

Exploiting the Alkaloid Extract from Waste material of *Nicotiana tabacum* as efficient Biomass Inhibitor for Mild Steel Corrosion in Acidic Media

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Abstract

Background

Extracts rich in alkaloid and derived from agricultural waste represent a scalable route to environmentally friendly corrosion inhibitors. In this study, a total alkaloid extract from discarded *Nicotiana tabacum* leaves (NTLE) was prepared and evaluated as a green inhibitor for mild steel corrosion in 0.5 M HCl.

Results

Chemical profiling confirmed selective enrichment in alkaloids, with nicotine amounting to 91%, and consistent with FT-IR signatures of heteroaromatic amine functionalities. Electrochemical measurements show that NTLE markedly reduces corrosion kinetics: potentiodynamic polarization indicates mixed-type inhibition with suppression of both anodic dissolution and cathodic hydrogen evolution, achieving up to 95% inhibition at 0.115 g·L⁻¹. EIS reveals increased charge-transfer resistance and decreased double-layer capacitance with concentration, consistent with interfacial film formation. Langmuir, kinetic–thermodynamic, and Flory–Huggins adsorption isotherms, and the Temkin model were used to investigate the mode of inhibition of NTLE extract. The free energy of adsorption showed that the corrosion inhibition takes place by spontaneous physical adsorption of NTLE molecules on the mild steel surface. Surface characterization using SEM shows mitigated acid attack in the presence of NTLE, contact-angle measurements indicate restoration of surface hydrophobicity, and four-point probe measurements evidence substantial recovery of electrical continuity relative to the corroded substrate.

Conclusions

Overall, alkaloid extracts obtained from unused biomass material of *Nicotiana tabacum* provides an effective, low-dose, and ecologically safer strategy for protecting mild steel in acidic media.

1. Introduction

Mild steel is widely used in petrochemical, oil and nuclear industries for the manufacture of reaction vessels, storage tanks and pipelines.” However, its poor resistance in acidic media severely limits its durability, causing acid pickling or cleaning, which ultimately results in severe corrosion. The latter is an unavoidable electrochemical process that leads to the gradual degradation of the metallic materials upon exposure to aggressive environments, driving them toward thermodynamically stable oxide states. Corrosion significantly compromises the mechanical integrity and functional performance of the industrial components, resulting in severe economic consequences. The annual global cost of corrosion was estimated at \$2.5 trillion during the last decade, equating roughly to 3.4% of the world's GDP, as published by NACE International, a corrosion-control standards and certification association.

Consequently, the development of effective and sustainable corrosion mitigation strategies remains a critical scientific and industrial priority.

Among the available protection methods, corrosion inhibitors represent one of the most efficient and economically viable approaches for reducing metal dissolution, particularly organic corrosion inhibitors. These compounds act primarily through adsorption at the metal–solution interface, forming a protective film that suppresses anodic and/or cathodic electrochemical reactions. On the other hand, while synthetic organic inhibitors often exhibit high inhibition efficiencies, their practical deployment is increasingly restricted due to environmental issues, poor biodegradability, and health hazards. This has prompted growing interest in environmentally benign alternatives derived from renewable resources. In particular, plant-based extracts have emerged as promising green corrosion inhibitors owing to their biodegradability, low toxicity, cost-effectiveness, and complex phytochemical composition. The corrosion inhibition performance of plant extracts is generally attributed to the formation of an adsorbed organic layer that impedes charge transfer and mass transport processes essential for corrosion reactions. Moreover, synergistic interactions among multiple phytochemical constituents often enhance inhibition efficiency beyond that of individual components. The increasing focus on plant-derived corrosion inhibitors reflects a broader shift toward sustainable and environmentally responsible corrosion protection strategies, offering a viable alternative to conventional synthetic inhibitors while maintaining high protective performance in aggressive acidic environments. These extracts typically contain alkaloids, flavonoids, tannins, and other heteroatom-rich organic molecules with π -electron systems that facilitate strong adsorption onto steel surfaces. Alkaloids are, particularly, significant due to their electron-donating properties and complex molecular structures, which facilitate strong adsorption onto metal surfaces, thereby providing effective corrosion inhibition. Doumane *et al.* tested the alkaloid extract of seed *Citrullus colocynthis* as novel green inhibitor for mild steel corrosion in one 1 M HCl acid solution. The obtained results showed that the extract exhibited an impressive inhibition efficiency, which reached 94.3% with a concentration of 2 g.L^{-1} at 25°C . Moreover, In a study conducted by Thapa et al., khasianine alkaloid was extracted from *Solanum xanthocarpum* stem and found to be a highly effective corrosion inhibitor for mild steel in 1 M H_2SO_4 . The inhibitor demonstrated a 98% efficacy rate when tested using electrochemical measurements and was shown to be a mixed type of corrosion inhibitor. Karki and his team reported that alkaloids extracted from *Acacia catechu* have inhibitory effects on mild steel exposed to 1 M H_2SO_4 . The plant extract exhibited physical adsorption and was effective up to 48°C , displaying an efficiency of 84.4% and had a maximum inhibitory efficiency of 93.9% after 3 h of immersion at 28°C . Additionally, Ugi et al. tested the Alkaloid and Flavonoid extracts of *Salvia Officinalis* Leaves as eco-friendly corrosion inhibitors of 817M40T Mild Steel in 0.5 M Hydrochloric acid concentrated environment.

In this study, we are particularly interested in exploiting the potency of alkaloid extracts obtained solely from the waste material of *Nicotiana tabacum*, a cultivated plant of high industrial interest, which include pre-harvest and post-harvest waste biomasses involving the upper parts of the plant and inflorescences, as inhibitor for Mild Steel corrosion in acidic media. The efficiency of such typically unused biomass was

investigated using mild steel electrodes immersed in aqueous solutions of 0.5 M HCl using electrochemical impedance measurements.

2. Experimental techniques

2.1. Specimen preparation and solution for corrosion tests

The mild steel working electrode contained (wt.%) (C:0.164, Mn:0.71, Si:0.0005, S:0.038, P:0.005, and Fe: balanced) with an area 0.7853 cm^2 was fixed in a rod of Teflon (Polytetrafluoroethylene PTFE) in such a way that only one side of the steel sample was left uncovered in contact with the solution. A copper wire was welded to the metal specimen. This wire was sheathed in a glass tube, which acted as both a holder and insulator. Before each experiment, the electrode was mechanically abraded with a series of emery papers 320, 600, and 800 starting with a coarse one and proceeding in steps to the fine grit up to a mirror finish, washed thoroughly with double-distilled water and finally dried by absolute ethanol, just before immersion in the tested solutions. Each experiment was carried out with newly polished electrode. The test solutions of 0.5 M HCl were prepared by diluting 37% concentrated grade acid purchased from Scharlab Chemical Industries with distilled water.

2.2. Plant Extract preparation

Nicotiana tabacum waste leaves were collected on June 2019 from Aitaroun, Southern Lebanon (33°07'N 35°28'E). The total alkaloids extracts (TAE) were obtained as described by Al-Sayegh with slight modifications. The first step was a solid–liquid extraction by maceration for 35 minutes of 20 g dried of *Nicotiana tabacum* leaf in 200 mL of MeOH. The second step consist a liquid–liquid extraction of the organic solution using 2% sulfuric acid. The acidic aqueous phases obtained sequentially were extracted sequentially with $3 \times 50 \text{ mL}$ portions of diethyl ether. The organic phase was separated, and the acidic layer was alkalinized to pH 9 with ammonium hydroxide (NH_4OH). Subsequently the aqueous layer was extracted three times by 50 mL each portion of dichloromethane. the combined organic layers were dried over anhydrous sodium carbonate, and dichloromethane was then removed under reduced pressure at 40°C . The resulting residue, *Nicotiana tabacum* leaf extract (**NTLE**) was stored at 4°C for future experimental analysis.

2.3. Total alkaloid content

The TAC was evaluated through the Bromocresol Green (BCG) spectrophotometry method, as described by El-Chamieyh et al. Briefly, various aliquots (0.2 ,0.4, 0.6, 0.8, and 1.0 mL) of atropine standard solution (0.1 mg.mL^{-1}) were transferred into different separate separatory funnels. Then, 5 mL of phosphate buffer (pH 4.7) along with 5 mL of BCG solution ($10^{-4} \text{ mol.L}^{-1}$), were added and shook with 5 mL of chloroform. After complete mixing, the funnel was left undisturbed for 3 minutes. The extracts were then collected in 10 mL volumetric flasks and diluted with chloroform to the mark. Similarly, TAE were prepared following the same method. The absorbance of the chloroform-solubilized complex was measured at 417 nm using a reagent blank (prepared identically but without atropine) as the reference.

The calibration curve was plotted for the calculation of the content of total alkaloids. The whole experiment was conducted in triplicates. The total alkaloid content was expressed as mg of AE/g of extract.

2.4. Antioxidant evaluation

With minor adjustments, the phosphomolybdenum, free radical scavenging (1,1-diphenyl-2-picrylhydrazyl (DPPH), and CUPRAC assays were used to assess the antioxidant activity of NTLE. For each of these tests, ascorbic acid was used as the standard to establish the final values.

