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Candidate's Name	**:**	A.Mathina
Candidate's Address with email	**:**	4/5 A,Palanikavundan Pudur, Vinayagar koil street,Vadavalli, Coimbatore-641 041. madhimohamed@gmail.com
Title of the thesis (i) In Roman Script (ii) In roman Script	**:**	Corrosion Inhibition and Adsorption Potential of Biomass Extracts-Leaves and Flowers of *Heliconia rostrata and Canna Indica* on Corrosion of Mild Steel / Aluminium 1100 in 1 M HCl.
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Name of Supervisor	**:**	Dr.R.Rajalakshmi
Designation of Supervisor	**:**	Professor and Head, Department of Chemistry
Centre/department/school in which research was conducted	**:**	Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, University,
University's Name & Address	**:**	Avinashilingam Institute for Home Science and Higher Education for Women, University, Coimbatore -641 043.

Abstract

Metals find multifarious applications in industrial facilities such as acid pickling, industrial cleaning and petrochemical processes to name a few. They are essential part of our present civilization and these metallic materials corrode in a variety of gaseous and aqueous environments. The corrosion of metallic materials in acidic solution causes considerable costs. Mild steel and aluminum find widespread industrial and structural applications due to their low cost, easy availability, stability, and low density, high thermal & electrical conductivity.

Acid solutions are widely used in industrial acid pickling, industrial acid cleaning and oil-well acidizing. The aggressive nature of these acids causes severe corrosion in the metal specimen causing serious corrosion problems. Comparing to other mineral acids such as sulphuric acid, nitric acid and phosphoric acid, use of hydrochloric acid in industrial processes is more economical, efficient and trouble free. Therefore it is of immense importance to protect metals from corrosion caused by hydrochloric acid. There are various methods used for the protection of metals against corrosion.

One of the methods for combating corrosion is the use of corrosion inhibitors. A very large number of inhibitors are reported in the literature for different corroding systems. Most of the effective corrosion inhibitors are synthetic chemicals with high cost. Such synthetic compounds are not only expensive but also toxic to humans and environment. For the safety of the global environment, efforts have been geared towards finding naturally occurring eco-friendly organic substances as suitable replacement of synthetic corrosion inhibitors. Many of these naturally occurring substances have proved their ability to act as corrosion inhibitors for the corrosion of different metals and alloys in different aggressive media and they are safe and can be extracted by simple and cheap procedures. Plants are great chemical factories that can supply us with the chemicals required to inhibit the corrosion process . The study of biomass extracts as metal corrosion inhibitor is beneficial for several reasons. Interestingly, extracts from natural products (biomass) contain several phytochemical constituents, including alkaloids, tannins, flavonoids, ascorbic acids, phenolic acids, pigments, resins, triterpenoids which possess electronic structures related to those of conventional organic corrosion inhibitors. In recent years, the research in corrosion is oriented towards the development of green corrosion inhibitors for sustainable environment.

As a contribution to the current interest to discover nontoxic, safe, easily available, environmentally friendly green corrosion inhibitors, the present work is carried out to study the

inhibitive effect of ***Heliconia rostrata*** and ***Canna indica*** as corrosion inhibitor for **Mild steel and Aluminium 1100** in acidic medium.

Objectives :

- To find out the phytochemical constituents present in leaves and flower extracts of ***Heliconia rostrata*** and ***Canna indica*** using preliminary phytochemical screening tests.
- To characterize the inhibitors using various analytical techniques such as GC-MS, UV and FT-IR.
- To evaluate the inhibition effect of a ***Heliconia rostrata*** and ***Canna indica*** as promising corrosion inhibitor for Mild steel and Aluminium 1100 in 1M HCl by Electrochemical measurements and conventional mass loss method.
- To arrive at a possible mechanism for the inhibition process.
- To ascertain the adsorption of the phytochemical constituents on Mild steel / Aluminium 1100 surface by surface analysis method.

Literature Survey

Review of Literature related to corrosion inhibition using plant extracts was carried out using various article data bases. Plants names and families were authenticated by Botanical Survey of India, Tamil Nadu Agricultural University Coimbatore.

Methodology

The present investigation is carried out in three phases.

