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Corrosion Inhibition properties of a Substituted Water Hyacinth on Mild Steel in 1M HCl

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ABSTRACT: Finishing of metallic surface is pre requisite for any mechanical component which is generally carried out by pickling using mineral acids. But metals get dissolved readily in such acids if treated without inhibitor. So many synthetic chemicals are used as corrosion inhibitors which are toxic in nature, therefore need of a green corrosion inhibition has been required; water hyacinth has been found an excellent naturally occurring corrosion inhibitior. The inhibition efficiency of aqueous extract solutions of water hyacinth was examined by weight loss method at 37˚C. The importance of inhibition efficiency was established conditional on the concentration of the inhibitor. A reduction in corrosion speed and growth in inhibition efficiency was practical with a gain in the concentration of the inhibitor. Inhibition efficiency expanded regularly with increasing concentration until reached the maximum. The maximum inhibition was found 97.7% at about 7% concentration of inhibitor. The increased inhibition was explained based on adsorption isotherms. The decreased corrosion rate and adsorption behaviour have been explained by Langmuir, Temkin and Freundlich adsorption isotherm. The constituents responsible for inhibition which were adsorbed on the surface of the metal were identified by Phytochemical analysis and Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy.

Keywords: Corrosion inhibitor, adsorption, weight loss, Langmuir, Temkin isotherm, FTIR.

INTRODUCTION

It is a natural method for metal to erode when susceptible to a harsh atmosphere like an acidic medium of downward pH. A significant stage of completing metal texture is pickling and descaling in which metals are treated with acids (Tanvar *et al.*, 2018). Since most, metals undergo corrosion in acidic mediums, especially mild steel; a certain level of protection is required. Mild steel is frequently used in machinery and other structural manufacturing units (Srivastava 2020; Sanaei *et al.*, 2019). Several organic compounds, natural and synthetic, serve the purpose of protecting metal from corrosion (Athareh and Fatemeh 2011; Okafor *et al.*, 2008). Many organic compounds, both natural and synthetic; have ability to adsorb on the surface of metal forming a barrier to further corrosion due to the presence of hetero atoms (Salhi *et al*., 2017; Kannan *et al.*, 2018; Zhang *et al*., 2015; Xiang and He 2020; Khadom *et al*., 2018; Rajendran *et al*., 2005; Qiang *et al.*, 2017; Nam *et al.*, 2018; El-Hajjaji *et al.*, 2020; Haldhar *et al.*, 2019; Bilgic, 2022). Such organic compounds are termed corrosion inhibitors.
Water hyacinth grows in all types of freshwater environments. Water hyacinth poses a variety of negative impacts once introduced into a freshwater environment. This aquatic species is a menace to aquatic bodies. It cannot be eradicated. Some studies on water hyacinth have been carried out for its corrosion inhibition activity (Dhanlaxsami and Cyril 2020). The results showed the protective nature of this natural product against corrosion in various corrosive environments (Subramanyam and Kumar 2016; Oloruntuba 2013; Orhorhoro *et al.*, 2017). It is a mixed-type inhibitor. The positive aspect is that the natural polyphenols present in the extract of water hyacinth were found to have good corrosion inhibition ability in an acidic medium (Godow and Fakeeh 2022).
The present work deals with the corrosion inhibition and adsorption behaviour of constituents of Water Hyacinth extract as an eco-friendly inhibitor. The work was carried out in 1M HCl at 37˚C. The rate of corrosion and inhibition efficiency was calculated by the weight loss method. FTIR spectroscopic studies were carried out to investigate the compound adsorbed on the surface of the metal (Verma et *al.*, 2021).

MATERIALS AND METHODS

Commercially available mild steel (C 0.15% by weight) was used for all experiments. The mild steel sheet was mechanically press-cut into 2.5×2.5×0.1 cm coupons. The steel coupons were pickled with 5% HCl to remove rust and sequentially polished using Silicon Carbide emery papers of grade 180, 220, 400, 600 and 1000, washed thoroughly with distilled water and degreased with carbon tetra chloride and acetone.

Chemicals used: 1M HCl solutions were prepared using analytical grade concentrated 37% HCl (Merck products) respectively and double distilled water.