2.4.1. DPPH Radical Scavenging Assay

Various concentrations of the extract ($100\text{--}1600\text{ mg.L}^{-1}$) were mixed with 3 mL of a methanolic solution containing 0.1 mM DPPH radicals. After an incubation period of 30 minutes, the absorbance was measured at 520 nm. The percent inhibition of activity was calculated using the formula: Percent Inhibition = $\frac{A_0 - A_e}{A_0} \times 100$, where A_0 is the absorbance without the extract, and A_e is the absorbance with the extract. The results were expressed as IC_{50} , which is the concentration of the sample required to inhibit 50% of the DPPH radicals.

2.4.2. Phosphomolybdenum Assay

The phosphomolybdenum assay was conducted following the method of Prieto et al. Aliquots of 0.1 mL of the sample solution at various concentrations ($600\text{--}1600\text{ mg.L}^{-1}$) were treated with 1 mL of reagent solution, which consisted of 0.6 M sulfuric acid, 28 mM sodium phosphate, and 4 mM ammonium molybdate. The mixtures were incubated for 30 min in a water bath at 80°C . After incubation, the samples were cooled to room temperature, and their absorbance was measured at 765 nm. The calibration curve was prepared by mixing ascorbic ($10\text{--}200\text{ mg.L}^{-1}$) with methanol. Methanol (0.1 mL) in the place of extract is used as the blank. The antioxidant activity is expressed as the number of equivalents of ascorbic acid.

2.4.3. Copper-Reducing Antioxidant Capacity (CUPRAC) Assay

The ability to reduce the cupric ions (Cu^{2+}) of NTLE was conducted based on the Hartati et al. work. Briefly, in a test tube a mixture of CuCl_2 solution ($1.0 \times 10^{-2}\text{ M Cu(II)}$), ammonium acetate (NH_4Ac) buffer (1.0 M, pH 7.0), and neocuproine ethanolic solution ($7.5 \times 10^{-3}\text{ M}$) (1:1:1) is prepared, followed by the addition the antioxidant sample (NTLE or standard) solution. The final volume was made up to 4.1 mL by completing the remaining volume with distilled water. The mixture is incubated for 30 min, after which the absorbance at 450 nm (A_{450}) is recorded and the results were expressed as $\text{TEAC}_{\text{CUPRAC}}$.

2.5. Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR analysis using a Bruker ALPHA II spectrometer with a platinum (Pt) ATR module and a spectral range of 400–4000 cm^{-1} was employed to identify functional groups in NTLE.

2.6. Gas Chromatography-Mass Spectroscopy Analysis

GC-MS (Gas chromatography and mass spectroscopy) analysis was carried out using a Shimadzu Nexis GC-2030 (Japan). The setup included an AOC-20i/s Plus liquid autosampler and the separation was performed on an HP-5MS Restek column (0.25 mm x 30 m, 0.25 μm film thickness). Helium was used as the carrier gas, and before and after each run, the injection needle was washed with three solvents (DCM, Ethyl acetate, and methanol). The injection volume was 1 μL , and a split ratio of 6.6 was employed. The column flow rate was 1.3 $\text{mL}\cdot\text{min}^{-1}$, and the injector temperature was maintained at 280°C throughout the experiment. The total run time was 100 min. Initially, the oven temperature was set at 60°C and then increased to 240°C with a ramp rate of 3°C $\cdot\text{min}^{-1}$. It was held at 240°C for 5 min, followed by an increase to 280°C with a ramp rate of 5°C $\cdot\text{min}^{-1}$ which was kept 15 min. Finally, the temperature was raised to 290°C with a ramp rate of 15°C $\cdot\text{min}^{-1}$ and maintained for 10 min. The ion source temperature was set to 220°C, and the transfer line temperature was set to 280°C. A detector (GCMS-QP2020 NX) voltage of 2.102 V and a 70-eV electron impact ASSP scan mode were utilized. The scan range covered from 41.00 to 500.00 m/z. LabSolutions software (Shimadzu, version 4.50 SP1) was used for instrument control, data acquisition, and processing. To identify the compounds, we compared their retention times and mass spectra with known standards from the NIST and Wiley libraries in the GC-MS system.

2.7. Electrochemical techniques

Electrochemical studies (Electrochemical impedance (EIS) and polarization measurement) were performed through a frequency response analyzer (FRA)/potentiostat supplied from ACM instruments (UK) in a three-electrode cell assembly at 30 °C.; saturated calomel electrode (SCE) and a platinum wire were used as reference and auxiliary electrodes. Before polarization and EIS measurements, the working electrode was left for 20 min to attain the open circuit potential in the used solution. The frequency range for electrochemical impedance spectroscopy (EIS) measurements was from 0.1 to 9.6×10^4 Hz with an applied potential signal amplitude of ± 10 mV around the rest potential. Polarization curve measurements were obtained at a scan rate of 60mV $\cdot\text{min}^{-1}$ starting from cathodic potential ($E_{\text{corr}} - 250$ mV) going to anodic direction ($E_{\text{corr}} + 250$ mV). All the measurements were done at 30 ± 0.1 °C using WiseCircu water bath (Germany) in solutions open to the atmosphere under unstirred conditions.

2.8. Scanning Electron Microscope (SEM)

Scanning Electron Microscopy (SEM) was employed to characterize the surface morphology using TESCAN MIRA3 LMH Schottky FE-SEM, operated at a magnification of 121,000, using an In-Beam secondary electron detector. SEM measurements were done for mild steel samples (1 cm^2) of same chemical composition similar to those used in electrochemical techniques. The elemental composition of the film formed on surface was analyzed by energy dispersive X-ray spectrometer at room temperature using Bruker D8 advance powder diffractometer with Cu-K α radiation ($\lambda = 1.54056$ Å) in the

range $10^{\circ} \leq 2\theta \leq 80^{\circ}$. The spectrophotometric measurements were performed using Thermo Fisher Scientific UV–Vis spectrophotometer GENESYS 150 and 10 mm Quartz cuvettes.

2.9. Water Contact Angle and Four-Point Probe measurements:

Contact angle measurements were performed using an Ossila Contact Angle Goniometer (L2004A1). The system is equipped with a high-resolution digital camera (1920 x1080) and an integrated monochromatic LED backlight to ensure high-contrast imaging of the liquid-solid interface. The stage was manually adjusted to maintain the substrate in a horizontal plane, and a 25 μ L glass syringe with a 22-gauge blunt-tip needle was used for droplet deposition. Sheet resistance and conductivity was measured using an Ossila Four-Point Probe System (T2001A3, Ossila Ltd., UK). The device utilized a co-linear four-probe head with 1.27 mm spacing and gold-plated, spring-loaded contacts to ensure non-destructive electrical coupling. Data were collected and processed using the Ossila Sheet Resistance software, which applied appropriate geometric correction factors based on sample dimensions. Measurements were conducted at room temperature.

3. Results and Discussion

3.1. Chemical composition and antioxidant activity

The total alkaloid content was determined using a spectrophotometric method after a chromogenic reaction with bromocresol green (BCG). Atropine sulfate served as the standard, and a series of concentrations (5 to 70 mg.L^{-1}) was prepared to construct the calibration curve. BCG forms an ion pair with alkaloids in general. Atropine is not an exception, and forms a yellow-colored complex, exhibiting a maximum absorbance at 417 nm. The absorbance of this complex demonstrated a linear relationship (Fig. 1A) with atropine concentration, adhering to Beer's law within the tested range ($R^2 = 0.9939$).

The content of alkaloids in NTLE calculated from the calibration curve for atropine sulfate, was found to be 60.21 mg AE/g dry weight. On the other hand, GC–MS analysis of the extract shown in the table of Fig. 1B revealed a predominant nicotine component (91.0%), alongside minor alkaloids and oxidative derivatives including cotinine (5.1%), anatabine (1.3%), nicotine-N-oxide (0.4%), and 2-pyridinepropionic acid (1.3%) (Fig. 1C). The obtained chromatogram confirms the selectivity of the extraction toward tobacco alkaloids (> 97%). Cotinine and nicotine-N'-oxide are known in vivo metabolites of nicotine, their occurrence indicates limited oxidative transformation of nicotine, likely originating from plant metabolism or mild oxidation during processing. Anatabine is reported as one of the most abundant alkaloids in tobacco. Whereas the detection of a pyridine carboxylic acid suggests further oxidation in minor amounts.

