CAAP Annual Report

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Section A: Business and Activities

(a) Contract Activities

- Contract Modifications: N/A
- Educational Activities:
 - Student mentoring:
 - Sevil Ozsut, a Ph.D. student in the Department of Civil and Architectural Engineering at the University of Miami, worked on the project starting at the 2nd quarter of this project.
 - Ashley Motola, an undergraduate research assistant, worked on the project during the summer of 2024. This was in collaboration with our NSF REU Site project.
 - Jason Houston, a master's student in the Department of Civil and Architectural Engineering at the University of Miami, started working on this project during the 4th quarter of this project.
 - Alexander Schwartz, an undergraduate research student, started working on the project during the 4th quarter of this project.
 - Student internship:

N/A

• Educational activities:

The PI, Dr. Ali Ghahremaninezhad, organized a science camp in the summer of 2024 where principles of corrosion and its importance were discussed with high school students, primarily from underrepresented minority groups in South Florida. The camp included in class lectures as well as hands-on activities.

• Career employed:

N/A

• Others:

N/A

• Dissemination of Project Outcomes:

Sevil Ozsut presented a research poster on bio-based corrosion inhibitors at the Research Day event in the College of Engineering at the University of Miami. The students had the opportunity to network with other researchers and industry experts and receive useful feedback on their research.

The results of the research obtained from this project are being currently prepared for a peerreviewed journal to be submitted soon.

• Citations of The Publications:

N/A

• Others:

N/A

(b) Financial Summary

- Federal Cost Activities:
 - PI/Co-PIs/students involvement: The PI and graduate and undergraduate students involved in this project held weekly meetings to monitor the research progress and discuss any issues that needed to be addressed.
 - Materials purchased/travel/contractual (consultants/subcontractors): Materials/consumables/supplies were procured to be used in various tasks of this project. In addition, The Advanced Materials Characterization Facility at the University of Miami was used per user fee to conduct chemical and imaging analyses in this project.
- Cost Share Activities:
 - Cost share contribution: N/A

(c) Project Schedule Update

• Project Schedule:

Table 1. Project schedule.												
Tasks		Yea	ar 1		Year 2			Year 3				
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1	✓											
Task 2		✓	✓	\checkmark								
Task 3				\checkmark								
Task 4												
Task 5												
Task 6												

• Corrective Actions: N/A

(d) Status Update of the 4th Quarter Technical Activities

1. Task 2: Electrochemical and Corrosion Testing

The inhibitive action of some proteins and thermally synthesized copoly-amino acids was examined using electrochemical and gravimetric analyses, and surface imaging methods. In this quarterly report, their electrochemical characteristics along with physical changes have been documented. The efficiency of the inhibitors was assessed using electrochemical measurements including open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) to allow a comparison among tested inhibitors.

The used inhibitors and their abbreviations are listed in Table 2.

Name	Abbreviation	Name	Abbreviation
Copolyaspartic glutamic acid	PAG	Whey Protein	WP
Lysozyme	LYS	Soy Protein	SP

Table 2: List of inhibitors and their abbreviations used in the 4th quarterly report.

The procedure of thermal polymerization was followed according to the literature [1]. The polymer PAG was prepared by first grinding together 10 g of L-Aspartic acid and 11 g of L-Glutamic acid and heating in a round-bottom flask equipped with a mechanical stirrer and an N₂ inlet. The mixture was heated at 170°C for 2 h and then at 200°C for 4 h. After cooling, the solidified polymer was slurried with 100 ml of water and filtered. The filtrate was dialyzed for 24 h through a Spectrapor membrane (m.w. cutoff of 3.5 kD) in 250 ml of constantly stirred water. Both parts that passed from the membrane and retained in the membrane were dried under a vacuum overnight at 50 °C. The results for the efficiency of the polymers that are retained in the membrane (i.e. molecular weight larger than 3.5 kD) have been presented in this quarterly report.

The corrosion behavior of mild steel in 0.5 M HCl in the absence and presence of 0.1% concentration of the inhibitors was studied using a weight loss technique and data obtained after 1 day, 3 days, and 7 days of immersion are shown in Table 3.

Table 3: The weight loss parameters obtained for mild steel specimens in 0.5M HCl solution without and with the concentration of 0.1% inhibitors.