Preparation of plant extract: Fresh leaves of Water Hyacinth were collected from Ramgarh Tal Lake of Gorakhpur city in U.P., India. The green leaves were air-dried and then kept in an oven maintained at 105°C for constant weight to remove the moisture content. Dried leaves were crushed and ground in an electric operated grinder to make a fine powder. The extract was prepared in 1M HCl for investigation. 50 g of dried powder of leaves were digested in 1000 mL 1M HCl and kept overnight. After 48 hours of soaking, it was filtered, and the filtrate volume was made up to 1000 mL using 1M HCl. The extract so prepared was taken as stock solutions from which 0.1, 0.2, 0.3, 0.4, 0.5, 1, 2, 3, 4, 5, 6, 7. 8, 9 and 10 % test solutions were prepared.

Phytochemical screening

Test for tannin: 1 g of powdered sample was boiled with 20 ml distilled water for five minutes in a water bath and filtered while hot.1 ml of filtrate was diluted to 5 ml with distilled water and a few drops of 10 % ferric chloride were added and observed. A bluish-black or brownish-green precipitate indicated the presence of tannins (Edeoga *et al.*, 2005).

Test for flavonoids: 1 g of the powdered dried leaves of the sample is boiled with 10 ml of distilled water for 5 minutes and filtered while hot. A few drops of 20 % sodium hydroxide solution were added to 1 ml of the cooled filtrate. A change to a yellow colour which on the addition of acid changed to a colourless solution indicates the presence of flavonoids and was also confirmed by analysing about 3 mL of dilute ammonia added to 2 mL aqueous filtrate of plant extract. This was followed by the addition of 1mL of concentrated sulphuric acid (H_2SO_4). The yellow colour in the extract showed the presence of flavonoids.

Weight loss studies The weight loss studies were carried out at 37°C by immersing steel coupons of known weight and surface area in 100 ml each of blank 1M HCl and test solutions containing various concentrations of extracts for 48 hours. The dissolution of iron takes place as follows with the subsequent release of hydrogen gas.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

$$Fe \rightarrow Fe^{2+} + 2e^-$$

After 48 hours of reaction in the absence and presence of different concentrations of extracts, the specimens were taken out, washed with water, dried and weighed.

Corrosion rates (in terms of $g.cm^{-2}h^{-1}$) were calculated using the following expression.

$$\text{Corrosion Rate (CR)} = \frac{W_i - W_f}{\text{Surface Area} \times \text{Time}}$$

Where,

W_i= initial weight of coupon,

W_f = weight of coupons after treatment

W_i-W_f = weight loss (g)

Surface Area (cm^2)

Time in hours

The surface coverage (θ) as a result of the adsorption of inhibitor and inhibition efficiency (n%) were calculated from corrosion rates using the following expression:

$$\theta = \frac{\text{CR (Blank)} - \text{CR (Inhibitor)}}{\text{CR(Blank)}}$$

$$\eta = \frac{\text{CR (Blank)} - \text{CR (Inhibitor)}}{\text{CR(Blank)}} \times 100$$

Where,

CR_{Blank} = corrosion rate in absence of inhibitor

$CR_{Inhibitor}$ = corrosion rate in presence of the inhibitor

Fourier transform infrared spectroscopy (FTIR). The identification of the corrosion inhibitor components in the extract was carried out by FTIR spectroscopy.

FTIR spectra were recorded for the aqueous extract of the leaves of water hyacinth.

RESULTS AND DISCUSSION

Analysis in 1M HCl. Table 1 shows the variation of corrosion rate, surface coverage (θ) and percent inhibition efficiency (η %) in 1M HCl at 37°C for 48 hours of studies. The graphs were plotted for corrosion rate and percent inhibition efficiency indicated that the corrosion rates were significantly lowered in presence of an inhibitor. The corrosion rate decreased with increasing extract concentration. The maximum lowering in corrosion rate was calculated in presence of 7% leaf extract of water hyacinth. 7% of extract concentration was also evaluated as the optimum concentration as on increasing the extract concentration above this no significant change in corrosion rate lowering was observed. Fig. 2 showed that in the case of leaf extract of the inhibitor, maximum inhibition efficiency (97.7%) was noticed and no considerable change in inhibition efficiency was observed after this.

It has also been observed that the rate of inhibition in the initial concentration of inhibitor 0.1% to 1.0% is more pronounced as compared to higher concentrations. The surface coverage data indicated that the extent of adsorption was rapid and more significant at the initial stage of adsorption.

Table 1: Corrosion rate, surface coverage and inhibition efficiency of aqueous extract of water hyacinth leaves in 1M HCl at 37°C for 48 hours studies.

