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Title of the thesis	:	Inhibitive performance of selected biomass-*Passiflora vitifolia, Pyrostegia venusta* and marine algae-*Sargassum polycystum, Padina boergesenii* on acid and alkali corrosion of mild steel and aluminium alloy – Experimental and Theoretical approach
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Abstract within 300 words:

Natural resources and infrastructure of any country are responsible for economic development. Corrosion is responsible for damaging bridges, airports buildings offices, irrigation systems, land and air transport, school buildings and industrial installations. Due to corrosion, the natural, industrial environments, efficiency and durability of the industrial equipment and infrastructure assets are affected. Human being and ecosystem are much affected by corrosion and pollution. The natural phenomenon of corrosion may be reduced by corrosion control methods.

The easy fabrication and cost-effectiveness of mild steel combined with excellent mechanical property is the main reason for using it in construction material, automobile Industries, petrochemical, chemical and metallurgical industries. Hydrochloric acid is used in many industries such as acidification, pickling bath, petrochemical processes. Mild steel suffers severe damage and it results in corrosion of the metal. Alkali solutions are used in alkaline cleaning, pickling and itching process.

Aluminium is the second largest attractive anode material after iron and it possesses excellent mechanical properties. It is an attractive anode material and it has high specific conductivity, high energy density, and high negative electrode potential compared to iron. It has many industrial applications namely construction purposes, automobile industries, aerospace industries, electrical power generation, ship hull and submerged pipelines.

Human health and safety considerations made the scientists concentrate on the use of natural compounds present in the plant parts which contained many organic compounds namely amino acids, alkaloids, pigments and tannins are used to replace the toxic and hazardous compounds. The inhibition mechanism mainly depends on the chemical properties of acids, parameters like concentration and temperature of the corrosive medium, dissolved organic and inorganic substance present in the acidic solution, mechanical behaviour of metals, structure and functional groups present in the investigated inhibitors.

This encouraged us to analyse the effectiveness of *Passiflora vitifolia, Pyrostegia venusta* (leaves) and *Sargassum polycystum*, *Padina boergesenii* (seaweed) for mitigating the MS and AA corrosion in hydrochloric and sodium hydroxide medium. The investigated plants/seaweeds were authenticated by Botanical Survey of India (BSI).

i) **Major objectives** :

- To find out the phytochemical constituents present in leaves extracts of *Passiflora vitifolia* (PAVL), *Pyrostegia venusta* (PVL) and marine algae-seaweed extracts of *Sargassum polycystum* (SP), *Padina boergesnii* (PB) using preliminary phytochemical screening analysis and characterised by HPTLC,GC-MS, UV and FT-IR.

- To examine the efficacy of acid/alkaline extracts of PAVL, PVL, SP and PB as eco-friendly corrosion inhibitors for MS/AA by electrochemical measurements and conventional mass loss method.
- To fit the suitable adsorption isotherm for all the investigated inhibitors using MS / AA in 1M HCl/1M NaOH.
- To assess the topography of MS/AA surface with and without using investigated inhibitors in 1M HCl/1M NaOH medium.
- To carry out quantum chemical calculation for the selected phytochemicals present in the investigated inhibitors.

ii) Methodology :

The present investigation is carried out in four phases.

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

Phase II : Evaluation of selected inhibitors as potential corrosion inhibitors for mild steel and aluminium alloy in 1MHCl/1M NaOH by Electrochemical measurements and conventional mass loss method.

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

Phase IV: To apply Quantum chemical calculations for correlating inhibition performance of inhibitors with electronic structural parameters.

Phase I:

Selection and identification of the inhibitors.

The leaves extract of *Passiflora vitifolia (PAVL), Pyrostegia venusta (PVL)* and seaweeds extract of *Sargassum polycystum (SP), Padina boergesenii (PB)* were selected for the present investigation. The plant parts were collected in and around Coimbatore and seaweeds were collected from Mandapam and shade dried. The plant specimens were authenticated in Botanical Survey of India (BSI/SRC/5/23/2016/Tech/729,731, BSI/SRC/5/23/2018/Tech/1742, 2019/Tech/3214) and voucher specimens were deposited in our university for further reference.

Preparation and Characterization of the investigated plant extracts.

25 g of the dried leaves / seaweeds were refluxed with 500 mL of 1M HCl/1M NaOH for 3 hours and kept overnight. The cooled extracts were filtered and made up to 500 ml (5% extract).Preliminary phytochemical examinations were carried out for all the extracts as per standard procedures mentioned in the literature.

