IE % LPR
0 (Blank)	−486.6	213.0	99.85	−110.73	54.5	−	−
0.116	−515.5	29.0	57.31	−73.42	339.64	86.38	83.95
0.232	−508.7	23.4	61.16	−75.90	499.18	89.01	89.08
0.348	−521.8	19.8	59.25	−80.71	576.39	90.70	90.54
0.464	−513.5	10.2	63.41	−83.62	907.02	95.21	94.00

The IE % acquired from Tafel plots as well as LPR values were calculated through Equations (4) and (5), respectively. Table 3 evidently indicates that with enhancing the inhibitor quantity, the I_{corr} values significantly falls because the obtained values are considerably less comparing to the uninhibited solutions. Conversely, due to the opposite trend concerning the I_{corr} and the R_p values, the polarization resistance (R_p) tends to significantly escalate as the inhibitor concentration rises, which in turn upsurges the inhibition efficiency. This advocates that the inhibitor concentration increases with increase in the adsorption amount of phytomolecule on the MS surface. This generates a physical barrier between mass and charge transfer and ultimately shields the metal through occluding the active spots [30]. It is also cleared from Table 3 that by adding the green inhibitor, both the anodic (β_a) and the cathodic Tafel constants (β_c) changes slightly, which shows that the **MAB** adsorption does not effect on the mechanism of anodic and cathodic reactions. Thus, the **MAB** can be classified as a mixed-type inhibitor with moderately cathodic efficacy because the addition of **MAB** shifts the E_{corr} values in the negative trend. However, this shift in E_{corr} measurements is not prominent. The extreme displacement in E_{corr} for **MAB** is only 29 mV in the direction of cathodic polarization, which suggest **MAB** as a mixed-type inhibitor with controlling cathodic efficacy [29]. In addition from the Figure 7, it is suggested that both anodic and cathodic mechanism are introverted in acidic solution, but the polarization in cathode is more diverged due to which the mixed-type inhibitor properties with dominant cathodic effect are revealed.

3.3.3. EIS Measurements

The **MAB** corrosion inhibitive action for MS was examined through EIS at 25 °C for an exposure duration of half an hour. The MS Nyquist plots attained at the interface with or without different concentrations of **MAB** are expressed in Figure 8.

Figure 8. Nyquist plots in the absence and presence of different quantities of **MAB**.

It is clear from Figure 8 that **MAB** concentration has pronounced effects on the impedance behavior of MS, and it can be clearly seen that the Nyquist plots diameter rises with increasing the quantity of **MAB** in the inhibitive media. It is pertinent to mention that the adsorption of **MAB** involved in developing an active shielding film on the MS that was further strengthened due to enhancing the **MAB** concentration to provide extra safeguard to MS in a destructive medium. Additionally, a typical solid electrodes in the Nyquist plots which involve a low semi-circle inside the real X-axis is more often mentioned to frequency dispersion because of the unevenness and roughness of the solid surface [31]. The impedance parameters derived from the Nyquist plots are displayed in Table 4.

Table 4. EIS parameters derived from the Nyquist plots for the MS corrosion in 1.0 M HCl with various concentrations of **MAB**.

Concentration (mM)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	θ	$IE\%$
0 (Blank)	57.1	533.0	-	-
0.116	385.0	352.3	0.85	85.17
0.232	479.7	348.2	0.88	88.10
0.348	634.0	222.3	0.91	91.00
0.464	886.4	118.4	0.94	93.56