The FT-IR spectrum presented in Fig. 1D, matches the expected profile for alkaloid totum from *N. tabacum*. It confirms the existence of heteroaromatic amines and aliphatic chains of alkaloids. First, the broad band around $3400\text{--}3200\text{ cm}^{-1}$ in alkaloids often corresponds to N–H stretching from secondary

or primary amines. Secondly, the weak shoulder $2920\text{--}2850\text{ cm}^{-1}$ can be attributed to the C–H stretching (sp^3) from aliphatic chains. Nicotine's pyrrolidine ring and alkyl side chains contribute to this. The strong band near $1630\text{--}1650\text{ cm}^{-1}$ indicates C = C stretching in aromatic rings or C = O stretching in conjugated systems. For alkaloids, this is often aromatic C = C from the pyridine ring. The peak corresponding to the C = N stretching of pyridine ring, appeared at 1540 cm^{-1} . C–N stretching in aromatic amines or heterocycles responsible of the bands between $1500\text{--}1400\text{ cm}^{-1}$, and those bands could also represent CH_2 bending in aliphatic groups. Additionally, the pyrrolidine ring (in nicotine and cotinine for instance) contributes to the C–N stretching vibrations showed up as a peak near $1250\text{--}1020\text{ cm}^{-1}$. Finally, the strong absorption near $1050\text{--}1000\text{ cm}^{-1}$, suggest the presence of C–O stretching and C–N vibrations in tertiary amines. By relating these results to those shown in the GC-MS analysis, the features are fully compatible with a nicotine-rich alkaloid mixture containing heteroaromatic rings and tertiary/secondary amine functionalities. The C = O band contribution around $1650\text{--}1700\text{ cm}^{-1}$ is consistent with cotinine and pyridine propionic acid. Moreover, in the fingerprint region ($900\text{--}500\text{ cm}^{-1}$), there are several small peaks corresponding to aromatic C–H out-of-plane bending, characteristic for substituted pyridine and other aromatic alkaloids. In this region also falls the relatively weak N–O stretch (bands 928 cm^{-1} to 971 cm^{-1}), confirming the presence of nicotine-oxide.

The antioxidant activity of NTLE was tackled using the DPPH, Phosphomolybdenum, and CUPRAC assays. Comparing to ascorbic acid as reference, the NTLE exhibited a noted antioxidant potential in the CUPRAC ($225.7\text{ mg AAE/g extract}$) and phosphomolybdenum ($1.74 \pm 0.32\text{ mg AAE/mg extract}$) methods, while its activity in the DPPH assay was comparatively low ($\text{IC}_{50}\text{ NTLE} > 300.\text{IC}_{50}\text{ AA}$). These findings highlight the influence of assay mechanisms and radical types on the apparent antioxidant capacity of natural products. Differences in the antioxidant results were obtained in agreement to methods described in previous work in the literature. The CUPRAC assay is based on the reduction of Cu (II) to Cu (I) by electron-donating ability, whereas the phosphomolybdenum assay measures the total reducing capacity of NTLE to reduce Mo(VI) to Mo(V) and subsequent formation of green phosphate/Mo(V) complex at an acid pH. Results from both methods indicate that NTLE has significant electron-donating and reducing properties. On the other hand, the DPPH radical scavenging assay evaluates the ability of NTLE to reduce DPPH radicals, a stable compound that can be reduced by hydrogen atoms transfer. The relatively weak activity, compared to the standard, observed here suggests that alkaloids in NTLE are more effective in single electron transfer (SET)-based mechanisms rather than hydrogen atom transfer (HAT). Such differences are consistent with the structural characteristics of alkaloids, many of which contain conjugated heteroatoms capable of donating electrons but not necessarily providing labile hydrogen atoms.

3.2. Open Circuit Potential Measurements

Open Circuit Potential (OCP) is a fundamental electrochemical technique used to monitor and evaluate corrosion inhibition processes. It measures the electrical potential of a metal working electrode relative to a reference electrode in a corrosive media, without any external current or potential applied. Figure 2 shows that the OCP of mild steel in the tested solutions was attained after 20 min of immersion.

Moreover, it was shifted towards more positive values in the presence of the extract. When the change in the corrosion potential (E_{corr}) value is higher than 85 mV, the inhibitor can be classified as an anodic or cathodic type. Since the largest displacement is approximately 30 mV, NTLE can be regarded as a mixed-type inhibitor of mild steel in 0.5 M HCl solutions.

3.3. Potentiodynamic polarization measurements

Figures 3 shows typical Tafel behavior. It is clearly observed that the addition of NTLE suppresses both anodic and cathodic parts of the polarization curves indicating that indeed it acts as a mixed-type inhibitor. We suggest that the extract retards the cathodic hydrogen evolution and reduces the anodic metal dissolution. Moreover, it is noted that the addition of NTLE has approximately no effect on the corrosion potential which can be classified as a pickling-type inhibitor for mild steel in HCl solution since its inhibition effect does not alters its potential. Table 1 shows the electrochemical corrosion results in the absence and the presence of different extract concentrations. The percentage of inhibition efficiency was calculated from polarization measurements using the relation: $\%P = [(i_0-i)/i_0] \times 100$ (Eq. 1) where i_0 and i , are the corrosion current densities in the absence and the presence of *Nicotiana tabacum* leaf extract, respectively.

The tabulated data revealed that with raising concentrations of NTLE, the corrosion current density (i_{corr}) values fall and %P values increase; this suggests that the extract is a good corrosion inhibitor for the case of mild steel. The slight variations in cathodic Tafel slopes (β_c), in the presence of plant leaf extract, indicates that increasing its concentrations has no effect on the cathodic hydrogen evolution.

Table 1
The electrochemical polarization parameters for the corrosion of mild steel in 0.5 M HCl containing different concentrations of NTLE at 30 °C.

Concentration	E _{corr}	$\beta_a \beta_c$		i _{corr}	%P
(g.L ⁻¹)	(mV vs. SCE)	mV/decade		(mA.cm ⁻²)	
Blank	-464	171	172	2.8130	-
0.0075	-472	168	136	1.5509	45
0.009	-465	140	130	1.1251	60
0.015	-446	144	110	0.8489	70
0.05	-460	121	139	0.5616	80
0.075	-467	100	115	0.1607	94
0.115	-447	89	139	0.1408	95

The inhibiting action is taking place by simply blocking the available cathodic sites on the metal surface, which reduces the exposed area necessary for cathodic reactions in parallel with the increase of inhibitor's concentrations. However, the shift in anodic Tafel slope β_a may be attributed to adsorption of the inhibitor molecules on surface of the mild steel (anodic sites).

3.4. Electrochemical Impedance measurements

Electrochemical impedance spectroscopy (EIS) measurement is an appropriate procedure that may help us to understand the action mechanism of corrosion inhibition. Fig. 4 shows that the impedance response consisted of characteristic semicircle of capacitive type indicating that the dissolution process occurs under activation control. Moreover, the circles are depressed in nature. Such observation is mostly referred to charge transfer control on the surface, as well as to frequency dispersion which could be attributed to different physical phenomena such as roughness and inhomogeneities of the solid surfaces.⁴² As seen, the size of the obtained semicircle increases with increasing NTLE concentrations. This may be explained on the basis of adsorption of the extract molecules on the mild steel surface and thereby producing a barrier for the metal to diffuse out to the bulk, while this barrier increases with increasing inhibitor concentrations.

Figure 5 shows the Bode impedance and Bode theta plots in the absence and presence of different concentrations of NTLE. It is clear that the presence of the leaf extract increases the modulus impedance indicating that it retards corrosion rates. On the other hand, the values of phase angle lower than 90 in Bode theta plots indicate the presence of non-ideal capacitances that confirm the depression and presence of inhomogeneities in the system.⁴⁴

The experimental and computer fit results of the Nyquist plot with the corresponding equivalent circuit model of 0.5 M HCl containing 0.115 g.L⁻¹ NTLE is demonstrated in Fig. 6. The equivalent circuit used to analyze the obtained Nyquist plots (Fig. 7, inset) includes the solution resistance R_s and the constant phase element (CPE) rather than pure capacitor since it can take depression of the obtained semi-circle into account. The CPE is in parallel to the charge transfer resistance element, R_{ct} . The R_{ct} value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate. To compensate for non-homogeneity in the system, the capacitances were employed as a constant Phase Element (CPE) that is defined by two values, Q and n . The impedance, Z , of CPE is represented by:

$Z_{CPE} = Q^{-1}(i\omega)^{-n}$ (Eq. 2), where $i = (-1)^{1/2}$, ω is the frequency in rad s⁻¹, $\omega = 2\pi f$, and f is the frequency in Hz. For a non-homogeneous system, n values are less than unity. The double layer capacitance could be obtained using the following equation: $C_{dl} = \frac{(Q_{dl} \times R_{ct})^{1/n}}{R_{ct}}$ (Eq. 3). The values of electrochemical impedance parameters, charge transfer resistance (R_{ct}), the non-ideal double layer capacitance (Q_{dl}) obtained from fitting the experimental data of mild steel in 0.5 M HCl solutions containing different NTLE concentrations to the used equivalent model are presented in Table 2.

The percentage inhibition efficiency (%P) can be calculated from impedance measurements according to the equation: $\%P = [(R_{ct} - R_{ct0})/R_{ct}] \times 100$ (Eq. 4), where R_{ct0} and R_{ct} are the values of the charge transfer resistance ($\Omega \cdot \text{cm}^2$) in the absence and the presence of leaf extract respectively.

Table 2

The electrochemical impedance parameters for the corrosion of mild steel in 0.5 M HCl containing different concentrations of *Nicotiana tabacum* leaf extract at 30°C.

