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Inhibitory action of *Macaranga peltata* leaves extract on the corrosion of mild steel in 0.5 M sulphuric Acid- Quantum chemical approach

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ABSTRACT

Weight loss and electrochemical impedance spectroscopy (EIS) method were used for testing the corrosion inhibition effect of *Macaranga peltata* leaves (MPL) extract on corrosion of mild steel in 0.5 M sulphuric acid solution. The inhibitory effect of MPL was studied at various concentrations of the extract and different time of immersion. In all cases an optimal efficiency was found out. Maximum inhibition efficiency was 92.6% for 5%v/v at 5 h. Nyquist and Tafel plots gave a confirmation about the inhibitory action of the plant extract, agreeing with the weight loss method. The surface content of mild steel after immersion was investigated using IR and the inhibition mechanism is suggested as adsorption of the phytochemical constituents from the results. The Quantum chemical energy calculations become an additional support of the suggested mechanism.

Selection and peer-review under responsibility of the scientific committee of the First International Conference on Frontiers in Chemical Sciences.

1. Introduction

The greater part of industrial work depends on the metals in acids such as pickling process. But the metals easily undergo corrosion. Corrosion inhibitors are used to prevent corrosion of metals from its acidic environment. There are many inhibitors, classified as organic and inorganic. Compounds containing S, O, N are more effective due to the presence of lone pairs [1-4]. These compounds form a covalent bond and make a thin film on the metal surface, which helps to prevent corrosion. The use of natural inhibitors increases day by day due to their availability and non toxicity. Different parts of plants such as leaves, flowers and seeds are used for the prevention of metal from corrosion. The inhibitory action varies with different parameters. The metal surface, components present in the inhibitor and the environment are the main parameters. There are several investigations on green inhibitors [5-14]. In this paper, effect of *Macaranga peltata* leaves (MPL) as an inhibitor for corrosion of mild steel in 0.5 M H_2SO_4 is presented.

2. Materials and methods

2.1. Preparation of samples

Mild steel coupons were prepared with an area of 15 cm^2 from the large sheet. It is degreased, cleaned and washed using double distilled water. These coupons were kept in desiccators to avoid the presence of moisture.

2.2. Preparation of MPL extract

Leaves of MP are collected and dried in the absence of sunlight. These dried leaves are ground well. 12.5 g of powdered leaves in 0.5 M H_2SO_4 is kept under reflux for 3 h. Left overnight, then filtered and made up to 250 ml.

2.3. Weight loss method

This is one of the easiest and most used methods to find out corrosion rate and inhibition efficiency. In this study weight of the metal is noted after and before the exposure to the corrosive medium. In the present work pre-weighed metal coupons were immersed in 100 ml of 0.5 M H_2SO_4 in the absence and presence of various concentrations of the MPL extract at different immersion

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periods. These coupons were cleaned, dried and re-weighed. The loss in weight of the metal was found out from these two weights.

Various parameters were used for weight loss studies such as,

Concentration of the inhibitor- 1, 2, 3, 5, 7 %v/v

Time of immersion – 1, 3, 5, 7, 24, 48 h

Surface coverage (θ) and inhibition efficiency (I.E.%) were found out using the data obtained from the study.

$\theta = (W_B\text{-}W_I)/W_B$

$\text{I.E. } (\%) = (W_B\text{-}W_I)100/W_B$

where W_B and W_I are the loss in weights for the mild steel sample in solutions devoid of the extract and solutions containing the extract respectively.

2.4. Electrochemical methods (Tafel and EIS)

The study was conducted in a glass cell with a capacity of 100 ml. Experiment was carried out by making platinum as a counter electrode and saturated calomel electrode as reference electrode. The working electrode was mild steel coupon used for weight loss method but lacquered as to expose an area of 1 cm^2. Potentiodynamic polarization was conducted using a Biologic – EC lab V111 2.0. Using Tafel regions from the potentiodynamic polarization curves, corrosion potentials and corrosion current densities were found respectively.

