

Article

Lady's Mantle Flower as a Biodegradable Plant-Based Corrosion Inhibitor for CO₂ Carbon Steel Corrosion

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Abstract: Due to issues with the corrosion problem in the petroleum industry and the use of less ecologically acceptable corrosion inhibitors, great emphasis, within research on corrosion inhibitors, is now being put on green corrosion inhibitors (GCIs). In this study, Lady's mantle flower extract (LMFE) has been observed as a plant-based GCI for carbon steel in a simulated CO₂-saturated brine solution. The effectiveness of the inhibitor in static and flow conditions has been determined using potentiodynamic polarization with Tafel extrapolation and electrochemical impedance spectroscopy (EIS). In static conditions, the inhibitor has been tested at concentrations from 1 g/L to 5 g/L with an increment of 1 g/L per measurement, while, in dynamic (flow) conditions, the inhibitor has been tested at concentrations from 3 g/L to 6 g/L with an increment of 1 g/L per measurement. All measurements were performed at room temperature. EIS and potentiodynamic polarization methods showed that LMFE achieves maximum effectiveness in protecting carbon steel from corrosion when added at a concentration of 4 g/L in static conditions and at a concentration of 5 g/L in flow conditions. The test methods proved that the inhibitory effectiveness of LMFE is greater than 90% in both test conditions (static and flow). The inhibitor efficiency was attributed to the adsorption of LMFE on the carbon steel surface, which was demonstrated by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). A biodegradability of 0.96 and a toxicity of 19.34% for LMFE were determined. The conducted laboratory tests indicate that LMFE could be used as an effective corrosion inhibitor for CO₂ carbon steel corrosion.

Keywords: Lady's mantle flower extract; plant-based corrosion inhibitors; CO₂ corrosion; carbon steel; biodegradability; toxicity



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1. Introduction

Since its beginning, the petroleum industry has been faced with the problem of corrosion, as most of the equipment and pipelines within the petroleum industry are mainly composed of carbon steel. During the production of hydrocarbons, depending on the type of reservoir, a certain amount of brine and other impurities (dissolved gases, sand, additives used in the production process, etc.) are also produced. As production progresses, i.e., as the production field matures, the amount of brine produced also increases. In addition to the aforementioned brine, the produced fluid may also contain carbon dioxide (CO₂) and hydrogen sulfide (H₂S) (among other impurities), which cause corrosion and damage equipment when dissolved in water (brine).

The flow of the produced fluid has a significant effect on the rate of corrosion and the processes that occur on the steel surface. If a protective layer of iron carbonate (FeCO₃) is formed on a steel surface, or the steel surface is covered with a corrosion inhibitor's film, the effect of the flow on the corrosion rate becomes insignificant, since the FeCO₃ layer or the inhibitor's film represent the main resistance to corrosion. However, the presence of a turbulent flow, typical for hydrocarbon production and transportation, as well as the transportation of brine during its reinjection into the reservoir, could disrupt the formation

of or mechanically damage the mentioned layer/film, which leads to a higher corrosion risk on a local basis [1].

Regarding its omnipresence, corrosion in the petroleum industry is a major problem. Its aftermaths can damage the equipment and, additionally, can influence the environment (i.e., potentially cause a spill). The mentioned environmental impact has a major economic impact. The International Measures of Prevention, Application, and Economics of Corrosion Technologies Study (NACE IMPACT report) gave estimates of the total costs caused by corrosion. It was reported that the overall cost of corrosion is approximately USD 2.5×10^{12} , or approximately 3.4% of the world's gross domestic product (GDP) [2].

Electrochemical corrosion will occur in systems where water is present. As mentioned earlier, production lines and flowlines are the most vulnerable parts of an oil and gas production and transportation system. The produced fluid that is transported through the flowlines has not yet been treated. This means that the fluid still contains brine and impurities such as CO₂. According to CONCAWE (CONservation of Clean Air and Water in Europe) data [3], there were fifteen leakage incidents caused by corrosion in a ten-year period (2012–2021). Corrosion has the largest share in spilled volume (1194.4 m³), and thus has the largest negative environmental impact compared to spills caused by mechanical failure (spill volume 109.2 m³) and operational causes (spill volume 63.1 m³). The corrosion problem can be alleviated by the use of corrosion inhibitors, among other things. Since conventional corrosion inhibitors are considered to be harmful to the environment, they are to be replaced by just as effective, less toxic, and biodegradable so-called green corrosion inhibitors (GCI). Plant extracts, derived either from flowers, roots, leaves, or fruit, are currently being tested as GCI. Most of them have been tested in strong acidic [4–24] and neutral environments [25–28], with only a few tests being performed in CO₂-saturated media [29–33].

Nowadays, in addition to the fact that a corrosion inhibitor must meet the criteria of high effectiveness in corrosion protection, it must also be environmentally friendly. Such corrosion inhibitors certainly include plant extracts that are rich in organic compounds that protect the metal from corrosion through a specific binding mechanism on the metal surface. Therefore, numerous tests are focused on the discovery of new plant extracts that show high inhibitory effectiveness in the protection of metals from corrosion [4–33].

Although tests show that plant extracts achieve comparable and higher effectiveness in corrosion protection than organic inhibitors, not all plant extracts are effective in all media, nor is the use of certain extracts as corrosion inhibitors justified (in the case of plants that are simultaneously used as food), and not all extracts are equally available in all parts of the world. Basically, finding an effective extract to act as a corrosion inhibitor in specific conditions is not easy.

Tests of plant extracts from different parts of the world (cashew nut, *Tridax procumbens*, *Chromolaena odorata*, kuding, olive leaf, *Jatropha curcas*, *Sida acuta*, *Coptis chinensis*, berberine, licorice, tobacco leaf, pomelo, *Calotropis procera*, corn oil, *Dimocarpus longan*, *Ginkgo biloba*, and *Momordica charantia*) were carried out in systems that simulate real ones in the production and transport systems of the oil industry, with a brine solution saturated with CO₂ [29,34–36].

The aim of this work is to examine the action of Lady's mantle flower (LMF) extract as a corrosion inhibitor in a brine solution saturated with CO₂. Although it can be cultivated, Lady's mantle is a plant that grows wild in the temperate regions of Europe, all the way to Siberia, but also in Asia, North America, and Greenland. It blooms from May to October [37,38]. The plant is characteristic of the Croatian climate, which is the reason for its selection as a potential corrosion inhibitor. The tests were carried out in a brine solution saturated with CO₂, which, in its composition, is similar to natural aquifers in Croatia.

This article presents the inhibitory effect of Lady's mantle flower extract (LMFE). The inhibitory effect was determined using electrochemical methods (potentiodynamic polarization with Tafel polarization and electrochemical impedance spectroscopy (EIS)). In addition, the results of scanning electron microscopy (SEM) and Fourier transform

infrared spectroscopy (FTIR) scans are presented to show surface characterization and determine how, and by which functional groups, the inhibitor was absorbed on the steel surface. Finally, biodegradability and toxicity tests were conducted to determine if LMFE is biodegradable and/or toxic.