Phase I: Selection and Identification of the inhibitor, preparation and Characterization of plant inhibitors, Selection of metal samples and test media.

Phase II: Assessment of selected inhibitors as promising corrosion inhibitors for mild steel and aluminum 1100 in 1M HCl by Electrochemical measurements and conventional mass loss method.

Phase III: Analysis of the metal surface by various surface analytical techniques.

Phase I:

Selection and identification of the inhibitors.

The leaves and flowers of ***Heliconia rostrata*** **(HR)** and ***Canna indica*** **(CI)** were selected for the present investigation and they were collected in and around Coimbatore and shade dried. The plant specimens were authenticated in Botanical Survey of India (BSI/SRC/5/23/2015/Tech/972 & 527) and voucher specimens were deposited in our university for further reference.

Preparation and Characterization of the investigated plant extracts.

50 g of the dried leaves / flowers were refluxed with 500 mL of 1M HCl for 3 hours and kept overnight. The cooled extracts were filtered and made up to 1000 mL (5% extract).Preliminary phytochemical examinations were carried out for all the extracts as per the standard procedures mentioned (Harborne, 1973).

Investigated plants HR/CI were subjected to UV-VIS Spectrophotometric characterization over 200-600 nm using PC based double beam spectrophotometer 2202. The FT-IR spectrum was recorded for **flower and leaves** of ***Heliconia rostrata*** and ***Canna indica*** extracts with a frequency ranging from 4000 to 400 cm^{-1} using Perkin Elmer FT-IR spectrophotometer with the SOFTWARE – OPUS version 6.5. The individual compounds in the ethanolic distillate of the extracts, were identified by using Fisons 800 Top GC coupled to Fisons MD 800 series MS quadrupole mass detector gas chromatograph-mass spectrometry (GC-MS).

Selection of the Metal samples- Mild Steel & Aluminium 1100

Mild steel (MS) specimens of the following chemical composition in wt % - carbon 0.081%, manganese 0.198%, silicon 0.009%, phosphorus 0.012%, sulphur 0.017%, chromium 0.022%,molybdenum 0.026% nickel 0.016% , iron 99.62% and Aluminium Alloy 1100(AA 1100) with the following composition- Copper 0.05 - 0.2%, Manganese 0.05% , Silicon + Iron 0.95%, Zinc 0.01 %, Aluminum 99% were used for the entire study.

Selection of Acid Media

Hydrochloric acid is widely used as pickling agents for the removal of rust and scale in several industrial processes. It is widely used for de-rusting, pickling, cleaning of refinery equipment and removal of calciferous deposits from boilers, radiators of vehicles, pipeline carrying water or petroleum products, heat exchangers etc. Hence 1M HCl was selected to study the inhibitive effect of **leaves and flowers** of ***Heliconia rostrata*** and ***Canna indica*** extracts on corrosion of **Mild steel (MS) and Aluminium 1100(AA1100)** .

Phase II:

Assessment of selected inhibitors as corrosion inhibitors for MS and AA1100 by Electrochemical measurements and conventional mass loss method.

Electrochemical and mass loss studies were carried out to assess the efficacy of the inhibitors. MS/AA1100 specimens of size 1 x 5 cm^2 were used for mass loss study and metal specimens with an exposed area of 1 cm^2 were used for electrochemical study. The specimens were mechanically polished, degreased, dried and stored in a desiccator.

Electrochemical measurements

In this setup, a three electrode system comprising of a platinum electrode, calomel electrode and **MS /AA 1100** specimens as auxiliary, reference and working electrodes respectively were immersed in acidic medium in the presence and absence of different concentration of the inhibitors (ASTM G 1-2).

Potentiodynamic measurements and Impedance Spectroscopy

Tafel polarization curves and the impedance spectral response of MS /AA 1100 in the absence and presence of the investigated extracts were recorded by using Biologic EC lab v10.4 software. The experiments were carried out over a frequency range of 20 kHz to 0.1Hz at open circuit potential.

Mass loss method

Pre weighed test pieces of MS and AA1100 were immersed in triplicate in 100 mL of the solution containing various concentration of the inhibitor and in the absence of inhibitor for a predetermined time period as per ASTM G 1-2. The test specimens were removed and then washed with de-ionised water, dried and reweighed.

