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Hibiscus leaves extract: A green corrosion inhibitor

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Corrosion is of great concern for chemical and process industries. Environment friendly corrosion inhibitors are need of hour in order to reduce toxic footprint and to achieve sustainable and green processes. The study reported here is a systematic experimentation conducted to examine the efficiency of Hibiscus leaves extracts as a potential green inhibitor for mild steel under acidic medium. High inhibition efficiency of almost 89% reported for 1 day protection at room temperature which gradually reduces to 80% in 4 days. The mechanism of inhibitive action was analysed to be physical adsorption and the Langmuir adsorption isotherm fitted well to the experimental data. The equilibrium adsorption constant (K_{ads}) and standard free energy ($\Delta G°$) evaluated for the system are in good agreement with the published values for green inhibitors.

Keywords: Corrosion inhibitor, green processes, Hibiscus leaves extract, adsorption, langmuir isotherm.

Introduction

Corrosion is the most omnipresent and omnipotent phenomenon in chemical process industries, as the main material of construction, mild steel is surrounded by aggressive media like, acids, salts, high temperature steams etc. for substantial time[1]. Despite of the development of corrosion control methods like cathodic protection, galvanising and use of protective coatings, the most efficient and widely used practice is the usage of corrosion inhibitors[2]. The corrosion inhibitors are chemical substances which on addition even in small quantity to the corrosive environment, retards the rate of corrosion. Conventionally chemicals like, mercaptobenzotriazole (MBT), ethylaniline and thiourea have been used as efficient corrosion inhibitors since early of 19th century[1].

However, most of these inhibitors are recognized to be toxic and hence being outlawed, especially in recent times of increased environmental awareness and subsequent regulations. Thus, the need of replacement of these traditional toxic corrosion inhibitors by so called green chemicals has urged the researchers to be curious in developing new generation green corrosion inhibitors. In past few years considerable efforts have been made in the development of green inhibitors from plant origins, such as Marigold flowers, Neem leaves, Apricot juice etc.[3,4]. In the present work, an attempt is made to synthesize a green corrosion inhibitor using acid extracts of Hibiscus leaves and monitor it's inhibition performance was on mild steel in acidic medium (0.5 *M* sulphuric acid solution).

Experimental

Synthesis of green corrosion inhibitor: Acid extracts of Hibiscus leaves:

Fresh leaves of Hibiscus plant were collected from nearby garden. The leaves were washed with deionized water and dried in an air-dryer at 80°C for approximately 45 min. A 15 g of dried leaves were taken and to that 10 mL of each of hydrochloric acid (HCl), sulphuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) were added, subsequently 300 mL of distilled water also added. The mixture was boiled for 30 min and then kept aside for next 16 h. The resultant mixture was filtered and the filtered solution was directly used as the green corrosion inhibitor for the subsequent experimentation. The chemicals and reagents used in the study were purchased from Merck, Mumbai (India) having 98% purity.

The metal specimen used:

Mild steel coupons of dimensions 4 cm×3 cm×0.1 cm were used as the metal for evaluation of corrosion inhibition

performance of the synthesized inhibitor. They were finely polished with emery paper of grade 200 followed by washing with distilled water and drying. The composition of the mild steel plates used was as provided in Table 1. The coupons were weighed before the insertion into acidic medium.

Table 1. Composition of the mild steel coupons

Element	Percentage
Carbon	0.07
Manganese	0.028
Silica	0.1
Sulphur	0.016
Phosphorous	0.018
Iron	Rest

Weight loss study:

The acidic solution of 0.5 *M* sulphuric acid (H_2SO_4) was prepared and used as the corrosive medium. 150 mL of this solution was poured in five bottles with a lid. The inhibitor was added to these five bottles in the range of 0 to 120 mL/L respectively. The mild steel plates were then inserted in these five bottles such that the plate did not touch the inner surface of the bottles and hanged with a string as shown in Fig. 1. Three sets of such five bottles were made and analysed for 1, 2, 3 and 4 days respectively at room temperature. After the specified period the plates were removed from the experimentation set up and washed, dried and re-weighed.