Inhibition efficiencies were calculated as follows,

$\text{I.E.} = (I_{corr} - I'_{corr}) \times 100/I_{corr}$

I_{corr} and I'_{corr} is the corrosion current densities in the solutions devoid of the extract and solutions containing the extract

A frequency range of 0.1 Hz–20 KHz, with a signal amplitude perturbation of 10 mV was selected for the a.c. impedance measurements. From the measurements Nyquist and Bode plots were plotted.

Values of R_{ct} and C_{dl} for different concentrations were found out from the graph using Zsimpwin software.

From R_{ct} values inhibition efficiencies were found out using the formula,

$\text{I.E.} = (R_{ct/inh}\text{–}R_{ct}) \times 100/R_{ct/inh}$

R_{ct} and $R_{ct/inh}$ are the charge transfer resistance values in solutions devoid of the extract and solutions containing the extract respectively.

2.5. Surface analysis

FTIR technique is used to identify the functional group of components in the inhibitor which leads to inhibition by adsorption. FTIR is carried out after the successful immersion of metal in acid medium containing inhibitor. Scratched the adsorbed layer from the metal surface and is used for FTIR analysis. Spectrum given by the analysis is used to find out the functional groups present in the components.

3. Result and discussion

3.1. Weight loss method

The I.E. obtained with MPL extract at its different concentrations and at various time intervals on the dissolution of mild steel in 0.5 M sulphuric acid is shown in Fig. 1. On increasing the amount of inhibitor, efficiency increases which results in the decrease of metal dissolution. Components present in the inhibitor adsorb on the metal surface and forms a thin film; this film prevents corrosion. The inhibition efficiency increases up to a concentration then it starts to decrease. This decrease in efficiency is due to desorption occurred by the replacement of components of inhibitor by water. After the optimum concentration the interaction between the metal and the inhibitor decreases, results in the loss of film formed on the metal. There occurs an optimum time of immersion also due to the same adsorption–desorption phenomena. Even though the efficiency of inhibition offered by 3% v/v solution is found to be stable after 5 h, the efficiency at lower time of immersion is greater with 5% v/v solution till 24 h. With 3% v/v of MPL, extending the time of immersion led to the decrease in I.E. to 84%. Hence the optimum concentration is taken as 5%v/v and the optimum time of immersion is 5hr.

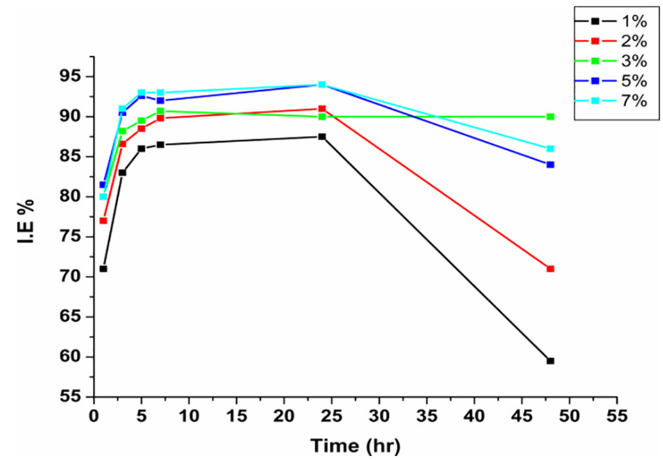

Fig. 1. Plot of I.E. vs immersion time of mild steel in 0.5 M H_2SO_4 for various concentrations of MPL extract.

3.2. Potentiodynamic polarization (PP measurements)

Reactions taking place in anodic and cathodic regions can be easily understood by using PP method. Work is carried out in the blank acid solution and in the presence of MPL extract at different concentrations. Anodic and cathodic behaviour of mild steel in 0.5 M H_2SO_4 is shown in the Fig. 2. The plot indicates that MPL extract is effective in controlling both cathodic and anodic reaction. Metal dissolution at the anode as well as hydrogen evolution at cathode was inhibited by MPL extract. The inhibitor effect on the anode is by adsorbing onto the metal surface and forming a boundary between the surface of the metal and the medium of immersion. Cathodic protection is by reducing H^+ formation. The MPL extract behaved as a mixed type of inhibitor.