Extract conc.%	Corrosion Rate ($g\ cm^{-2}h^{-1}$) 10^{-5}	Surface Coverage (θ)	% Inhibition efficiency(%η)
Blank	96.3	—	—
0.1	59.5	0.382	38.2
0.2	48.2	0.499	49.9
0.3	33.2	0.655	65.5
0.4	29.1	0.698	69.8
0.5	20.4	0.788	78.8
1.0	16.7	0.826	82.6
2.0	11.5	0.880	88.0
3.0	8.8	0.909	90.9
4.0	5.2	0.946	94.6
5.0	3.5	0.963	96.3
6.0	2.7	0.972	97.2
7.0	2.2	0.977	97.7
8.0	2.3	0.976	97.6
9.0	2.2	0.977	97.7
10.0	2.3	0.976	97.6

Table 2: % Inhibition Efficiency observed for 7% concentration of aqueous extract of Water Hyacinth for consecutive days of analysis.

Day	% Inhibition Efficiency
1	99.48
2	99.52
3	99.58
4	99.59
5	99.60
6	99.62
7	99.64

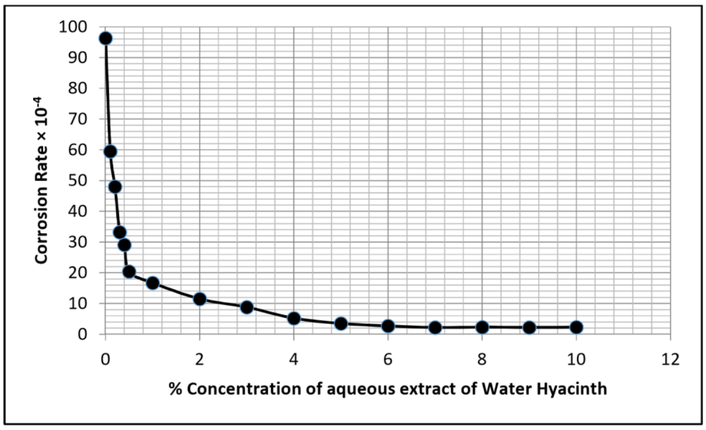

Fig. 1. Plot of Concentration versus Corrosion Rate in presence and absence of inhibitor.

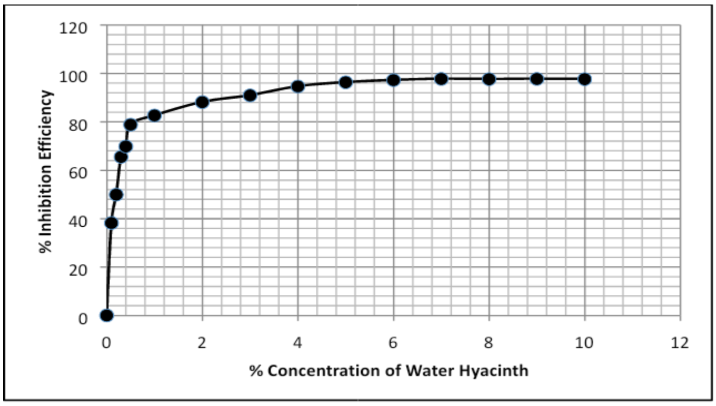

Fig. 2. Plot of % Concentration versus % Inhibition efficiency of Water Hyacinth Inhibitor.

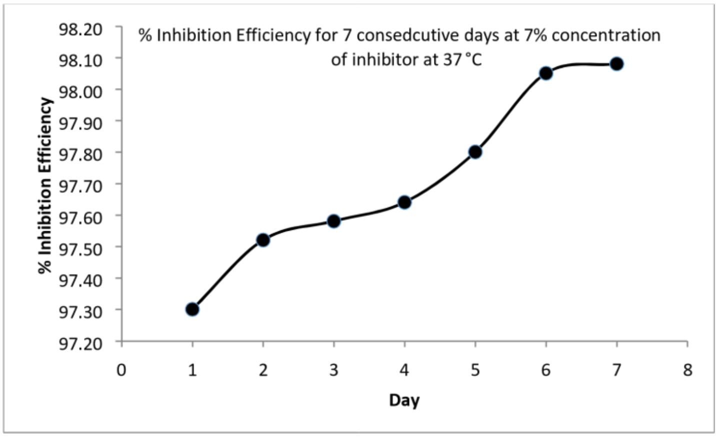

Fig. 3. Plot of % Inhibition Efficiency for 7 consecutive days at 7% concentration and 37ºC.