Inhihiton /	Day 1		Day	3	Day 7	
Concentration	CR (mm/year)	IE (%)	CR (mm/year)	IE (%)	CR (mm/year)	IE (%)

Control	0.48	-	1.22	-	1.81	-
SP	0.22	54.5	0.40	67.4	0.93	48.9
LYS	0.19	59.8	0.41	66.2	1.20	33.7
PAG	0.27	44.1	0.46	62.7	1.30	28.2
WP	0.29	39.1	1.32	-7.7	2.95	-63.3

In Table 4, the electrochemical parameters, R_s and R_{ct} , obtained from the EIS tests are presented. Moreover, their IE values with respect to the control specimen are summarized. For all the tested inhibitors, IE values increased with an increase in their concentration in the 0.5M HCl solution. In Table 4, the inhibitors are sorted by increasing IE, and all results are presented for 0.1% concentration of inhibitors.

Table 4: EIS parameters for mild steel in 0.5 M HCl and the presence of the investigated inhibitors.

Inhibitors	$R_s (\Omega \ cm^2)$	$R_{ct} (\Omega \ cm^2)$	IE (%)
Control	4.4	242.9	-
SP	3.6	717.9	65.2
LYS	3.7	574.5	57.5
WP	3.6	535.2	53.7
PAG	3.6	392.9	37.7

2. Task 3: Advanced Microscopy and Chemical Characterization

Fourier transform infrared spectroscopy (FTIR) of the inhibited mild steel specimens was examined to shed light on the corrosion inhibition behavior of the inhibitors. Moreover, the corrosive solutions for the case of inhibitors were analyzed by UV-visible spectrometry (UV-vis). The adsorption behavior and morphology of the select proteins were analyzed by atomic force microscopy (AFM).

AFM was used to visualize WP and SP to gain insight into their shape and distribution at natural pH. Mica has been selected as a base surface for adsorption studies because its smooth surface, on the scale of the adsorbing molecules, makes it an excellent substrate for imaging biomolecules. Additionally, proteins can effectively bind to it in common buffer solutions [2].

The obtained 3D views and cross-section topography images of the proteins are shown in Figure 1. It was observed that higher concentrations showed higher surface coverage on the mica surface for both proteins. Moreover, the individual larger aggregates were obtained for the case of lower concentration value of the solutions, which shows that different behaviors can be naturally encountered in the same concentration state [2]. On the other hand, both proteins created the multilayer on the mica surface, however, the layer thickness of the samples cannot be observed exactly since the mica surface cannot be observed and used as a zero-height [3].

Figure 1 (a) illustrates the height of the SP of 0.001% concentration, which was observed as 1.0 \pm 0.5 nm. The result appears to be consistent with the literature [4]. In addition, SP showed a more balanced cross-section topography in terms of height for its concentration of 0.01%. It can be explained as the fractional coverage increases with an increase in concentration [5]. From Figure 1 (b), it is found that the height of WP was 6.0 ± 0.5 nm for the lower concentration. Moreover, the variation of the height was lower for the ten times greater concentration as also observed in the case of SP.

It is suggested that the shape and adsorption behavior of proteins depend strongly on pH level [2]. If the pH is significantly different from the protein's isoelectric point and the ionic strength is low, intermolecular electrostatic repulsion becomes the dominant force. So, the protein network in a solution becomes coarser and composed of more particulate aggregates [6]. On the other hand, it is argued that the proteins are tightly bound to mica, and the contamination does not occur at acidic pH [2]. Therefore, the adsorption behavior and the shape of the inhibitors will be analyzed in the HCl solution as well.





Figure 1: 3D views and cross-section topography images of the mica surface with (a) SP and (b) WP.

3. Conclusions

The effect of inhibitors, including synthesized copoly-amino acids and proteins on mild steel in 0.5 M HCl was investigated using electrochemical measurements. The film formation on the mild steel surface was studied using FTIR and UV-vis. The obtained results showed that the used inhibitors showed higher IE with increasing their concentration. The mechanism for the inhibition could be explained by the adsorption of the inhibitor molecules on the metal surface by their functional groups. The adsorbed molecules of inhibitors formed a complex film on the metal and effectively blocked the steel surface from being attacked by the corrosive media.