2. Materials and Methods

Carbon steel was used as a metal sample for the measurements conducted in this study. The composition (wt.%) of the carbon steel was 0.32 C, 0.25 Si, 1.38 Mn, 0.016 P, 0.009 S, 0.24 Cr, <0.01 Mo, 0.02 Ni, 0.01 Cu, and balance Fe. It was determined using optical emission spectrometry on the Laboratory Equipment Companies' (LECO) Glow Discharge Atomic Emission spectrophotometer GDS 850 A. Prior to conducting each corrosion rate progression measurement, the carbon steel sample was ground with 300, 600, and 1200 grit paper. After grinding, the carbon steel sample was washed using distilled water and degreased with ethanol (96%). The area of the carbon steel sample exposed to the corrosive solution was 1 cm². Considering that the brine is corrosive media for the carbon steel in the petroleum industry, it was necessary to simulate the brine for the laboratory measurements. Simulated brine solution contained 30 g/L of NaCl, 0.1 g/L of NaHCO₃; and 0.1 g/L of CaCO₃. For the measurements, the commercially available powder of Lady's mantle flower extract, DARvitalis, Croatia, was used.

Prior to the start of the measurements, the prepared solution was saturated with carbon dioxide (CO₂) for 45 min and continued to be saturated during the measurements. LMFE was added at a concentration from 1 g/L to 5 g/L, which increased by 1 g/L per measurement in static conditions. For the measurements in flow conditions, the added concentration of LMFE was 3 g/L to 6 g/L, also with an increase of 1 g/L per measurement. All measurements were performed at room temperature.

After saturation, the carbon steel sample was immersed in the prepared solution and the electrode was stabilized for 1 h before the electrochemical measurement was performed. The measurements that were performed in static conditions were performed by using a three-electrode corrosion cell (see Figure 1a). For the measurements in flow conditions, a three-electrode flow-through corrosion cell was used (see Figure 1b). Two graphite rods were used as counter electrodes for the measurements in static conditions and a platinum electrode was used for the measurements in flow conditions. In both cases, a saturated calomel electrode (SCE) was used as the reference electrode. In maximum flow conditions of 50 cm³/min, which is equal to a maximum flow rate of 400 cm/min for the flow cell used in this case, the measurements were conducted for a simulation of flow. The electrochemical measurements were performed, using the SP1 potentiostat and SmartManager software (ver6743), with the DC data analysis software IVMANTM 1.5 and Impedance Data Analysis Software ZMANTM 2.5 to analyze the data. All the measurements were taken three times, resulting in a reproducibility of less than 5% of relative standard deviation.

For potentiodynamic polarization with Tafel extrapolation, the corrosion potential was adjusted to ± 250 mV opposite to the open-circuit potential after a 1 h stabilization of the electrode. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 100 kHz to ~ 10 mHz. By repeating the measurements, the obtained results indicated a negligible change in the values after 10 mHz and had no effect on the results or the chosen equivalent electrical circuits. The characterization of the steel sample surface, with or without the corrosion inhibitor, was performed using the non-destructive EIS method. In addition to electrochemical measurements, surface methods (SEM and FTIR) were used to determine the presence of inhibitory film and the mode of the adsorption on the steel surface. To perform these methods, the carbon steel sample was immersed in the solution containing the most effective concentration of the LMFE for four hours, after which it was compared to the carbon steel samples, which were exposed to the solution without the addition of the extract. To determine the impact of the LMFE as a GCI on the environment, the biodegradability and toxicity of the LMFE were studied. The value of chemical oxygen demand (COD) was determined spectrophotometrically, and biochemical

oxygen demand (BOD) was determined using the Winkler method. The bioluminescent bacterium *Vibrio fischeri* was used to determine the toxicity.

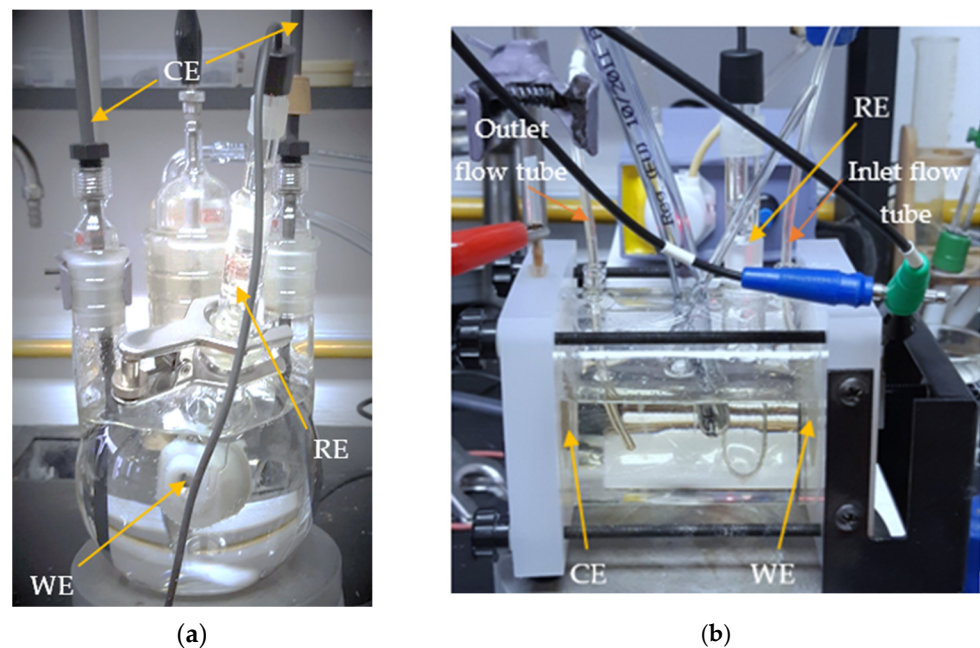


Figure 1. Three-electrode corrosion cell used for measurements in static conditions (a); three-electrode flow-through corrosion cell used for measurements in flow conditions (b); CE—counter electrodes, RE—reference electrode, WE—working electrode.

3. Results and Discussion

3.1. Electrochemical Measurements

3.1.1. Potentiodynamic Polarization

To detect the efficiency of LMFE as a GCI, a potentiodynamic polarization measurement was conducted. Figures 2 and 3 show polarization curves that were scanned during the measurements in static and flow conditions. By applying Tafel extrapolation on the recorded polarization curves, some electrochemical parameters could be determined. These parameters are corrosion potential (E_{corr}), corrosion current (j_{corr}), anodic and cathodic Tafel slopes (β_a and β_c , respectively), and corrosion rate (v_{corr}) (see Tables 1 and 2). Inhibitor efficiency was calculated using Equation (1) [39], as follows:

$$IE(\%) = \frac{v_{corr}^0 - v_{corr}^{inh}}{v_{corr}^0} \times 100 \quad (1)$$

where IE is the inhibitor efficiency (%), v_{corr}^0 is the corrosion rate of the sample in the uninhibited solution (mm/year), and v_{corr}^{inh} is the corrosion rate of the sample in the inhibited solution (mm/year).