The experiments were performed for various parameters such as:

• Concentration variation (0.1%, 0.2%, 0.3%, 0.4%, 0.5%.0.6%, 0.7%)

• Different time intervals (½ h , 1 h , 3 h , 6 h , 12 h and 24 h)

• Temperature variation (303 K, 313 K, 323 K, 333 K , 343 K,353 K)

Molecular Modelling Studies:

Molecular modeling studies were carried out using Mopac software.

Phase III: Analysis of the metal surface by various analytical techniques

Surface examination of the **MS/AA 1100** in the presence and absence of the inhibitors were carried out by Scanning Electron Microscope, Energy dispersive X-ray analysis, XPERT-PRO X-ray diffractometer,Zeta-20 Optical Profiler,. FTIR spectra and UV-Visible spectrophotometer.

Salient features:

The salient features of the present study entitled **"Corrosion Inhibition and Adsorption Potential of Biomass Extracts-Leaves and Flowers of *Heliconia rostrata and Canna indica* on Corrosion of Mild Steel / Aluminium 1100 in 1M HCl"** are summarized below:

- Preliminary phytochemical screening tests reflected the presence of phytochemical constituents in the plant extracts.
- Various techniques namely FT-IR,UV-Vis and GC-MS were used for the characterization of the investigated plant inhibitors. The results confirmed the presence of N and O atoms which are the pre requisites for the extracts to act as corrosion inhibitors.
- The investigated inhibitors, performed in an effective manner to minimize the corrosion of **MS/AA1100** in 1M HCl medium.
- The Potentiodynamic polarisation curves inferred that the anodic (b_a) and cathodic (b_c) curves shifted towards low corrosion current density values in the presence of the inhibitors. This supports the fact that the inhibitors were able to suppress both the anodic dissolution and cathodic hydrogen evolution.
- Considerable reduction in the I_{corr} values reflected the inhibitive nature of studied inhibitors. The IE was found to increase with increase in concentration of the inhibitors.
- The impedance spectra obtained for **MS** in the presence and absence of the inhibitors at room temperature exhibited single capacitance loop indicating that the corrosion was controlled by charge transfer process. The diameter of the semi circle increased with increase in concentration of the studied inhibitors and the shape of the semi circle was similar in the presence of the inhibitors implying that there was no change in the mechanism of MS dissolution in the presence of the investigated inhibitors.
- In the case of **AA1100**, at room temperature, a capacitance loop at high frequency range and an inductive loop at the low frequency range were observed. The appearance of the inductive loop might be due to the relaxation of adsorbed species H_{ads}^{+} /Cl^{-} /O^{2-} ions /adsorbed phytoconstituents or redissolution of the oxide layer surface or Al dissolution. Neverthless the shape of the capacitive and inductive loops increase with increasing concentration of the inhibitors, thereby indicating the inhibitive properties of the inhibitors.
- The data obtained by impedance spectroscopy was analysed by proposing an equivalent circuit .Excellent fit for the results were obtained. The results reflected the increase of charge transfer resistance (R_{ct}) with increase in concentration of inhibitor. This might be due to the adsorption of the Phytochemical constituents adsorbed onto the MS/AA 1100 surface. The value of C_{dl} decreased with inhibitor concentration which might be due to decreased value of dielectric constant and/or due to the adsorbed film formed at acid/metal interface.
- Analysis of the results of the mass loss measurements of **MS / AA 1100** inferred that the inhibition efficiencies increased with increasing concentration of the inhibitors. Immersion studies reveal that as the time of immersion increased from ½ hr to 12h/6h the inhibition efficiency also increased. After 12 h/6h there was a slight decline in the inhibition efficiency at 24 h. The decrease in inhibition efficiency at longer immersion time might be due to the desorption of the protective layer formed in the presence of the inhibitors on the metal surface. All the investigated inhibitors could furnish an efficiency of 90-98% at a maximum concentration of 0.7%.
- The Kinetic and mechanistic aspects of corrosion may be gained by studying the effect of temperature on the corrosion of **MS/AA1100** in the presence and absence of the inhibitors.