Concentration (g.L ⁻¹)	R _s ($\Omega \cdot \text{cm}^2$)	R _{ct} ($\Omega \cdot \text{cm}^2$)	Q _{dl} ($\mu\text{F} \cdot \text{cm}^{-2}$)	n	C _{dl} ($\mu\text{F} \cdot \text{cm}^{-2}$)	% P
Blank	2.450	9.77	483	0.83	2732	-
0.0075	2.269	14.65	671	0.87	2650	33
0.009	2.299	19.75	586	0.87	2372	51
0.01	2.622	24.81	470	0.86	2148	61
0.015	2.393	28.69	253	0.83	1563	66
0.06	2.573	39.77	263	0.84	1533	75
0.077	2.611	81.42	190	0.84	1193	88
0.09	2.275	88.60	182	0.84	1152	88.97
0.115	2.515	89.99	217	0.86	1084	89.14

The tabulated data revealed that increasing NTLE leads to an overall increase in the charge transfer resistance that is associated with a decrease in ideal double layer capacitance C_{dl} , the change in the R_{ct} and C_{dl} values is due to the gradual replacement of water molecules by the organic molecules on the metal surface, decreasing the extent of the metal dissolution. The decrease in C_{dl} values with concentration is due to the increase in the thickness of the electrical double layer, suggesting that *Nicotiana tabacum* leaf extract molecules act by adsorption at the metal/solution interface. Moreover, it revealed that increasing its concentration leads to an increase in the percentage of inhibition.

3.5. Adsorption Isotherms

Figure 7 shows the variation of degrees of surface coverage values obtained from AC impedance measurements using equation ($\theta = \%P/100$) as function of concentration of NTLE. The curve is characterized by an initial rising part indicating the formation of a mono-layer adsorbate film on the metal surface followed by an approximately constant part at higher concentrations indicating complete saturation of the surface by the inhibitor molecules. The adsorption isotherm is an interesting investigation that can help in understanding the interaction nature that happens between inhibitor structures and the studied metallic surfaces. Therefore, several adsorption isotherms models like Langmuir, kinetic-thermodynamic adsorption isotherms and Flory Huggins models were evaluated using

the inhibition percentage obtained by EIS measurements as shown in Fig. 7 (B–D) and the obtained parameters presented in Table 3.

Table 3
Linear fitting parameters of NTLE according to all isotherms in mild steel surfaces in 0.5 M HCl at 30 °C.

Inhibitor	Langmuir	Kinetic Model		Flory-Huggins	
NA	K	K	1/y	K	x
<i>Nicotiana tabacum</i>	97	109	1.02	108	0.92

Experimental data fitted all the applied adsorption isotherms. Fitting of Langmuir isotherm gives a straight line that passes through the origin indicating the ideal behavior in the adsorption processes of NTLE. Such observation indicates a near ideal behavior of NTLE. The number of active sites occupied by a single inhibitor molecule, 1/y, is nearly equal in unity indicating that each molecule of the leaf extract was adsorbed onto one active site. This is confirmed by the value of the size parameter x, which indicates the number of adsorbed water molecules replaced by a given inhibitor molecule.³

In addition, the binding constants of the kinetic thermodynamic model were used to calculate the Gibbs free energy of adsorption (ΔG_{ads}): $K_{ads} = 1/55.5 e^{(-\Delta G_{ads}/RT)}$ (Eq. 5), where R is the ideal gas constant, T is the temperature in Kelvin and 55.5 is the concentration of water at the metal surface interface expressed in molar. The ΔG_{ads} value was $-21.93 \text{ kJ.mol}^{-1}$ for NTLE. The negative value indicates the spontaneity and stability of the adsorption processes of the extract. Moreover, it proves that the adsorption of NTLE molecules takes place through a physical adsorption mechanism.

3.6. Activation Parameters

The calculation of the activation parameters is fundamentally important to illustrate the inhibition mechanism. The thermodynamic parameters (ΔE^* , ΔH^* , ΔS^* , and ΔG^*) for the dissolution of mild steel in HCl solution in the absence and presence of 0.115 g.L^{-1} NTLE were obtained using Arrhenius with the transition state equations. The obtained parameters are depicted in Table 4. Nyquist plots at different temperatures (Fig. 8) were used to obtain the corrosion rates that were taken as the reciprocal of R_{ct} values. It is clear that increasing temperature decreases the size of the depressed semicircles which indicates an increase in the corrosion rate of mild steel. This behavior could be explained on the basis that the increase in temperature results in desorption of the metal complex from mild steel surface.

Table 4
Activation parameters for mild steel in 0.5 M HCl with and without
0.115 g.L⁻¹ *Nicotiana tabacum* leaf extract

Plant Leaves Extract	E _a (KJ.mol ⁻¹)	ΔH* (KJ.mol ⁻¹)	ΔS* (J.mol ⁻¹ .K ⁻¹)
<i>n.a.</i>	33	30	-162
<i>Nicotiana tabacum</i>	24	21	-211

Table 4 showed that E_a and ΔH* values decrease with *Nicotiana tabacum* leaf extract revealing that the elevated temperature doesn't affect the effectiveness of *Nicotiana tabacum* leaf extract on the corrosion of mild steel. The activated complex formation process is endothermic in nature as verified by the positive ΔH* values. Moreover, the transition state complex denotes an association rather than dissociation step as suggested by negative ΔS* values.

3.7. Surface Analysis

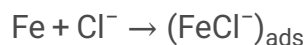
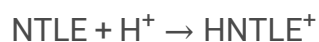
Figures 9 (A–C) show the SEM of mild steel samples before and after immersion in 0.5 M HCl solution for 1 hour in the absence and presence of 0.115 g.L⁻¹ NTLE. Figure 9B shows clear polished marks of smooth and homogeneous steel surface before immersion in the acid solutions. Figure 9A shows rough and highly damaged steel surface. However, Fig. 9C shows that the mild steel surface in presence of 0.115 g.L⁻¹ NTLE is not severely damaged as that obtained in the absence of the extract. This indicates that indeed, the leaf extract is effectively hindering the dissolution of steel in acidic media. Contact angle measurements were used to evaluate the hydrophilicity of the steel surface. For untreated bare mild steel, the contact angle was 79.38°, indicating that the surface is still relatively wettable (tending to be hydrophilic). Figure 10E, after immersion in 0.5 M HCl, the contact angle decreased to 26.06°, showing that the surface became more hydrophilic due to corrosion attack, which makes it easier for water molecules to adhere to the mild steel surface. However, when the steel was immersed in 0.5 M HCl containing 0.115 g.L⁻¹ NTLE, the contact angle sharply increased to 54.48°. This significant increase demonstrates that the steel surface became more hydrophobic because of the protective layer formed by the adsorbed extract molecules. As a result, water molecules are less likely to attach, and the corrosion rate is effectively reduced.

In addition, four-point probe measurements were conducted on the pristine surface showing a conductivity of 9.0 x10⁷ S.m⁻¹ and sheet resistance of 19.4 x10⁻³ Ω.square⁻¹ (Fig. 9G), characteristic of unhindered electron flow. Upon immersing the metal in acidic media, the conductivity decreased to 7.9 S.m⁻¹ accompanied with an increase in sheet resistance to 221.2 x10³ Ω.square⁻¹. The result is an effect of acidic corrosive nature that contributes to the oxidation of the metallic surface, forming a barrier to electrical continuities. The presence of NTLE (0.09 g.L⁻¹) in the medium mitigated the conductivity compared with the pristine MS to 1.7 x 10⁴ S.m⁻¹ (≈ 2000% improvement over the corroded

sample) and a recorded sheet resistance of $1.1 \times 10^2 \Omega \cdot \text{square}^{-1}$. This data suggests an adsorption behavior of the extract by the heteroatoms (nitrogen of alkaloids) with the empty *d*-orbitals of iron, forming a film that protects the mild steel from corrosion. This is also supported by the standard free energy of adsorption ΔG_{ads} which shows a physical adsorption mechanism on the electrode, as discussed in section 3.4 (*vide supra*). Moreover, this is sustained further by the fact that applying extra force on the film that protects the mild steel with the four-point probe results in conductivity and sheet resistance measurements identical to the pristine electrode, suggesting that the probes had ruptured the top organic thin film.

3.8. Mechanism of the corrosion Inhibition

The adsorption mechanism of organic inhibitors in acidic environments involves either protonated or neutral molecular species. In hydrochloric acid solutions, the mild steel surface carries a net positive charge,² which hinders the direct adsorption of protonated species. Nevertheless, the specific adsorption of chloride ions on the steel surface induces surface charge modification, thereby enhancing electrostatic interactions and facilitating the physical adsorption of the protonated inhibitor molecules. Consequently, the corrosion inhibition performance of NTLE is predominantly governed by a physisorption mechanism as follows:



4. Conclusion

To conclude, our study demonstrates that alkaloid-rich extracts derived from waste material of *Nicotiana tabacum* leaves constitute an effective and sustainable corrosion inhibition strategy for mild steel in acidic environments. The extraction protocol selectively enriches tobacco alkaloids, with nicotine as the dominant component. Electrochemical investigations confirm that NTLE acts as a mixed-type inhibitor, significantly suppressing both anodic metal dissolution and cathodic hydrogen evolution, achieving inhibition efficiencies up to 95% at low concentration ($0.115 \text{ g} \cdot \text{L}^{-1}$). Impedance analysis further reveals a marked increase in charge-transfer resistance and a decrease in double-layer capacitance, consistent with the formation of a protective adsorbed film at the metal–solution interface. Adsorption studies indicate that NTLE follows near-ideal isotherm behavior, with a negative Gibbs free energy of adsorption, supporting a spontaneous, predominantly physisorption-driven mechanism. SEM confirms mitigation of acid-induced damage, contact angle measurements demonstrate partial restoration of surface hydrophobicity, and four-point probe data reveal substantial recovery of electrical conductivity relative to the corroded state. Together, these results establish a coherent inhibition mechanism based on the

adsorption of heteroatom-rich alkaloids forming a barrier that limits charge transfer and mass transport processes.