For the specified test conditions, the anodic corrosion reaction is the dissolution of iron from the steel, according to Equation (2), as follows:



Although there were disagreements about the cathodic corrosion reaction, it was determined that, under the tested conditions, the dominant cathodic reaction is the reduction of hydrogen ions produced by the dissociation of carbonic acid (the so-called “buffering effect”, shown in Equation (3)) [40–42], as follows:



Figures 2 and 3 show the polarization curves scanned on carbon steel in static and flow conditions, while Tables 1 and 2 contain electrochemical parameters determined from these polarization curves.

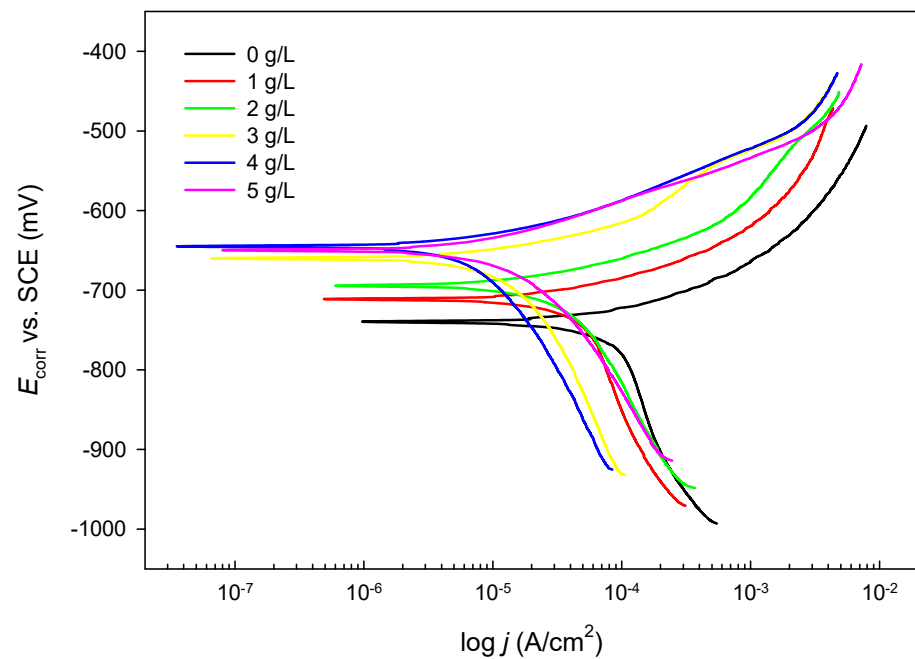


Figure 2. Polarization curves of carbon steel samples in the simulated brine solution saturated with CO_2 with different concentrations of LMFE as a corrosion inhibitor in static conditions (adapted from [43]).

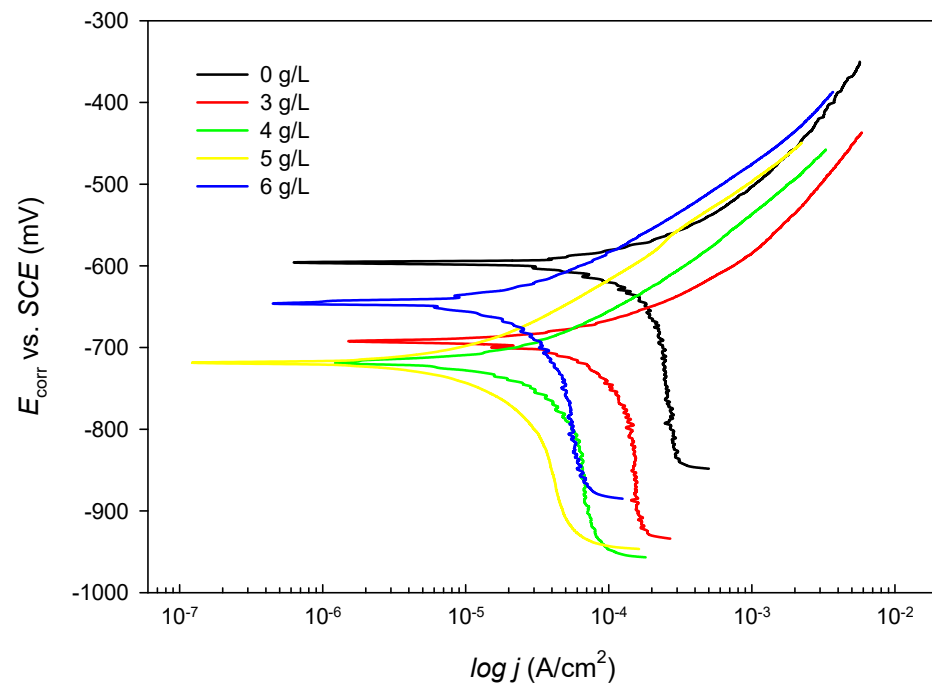


Figure 3. Polarization curves of carbon steel samples in the simulated brine solution saturated with CO_2 with different concentrations of LMFE as a corrosion inhibitor in flow conditions (adapted from [43]).

Table 1. Electrochemical polarization parameters for carbon steel samples in the simulated brine solution saturated with CO₂ with different concentrations of LMFE as a corrosion inhibitor in static conditions (adapted from [43]).

γ (g/L)	E_{corr} (mV)	j_{corr} ($\mu\text{A}/\text{cm}^2$)	$-\beta_k$ (V/dec)	β_a (V/dec)	v_{corr} (mm/year)	IE (%)	σ
0	−741	97.627	0.517	0.065	1.136	-	-
1	−699	46.199	0.375	0.054	0.538	52.64	1.49
2	−685	34.675	0.287	0.053	0.404	64.44	1.92
3	−662	13.370	0.275	0.053	0.156	86.27	2.51
4	−641	5.516	0.182	0.038	0.064	94.37	1.44
5	−640	12.352	0.188	0.057	0.144	87.32	1.59

Table 2. Electrochemical polarization parameters for carbon steel samples in the simulated brine solution saturated with CO₂ with different concentrations of LMFE as a corrosion inhibitor in flow condition (adapted from [43]).

γ (g/L)	E_{corr} (mV)	j_{corr} ($\mu\text{A}/\text{cm}^2$)	$-\beta_k$ (V/dec)	β_a (V/dec)	v_{corr} (mm/year)	IE (%)	σ
0	−613	175.441	0.686	0.145	2.042	-	-
3	−683	86.783	0.626	0.085	1.010	50.54	1.49
4	−708	32.193	0.347	0.099	0.351	82.81	1.18
5	−713	8.845	0.158	0.084	0.103	94.96	2.77
6	−642	18.330	0.206	0.078	0.213	89.57	2.28

Potentiodynamic polarization in static conditions

Corrosion current densities, j_{corr} , and corrosion potentials, E_{corr} , were determined using the Tafel method, i.e., as the intersection of the extrapolated linear parts of the cathodic and anodic branches of the polarization curves in the $E_{\text{corr}} \pm 100$ mV range.