Fig. 1. Experimental set up for the Hibiscus leaf extracts as corrosion inhibitor.

Results and discussions

The corrosion rates of both uninhibited and inhibited systems were calculated using following eq. (1)

$$C_R = \frac{\text{Weight loss}}{\text{Area} \times \text{Time}} \quad (1)$$

The inhibition efficiency of the inhibitor was the calculated using eq. (2) as,

$$IE\% = \frac{\text{Corrosion rate of unihibited system} - \text{Corrosion rate of inhibited system}}{\text{Corrosion rate of unihibited system}} \times 100 \quad (2)$$

The corrosion rates and respective inhibition efficiencies as obtained through systematic experimentation are as shown in Table 2. All the experiments are repeated twice and average values are reported here.

Langmuir adsorption isotherm:

The Langmuir adsorption isotherm is given by eq. (3) as,

$$\frac{C}{\theta} = C + \frac{1}{K_{ads}} \quad (3)$$

where, C is the concentration of inhibitor in g/L, θ is the fraction of the metal surface covered with the inhibitor, and K_{ads} is the equilibrium adsorption constant in L/g. The equilibrium adsorption constant is calculated by taking reciprocals of the Langmuir adsorption isotherms.

Langmuir adsorption isotherms for the Hibiscus extracts for 1, 2, 3 and 4 days respectively are represented in the Figs. 2 to 5.

The equilibrium constant of adsorption K_{ads} can be expressed in terms of change in standard Gibb's free energy, ΔG°_{ads} (kJ/mol) as,

$$K_{ads} = \frac{1}{C_{H_2O}} \exp \frac{-\Delta G^\circ_{ads}}{RT} \quad (4)$$

where, $-\Delta G^\circ_{ads}$ denotes change in standard Gibb's free energy (kJ/mol), C_{H_2O} = 1000 g/L in solution[4]. R represents universal gas constant and T is absolute temperature. The equilibrium adsorption constants and the respective changes in standard Gibb's free energy were calculated and tabulated in Table 3.

The detailed experimental study indicated that inhibition efficiency of Hibiscus leaf extract is almost 89% at room temperature for the first day of operation; however, it is decreased as the number of days is increasing.

Table 2. Corrosion rate and inhibition efficiencies of Hibiscus leaves extracts

Number of days	Inhibitor concentration (g/L)	Corrosion rate (g/m².day)	Inhibition efficiency (IE%)	θ (–)	C/θ (g/L)
1	0	432.083	–	–	–
1	1.3636	45.833	89.3925	0.8939	1.5254
1	2.7272	54.167	87.4638	0.8746	3.1181
1	4.0908	50	88.4281	0.8843	4.6261
1	5.4545	45.833	89.3924	0.8939	6.1017
2	0	416.458	–	–	–
2	1.3636	46.6667	88.7944	0.8879	1.5357
2	2.7272	46.6667	88.7944	0.8879	3.0714
2	4.0908	54.1667	86.9935	0.8699	4.7024
2	5.4545	47.9167	88.4942	0.8849	6.1637
3	0	431.944	–	–	–
3	1.3636	83.3333	80.7074	0.8071	1.6896
3	2.7272	88.8889	79.4212	0.7942	3.4338
3	4.0908	81.9444	81.0289	0.8103	5.0486
3	5.4545	55.5556	87.1383	0.8714	6.2596
4	0	482.917	–	–	–
4	1.3636	96.9792	79.918	0.7992	1.7062
4	2.7272	65.625	86.4107	0.8641	3.1561
4	4.0908	81.25	83.1752	0.8318	4.9183
4	5.4545	134.375	72.1743	0.7217	7.5574

The research work conclusively demonstrates that Hibiscus leaf extract can be used as green corrosion inhibitor for mild steel in acidic medium with an average efficiency of about 80% for a four day operation. It can be injected with the corrosive fluid at one point and can effectively provide