Investigated plants/seaweeds were subjected to UV-VIS Spectrophotometric characterization over 200-800 nm using AU-2701double beam spectrophotometer. The FT-IR spectrum was recorded for all the studied inhibitors by Shimadzu IR Affinity-1S Fourier Transform Infrared Spectrometer with a frequency ranging from 4000 to 400 cm^{-1}.The various compounds present in the methanolic extracts of the inhibitors 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 Alloy

Mild steel (MS) specimens of the following chemical composition in wt % - C 0.019%, Mn 0.352%, Si 0.049%, P 0.019%, S 0.013%, Cr 0.010%, Mo 0.008%, Ni 0.010%, Cu 0.026% and Fe 99.33% were used for the entire study.

Aluminium Alloy(AA) with the following elemental composition- Si 0.056%, Fe 0.184%, C 0.010%, Mn 0.013%, Mg 0.015%, Cr 0.010%, Ni 0.053%, Zn 0.040%, Sn 0.026%, Ti 0.013%, Pb 0.029%, Bi 0.021%, Cd 0.013%, Ga 0.024% and Al 99.49% were used for the entire study.

Selection of Acid/Alkaline Media

Acid solutions as a medium are widely used in the acid-cleaning, acid descaling, acid pickling and oil well acidizing industries where it is desperate for corrosion inhibitors to control the acid induced corrosion attack on metals. The pickling of Al in caustic alkalis for degreasing before anodizing or to give an attractive matter finish is common practice, Alkalis destroy the protective Al film very quickly, possibly because OH^- ions are positively absorbed and hence the dissolution rate of aluminium is very high. In the current study, the following systems are investigated

1. PAVL, PVL, SP, PB in MS/HCl
2. PAVL, PVL, SP, PB in AA/HCl
3. PAVL, PVL, SP, PB in AA/NaOH

Phase II:

Electrochemical measurements and conventional mass loss method.

Electrochemical and mass loss studies were performed to determine the efficacy of the inhibitors. MS/AA specimens of size 1 x 5 cm^2 were used for mass loss method and metal specimens with an exposed area of 1 cm^2 were used for electrochemical measurements. The specimens were mechanically polished, degreased, dried and stored in desiccators [ASTM G1-03].

Electrochemical measurements

In this setup, a three electrode system comprising of a platinum electrode, calomel electrode and MS /AA specimens as auxiliary, reference and working electrodes respectively were exposed in acidic/basic medium in the presence and absence of different concentration of the inhibitors. Potentiodynamic measurement and EIS measurements were performed using a Frequency response analyser (Biologic model V10.23).

Potentiodynamic measurements and Impedance Spectroscopy

Tafel polarization curves and the impedance spectral response of MS/AA in the absence and presence of the studied inhibitors in the acid and alkaline corrosion 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 AA 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)

Phase III:

Surface examination of the MS/AA in acid and alkaline corrosion in the presence and absence of the inhibitors were performed by Scanning Electron Microscope, Energy dispersive X-ray analysis, Zeta-20 Optical Profiler, FTIR spectra and UV-Visible spectrophotometer.

Phase IV: Molecular Modelling Studies:

Molecular modelling studies were carried out using Mopac software. Quantum chemical studies were conducted for the selected phytochemicals commonly present in investigated inhibitors.

iii) Findings:

Salient features:

The salient features of the present study entitled "Inhibitive Performance of selected biomass- *Passiflora vitifolia, Pyrostegia venusta* and marine algae-*Sargassum polycystum, Padina boergesenii* on acid and alkali corrosion of mild steel and aluminium alloy – Experimental and Theoretical approach*"* are summarized and discussed under different phases as per the methodology adopted

Phase I:

- Preliminary phytochemical screening of the leaves extract of PAVL, PVL and seaweed extract of SP, PB were carried out using standard procedure (J.B. Harbone, 1973).
- The prepared extracts were characterized using GC-MS, HPTLC, FT-IR and and UV.

- HPTLC analysis revealed the presence of flavonoid, alkaloid and steroid in the studied inhibitors.
- The results of FT-IR and UV studies proved that the phytochemical constituents present in the PAVL, PVL, SP and PB were absorbed over the metal surface and metal surface can be protect from corrosion.

Phase II:

Polarisation studies for PAVL, PVL, SP, PB using MS, AA in acidic and alkaline medium

- Analysis of Potentiodynamic polarization results reveal that the E_{corr} for PAVL, PVL, SP and PB in acid/alkaline media do not change appreciably with the addition of the inhibitors and thus affect the anodic dissolution as well as cathodic hydrogen evolution reactions and act as mixed type inhibitors.
- I_{corr} values decreases significantly in the presence of inhibitors showing that all the inhibitors are effective in controlling corrosion.
- Tafel constants b_a and b_c for the studied systems and polarization curves of a MS/AA in acidic and alkaline medium inferred that all the studied inhibitors behave like mixed type inhibitor.
- R_p values increases with increase in inhibitor concentration indicating a better corrosion protective ability of the inhibitors under study.