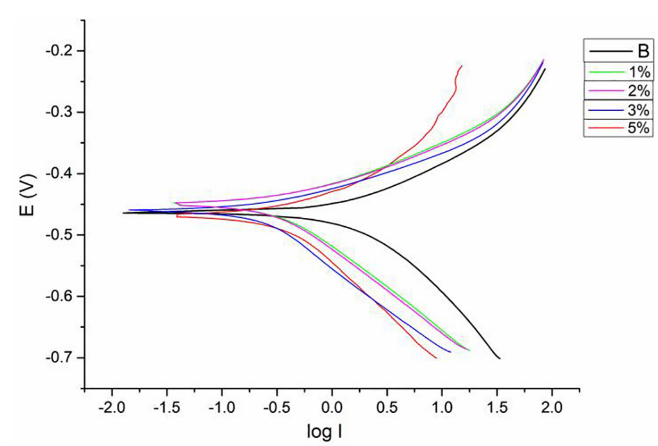

Fig. 2. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 for various concentrations of MPL extract.

Table 1
Electrochemical kinetic parameters.

Concentration (%v/v)	-Ecorr (mV)	Icorr (mA/cm^2)	Ba (mV/decade)	Bc (mV/decade)	I.E. (%)
Blank	486.76	2631	150.8	186.1	
1	522.68	745.52	197.2	166.9	71.7
2	501.79	705.72	123.2	136.6	73.2
3	491.54	656.53	116.4	136.3	75.0
5	530.13	643.24	129.8	132.2	75.5

From Table 1, it is clear that on increasing concentration of the inhibitor I_{corr} value also increases, but after a certain concentration it decreases. There is no regular trend for E_{corr} value, which indicates inhibitor acts as a mixed type. From I_{corr} values I.E. of MPL extract is calculated, it gave maximum of 75.5% efficiency. ßc values decrease with increasing concentration of the inhibitor. There is no regular trend for ßa values. A displacement of 85 mV or more in the corrosion potential from that of the blank solution is considered as anodic or cathodic type [15,16]. The shift in E_{corr} to a more positive value than that of blank confirms the protective nature of the extract used [17]. Here maximum shift in corrosion potential is 43.37 mV. This suggests that MPL extract is a mixed type of inhibitor. In the presence of MPL extract, a sheath is formed on the surface of the metal and blocking the active sites for corrosion. This would lead to decrease in corrosion current for increase in the extract concentration.% I.E. is calculated from the corrosion current values. The increase in I.E. with increasing concentration of the plant extract indicates that MPL is a good corrosion inhibitor (Table 2).

3.3. Electrochemical impedance spectroscopy

Metals in solution can undergo corrosion by charge transfer and mass transport at the metal/electrolyte interface. Electrochemical impedance method is fast and provides details about the kinetics of the electrode processes. EIS is also used to understand the surface kinetics. Efficiency of the inhibitor can be found out from the variables given by the study.

The diameter of the Nyquist plot increased on increasing concentration of the extract. Increase in diameter indicates that the strength of the film formed due to adsorption increases with increase in concentration of the extract. Nyquist plots without loop suggests that, there occurs a charge transfer resistance control between the metal and the inhibitor [18]. Fig. 3 indicates that the extract components are selectively adsorbed in specific places on the surface of the metal surface. The equivalent circuit used for finding the R_{ct} values is provided below Fig. 4.

From the data obtained from the study, charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) are found out. From that I.E. for different concentrations are also found.

On increasing concentration of the inhibitor R_{ct} value increases, but C_{dl} values have no trend. For 5%v/v R_{ct} value increased by 60.48 O and C_{dl} value decreased by 25.67 $\mu F/cm^2$ C_{dl} values in the presence of MPL extract are lower than the blank acid solution. This indicates that inhibitor forms a protective layer on the surface of the metal [19]. Maximum I.E. of 83.99% is obtained for 5%v/v concentration of the inhibitor. So, the study indicates that 5%v/v concentration of the inhibitor is more effective for preventing corrosion of the mild steel in 0.5 M H_2SO_4.