In the presence of LMFE, a shift of the cathodic and anodic part of the polarization curve towards lower values of the corrosion currents is observed, which implies lower values of the corrosion rate. Corrosion rates decrease (from 1.136 mm/year to 0.064 mm/year) with an increase in extract concentration (from 0 g/L to 5 g/L). In the presence of LMFE in the highest concentrations (5 g/L), a decrease in the effectiveness (increase in corrosion rate to 0.144 mm/year) of LMFE was observed, which is often mentioned in the literature for organic inhibitors at higher concentrations as the phenomenon of critical inhibitor concentration (CMC) and is associated with adsorption [44–46].

As can be seen in Figure 2, the anodic Tafel slope (β_a) in simulated brine solution saturated with CO₂ without the LMFE was 65 mV/dec, which indicates that, in the tested condition, anodic dissolution of the carbon steel sample occurs [47]. The cathodic Tafel slope in the simulated brine saturated with CO₂ without the LMFE was very high ($\beta_c = -517$ mV/dec). This high value is characteristic for saturated CO₂ solutions, and it is a result of the diffusion of dissolved CO₂ on the reduction process [48].

Regarding the polarization curves and the values of the slope of the anodic Tafel lines in the presence of LMF extract, it is evident that they change only slightly when compared to the uninhibited system. A significant increase in the anodic slope of the Tafel lines would indicate the effect of the extract on the reaction mechanism. Since only small decreases in the anodic Tafel slopes are evident, this indicates the adsorption of the extract on the surface of the steel and its inhibitory effect by blocking the surface, without affecting the reaction mechanism [49,50]. A more significant change in the anodic Tafel slope is observed at an extract concentration of 4 g/L, which also corresponds to the greatest reduction in the corrosion rate (0.064 mm/year), i.e., the greatest inhibitory effectiveness (94.37%).

The dominant cathodic reaction in the tested conditions is the reduction of hydrogen ions produced by the dissociation of carbonic acid [40]. The cathodic Tafel slopes in the presence of LMFE decrease compared to the uninhibited system, which indicates a reduction in the influence of the diffusion process on the cathodic reaction [45]. This change is especially noticeable at an extract concentration of 4 g/L.

The corrosion potential of a carbon steel sample in a simulated brine solution saturated with CO₂ without the LMFE was −741 mV, which is in accordance with the values of corrosion potential under similar test conditions [51].

In the presence of the LMFE, a shift of the corrosion potential (E_{corr}) in the direction of more positive values was observed. The shift in the positive direction increases with an increase in extract concentration, and, at the extract concentration of 4 g/L, it was −641 mV vs. SCE, which is 100 mV more positive compared to the uninhibited system ($E_{\text{corr}} = -741$ mV). The shift of the corrosion potential in the direction of more positive values indicates the preferential inhibition of the anodic reaction of iron dissolution and is attributed to the formation of a protective film on the steel surface [48].

Since the value of the corrosion potential at a concentration of LMFE of 4 g/L is greater than 85 mV compared to the uninhibited system, LMFE can be considered as an anodic corrosion inhibitor of carbon steel in brine solutions saturated with CO₂ in static conditions [39,52–56]. The polarization curves scanned at higher concentrations of the extract, 4 g/L and 5 g/L, show a more significant change in the shape of the anodic part of the curve, which also supports the action of the extract on the anodic process.

The inhibitory efficiencies, IEs, given in Table 1 show that the LMFE inhibits the corrosion of carbon steel in a brine solution saturated with CO₂ under static conditions. The highest inhibitory effectiveness was achieved by the LMFE at a concentration of 4 g/L and is 94.37%. The inhibitory effect is attributed to the adsorption of the LMFE on the steel surface.

Although the tested extract also showed an action on the cathodic reaction, the shift of the corrosion potential in the anodic direction greater than 85 mV, a significant decrease in the anodic current densities, in comparison with the decrease in the cathodic current densities in the presence of the extract, and an obvious change in the shape of the anodic branch of the polarization curves at concentrations of 4 g/L and 5 g/L extract, categorize the extract as an anodic corrosion inhibitor for carbon steel in a brine solution saturated with CO₂ under static conditions.

Potentiodynamic polarization in flow conditions

Scanned polarization curves for measurements conducted in flow conditions are shown in Figure 3. In Table 2, the parameters determined from the Tafel extrapolation of scanned curves are given.

The corrosion potential in the non-inhibited system ($E_{\text{corr}} = -613$ mV) takes on a more positive value compared to the non-inhibited system in static conditions ($E_{\text{corr}} = -741$ mV), which is consistent with the tests of the influence of flow on the corrosion potential [57].

In the presence of the extract, a shift of the corrosion potentials towards more negative values is observed (Figure 3), and the shift is more significant with an increase in the concentration of the extract, which indicates the inhibition of the cathodic reaction [58].

The change in corrosion potential in the cathodic direction for 3 g/L, 4 g/L, and 5 g/L of LMFE is greater than 85 mV (Table 2), which means that LMFE exhibits the behavior of a cathodic corrosion inhibitor in flow conditions.

In the presence of LMFE, a shift of the cathodic parts of the polarization curves towards lower current densities was observed when compared to the system without extract. This proves the effect of the extract on the cathodic reaction, such that it suppresses the reduction of hydrogen ions [59]. On the other hand, the anodic parts of the polarization curves show active corrosion for the uninhibited and inhibited systems, which means that the LMFE does not significantly affect the anodic reaction under flow conditions [58].

With an increase in the concentration of the extract (from 0 g/L to 5 g/L), a decrease in the rate of corrosion (from 2.042 mm/year to 0.103 mm/year) and an increase in the

effectiveness of the extract (up to 94.96%) as a corrosion inhibitor can be observed. Even in flow conditions, at the highest tested concentration, 6 g/L, an increase in the corrosion current density and a decrease in effectiveness compared to a lower extract concentration were observed, which is also attributed to the CMC. LMF extract showed a maximum effectiveness of 94.96% as a corrosion inhibitor at a concentration of 5 g/L.

The values of the parameters obtained by Tafel extrapolation, shown in Table 2, indicate a slight change in the anodic Tafel slopes (maximum 0.067 V/dec) and a significant decrease in the cathodic Tafel slope (maximum 0.528 V/dec) in the presence of the extract compared to the uninhibited system [60]. This significant decrease in the cathodic Tafel slope indicates the action of the extract as a cathodic corrosion inhibitor, in a way that affects the mechanism of the cathodic reaction. Such behavior may be the result of the formation of a protective film on the surface of the steel, which reduces the diffusion of electroactive species of the cathodic reaction (H^+ ions) to the surface of the steel, increases the resistance on the surface of the metal, and reduces the rate of corrosion [58,61].

All of the above indicate the effect of the LMFE as a cathodic corrosion inhibitor on carbon steel corrosion in brine solution saturated with CO_2 in flow conditions.

3.1.2. Electrochemical Impedance Spectroscopy

Phenomena at the electrolyte–steel surface interface were investigated using the electrochemical impedance spectroscopy method. Figure 4 shows impedance spectra (Nyquist and Bode plots) recorded on the surface of carbon steel with and without the presence of LMF extract in a brine solution saturated with CO_2 in static and flow conditions.