FTIR Analysis of Leaf Extract shows the stability of corrosion inhibition which was determined by monitoring the test sample by keeping in corrosive 1M HCl solution in presence of 7% aqueous extract of Water Hyacinth corrosion inhibitor at 37°C (Noor, 2009). A regular increase with a very slight variation of inhibition efficiency revealed that the adsorption of inhibitor is quite stable. Since the adsorption is constantly increasing with a very nominal amount with the duration of exposure, it indicates the adsorption is of a chemisorption nature in which molecules are bonded and adhered well on the surface giving metal excellent protection (Jahdaly & Awad 2016). The chemisorption was also confirmed by obeying the Langmuir adsorption isotherm.

Adsorption is a well-known phenomenon in which certain molecules get attached to the surface of the metal through coordinate bonding. The hetero atoms having lone pairs of electrons play a significant role in adsorption. The decreasing corrosion rate and increasing inhibition efficiency were attributed to the fact that the adsorption of inhibitor on the metal surface. Adsorption of compounds present in water hyacinth extract depends on the chemical constituents present in the aqueous extract (Prabakaran *et al.*, 2016). The phytochemical analysis revealed that the presence of tannins and phenolic compounds might be the possible reason for inhibition. It was further confirmed by FTIR spectroscopic studies. Polyphenolic naturally occurring compounds, which have oxygen atoms with lone pair of electrons for coordinate bonding on the surface of metal are responsible for corrosion inhibition (Singh *et al.*, 2010).

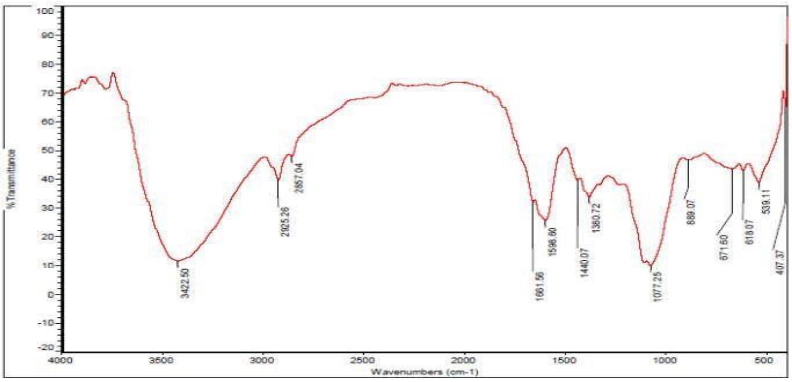

Fig. 4. FTIR Analysis.

Fig. 4 shows FTIR spectra. FTIR data for aqueous extract of leaves and prominent peaks are given as below. The data furnished relevant information that reflects the corrosion inhibition was due to adsorption of such groups present in the extract. The FTIR spectra confirmed the presence of phytochemicals containing functional groups, hydroxyl –OH at 3422.50 cm^{-1}, carbonyl C=O stretching at 1661.56 cm^{-1}, amine -C-N stretching at 1380.72 cm^{-1}, and saccharide linkage O-CO at 1077.25 cm^{1}. The FTIR spectra also included aromatic Ar-H stretching at 2925.26 cm^{-1}, C-H stretching at 2857.04 and aromatic rings at 1598.60 cm^{-1}.

Flavonoids. The phytochemical analysis showed the presence of Tannin and flavonoids. On the basis of FTIR spectra it has been confirmed that certain polyphenols are present on the surface of metal that acted as a barrier and imposed inhibitory effect (Khalid, 2010).

Flavonoids are the compounds with conjugated system; they have hetero atoms and carbonyl groups which are electron rich species which can readily get adsorbed on the surface of the metal to form a thin, stable and well adhered protective film (Rebecca *et al*., 2016).

Adsorption behavior Langmuir adsorption isotherm. A plot of C/θ against Concentration C (Fig. 5) showed a straight line indicating that adsorption follows the Langmuir adsorption isotherm (Alamry *et al.*, 2022). This trend of adsorption indicated the formation of a stable protective film of inhibitor on the surface of metal (Srivastava and Srivasatva 1981).