Section B: Detailed Technical Results in the Report Period

1. Background and Objectives in the 1st Annual Report Period

1. Background

There are several methods to mitigate or prevent corrosion processes occurring on the metal surface, specifically pipeline systems for the oil and gas industry. Corrosion inhibition, anodic protection, cathodic protection, coating, alloying etc are the available methods to mitigate the corrosion process [7]. Among all the methods, corrosion inhibitors, which is the method based on the addition of chemicals, are widely used due to their effectiveness and cost efficiency. In recent decades, the pursuit of environmentally friendly corrosion inhibitors has gained significant attention [8], [9]. The research in the field of corrosion inhibitors has been to replace environmentally harmful substances with affordable, efficient molecules that have little to no environmental impact [10]. These inhibitors can be classified into two categories, which are namely organic and inorganic eco-friendly inhibitors. The types of organic inhibitors are easy to degrade, low toxic, accessible and sustainable and they are, generally, derived from various sources, including natural plants, animals, and microorganisms [9]. The working principle for the organic inhibitors is to create a protective layer on the metal surface. The heteroatoms localized on functional groups or aromatic rings in the molecular structure of the organic inhibitors, basically biopolymers can interact chemically or electrostatically with a metal surface. That interaction of the biopolymer and the metal surface leads to the formation of an adsorbed molecular layer which prevents or slows down the reaction between metal and the surrounding environment, thereby reducing the rate of corrosion [10], [11].

2. Objectives in the 1st Annual Report Period

During the 1st year of our project, we accomplished several important objectives as described in this report. Our main goal was to investigate the effectiveness of various bio-based green corrosion inhibitors through electrochemical and gravimetric tests as well as chemical and imaging techniques. The following objectives were achieved:

Task 1: Completed a comprehensive Literature Review regarding bio-based and green corrosion inhibitors suitable for the oil and gas industry. A comprehensive review of existing research was carried out, yielding important insights into the working mechanisms of bio-based corrosion inhibitors. This in-depth literature review formed the basis for our subsequent analyses.

Task 2: Evaluated the corrosion inhibition efficiency of bio-based corrosion inhibitors using electrochemical and gravimetric tests.

Task 3: Investigated the effect of bio-based corrosion inhibitors on the chemical and topographical characteristics of metal surfaces subjected to the corrosive environment

2. Experimental Program in the 1st Annual Report Period

2.1 Materials

Tests were performed on a mild steel specimen of the percentage composition C: 0.059, Si: 0.18, Mn: 0.4610, P: 0.01, S:0.011, and the rest of Fe. The steel bar was purchased from McMaster-Carr, US. The specimens of size 10mm x 10mm x 2mm were cut from the mild steel bar. Before both the gravimetric and the electrochemical tests, the specimens' surfaces were physically polished with silicon carbide (SiC) paper ranging from grade #180 to #1200. This was followed by rinsing with distilled water, degreased with acetone, and finally dried in air. Before any experiment, the substrates were treated as described and freshly used with no further storage.

Amino acids, proteins and chitosan were used as the inhibitors. The amino acids (reagent grade \geq 98%) and chitosan (from shrimp shells \geq 75%) were purchased from Sigma-Aldrich and were used with no further purification. The proteins studied in this investigation were obtained from various commercial vendors and used as received. Due to the considerable quantity of proteins required for both experiments and practical applications, for inhibiting steel corrosion, acquiring extremely pure proteins at the necessary scale was too expensive, resulting in the proteins being obtained in bulk with anticipated impurities. The used inhibitors and their abbreviations are listed in Table 5.

The molecular structures of select amino acids are presented in Figure 2. The electrolytic solution of 0.5M HCl was prepared from dilution of 37% analytical grade HCl. The test inhibitors were dissolved in 0.5 M HCl to obtain the desired concentration (0.002% - 0.02% wt).

Name	Abb.	Name	Abb.	Name	Abb.		
Amino Acids							
L-Methionine	MET	L- Cysteine	CYS	L- Isoleucine	ILE		
L-Arginine	ARG	Glycine	GLY	L- Phenylalanine	PHE		
L-Glutamic Acid	GLU	L-Aspartic Acid	ASP	L- Alanine	ALA		
L- Threonine	THR	L- Histidine	HIS	L-Leucine	LEU		
L- Proline	PRO	L- Valine	VAL	L- Lysine	LYS		
L- Tryptophan	TRP	L- Asparagine	ASN	L- Serine	SER		

Table 5: List of inhibitors and their abbreviations used in the study

L- Tyrosine	TYR	L- Glutamine	GLN	L- Ornithine monohydrochlori de	H- ORN
		Proteins			
Lysozyme	LYS	Albumin	ALB	Mild Silver Protein	MSP
Whey Protein	WP	Soy Protein	SP	Bovine Serum Albumin	BSA
Sodium Caseinate	SC	Trypsin	TRY	Non-fat Milk Powder	NFMP
Collagen Peptides	СР	Pepsin	PEP	Hemoglobin Powder	HEM



Figure 2: Molecular structure of used amino acids.