By fitting the recorded impedance spectra with the assumed theoretical models (equivalent circuits), which can be seen in Figure 5, the values of the electrochemical parameters shown in Table 3 were obtained. On the graphs shown (Figure 5), points represent measured values, and lines represent fitted results. The fitted and measured values show good agreement (more precisely, the error in disagreement for all spectra is less than 5%). The listed electrical equivalent circuits (and similar) are used commonly in the interpretation of EIS results for the conditions and systems described in this paper [62].

Table 3. EIS parameters for the carbon steel sample in the simulated brine solution saturated with CO_2 with different concentrations of LMFE as a corrosion inhibitor in static and flow conditions (adapted from [43]).

Static Conditions									
γ (g/L)	R_s ($\Omega\text{ cm}^2$)	Y_{dl} ($\mu\Omega^{-1}s^n$)	n_1	R_p ($\Omega\text{ cm}^2$)	Y_{inh} ($\mu\Omega^{-1}s^n$)	n_2	R_{po} ($\Omega\text{ cm}^2$)	IE (%)	σ
0	3.12	408	0.83	142.78	-	-	-	-	-
1	5.56	407	0.77	359.05	-	-	-	60.23	2.97
2	7.04	331	0.73	371.56	-	-	-	61.57	2.94
3	8.34	82.2	0.75	634.37	77.3	0.94	10.85	77.49	2.11
4	5.31	77.5	0.70	1629.61	67.5	0.94	12.97	91.24	1.60
5	5.18	65.2	0.73	516.37	68.1	0.95	16.04	72.35	1.16
Flow Conditions									
γ (g/L)	R_s ($\Omega\text{ cm}^2$)	Y_{dl} ($\mu\Omega^{-1}s^n$)	n_1	R_p ($\Omega\text{ cm}^2$)	Y_{inh} ($\mu\Omega^{-1}s^n$)	n_2	R_{po} ($\Omega\text{ cm}^2$)	IE (%)	σ
0	12.31	1840	0.75	113.68	-	-	-	-	-
3	14.03	1570	0.97	219.87	310	0.83	371.86	48.30	2.18
4	14.20	230	0.79	384.28	291	0.71	512.91	70.42	2.57
5	14.81	140	0.83	2884.45	186	1.00	832.84	96.06	1.54
6	14.26	18220	0.80	1288.80	170	0.82	454.16	91.18	3.72

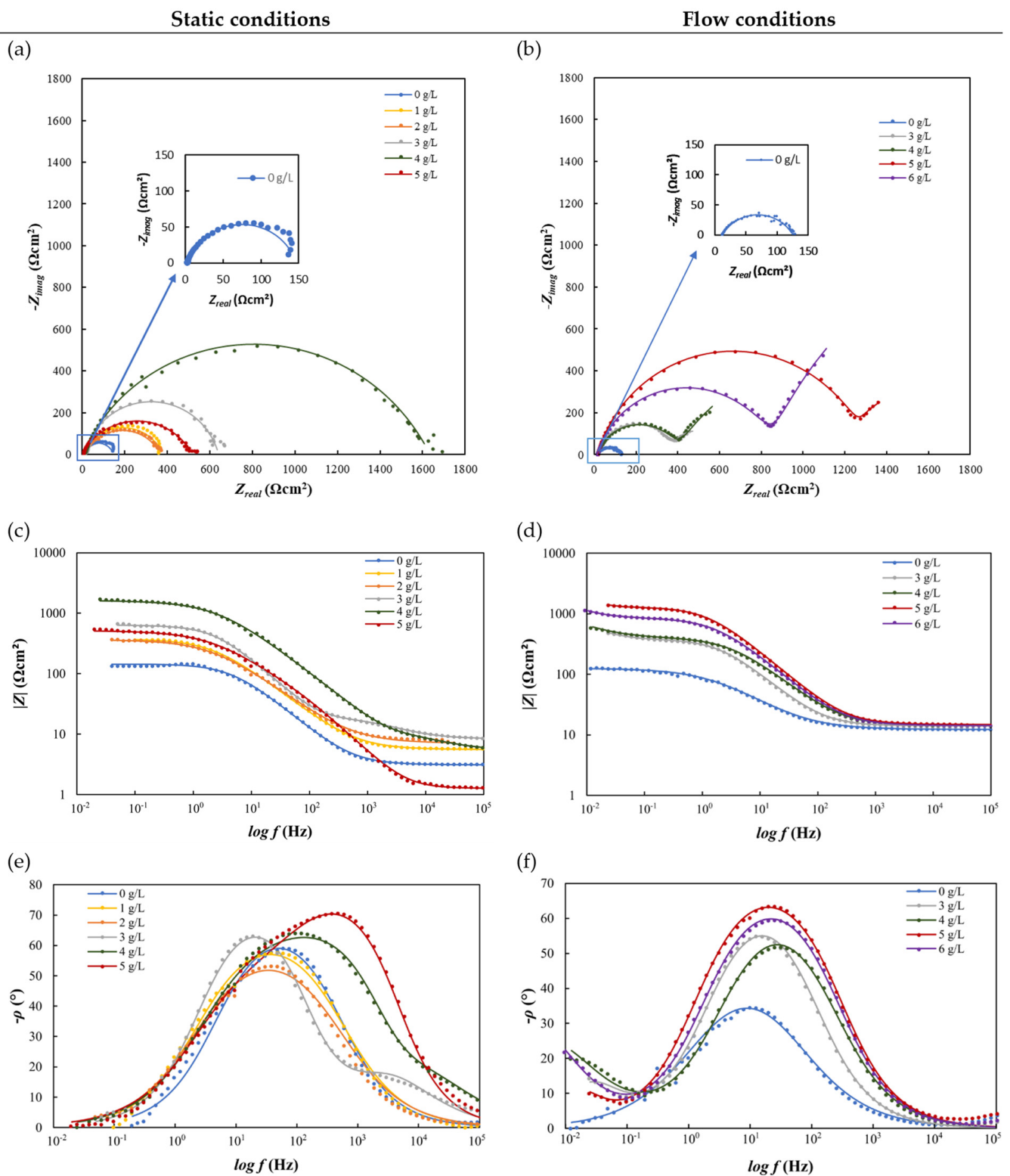


Figure 4. (a,b) Nyquist and (c–f) Bode plots for the carbon steel samples in the simulated brine solution saturated with CO_2 with different concentrations of LMFE as a corrosion inhibitor in static and flow conditions (adapted from [43]).