Impedance studies

- The data obtained by impedance spectroscopy was analyzed by proposing an equivalent circuit. Excellent fit for the results were obtained. The results reflected an increase in charge transfer resistance (R_{ct}) values with increase in concentration of inhibitor. This might be due to the adsorption of the Phytochemical constituents adsorbed onto the MS/AA surface. The value of $_{Cdl}$ 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**.**
- The increase of absolute impedance at low frequencies in Bode plot confirms the higher protection with increasing concentration of the inhibitors, which is related to adsorption of inhibitors on MS/Al surface.

PAVL, PVL, SP, PB /MS/1M HCl

- The impedance spectra obtained for MS in the presence and absence of the inhibitors 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.

PAVL, PVL, SP, PB/AA/1M HCl

- In the case of AA, 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. Nevertheless the shape of the capacitive and inductive loops increase with increasing concentration of the inhibitors, thereby indicating the inhibitive properties of the inhibitors.

PAVL, PVL, SP, PB in AA/1M NaOH

- In case of aluminum alloy corrosion in 1M NaOH medium depicted two depressed capacitive semicircles at higher and lower frequency regions, separated by an inductive loop at low frequencies. Inductive loops can be explained by the occurrence of adsorbed intermediate on the surface. Therefore, adsorbed intermediate species such as Al^{+} and Al^{3+} might be involved in Al dissolution process. The capacitive semicircle at higher frequencies is attributed to the redox Al–Al^{+} reaction of the charge transfer process. Therefore, the resistance value obtained from intercepts of the first capacitive semicircle with real axis corresponds to the Al–Al^{+} charge transfer resistance. On the other hand, the second capacitive semicircle could be attributed to the fast complementary redox Al^{+}–Al^{3+} reaction. The curve manifested that addition of extract to alkaline NaOH solution leads to increase in the size of the capacitive semicircles, indication for increasing the resistances and decreasing corrosion rate.

Mass loss Measurements

- Analysis of the results of the mass loss studies of MS / AA in HCl/NaOH inferred that the inhibition efficiencies increased with increasing concentration of the inhibitors. Immersion studies reveal that as the time of immersion increased from ½ h to 24h the inhibition efficiency also increased. All the studied inhibitors are found to be promising candidates.
- Kinetic and mechanistic aspects of corrosion may be gained by studying the effect of temperature on the acid/alkaline corrosion of MS/AA in the presence and absence of the inhibitors. It can be noted that the maximum I.E. obtained was in the range of 79- 99 percentage in 1M HCl/1M NaOH for the studied inhibitors. When the temperature increased, IE increased up to a particular temperature (333K) and it indicates temperature decreased. This may be due to the adsorption of the inhibitor up to a particular temperature and then desorption of the inhibitor at higher temperature.
- Statistical Analysis of the inhibitors using SPSS reflected that all the investigated inhibitors followed Langmuir adsorption isotherm.
- In the present investigation, E_a 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 ($\Delta H_a°$) reflected the endothermic nature of the metal dissolution process. The positive values of entropy of activation ($\Delta S_a°$) in the presence of the inhibitors

in MS/Al/1M HCl/1M NaOH implied an increase in disorderness takes place on going from reactants to the activation complex.

- The negative values of ΔG^o_{ads} for the studied systems demonstrate that the inhibitors were spontaneously adsorbed onto the MS/AA surface. In the present study, the calculated values of ΔG^oads obtained for the investigated systems range between -12 kJ/mole to -23 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} indicated 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 surface by inhibitor molecules all the studied inhibitors (AA/1M HCl). The negative values of entropy (ΔS^o_{ads}) in the presence of all the studied inhibitors using MS/AA in 1M HCl/1M NaOH implied the inhibitor molecules, freely moving in the bulk solution were adsorbed in an orderly manner onto the metal surface.

Phase III:

- Surface morphology of the metal surfaces using SEM and EDX indicated that the surface of the metal was found to be rough after exposed MS/AA specimens in the acid/alkaline 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 spectral values revealed the adsorption of the inhibitor molecules on metal surface.
- 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.

Phase IV: Quantum chemical studies, confirmed the probable adsorption centres through which the Fe/Al atom is linked to form Fe/Al – inhibitor complex.

Conclusion

The following conclusion could be deduced

Potentiodynamic polarization curves indicate that the studied inhibitors acts as mixed type inhibitors and it retards both anodic metal dissolution and cathodic hydrogen evolution reaction. EIS studies show that the inhibition is due to a charge transfer mechanism. From the mass loss studies, it has been found that there was an enhancement in inhibition efficiencies with increase of the inhibitor concentration. The adsorption of the inhibitors was found to obey Langmuir adsorption isotherm. Thermodynamic parameters confirmed strong interaction of the inhibitor with the MS/AA surface. Surface analytical techniques confirmed that the phytochemical constituents present in the inhibitors are adsorbed on metal surface. Quantum chemical studies, confirmed the probable adsorption centres through which the Fe/Al atom is linked to form Fe/Al – inhibitor complex.

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