2.2 Gravimetric Measurements

The mild-steel coupons with almost equal sizes and masses were used to determine the inhibition efficiency via gravimetric mass-loss measurements. The weight loss was measured as the difference between the weight at a given time and the initial weight of the specimens. Mild steel coupons (10mm x 10mm x 2mm) were immersed in 0.5 M HCl for 24 h in the absence and presence of amino acid inhibitors with different concentrations of 0.002% to 0.02% wt. Then, the steel coupons were rinsed with acetone, dried in air, and reweighted. The average relative mass loss of the mild-steel coupons was determined from three individual measurements. All the measurements were taken at room temperature. The corrosion rate (CR) and inhibition efficiency (IE) were calculated by the following equations:

$$CR \ (mmy) = \frac{KW}{\rho At} \tag{1}$$

where W is the weight loss (in g), ρ is the density (gcm⁻³), A is the exposed area of the specimen (cm), and t is the exposure time (h). K is a constant that can be varied to calculate the corrosion rate in various units. For the case of mm/year for corrosion rate calculation, K is equal to 8.75×10^4 .

$$IE_{WL}(\%) = \frac{CR_0 - CR_i}{CR_0} \times 100$$
(2)

where CR_0 and CR_i are the corrosion rate of mild steel in the absence and presence of inhibitor respectively.

2.3 Electrochemical Measurements

Electrochemical experiments were conducted in a conventional three-electrode glass cell, using a Gamry Reference 600 potentiostat. Mild steel coupons were used as the working electrode. The saturated calomel electrode (SCE) and platinum sheet electrode were used as reference electrode and counter electrode, respectively. Before carrying out the electrochemical tests, the working electrode was immersed in electrolytic solution for 30 minutes to ensure that there is a steady-state potential on the electrode surface. The open circuit potential (OCP) of the corroding system was monitored for 30 minutes to ensure a steady-state condition. In this work, all the electrochemical experiments were repeated three times to examine the reproducibility of the electrochemical data.

Electrochemical impedance spectroscopy (EIS) was conducted at corrosion potentials (*E*corr) over a frequency range of 100 kHz–10 MHz, with amplitude signal of 10 mV acquiring 10 points/decade. The obtained EIS data were interpreted with Gamry Echem Analyst. With EIS results, the corrosion inhibition efficiency was obtained according to Equation 3.

$$IE_{EIS}(\%) = \frac{R_{ct} - R_{ct,0}}{R_{ct}} \times 100$$
(3)

where R_{ct.0} and R_{ct} are the charge transfer resistance without and with inhibitor, respectively.

The potentiodynamic polarization (PDP) curves were carried out under the potential from -250 mV to +250 mV vs. OCP at a scan rate of 0.5 mV/s. The PDP test was conducted only for the L-Methionine test series. The inhibition efficiency was calculated from the measured Icorr values using the relationship:

$$IE_{PDP}(\%) = \frac{I_{corr,0} - I_{corr}}{I_{corr,0}} \times 100$$
(4)

where $I_{corr.0}$ and I_{corr} are the corrosion current density without and with inhibitor, respectively.

2.4 Chemical and Topographical Characterization

2.4.1 FTIR

The FTIR analysis was performed using a PerkinElmer Frontier spectrometer with an Attenuated Total Reflectance (ATR) accessory, to determine the structure and bond configuration of the Albumin protein and the formed film on the mild steel surface. To this end, a 12% concentration of protein by mass in a 0.5M HCl solution was prepared. The Albumin-HCl solution was mixed using a stirring rod for 30 min to ensure total dissolution of protein particles before testing. The mild steel specimens with dimensions of 20mm x 10mm x 2mm were used. Mild steel specimens' surfaces were mechanically polished with silicon carbide (SiC) papers with a grit size of #180, #320 and #600. This was followed by rinsing with deionized water, acetone, and drying in air. FTIR was carried out on 12% concentration of ALB by mass in 0.5M HCl solution, and on mild steel surfaces after 24h immersion in 0.5M HCl solution in the presence and absence of 0.1% of ALB. The transmission infrared spectra of the specimens were recorded in the range between 650 cm⁻¹ and 4000 cm⁻¹ at a resolution of 4 cm⁻¹ with 3 scans per specimen. An average of three replicates is reported in this study. The background noise was also collected and removed from both the protein and mild steel spectra. After obtaining the spectra, baseline correction was applied on the spectra to fix both the sloping shape of the spectra and the offset in absorbance.