This work highlights the valorization of agricultural waste into high-performance corrosion inhibitors. The combination of low dosage, high efficiency, and scalable sourcing positions NTLE as a promising candidate for industrial acid pickling and cleaning applications. Future work may focus on isolating structure–activity relationships among individual alkaloids, and study the contribution of minor alkaloids and possible synergistic interactions, and extending performance assessments to higher temperatures and dynamic flow conditions to further support real-world deployment.

Declarations

Conflicts of Interest

The authors declare they have no known competing financial and/or non-financial interests in relation to the work described.

Data availability

Information which led to this research are included in the paper, further information can be attained from the corresponding authors.

Consent to Publish declaration: Not applicable.

Ethics and Consent to Participate declarations: The guidelines for cultivation and collection of the plants/plant parts used in this study for *Nicotiana tabacum* were followed and complied with local and national guidelines. No specific permissions or licenses were required for the collection process.

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Figures

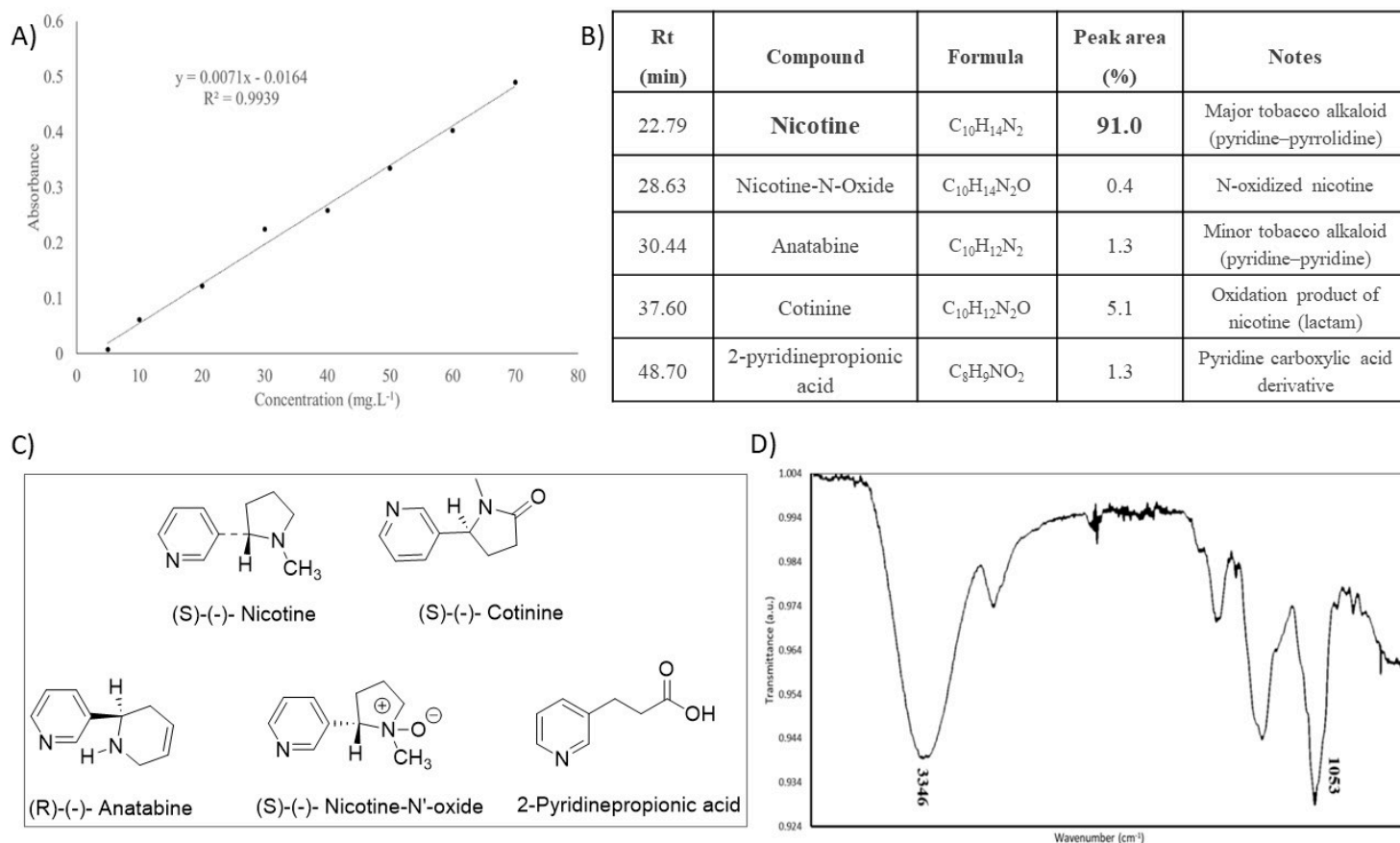


Figure 1

A) absorbance of the BCG-alkaloids complex as function of atropine concentration, B) GC-MS analysis of the NTLE C) chemical structures of the detected alkaloids in the extract, and D) FT-IR spectrum of the extract.

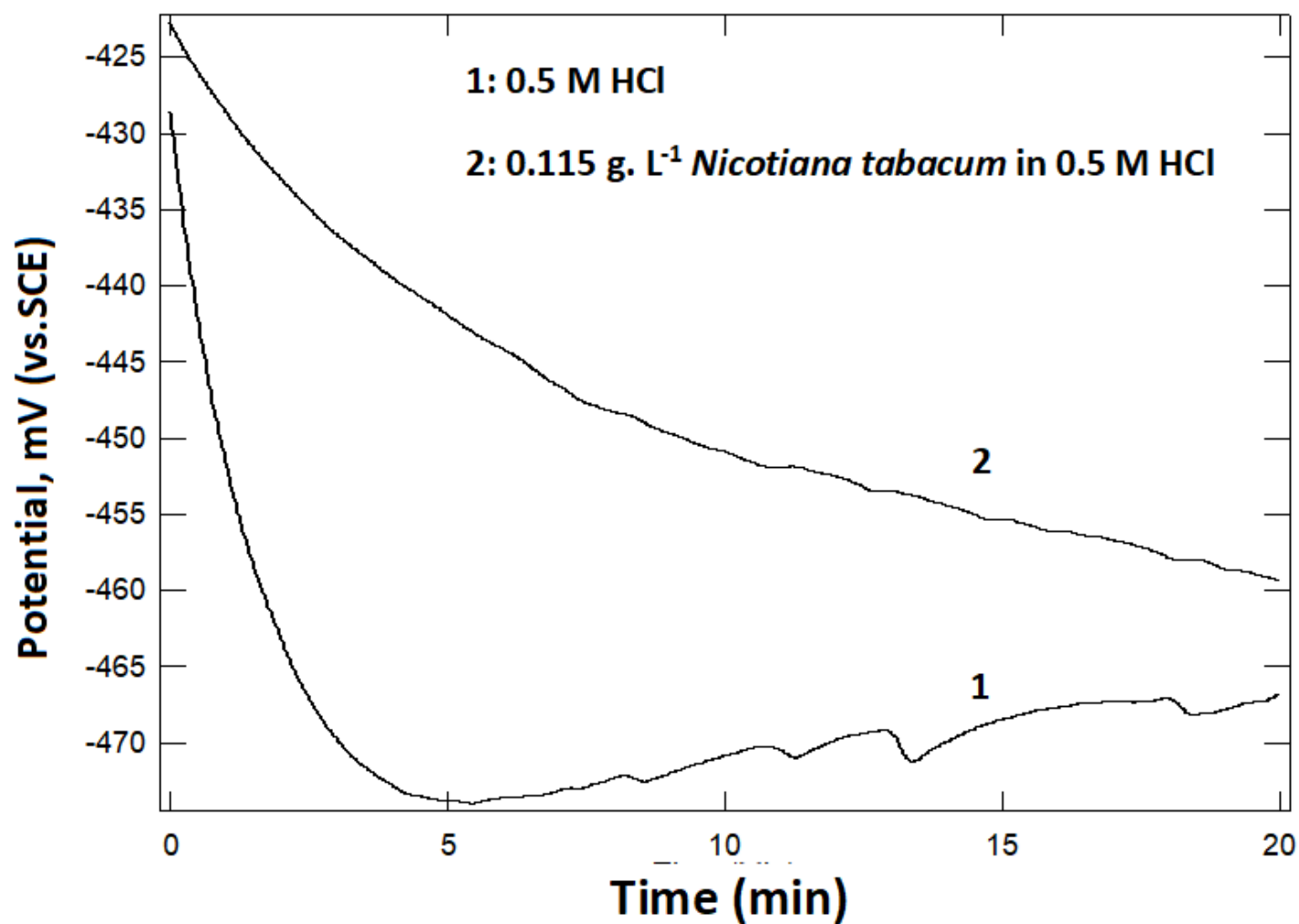


Figure 2

The variation of open circuit potential as a function of time for mild steel in 0.5 M HCl solution in the absence and presence of 0.115 g.L⁻¹ NTLE.