It can be noted that the maximum I.E. obtained was in the range of 90- 94 percentage (313 K/333 K) in 1M HCl and then a slight decrease was observed from 343K to 353K.The IE was found to be at 80-85 percentage for the investigated inhibitors. This may be due to the adsorption of the inhibitor up to a particular temperature and then desorption of the inhibitor at higher temperature.

- Analysis of the mass loss data obtained from the investigated inhibitors using **SPSS** statistical package reflected the applicability of Langmuir adsorption isotherm.
- In the present investigation, Ea values were found to be greater than those calculated in the absence of the inhibitors. The higher values of E_a in the inhibited solution can be correlated with the increased thickness of the double layer, thereby enhancing the activation energy of the corrosion process.
- The positive value of the enthalpy of activation (ΔHa°) reflected the endothermic nature of the metal dissolution process. The positive values of entropy of activation (ΔSa°) in the presence of the inhibitors in 1 M HCl imply that the inhibitor molecules, freely moving in the bulk solution were adsorbed in an orderly fashion onto the metal surface.
- The negative values of ΔG^{o}_{ads} demonstrate that the inhibitors were spontaneously adsorbed onto the MS/AA 1100 surface. In the present study, the calculated values of ΔG^{o}ads obtained for the investigated systems range between -12 kJ/mole to -18 kJ/mole indicating that the adsorption of the inhibitors on the surface of the metal were through physical means of adsorption but chemisorption cannot be excluded.
- The negative sign of ΔH^{o}_{ads} indicated that the adsorption of the inhibitors on metal surface was exothermic in nature.The positive sign of ΔS^{o}_{ads} arised from substitutional process, which can be attributed to the increase in the solvent entropy and more positive water desorption entropy. This led to an increase in disorder due to the fact that more water molecules can be desorbed from the metal **s**urfac**e** by one inhibitor molecule. The negative values of entropy (ΔS^{o}_{ads}) in the presence of the inhibitors in 1 M HCl implied the inhibitor molecules, freely moving in the bulk solution were adsorbed in an orderly fashion onto the metal surface.
- Surface morphology of the metal indicated that the surface of the metal was found to be rough after subjecting the **MS/AA 1100** specimens in the acid medium and this reflected the aggressive nature of the inhibitors under study. The inhibited surface was found to be smooth and this revealed that the surface of the metal was protected by the adsorption of the active constituents of the plant species. The EDX patterns corroborated the results of SEM analysis.
- FT IR spectrum implied the presence of O and N atom containing functional groups, that act as a prerequisite for a molecule to function as a corrosion inhibitor.
- UV spectral data confirmed the formation of protective layer of metal-inhibitor complex on the metal surface.
- The morphology of the specimens using XRD and 3D Optical Profiler further confirmed the inhibitive nature of the inhibitors under study

Conclusion

- Tafel studies, linear polarization and impedance studies revealed that the inhibitors act as mixed type inhibitors
- The investigated inhibitors act as potential inhibitors for the corrosion of **MS/AA1100** in 1M HCl.
- The inhibition efficiency increased with increase in concentration of the inhibitors.
- The adsorption of the inhibitors was found to obey Langmuir adsorption isotherm.
- Thermodynamic parameters confirmed strong interaction of the inhibitor with the MS/AA 1100 surface.
- Quantum chemical studies, confirmed the probable adsorption centers through which the metal atom was linked to form metal – inhibitor complex.
- FTIR and UV-Visible spectroscopic studies confirmed the formation of metal- inhibitor complex.
- SEM –EDAX, XRD, 3 D Laser profilometry studies ascertained the inhibitive nature of the inhibitors under study.

Examiners :

Internal Examiner : Dr. T.V.Venkatesha, Professor
Department of Chemistry,
Kuvempu University,
Shankaraghatta,
Shivamogga District,
Karnataka-577451
drtvvenkatesha@yahoo.co.uk

External Examiner : Dr. Saviour A. Umoren,
Centre of Research Excellence in Corrosion Research Institute,
King Fahd University of Petroleum and Minerals,
Dhahran 31261, Saudi Arabia
saviourumoren@yahoo.com, umoren@kfupm.edu.sa