2.4.2 UV-vis

UV-vis analysis was carried out using Shimadzu UV-2600 spectrophotometer in a range of 200–800 nm. The UV-vis spectra were collected for the solutions of the 0.02% Albumin in the 0.5M HCl recorded prior to immersion of the mild steel, and solutions of 0.02% Albumin in the 0.5M HCl after 2h immersion of the mild steel. The spectral profiles were then compared to predict whether a complex is formed with the metal surface by adsorption of ALB on mild steel surface. The mild steel specimens were prepared similar to that described in the FTIR section.

2.4.3 3D profilometry

The 3D profilometry analysis was performed using a Nanovea CHR 150 chromatic confocal profilometer. It measures the surface profile and topography of the mild steel specimens. Mild steel specimens with dimensions of 20mm x 20mm x 2mm were used in this test. Mild steel specimens' surfaces were mechanically polished with silicon carbide (SiC) papers with a grit size of #180, #320, #600 and #1200. This was followed by rinsing with deionized water, acetone, and finally drying in air. The surface of the metal specimens was measured for the polished specimen and the mild steel specimens that were immersed in the 0.5M HCl without and with 0.1% of ALB for 24h. An area of 3mm x 3mm on the specimen surface was scanned with the step size of 1.5 μ m in both 2D directions. Scan velocity was 1.50 mm/s. The data were processed with Professional 3D software to calculate surface topography before and after corrosion.

2.4.4 AFM

The AFM technique was used to investigate the topographical characteristics of the mild steel surface in the corrosive solution without and with ALB. The Cypher S AFM from Oxford Technologies (former Asylum Research) was used for the analysis. The mild steel specimens were prepared in a similar way to that used in the 3D profilometry analysis and inserted in the corrosive solution without and with 0.1% of ALB for 24h. After 24h, the specimens were removed, carefully rinsed with deionized water and dried in air. The surface examination was performed in tapping mode (intermittent contact), and the topographic AFM images of 256 by 256 pixels for the scanned area of 10x10 μ m were obtained at 1 Hz per line. The images were obtained using the probe (AC160) from Oxford Technologies with a spring constant of 26 N/m. The image analysis was processed using Igor software to determine surface roughness of the specimens before and after corrosion.

2.5 Results and Discussions

2.6 Task 1: Literature Review

The working principle for the organic inhibitors is to create a protective layer on the metal surface. The heteroatoms localized on functional groups or aromatic rings in the molecular structure of the organic inhibitors, basically biopolymers can interact chemically or electrostatically with a metal surface. That interaction of the biopolymer and the metal surface leads to the formation of an adsorbed molecular layer which prevents or slows down the reaction between metal and the surrounding environment, thereby reducing the rate of corrosion [10], [11]. Many research groups have reported the successful use of biopolymers as corrosion inhibitors for metals in various corrosive media. In recent years, large numbers of novel materials have been developed which are bioinspired materials from lotus leaves, shrimp waste protein, chitosan-based protein, rose petals and nepenthes pitcher plants [12] Researchers have used bioinspired substances as corrosion inhibitors to test their efficiency on metallic materials in an acidic medium. They have performed several test methods to observe both electrochemical and surface analyses to investigate the effect of corrosion inhibitors for mitigating the corrosion process. Some of these test methods can be listed as weight measurement, electrochemical impedance spectroscopy, potentiodynamic polarization scanning electron microscopy analyses etc.

A study performed by Farag et al. [13] shows the use of recovery shrimp waste protein to characterize its inhibition effects as a corrosion inhibitor for carbon steel. They found that the corrosion rate decreases with increasing inhibitor concentration. In this study, the inhibition action of the used inhibitor depends on the adsorption on the steel surface by applying Langmuir adsorption isotherm. The obtained free energy of adsorption showed the inhibition process was spontaneous and chemically adsorbed onto the steel surface. In addition, some researchers have focused on the ability of natural proteins to inhibit the corrosion of metals in acidic media. In this regard, a casein which is a milk protein was used to inhibit the corrosion of mild steel in an acidic electrolyte [14]. Authors have pointed out that an increase in the concentration of casein resulted in an 88 % decrease in the corrosion rate of mild steel. They have also stated that temperature increase had adverse effects on the surface coverage and the corrosion inhibition

efficiency of casein. They have also analyzed the surface improvements of the sample by atomic force microscopy, and they stated the surface of the mild steel has become smoother with the addition of casein as an inhibitor. Liao et al. [9] reported that the Fructus cannabis protein extract powder as a green and effective corrosion inhibitor shows very high corrosion inhibition efficiency with 98 % on carbon steel in an acidic medium. Moreover, the tested carbon steel shows higher hydrophobicity of the surface, making it less prone to interact with water, and greater adhesion force obtained by adsorption of the Fructus cannabis protein. The study also points out that high temperatures affect the bond between the inhibitor and the steel surface weakens or breaks due to increased thermal energy.