Table 2
Impedance parameters.

Concentration (%v/v)	Rct (ohm)	I.E. (%)	Cdl ($\mu F/cm^2$)	I.E. (%)
Blank	11.53		78.7	
1	33.42	65.49	51.49	34.57
2	46.73	75.33	69.71	11.42
3	48.9	76.42	58.38	25.82
5	72.01	83.99	53.03	32.62

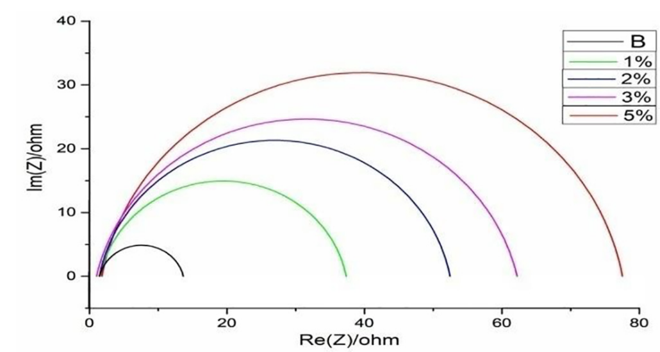

Fig. 3. Nyquist plots for mild steel in 0.5 M H_2SO_4 in the absence and in the presence of various concentrations of MPL extracts.

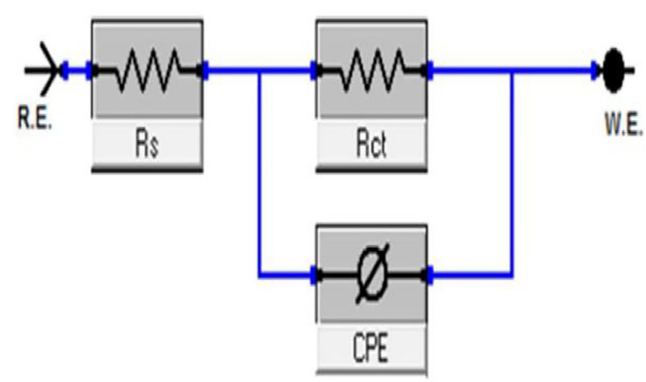

Fig. 4. Equivalent circuit used to model impedance data for mild steel in 0.5 M H2SO4.

3.4. Surface analysis

3.4.1. IR analysis

IR analysis is used to identify the functional groups adsorbed on the surface of the metal. IR plot is used to identify the organic groups that reduce the corrosion of metal. The different peaks in the IR plot show that the inhibitor contains OH, C = O, C-O Fig. 5. The shift in the IR frequencies may be due to the covalent bond formed by the phytochemical constituents of MPL with the metal. It indicates that the inhibitory effect is due to the presence of phytochemical components containing these organic groups. IR analysis proves that some of the phytochemicals are adsorbed on the surface of the metal.

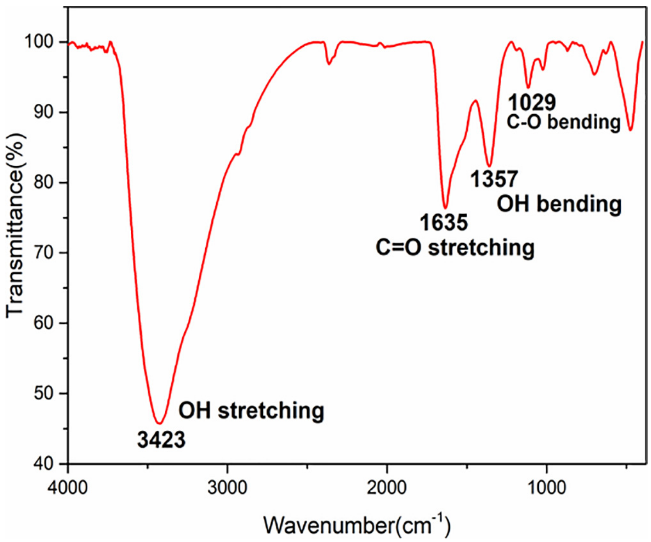

Fig. 5. FTIR spectra of the film formed on the mild steel sample during immersion of mild steel in the acidic medium in presence of the MPL extract.