The $IE\%$ were determined by Equation (6), while the double-layer capacitance (C_{dl}) was expressed by the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (7)$$

where f_{max} is the frequency at the Nyquist plots apex and R_{ct} is defined as charge transfer resistance. It is clear from Table 4 that the R_{ct} values increases with the increase in **MAB** concentration. This phenomenon of increment in R_{ct} values can be arisen because of the creation of phytomolecules shielding layer on the MS surface, which in turn increases the IE values [32]. Furthermore, it is implied that the C_{dl} values shows inverse effect with inhibitor concentration, which may be possible due to the increase in electrical double layer thickness and/or decrease in local dielectric constant [33]. This result advocates that this naturally occurring phytomolecule **MAB** functions through adsorption at the MS/solution interface [31]. It is also believed that due to this adsorption phenomenon of **MAB** on the MS surface and the water molecules progressive replacement, C_{dl} decreases. This ultimately provides extra surface veil to the MS active site by **MAB**. As a result, it decreases the MS dissolution magnitude as well as the charge transfer [34]. Moreover, it is revealed that through the EIS measurements green inhibitor, **MAB** shows potent anticorrosive activity for MS with the maximum IE (94%) at 0.464 mM of **MAB**. Thus, the data obtained through weight loss, EIS, and potentiodynamic polarization experiments are coherent with each other (Figure 9).

Figure 9. Comparison of IE achieved from numerous methods at optimal concentration of **MAB**.

3.3.4. Adsorption Isotherm and Mechanism of Inhibition

The isotherm of adsorption provides elementary evidence regarding the surface of metal and corrosion inhibitors. In an aqueous solution, a compound can be regarded as a powerful corrosion

inhibitor, when the interaction potency of the metals and the inhibitive compounds is more than that of the metal and H₂O molecules [35].

Generally, Frumkin, Temkin, and Langmuir adsorption isotherms are known to be most important and useful isotherms. As stated by these isotherms the concentration of inhibitive compound and surface coverage, (θ) is associated as:

$$\log \left(\frac{\theta}{C} \right) = \log K - g\theta \text{ (Temkin isotherm)} \quad (8)$$

$$\frac{C}{\theta} = \frac{1}{K} + C \text{ (Langmuir isotherm)} \quad (9)$$

$$\log \left\{ \frac{\theta}{(1-\theta)C} \right\} = \log K - g\theta \text{ (Frumkin isotherm)} \quad (10)$$

where K = adsorption-desorption equilibrium constant, C = inhibitor concentration, and g = adsorbate parameter.

Employing θ values that achieved with different concentrations of **MAB** at 25 °C, efforts were put through to fit the aforementioned isotherms where the Langmuir isotherm displayed the best result with r^2 (coefficient of regression) value 0.9989 for **MAB** (Figure 10).

Figure 10. Langmuir isotherm with various **MAB** concentrations.

This result advocates that **MAB** develops a monolayer on the MS surface [36].

The ΔG_{ads}° (free energy) values of adsorption process was measured through the following equation:

$$\Delta G_{ads}^{\circ} = -RT \ln(K \times 55.5) \quad (11)$$

where K = adsorption process equilibrium constant.

In this study, the calculated ΔG_{ads}° value is $-19.66 \text{ kJ mol}^{-1}$ (Table 5). This value of ΔG_{ads}° specifies that **MAB** is adsorbed on the MS surface by a physisorption process [28]. Moreover, similar results were confirmed from the weight loss experiment, where it was found that *IE* decreased with an elevation of inhibitive solution temperature. Thus, this shows that **MAB** undergoes physisorption process with the MS surface [37]. Therefore, due to temperature elevation, *IE* and the adsorbed **MAB**

on the MS are decreased [38]. The important adsorption parameters such as entropy (ΔS_{ads}°) and enthalpy (ΔH_{ads}°) were computed employing the following equations:

$$\Delta H_{ads}^\circ = E_a - RT \quad (12)$$

$$\ln C_R = \ln A - \frac{E_a}{RT} \quad (13)$$

$$\Delta G_{ads}^\circ = \Delta H_{ads}^\circ - T\Delta S_{ads}^\circ \quad (14)$$

Table 5. ΔG_{ads}° , ΔH_{ads}° and ΔS_{ads}° values for MS in 1.0 M HCl with **MAB** (0.464 mM).

Compound	ΔG_{ads}° (kJ mol ^{−1})	ΔH_{ads}° (kJ mol ^{−1})	ΔS_{ads}° (J K ^{−1})
MAB	−19.66	10.23	−31.64

The results in Table 5 suggests that **MAB** adsorption on MS surface is exothermic as acquired ΔH_{ads}° values shows the negative sign [30].