2.7 Task 2: Electrochemical and Gravimetric Corrosion Testing

The inhibition performance of amino acids, proteins and chitosan for mild steel corrosion in 0.5M HCl solution was investigated using the EIS measurements. The obtained results in EIS were analyzed using an electrical equivalent circuit.

In Table 6, the electrochemical parameters, R_s and R_{ct} , obtained from the EIS tests are presented. Moreover, their inhibition efficiencies with respect to the control specimen are summarized. For all the tested inhibitors, inhibition efficiencies increased with an increase in their concentration in the 0.5M HCl solution. In Table 6, the inhibitors are sorted by increasing inhibition efficiency, and all results are presented for 0.02% concentration of inhibitors.

#	Inhibitors	$R_s (\Omega \ cm^2)$	$R_{ct} (\Omega \ cm^2)$	IE (%)
0	Control	3.561	196.091	-
1	Albumin	4.517	539.907	63.68
2	Lysozyme	4.392	502.231	60.61
3	Collagen Peptides	4.112	492.346	60.17
4	Soy Protein	3.981	487.972	59.82
5	Pepsin	4.049	413.886	52.62
6	Chitosan	3.706	408.900	52.04
7	Non-fat Milk Powder	3.838	391.913	49.97
8	Mild Silver protein	4.202	390.557	49.79
9	Trypsin	4.532	373.572	46.86

Table 6: EIS parameters for mild steel in 0.5 M HCl and the presence of the investigated inhibitors.

10	L-Methionine	3.866	364.734	46.24
11	Whey-Protein	3.720	345.991	43.32
12	Bovine Serum Albumin	4.178	345.593	43.26
13	Hemoglobin	4.372	292.821	33.03
14	L-Asparagine	4.177	290.523	32.50
15	L-Arginine	3.493	284.195	31.00
16	L-Cysteine	4.283	279.117	29.75
17	L-Histidine	3.904	256.026	23.41
18	Sodium Caseinate	4.060	253.068	22.51
19	L-Tryptophan	3.676	249.390	21.37
20	L-Valine	3.708	245.272	20.05
21	L-Lysine	3.814	236.280	17.01
22	L-Tyrosine	3.855	233.133	15.89
23	L-Isoleucine	4.146	230.839	15.05
24	L-Glutamine	3.541	229.932	14.72
25	L-Aspartic Acid	3.839	225.036	12.86
26	L-Glycine	4.804	218.196	10.13
27	L-Leucine	3.542	220.882	9.40
28	L-Phenylalanine	5.977	213.323	8.08
29	L-Proline	4.908	215.092	8.83
30	L-Threonine	5.421	210.979	7.06
31	L-Glutamic Acid	4.658	203.072	3.44
32	L-Alanine	4.189	201.633	2.75

33	DL-Serine	3.785	178.913	-9.60

From Table 6, it is observed that there was a significant enhancement in the change of R_{ct} for most of the inhibitors. An increase in R_{ct} manifests the formation of a protective layer on the metal surface, which provides higher resistance toward the charge transfer reactions occurring at the metal-electrolyte interface [15]. The obtained R_{ct} allowed to calculate their efficiency in terms of inhibition of corrosion. For example, proteins ALB and LYS, and amino acids MET and ASN showed positive effects for corrosion inhibition with an increase in their charge transfer resistance.

The corrosion behavior of mild steel in 0.5 M HCl in the absence and presence of different concentrations of amino acids was studied using a weight loss technique and data obtained after 24 h of immersion are shown in Table 7. The corrosion rate of mild steel is reduced in the presence of inhibitors as compared to free acid solution and depends upon the used inhibitor concentration. For all amino acids tested, the IE increases with increasing concentration of inhibitor.

Table 7: The weight loss parameters obtained for mild steel in 0.5M HCl solution without and
with various concentrations of amino acids.