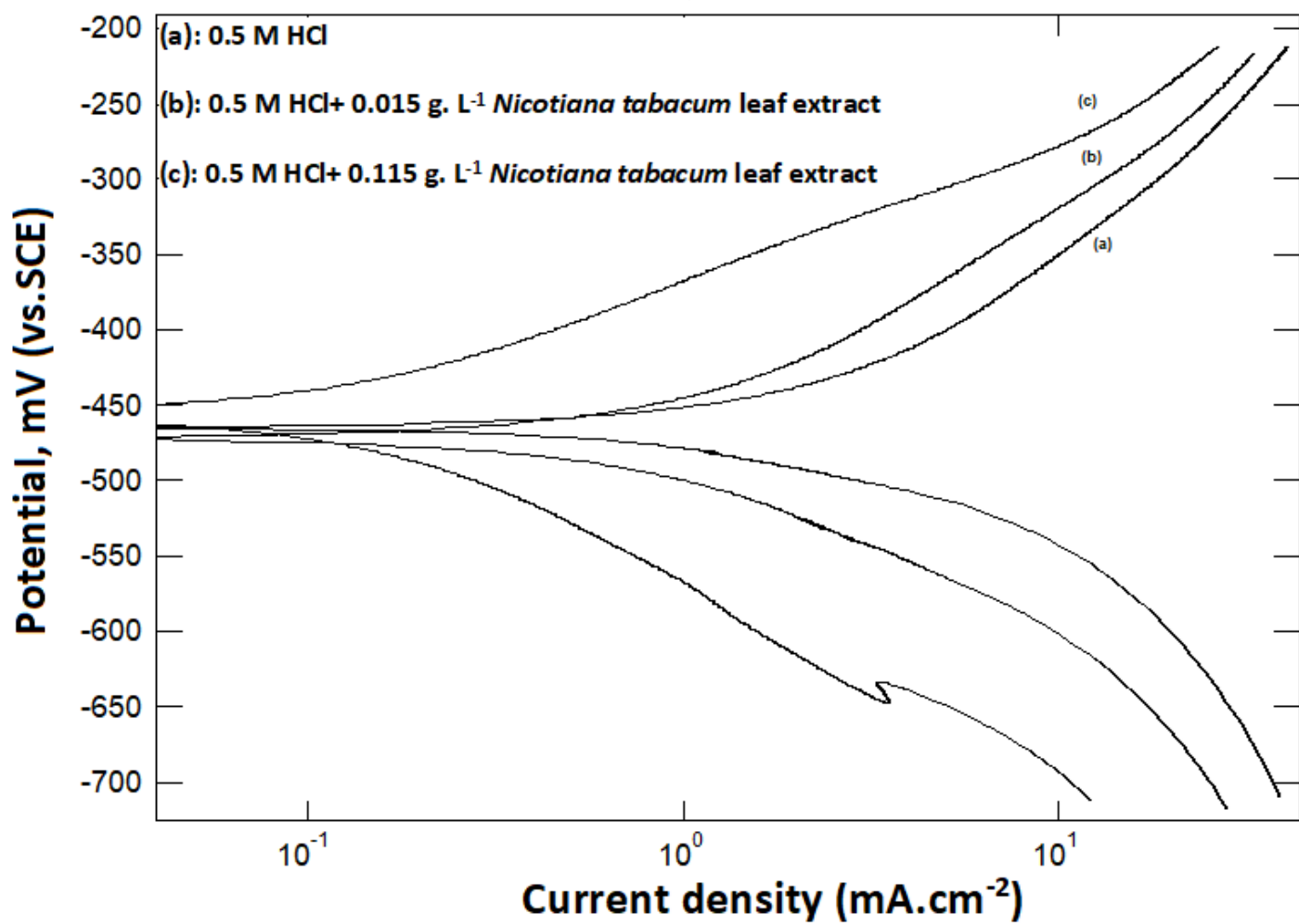


Figure 3

Potentiodynamic polarization curves for mild steel in 0.5 M HCl in the absence and presence of different concentrations of NTLE at 30 .

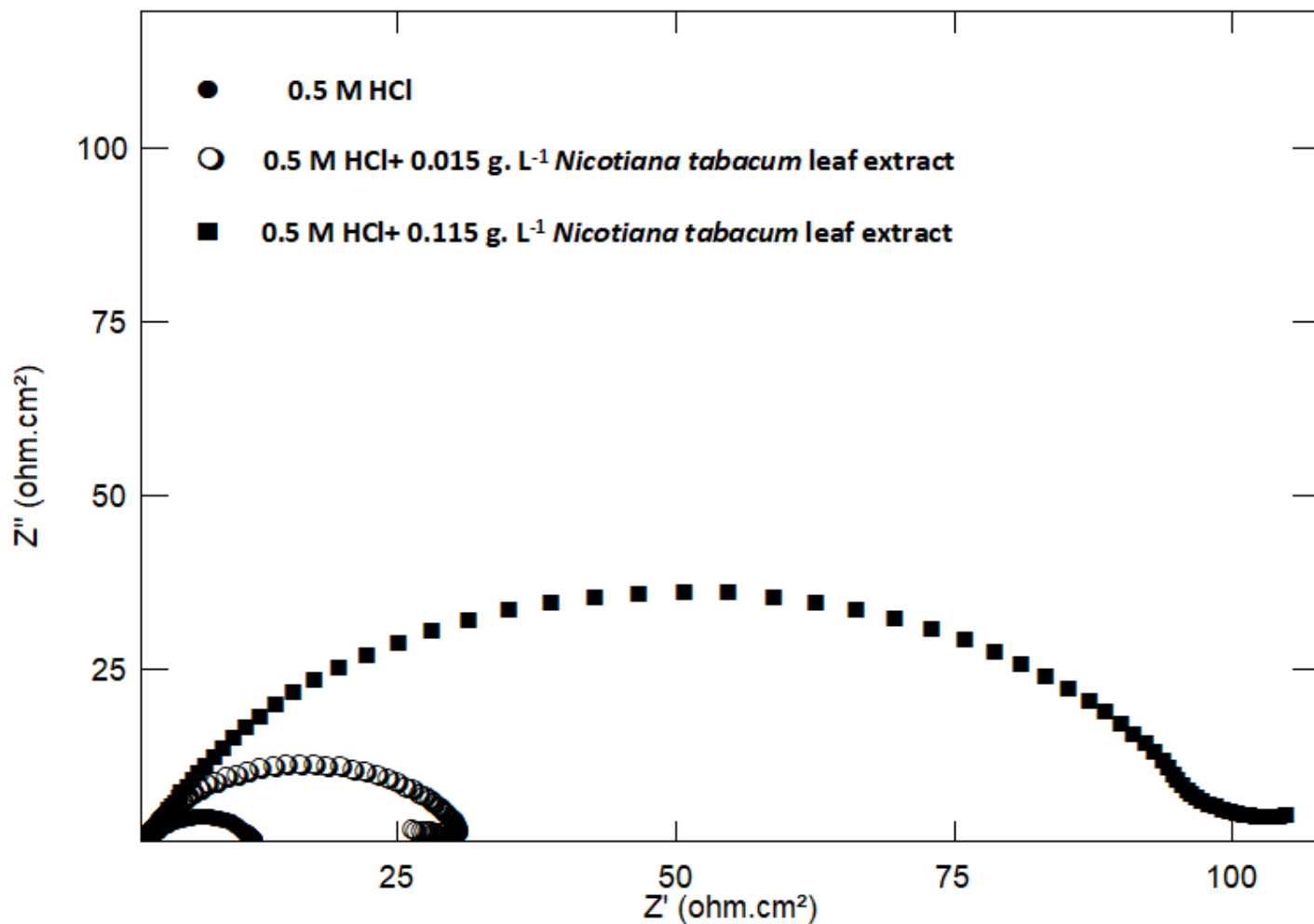


Figure 4

Nyquist Impedance plot for mild steel in 0.5 M HCl in the absence and presence of different concentrations of NTLE at 30