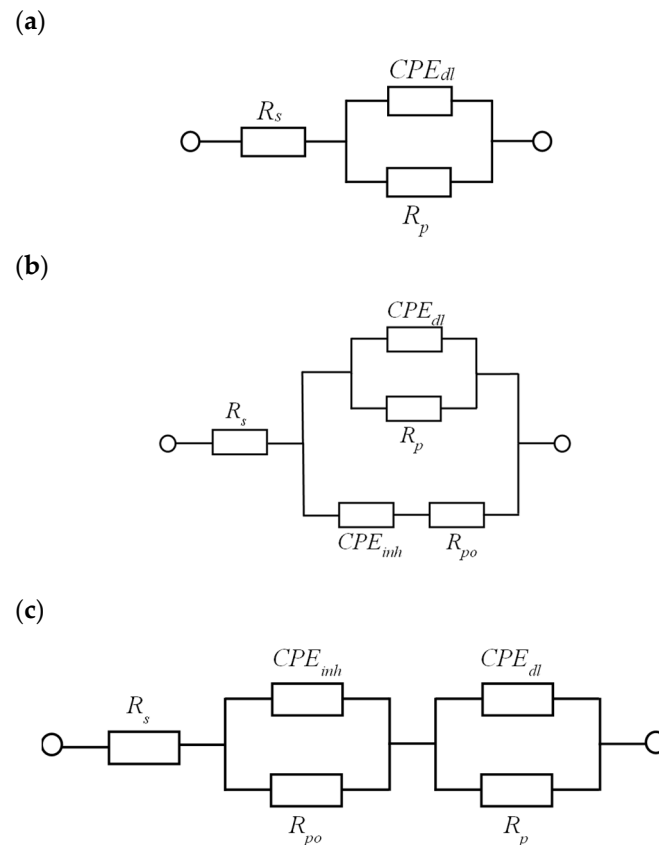


Figure 5. Equivalent circuit models used to analyze the impedance data; (a) uninhibited solution, (b) inhibited solution in static conditions, and (c) inhibited solution in flow conditions.

Three equivalent circuits were used to analyze the experimental data. For the measurements performed in static and flow conditions for the uninhibited solutions, the circuit system shown in Figure 5a was used. This theoretical model (Figure 5a) was also used for the solution that contained 1 and 2 g/L of LMFE in static conditions. For the solution with all the other LMFE concentrations (3–5 g/L) in static conditions, the equivalent circuit shown in Figure 5b was used. In the interpretation of test results of inhibited systems in flow conditions, the equivalent circuit shown in Figure 5c was used.

In the shown equivalent circuits, there were the following parameters: R_s , electrolyte resistance; R_p , charge transfer resistance; R_{po} , resistance of inhibitor film pores; CPE_{dl} , constant phase element representing the capacity of the electrochemical double layer; and CPE_{inh} , constant phase element representing the capacity of the inhibitor film. A constant phase element, CPE , replaces capacitors in equivalent circuits in order to compensate for surface inhomogeneity, roughness and geometric irregularity, porosity of electrodes, etc. [33,63].

Electrical equivalent circuits, EECs, for systems in the presence of LMFE represent a parallel/series connection of two CPE s, which refer to the metal surface and the coating film. The impedance of CPE s is defined by Equation (4), as follows:

$$Z_{CPE} = \frac{1}{Y} (j\omega)^{-n} \quad (4)$$

where Y is the proportionality factor, $j = \sqrt{-1}$, $\omega = 2\pi f$, and n is the dispersion coefficient associated with surface inhomogeneity. CPE can represent different electrical elements, depending on the value of n : for the value of $n = 0$, Y represents a resistor, $R = Y^{-1}$, and for $n = 1$, a capacitor, $C = Y$ [64–68].

The inhibitory effectiveness of the extract was calculated from the charge transfer resistance according to the expression (Equation (5)), as follows:

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

where R_p^{inh} and R_p^0 are charge transfer resistances for carbon steel in a solution without and in the presence of the extract, respectively.

Nyquist plots recorded for the uninhibited system under static and flow conditions show a single capacitive half-circuit, as seen in Figure 4. The irregular shape of the Nyquist diagram is an indicator of the impedance frequency dispersion at the phase boundary and is characteristic of an inhomogeneous metal surface [69–74].

Since Y is proportional to C , changes in the value of Y correspond to changes in C . The value of Y_{dl} of an uninhibited system under flow conditions, $Y_{dl} = 1840 \mu\Omega^{-1}s^n$, is significantly higher than $Y_{dl} = 408 \mu\Omega^{-1}s^n$ under static conditions, which also means a higher value of C_{dl} under flow conditions compared to static conditions. Namely, the increase in the capacity of the double layer, C_{dl} , is related to the increase in the surface area available for the deposition of corrosion products. This is interpreted as the preferential dissolution of ferrite, while cementite (Fe_3C) stays behind and protrudes on the carbon steel surface [33,75].

The charge transfer resistance for uninhibited systems in static conditions, $R_p = 142.78 \Omega cm^2$, and flow conditions, $R_p = 113.68 \Omega cm^2$, are low, which indicates an active corrosion process and the formation of corrosion products that do not have protective properties. A lower resistance to charge transfer indicates a higher corrosion rate under flow conditions. The phase angle maximum, φ , of the Bode diagram under flow conditions for the uninhibited system takes on a lower value compared to the phase angle maximum under static conditions, which is attributed to the more intense corrosion of carbon steel under flow conditions. The existence of one phase angle peak (one time constant) on the Bode diagram indicates an active corrosion process [48].

The Nyquist diagrams show an increase in the real and imaginary components in the presence of the extract compared to the system without the extract. Also, this increase is consistent with the increase in extract concentration, which is attributed to the formation of a protective film on the steel surface in the presence of the LMFE [76]. The amount of impedance modules on the Bode diagram also increases with increasing extract concentration. The exception is the behavior of the extract at the highest concentrations (5 g/L in static conditions and 6 g/L in flow conditions) when, due to the CMC, there is a drop in resistance to charge transfer. For the same concentration values of LMF extract in static conditions, there are higher resistances to charge transfer compared to flow conditions (a comparison is only possible for the same concentrations in flow and static conditions, which are 3 g/L and 4 g/L, with the fact that 5 g/L was not taken into consideration since the CMC was reached in static conditions at that concentration).

In the presence of the extract in static conditions, the Bode diagram shows the formation of a time constant in the area of high frequencies, i.e., the presence of the extract changes the corrosion process with one time constant into a process with two time constants. The rate of corrosion is influenced by charge exchange at low frequencies and the formation of an inhibitory film at higher frequencies, which is evident from the shape of the Nyquist and Bode diagrams for static conditions, as shown in Figure 4 [48,77,78].

The existence of a time constant in the region of high frequencies means the existence of a protective inhibitory film on the surface of the electrode, while the shift of the phase angle maximum towards higher frequencies is associated with the growth of the inhibitory film [79]. In flow test conditions, although no clear formation of the second time constant is visible on the Bode diagram, an increase in the maximum of the phase angle is visible, as well as its shift towards higher frequencies, which is attributed to the formation of an inhibitory film on the carbon steel surface in flow conditions [48].

According to the values given in Table 3, for flow and static conditions, the values of Y_{dl} in the presence of the extract decrease (as does C_{dl}), which indicates the adsorption of the extract on the surface of the steel sample. The decrease is in accordance with the increase in the concentration of the extract. Also, the charge transfer resistances increase with an increase in the extract concentration, except for the highest concentrations, at which the drop in the charge transfer resistance, i.e., the decrease in the radius of the Nyquist diagram, is attributed to the achievement of the CMC.