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Amino Acid	Concentration (%wt)	Corrosion Rate (mm/year)	Inhibition Efficiency (%)
Control ¹	0	10.91	-
	0.002	9.96	8.73
L-Methionine	0.008	2.13	80.48
	0.02	2.10	80.75
	0.002	10.78	1.12
L-Arginine	0.008	2.19	79.88
	0.02	2.16	80.21
Control ²	0	9.33	-
	0.002	10.21	-9.44
L-Glutamic Acid	0.008	9.82	-5.30
	0.02	9.40	-0.82
L-Threonine	0.002	10.57	-13.30

0.008	9.90	-6.17
0.02	8.71	6.62

Control¹: Control sample for test series of L-Methionine and L-Arginine Control²: Control sample for test series of L-Glutamic Acid and L-Threonine

For Methionine, IE reached its maximum of 80.75% at the concentration of 0.02%wt. The increased IE with increasing inhibitor concentrations indicates that more L-Methionine molecules are adsorbed on the steel surface at higher concentrations, leading to greater surface coverage and hence the formation of a protective film [16]. Arginine has shown similar behavior with Methionine in terms of concentration-based increase in IE, and the maximum IE of 80.21% was obtained at the concentration of 0.02%wt.

The corrosion rate value decreased with increasing concentration of Threonine. In terms of IE, Threonine showed mitigation of corrosion for mild steel in 0.5 M HCl for the highest concentration (0.02%wt). The photos taken before and after the immersion of the Threonine test samples were provided in Figure 3.



Figure 3: Mild steel samples tested for weight loss measurement before and after the test in 0.5M HCl with different concentrations of L-Threonine

2.8 Task 3: Chemical and Topographical Characterization

2.8.1 FTIR

The mild steel surface was analyzed using FTIR to observe the formation of the protective layer. The spectra for the LYS and PAG in HCl solution, and the surface of mild steel immersed in 0.5M HCl with 0.1% LYS and PAG are presented in Figure 4 and Figure 5, respectively.



Figure 4: FTIR spectra of (a) LYS in HCl solution and (b) surface-adsorbed layer of the mild steel immersed in 0.5M HCl in the presence of 0.1% LYS.

According to the FTIR spectra of the LYS, the bands at 3306 cm⁻¹ and 1633 cm⁻¹ were the dominant peaks for the O-H functional group and C-O stretching vibration of amide I, respectively [17]. Compared with the FTIR spectrum of the mild steel specimen immersed in 0.5M HCl solution in the presence of 0.1% LYS, the C-O stretching at 1633 cm⁻¹ tended to disappear. The O–H stretching peak was shifted to 3683 cm⁻¹. Moreover, the observed peak at 2983 cm⁻¹ is attributed to C-H stretching vibration. All these reveal the adsorption and interaction of the oxygen heteroatoms in LYS with the mild steel specimen surface [18]

From Figure 5 (b), the characteristic peak was observed at 3342 cm⁻¹ which corresponds to the O-H stretch vibration of PAG. The absorptions at 1635 cm⁻¹ can be assigned to the carbonyl C=O stretch. A strong band of high intensity at 1031 cm⁻¹ corresponds to the N-H bending vibration of the polymer [19]. The FTIR spectra of the mild steel specimen immersed in 0.5M HCl in the presence of 0.1% PAG confirm the PAG adsorption on the mild steel specimen. The O-H stretching peak was shifted to 3681 cm⁻¹. The peak from the N-H bending vibration was shifted to 1025 cm⁻¹. In addition, the observed peak at 2969 cm⁻¹ is attributed to C-H stretching vibration.



Figure 5: FTIR spectra of (a) PAG in HCl solution and (b) surface-adsorbed layer of the mild steel immersed in 0.5M HCl in the presence of 0.1% PAG.

2.8.2 UV-vis

The UV-vis spectra for LYS and PAG are shown in Figure 6 and Figure 7, respectively. The spectra were obtained for the solution that contains 0.1% inhibitors in 0.5M HCl before and after the immersion of the mild steel specimen for 24 hours. It was shown that after immersion of the mild steel specimen, the obtained absorption spectra in the UV-vis region shifted to a lower absorbance value for both tested inhibitors. This implies that there might be an interaction between Fe²⁺ and the inhibitor molecules in the solution [20]. Moreover, a displacement in the absorption peaks indicates the interaction between the tested molecules and Fe²⁺ ions in the solution. Therefore, these results could potentially show the formation of a complex between the Fe²⁺ ions and the LYS and PAG molecules in 0.5 M HCl solution [21], [22].