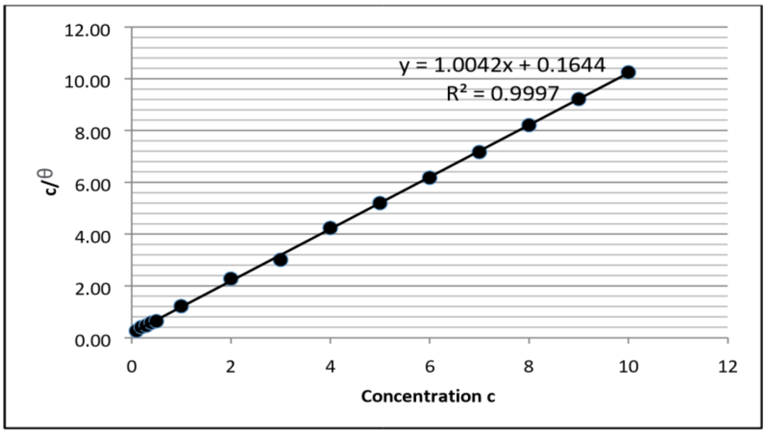

Fig. 5. Langmuir Adsorption isotherm for Water Hyacinth.

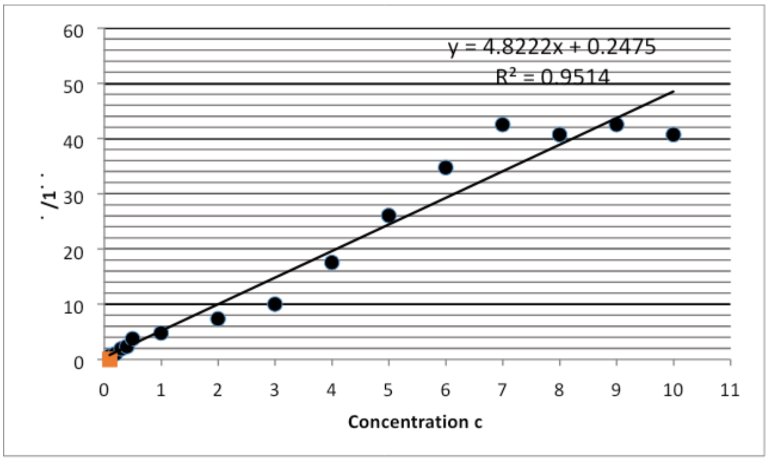

Fig. 6. Freundlich Adsorption isotherm in 1M HCl for Water Hyacinth.

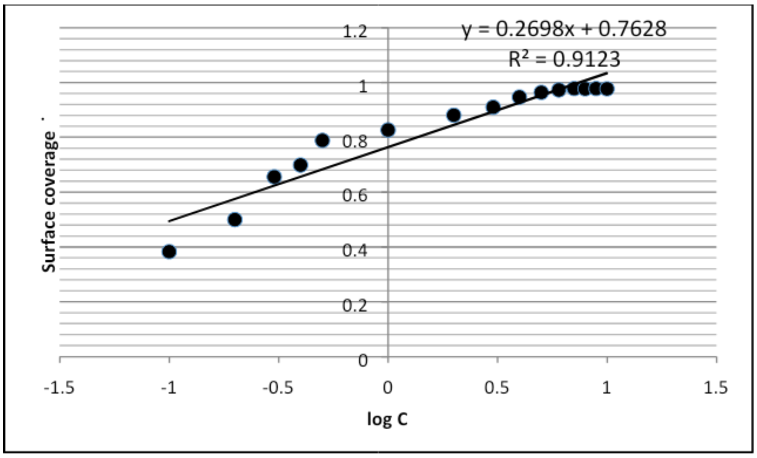

Fig. 7. Temkin adsorption isotherm in 1M HCl for Water Hyacinth vs log C.

Temkin adsorption isotherm. A plot between surface coverage and log C showed straight line indicating Temkin adsorption isotherm (Abdel-Gaber *et al.*, 2020) Fig. 7.

CONCLUSIONS

1. The aqueous extract of Water hyacinth (Jalkumbhi) has been found an excellent natural corrosion inhibitor for mild steel in 1M HCl solution.

2. The corrosion rate significantly decreased and inhibition efficiency increased with increasing concentration of inhibitor.

3. The adsorption was of chemisorptions nature that provided a good protection.

4. It was adsorbed molecules were poly phenols which was identified by chemical analysis and FT-IR analysis.

5. The decreased corrosion rate was due to adsorption of plant extract which was discussed on the basis of

Langmuir, Freundlich and Temkin adsorption isotherm.

FUTURE SCOPE

The present work deals with the corrosion inhibition and adsorption behaviour of constituents of Water Hyacinth extract as an eco-friendly inhibitor as they offer a sustainable, non toxic, high –quality, and aesthetically pleasing option for painting homes and other spaces.

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