Changes in the double layer capacitance and inhibitor film capacitance provide information about the inhibitor film. The capacity of the electrochemical double layer is calculated according to the Helmholtz model (Equation (6)), as follows:

$$C_{dl} = \frac{\epsilon \epsilon_0 A}{d} \quad (6)$$

where d is the thickness of the layer, ϵ is the dielectric constant of the medium, ϵ_0 is the permittivity of the vacuum, and A is the effective area of the electrode. In the presence of the extract, the decrease in the Y_{dl} value, or C_{dl} , can be interpreted as a decrease in the value of the dielectric constant due to the replacement of water molecules (with a high dielectric constant) with inhibitor molecules (with a low dielectric constant) on the surface of the steel sample. Also, this trend of C_{dl} value changes can be interpreted as an increase in layer thickness (according to Equation (6), the C_{dl} value will decrease), due to the adsorption of larger organic inhibitor molecules [80–84].

According to the literature, the values of the parameter n_1 range from 0.7 to 0.9, which was mostly achieved in this work, and they play a role in describing the experimental data [67]. The parameter n is a measure of the unevenness of the electrode surface, although its physical meaning has not been fully clarified [67].

The values of Y_{inh} , i.e., the capacities of the inhibitory film, C_{inh} , decrease with increasing LMFE concentration, while the pore resistance values, R_{po} , of the inhibitory film increase, which indicates a compact surface of the inhibitory film with protective properties against corrosion.

The electrolyte resistance values, R_s , are different for static and flow conditions. The reason for this is the different geometric performance of the electrolytic cell in static and flow conditions; that is, in the flow cell, the distance between the reference and working electrodes is greater than in the cell for static tests.

Charge transfer resistances increase with an increase in the concentration of the LMFE for static conditions up to 4 g/L, and up to 5 g/L for flow conditions, which means that the adsorbed extract increases the resistance to the dissolution of iron from the steel or blocks the reaction surface [33]. At the highest extract concentrations (5 g/L for static and 6 g/L for flow conditions), a drop in the resistance to charge transfer was observed due to the reaching of the CMC. The highest value of charge transfer resistance ($R_p = 1629.61 \Omega$) and the highest inhibitory efficiency in static conditions ($IE = 91.24\%$) was shown by the LMFE at a concentration of 4 g/L, and in flow conditions ($R_p = 2884.45 \Omega$, $IE = 96.06\%$) in a concentration of 5 g/L. The results obtained by the EIS method are comparable to the results of potentiodynamic polarization.

3.2. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR)

Surface scans of the carbon steel sample, after its 4-h immersion in the uninhibited simulated brine solution saturated with CO_2 in static and flow conditions, in the presence of the most effective concentration of LMFE as a corrosion inhibitor (4 g/L in static conditions and 5 g/L in flow conditions), are shown in Figure 6a–d.

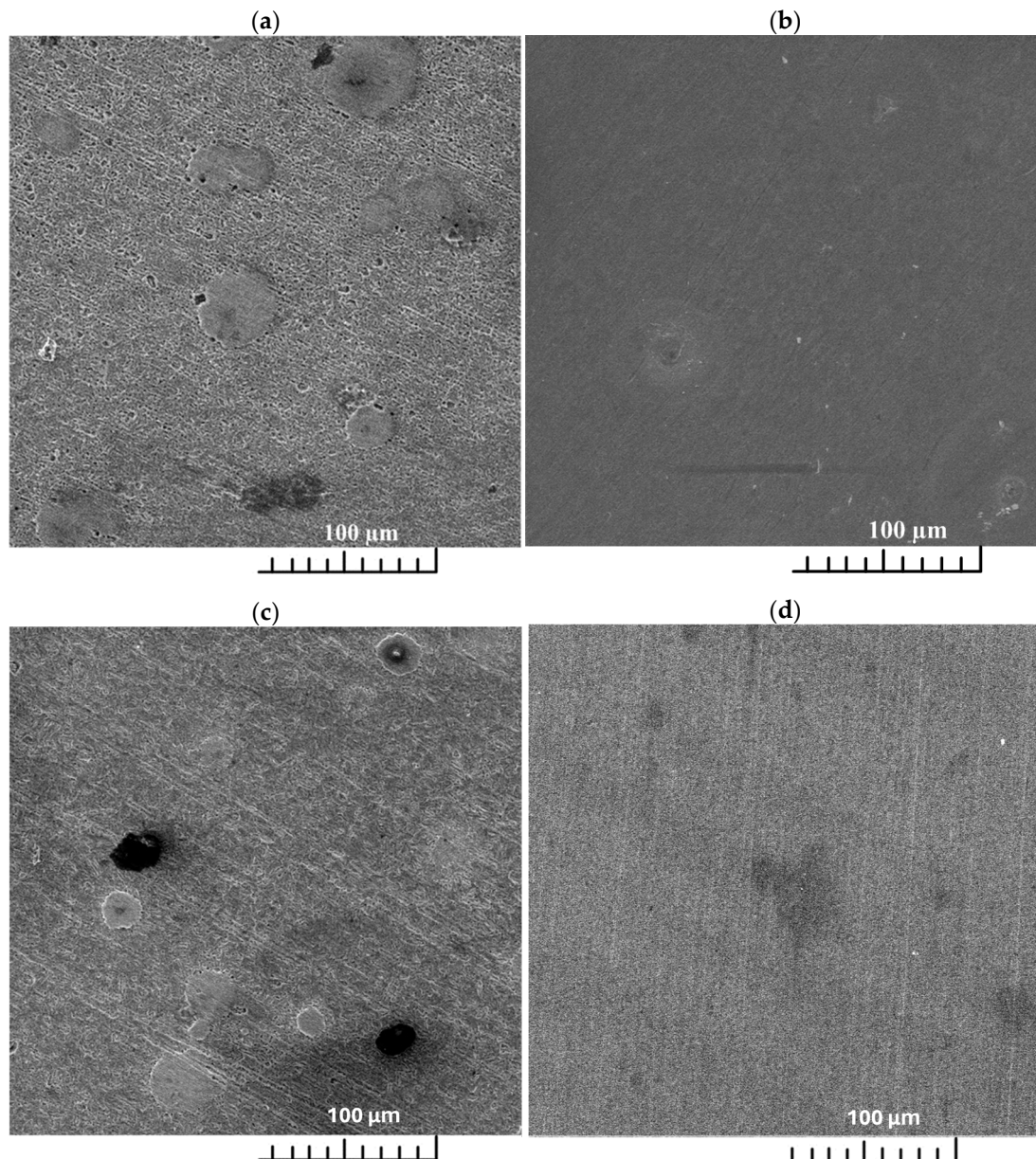


Figure 6. Carbon steel SEM scans after a 4-h immersion in the simulated brine solution saturated with CO_2 without the extract (a) in static and (c) in flow conditions and with LMFE (b) in static (4 g/L of LMFE) and (d) flow conditions (5 g/L of LMFE) (adapted from [43]).

Carbon steel surfaces after exposure to an uninhibited system in static and flow conditions (Figure 6a,c) are uneven and rough, which is a consequence of active corrosion, i.e., dissolution of iron from the steel. Under the test conditions, no corrosion products of protective properties are formed, so the rough surface can be interpreted as the dissolution of ferrite, while cementite rises from the surface of carbon steel [33,75].