Figure 6: UV-vis spectra of the solutions with 0.1% LYS in the 0.5M HCl recorded before and after immersion of the mild steel specimen.



Figure 7: UV-vis spectra of the solutions with 0.1% PAG in the 0.5M HCl recorded before and after immersion of the mild steel specimen.

This observed data is explained by having some electronic transitions between the metal surface and the inhibitor molecules, thus, the formation of a film complex on the surface of the mild steel. The electronic transition can be classified as $n \rightarrow \pi$ or $n \rightarrow \pi^*$ [23]. Having an adsorbed protective film, which was formed by the interaction between the inhibitor molecules and mild steel surface, can reduce the acid attack on the metal surface. Therefore, corrosion on the surface can be reduced.

2.8.3 3D profilometry

Surface topology of the metal specimens was measured on the polished mild steel specimen and the mild steel specimens that were immersed in the 0.5M HCl without and with 0.1% ALB. The scanned area was $3x3 \text{ mm}^2$ for all the specimens. The surface topography of the samples before and after immersion in corrosive solution is shown in Figure 8. The parameter of root mean square deviation of the roughness (R_q) was obtained from the 3D profilometry test scan and presented in Table 8.

For the mild steel specimen immersed in 0.5M HCl solution with 0.1% ALB had lower value of R_q than the mild steel immersed in 0.5M HCl without any inhibitor. This implies that the ALB molecules could create a bond with the mild steel surface, and this could suppress the corrosion of the metal [20]. In other words, having ALB in the solution helped to form a complex film on the mild steel surface to prevent corrosion.



Figure 8: Surface topography of (a) polished mild steel, (b) mild steel specimen immersed in 0.5M HCl, and (c) mild steel specimen immersed in 0.5M HCl with 0.1% ALB

Table 8: Surface roughness parameters obtained by profilometer of the polished mild steel, and mild steel specimen immersed in 0.5M HCl with and without 0.1% ALB.

Specimen	Rq
Polished mild steel	600 nm
Mild steel immersed in 0.5M HCl	900 nm
Mild steel immersed in 0.5M HCl + 0.1% ALB	600 nm

2.8.4 AFM

The 2D and 3D surface profiles of the samples before and after immersion in 0.5 M HCL solution are shown in Figure 9. The values for the parameter of root mean square roughness (R_q) are presented in Table 8. From Table 9, R_q for polished mild steel surfaces, inhibited and uninhibited mild steel surfaces were 16.76 nm, 32.53 nm, and 114.37 nm respectively. The results showed that the R_q value for the mild steel surface immersed in 0.5M HCl with 0.1% ALB solution is lower than that of the steel surface immersed in 0.5M HCl without inhibitor. This indicates that the use of ALB controlled the corrosion process by the formation of a film on the mild steel surface. The reduced value of R_q for the treated surface with ALB also indicated the homogeneity of the film on the surface. Moreover, the formed film prevented the metal from corrosion [24]. The AFM results seem to be in a good agreement with the FTIR, UV-vis and 3D profilometry analyses.





Figure 9: 2D and 3D images of the profiles obtained by AFM of (a) polished mild steel, (b) mild steel specimen immersed in 0.5M HCl, and (c) mild steel specimen immersed in 0.5M HCl with 0.1% ALB.

Table 9: Surface roughness parameter obtained by AFM measurement of the polished mild ste	eel,
and mild steel specimens immersed in 0.5M HCl with and without 0.1% ALB.	

Specimens	Rq
Polished mild steel	16.76 nm
Mild steel immersed in 0.5M HCl	114.37 nm
Mild steel immersed in 0.5M HCl + 0.1% ALB	32.53 nm

3. Future work

It is stated that the presence of heteroatoms and conjugated π electrons system on the molecular structure of polymers make them potential environmentally friendly organic corrosion inhibitors for metal. It is important to highlight that the effectiveness of the inhibition capability of the polymers depends on their molecular structure, concentration, corrosive environment, nature of the metal surface, etc [25]. Moreover, studies suggest that the presence of -SH groups in the amino acids and the polymers increases the adsorption of the inhibitors, which results in greater blockage of active sites at the steel surface [26], [27]. Therefore, the methionine functionalized

poly amino acids will be synthesized and used as a corrosion inhibitor. The adsorption behavior and the shape of the inhibitors will be analyzed in the HCl solution to observe their behavior in low pH conditions. In addition, it is planned to use the steel API 5L as a specimen to better simulate real-world conditions.

4. References

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