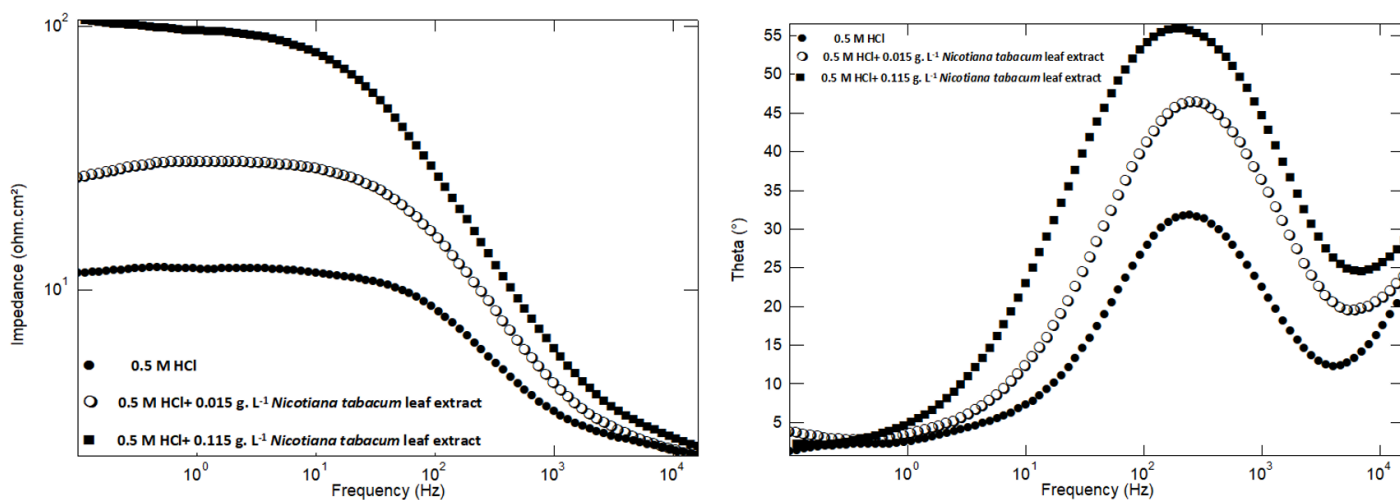


Figure 5

Bode impedance (left) and bode theta (right) plots of mild steel in 0.5 M HCl in the absence and presence of different concentrations of NTLE.

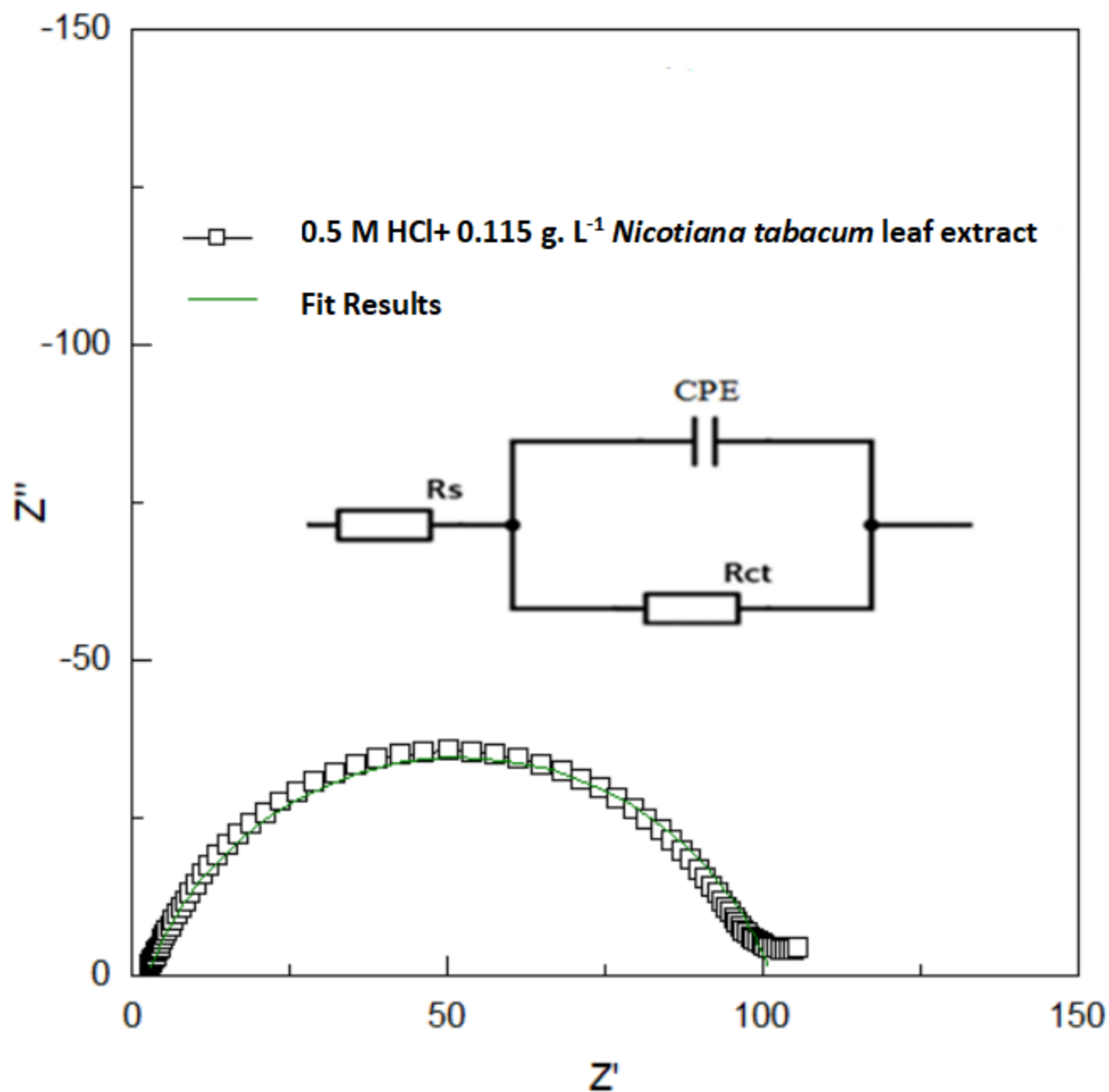


Figure 6

The experimental and computer fit results of Nyquist plot of 0.115g.L⁻¹ of the extract in 0.5 M HCl

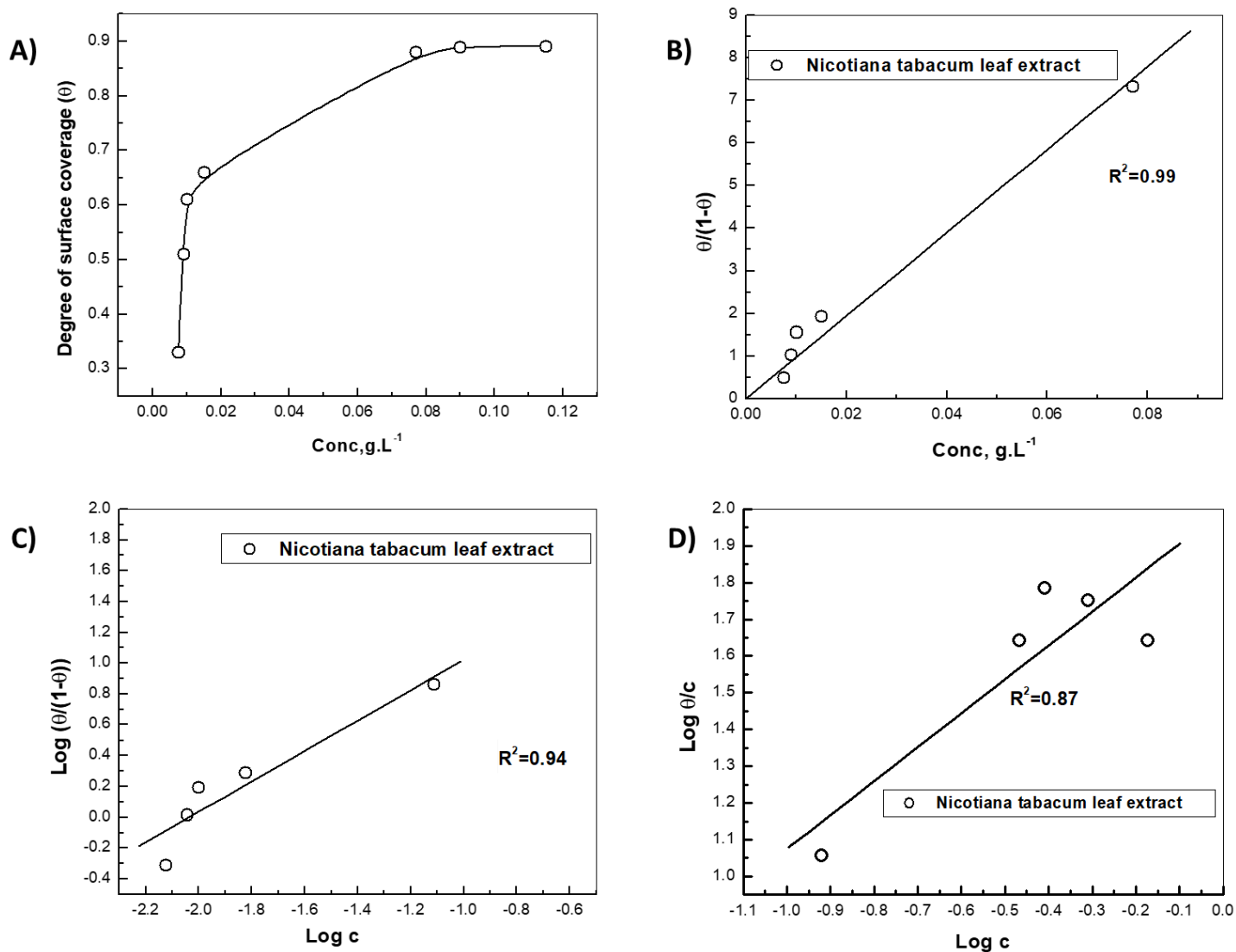


Figure 7

Variation of the degree of surface coverage (θ) with different concentrations of NTLE at 30°C (A), and the application of Langmuir adsorption isotherm (B), Kinetic-thermodynamic adsorption isotherm (C), and Florry-Huggins model (D) to the results of impedance.