3.5. Quantum chemical calculations

Plant extract is a mixture of various phytochemical components. Quantum chemical studies are used to determine the molecular, electronic structure and reactivity [20,21]. From the values given by the study it is understood that adsorption facilitates the inhibition effect of the inhibitor molecules on the metal surface. Phytochemical studies of Macaranga genus [22] confirm that the species contains Betulin, Sumatrol, Sitosterol, 6,7-dimethoxy-3′,4′-methylenedioxyflavanone, Trimethoxyflavanone and Lupeol. Here the quantum chemical studies are carried out for two major components. There are some parameters which influence directly on the electronic interaction between inhibitor molecules and the metal surface. These are mainly E_{HOMO}, E_{LUMO}, ΔE (E_{LUMO}–E_{HOMO}), dipole moment and Mulliken charges. According to FMO, electron transition occurs through interaction between HOMO and LUMO [23]. E_{HOMO} and E_{LUMO} are associated with the donor and acceptor ability respectively. The tendency of a molecule to be an electron donor is indicated by the higher E_{HOMO}. The lowest value of E_{LUMO} is most favourable for accepting electrons [24]. Values of ΔE are an indication of the stability of the formed complex on the metal surface. Higher stability is shown by low ΔE val-

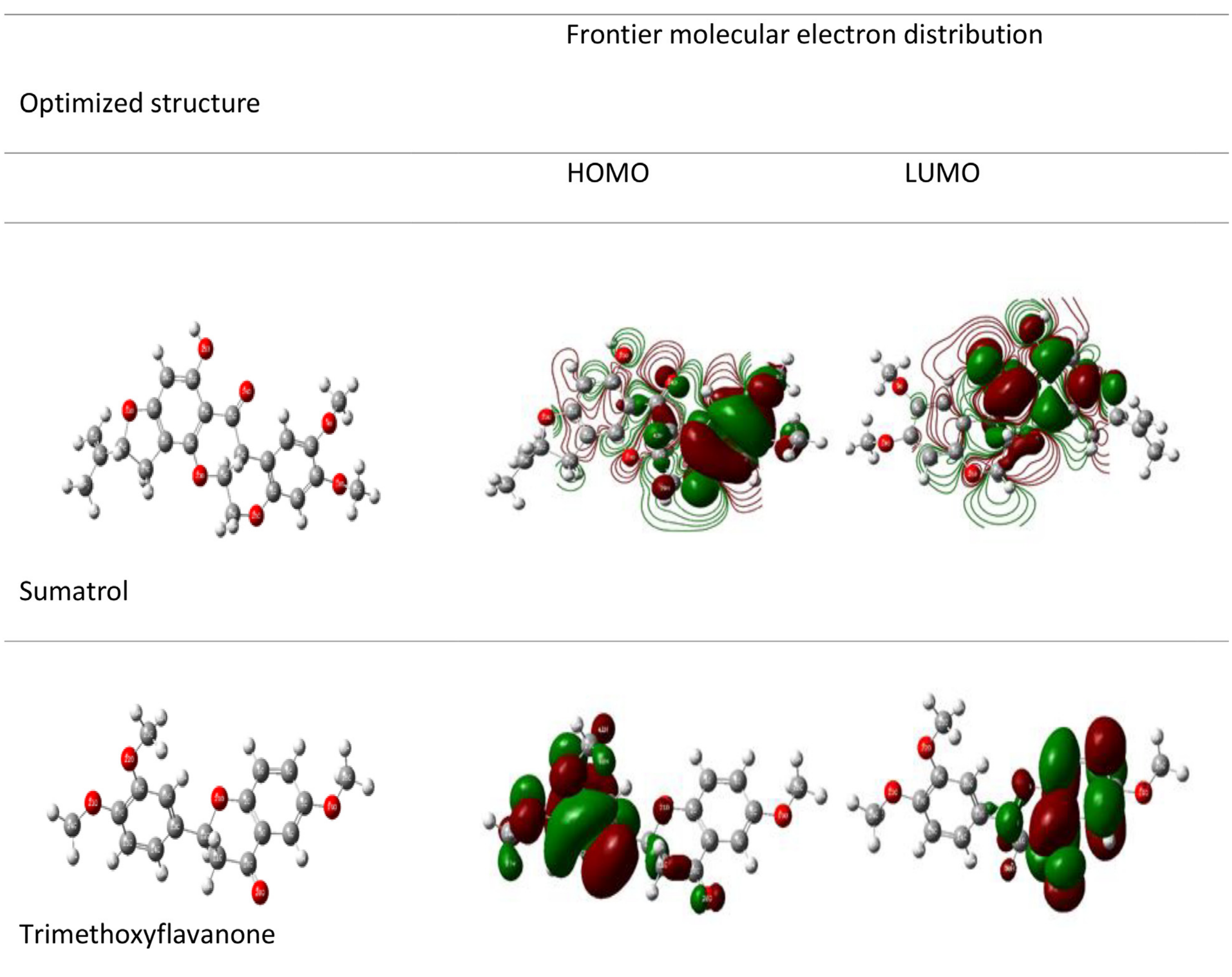

Fig. 6. Optimized structures, highest occupied and lowest unoccupied FMO pictures of active phytochemicals present in Macaranga genus.

Table 3
Quantum chemical parameters for the active constituents of Macaranga species.

Constituents	E_{HOMO}	E_{LUMO}	ΔE	Total energy (a.u.)	Dipole moment (Debye)
Sumatrol	−0.19927	−0.03995	0.15932	−1416.21757791	4.5582
Trimethoxyflavanone	−0.20396	−0.05382	0.15014	−1072.86023609	3.4628