3.3.5. EDS and SEM Analysis

The images obtained through a scanning electron microscope (SEM) techniques has been regarded as a vital tool to analyze the external quality of MS surface [30]. To understand the effects of **MAB** on the MS surface, SEM analysis were apprehended for MS specimens with or without the optimal **MAB** concentration. Results are displayed in Figure 11.

Figure 11. SEM images of (a) smoothed MS specimen, (b) MS specimen in corrosive solution, (c) MS specimen in corrosive solution with **MAB** (0.464 mM).

Figure 11a indicates the SEM picture of newly rubbed up MS specimen prior to any application. This image shows a very neat and fine MS surface, except for a few notable scratches that might have ascended during abrasion, whereas Figure 11b indicates the image of MS sample in a corrosive solution for 3 h. In this image, a highly corroded MS exterior could be seen due to the highly corrosive character of aggressive solution (1.0 M HCl). In contrast, the image of MS specimen in a corrosive solution with ideal concentration of **MAB** (Figure 11c) shows a conspicuously fine MS surface without scratches and is analogous with the freshly rubbed up MS specimen (cf. Figure 11a) which unveils that a shielding film developed by **MAB** on the surface of MS significantly prevents the corrosion of MS specimen [30].

Moreover, results of EDS analysis to detect chloride content of freshly rubbed MS specimen untreated and treated with ideal **MAB** concentration in a corrosive solution MS specimen are shown in Figure 12.

Figure 12. EDS of (a) smoothed MS specimen, (b) MS specimen in corrosive solution, (c) MS specimen in corrosive solution with **MAB** (0.464 mM).

Figure 12a reveals the chlorine free EDS image of the polished mild-steel specimen, whereas Figure 12b indicates the presence of significant chlorine (4.6%) on the MS sample in aggressive media due to the corrosive nature of the aqueous hydrochloric acid solution. Figure 12c demonstrates the EDS outcomes for MS specimen treated with an optimum **MAB** concentration (0.464 mM) in corrosive media. This displays an insignificant quantity of chlorine content on the MS exterior when **MAB** was used in aggressive solution, suggesting this green inhibitor **MAB** is capable of providing excellent protection to MS specimen from aggressive solution [30].

4. Conclusions

In the present study, chemical investigation and anticorrosive evaluation of various *M. aurea* extracts for MS in acidic solution led to the identification of an efficient anticorrosive component **MAB** from the *n*-butanol extracts of *M. aurea*. Based on different spectroscopic (ESI-MS, UV, 1D, and 2D-NMR) data and their literature values, the chemical structure of **MAB** was characterized as Apigetrin. Chemical investigation of this plant is very sporadic and this compound was identified for the first time from *M. aurea*. The comprehensive study on the corrosion inhibitive properties of **MAB** revealed the following outcomes:

- The corrosion inhibitive capability of **MAB** increases with increasing the concentration of **MAB**, and highest *IE* (94.0%) was achieved at 0.464 mM.
- Electrochemical studies demonstrated a mixed-type inhibitor for **MAB** with the inclining cathodic efficacy.
- This novel green inhibitor **MAB** obeys Langmuir adsorption method isotherm, protects MS specimen through physical adsorption route, and process was exothermic and spontaneous.
- EDS and SEM analysis showed highly improved surface of MS specimen with **MAB** in corrosive media.
- Corrosion inhibitive properties evaluation of **MAB** using different methods such as weight loss, Tafel plots, EIS, SEM, and EDS analysis revealed that **MAB** has excellent inhibitive properties for MS sample in HCl corrosive environment.
- Corrosion inhibitive properties of *M. aurea* extracts and its isolated compound **MAB** is being reported here for the first time.
- The consistent results of the electrochemical and weight loss experiments is evident that this green inhibitor can be effectively utilized as a potent corrosion inhibitor for MS in aggressive solution (1.0 M HCl).

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