In comparison with the exposure of steel to the inhibited solution, Figure 6b,d show that, after exposure to the action of LMFE, the carbon steel surface was smoother and more even, which can be related to the adsorption of LMFE on the carbon steel surface.

The mode of the adsorption of the LMFE compounds' functional groups on the carbon steel surface was examined using the FTIR method. The FTIR spectra of LMFE powder and the carbon steel surface, after its immersion for 4 h in the simulated brine solution saturated with CO_2 in the presence of 4 g/L of LMFE, are shown in Figure 7.

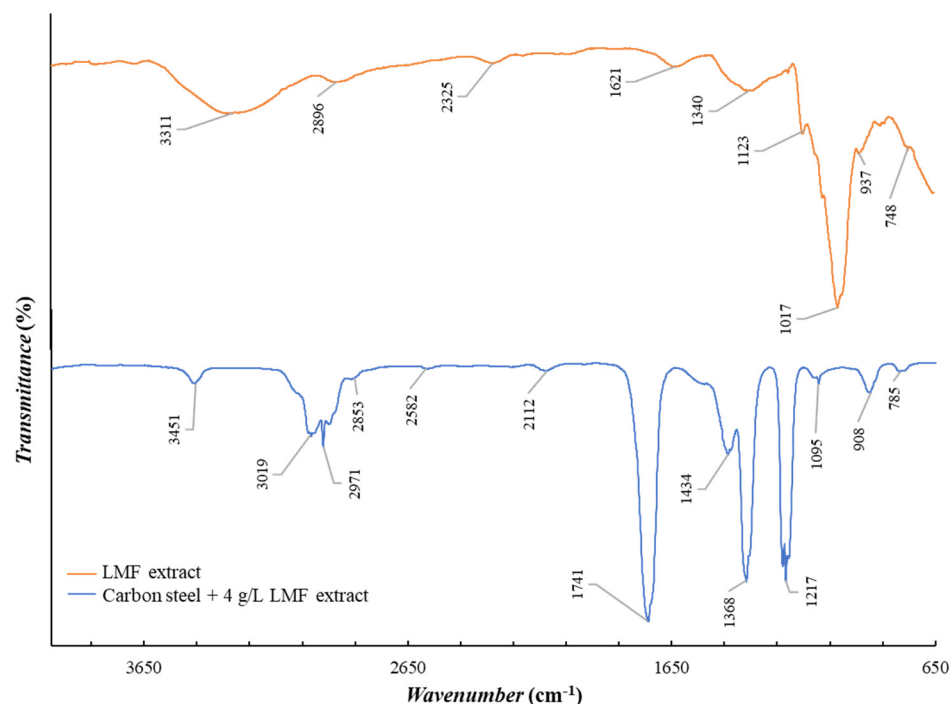


Figure 7. FTIR spectra of LMF extract powder and FTIR spectra of the carbon steel sample after 4 h of immersion in the simulated brine solution saturated with CO₂ and 4 g/L of the LMF extract (adapted from [43]).

According to the FTIR spectra of the LMFE, from the IR bands at 1017 cm^{−1}, 1340 cm^{−1}, and 3311 cm^{−1}, the dominant functional group was C-N, followed by the C-C and O-H functional groups, respectively. On the other hand, from the FTIR spectra of the inhibitors' film on the carbon steel sample surface, the vibration bands reveal the presence of some functional groups that were not seen on the LMFE spectra, but on the spectra of the inhibitors' film they were more noticeable. This means that, in the extract, some non-dominant functional groups exist, and through them, adsorption on the steel surface is achieved. From Figure 7, it can be seen that there was adsorption of the LMFE on the carbon steel sample surface through the C-N (1217 cm^{−1}), C-C (1368 cm^{−1}), C=O (1741 cm^{−1}), and C-H (2971–3019 cm^{−1}) functional groups [85]. The FTIR spectra results confirm the LMFE adsorption on the carbon steel sample surface, which was also proven by electrochemical methods.

3.3. Biodegradability and Toxicity Measurements

The chemical properties and toxicity of LMFE are given in Table 4, where COD is the chemical oxygen demand, BOD is the biochemical oxygen demand, EC₅₀ is the effective concentration, and TU is the toxic unit.

Table 4. Chemical properties and toxicity of LMFE (adapted from [43]).

Parameter	BOD ₅ (mgO ₂ /L)	COD (mgO ₂ /L)	BOD ₅ /COD	EC ₅₀ (%)	TU (%)
LMFE (γ = 4 g/L)	4209	4363	0.96	5.17	19.34

High values of the extracts' CODs indicated that the extract contains a high concentration of organic substance. The BOD/COD ratio indicated high biodegradability. Even though the 19.34% of the TU value puts the LMFE in the toxic category, those values need to be observed with respect to the applied concentration. A high TU value was the consequence of the applied high concentration of the LMFE (4 g/L). In the case of pipeline leakage

and spillage of fluid into the environment, with LMFE as a corrosion inhibitor, no matter the high concentration and the *TU* value, the extract would be completely biodegraded.

The *COD* value indicated a high concentration of organic substances in the LMFE. The ratio of *BOD*₅ and *COD* was almost equal to one (0.96), which indicated a high biodegradability of LMFE [86]. In general, the compound is classified as toxic if the value is between 1% and 40% [86]. Although LMFE falls into the category of toxic compounds, the higher *TU* value (19.34%), in this case, depends mainly on the high LMFE concentration used and, thus, the increased presence of organic substances.

4. Conclusions

The extract from Lady's mantle flower has been studied as a GCI for carbon steel in simulated brine solution saturated with CO₂ in static and flow conditions, using potentiodynamic polarization and electrochemical impedance spectroscopy. The results showed that LMFE is an effective corrosion inhibitor in both static and flow conditions.

The tested LMFE achieved the best performance as a corrosion inhibitor at a concentration of 4 g/L in static test conditions and 5 g/L in flow conditions, with efficiencies greater than 90%. Both electrochemical test methods (EIS and potentiodynamic polarization) showed comparable results. Based on the results of potentiodynamic polarization, LMFE can be categorized as an anodic corrosion inhibitor in static conditions, while, in flow conditions, it can be categorized as a cathodic corrosion inhibitor.

The comparison of the SEM scans of the carbon steel surface after immersion in the uninhibited and the inhibited solutions show that the carbon steel surface, which was immersed in the inhibited solution, has a more uniform surface. The scans indicate that the inhibitor was absorbed on the tested carbon steel surface. Also, FTIR scans confirmed the adsorption of the LMFE by the functional groups C-N (1217 cm⁻¹), C-C (1368 cm⁻¹), C=O (1741 cm⁻¹), and C-H (2971–3019 cm⁻¹). The biodegradability and toxicity analysis show that LMF extract is almost completely biodegradable (*BOD*₅/*COD* = 0.96) and that it has a toxicity value of 19.34%. Even though this is a slightly higher value, due to the increased levels of organic substance present in the extract, it can be concluded that LMFE is environmentally acceptable as a GCI. Considering the obtained results, it can be concluded that LMFE proved to be a very effective corrosion inhibitor of carbon steel corrosion in a brine solution saturated with CO₂, in static and flow conditions.

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