ues [25,26]. If the ΔE values are low, then the energy required to remove an electron from the last occupied orbital will be low. So, it will have higher inhibition efficiency [27]. The higher total energy values are the indication of higher stability [28]. The dipole moment is the electron distribution in a molecule and shows polarity of the covalent bond [29,30]. The Mulliken population analysis is used to quantify the adsorption centres of inhibitors [25,31]. The more negatively charged heteroatom adsorbs effectively on the surface of the metal [32,33].

The FMO electron distribution of the phytochemicals namely Sumatrol and trimethoxyflavanone of Macaranga genus are shown in the Fig. 6.

Various quantum chemical calculations of phytochemical constituents are given in the Table 3. It shows that the sumatrol has the highest and trimethoxyflavanone has the lowest value of E_{HOMO} indicates that sumatrol has more donating ability. Trimethoxyflavanone has less ΔE value, suggests that it has highest chemical reactivity. Due to its high reactivity it forms a complex with Fe^{2+} on the surface of mild steel and inhibits the corrosion.

4. Conclusion

•The selected part of the plant Mecaranga peltata acts as a corrosion inhibitor for the mild steel in 0.5MH2SO4•From the weight loss studies, maximum I.E. of MPL extract was obtained as 92.6% in 5 h immersion periodfor 5%v/v concentration.

•Potentiodynamic polarization studies show that MPL extract is a mixed type of inhibitor.

• From the Nyquist plot it is understood that the coating formed is uniform and effective. The high I.E.indicates MPL extract is a good inhibitor.

•The I.E. obtained from Weight loss studies and Electrochemical studies are comparable.

CRediT authorship contribution statement

K.K. Athul: Formal analysis, Investigation, Project administration, Writing - original draft. **P. Thilagavathy:** Conceptualization, Supervision, Writing - review & editing. **D. Nalini:** Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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