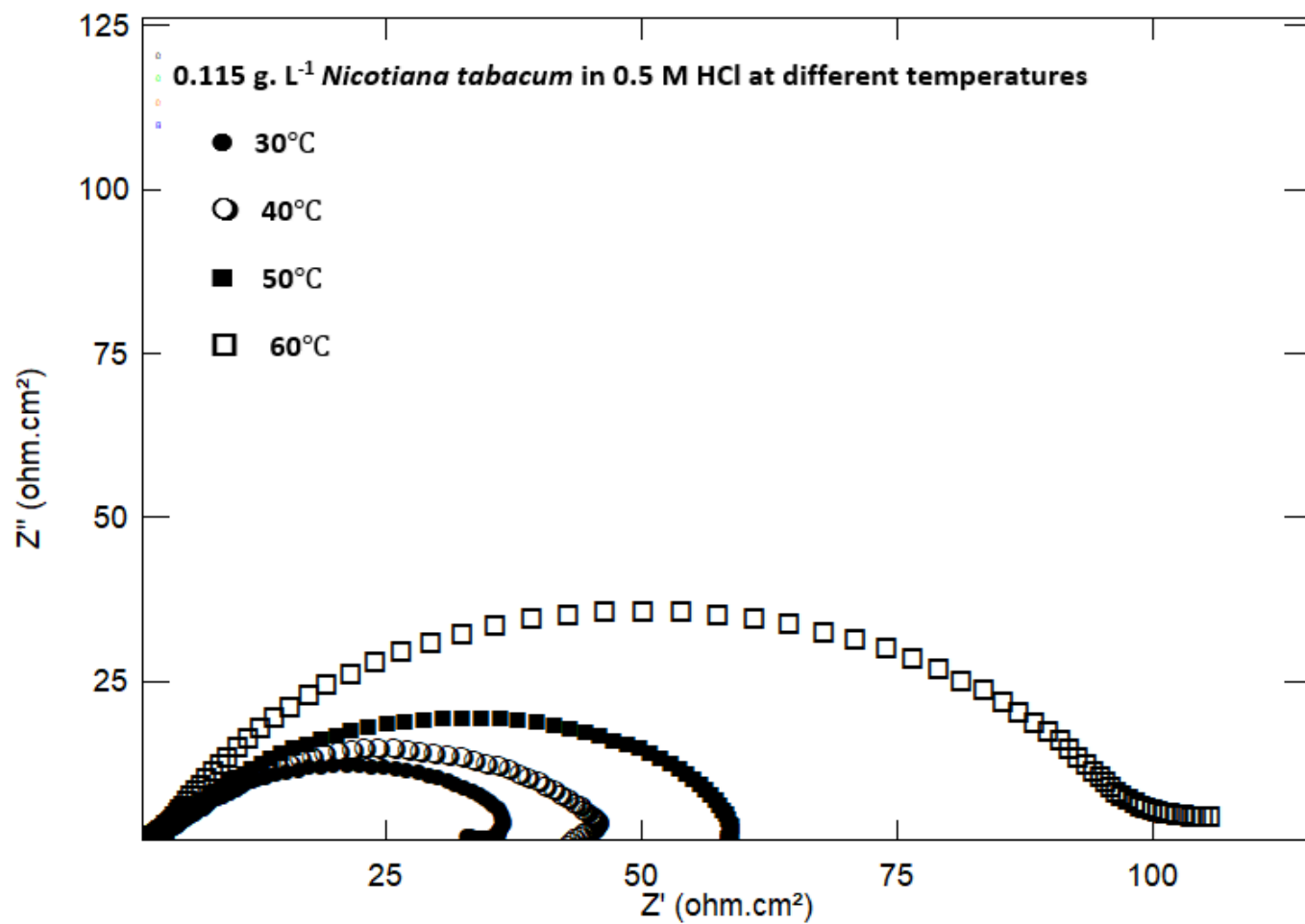


Figure 8

Nyquist plots for the mild steel in the presence of 0.115 g.L⁻¹ NTLE at different temperatures.

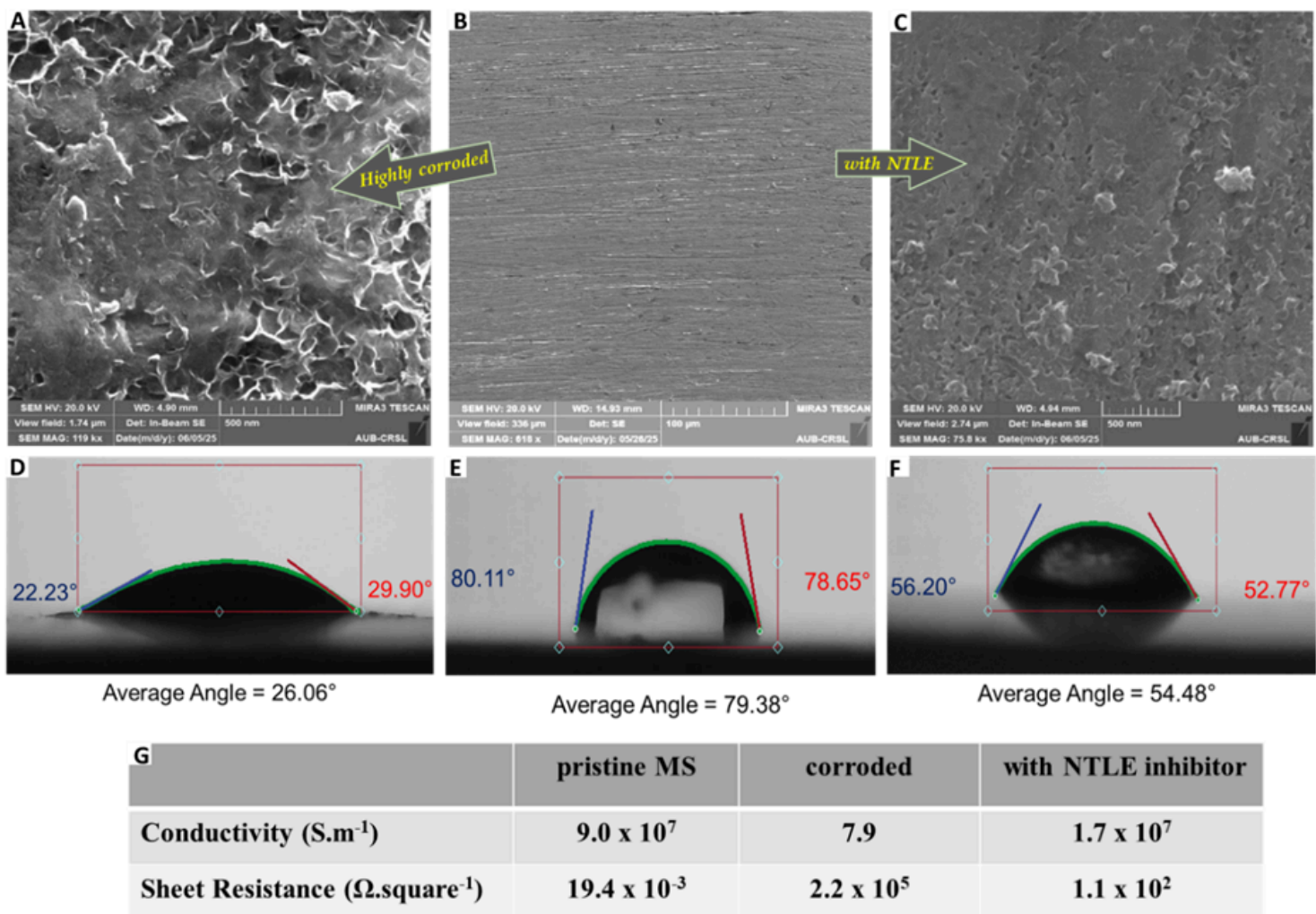


Figure 9

Figure 10. SEM images of mild steel before (B) and after immersion in 0.5 M HCl solution for 1 h in absence (A) and presence of 0.115 g.L⁻¹ NTLE (C). Contact angle images of the clean and polished mild steel surface (E), after exposure to HCl solution (D), and exposure to HCl in presence of the extract (F). Solutions were immersed for 1h. (G) Table with four-point probe measurements of conductivity of and sheet resistance.