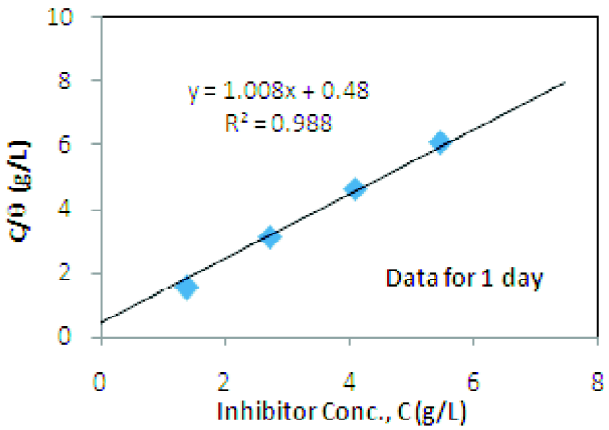

Fig. 2. Langmuir adsorption isotherms for Hibiscus leaves extracts for 1 day of study.

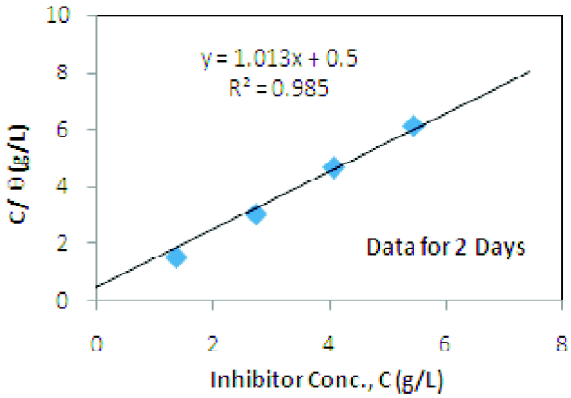

Fig. 3. Langmuir adsorption isotherm fitted for the leaves extracts for 2 days of study.

inhibition downstream for a prolonged period. It is suggested that the inhibitive action is physical adsorption and the Langmuir adsorption isotherm fitted well (kindly refer Figs. 2 to 5). The equilibrium adsorption constant (K_{ads}) obtained are in the range of 1.82 to 2.08 L/g (provided in Table 3), is in good agreement with the earlier reported values of 1.58 L/g[5]. The standard free energy ($\Delta G°$) evaluated for the system

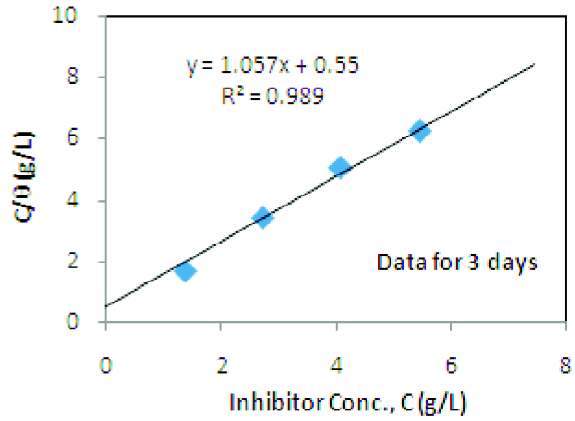

Fig. 4. Langmuir adsorption isotherms for the extracts for 3 days of study.

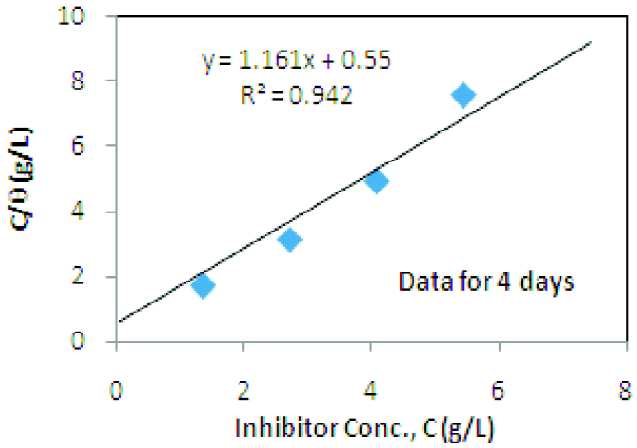

Fig. 5. Langmuir adsorption isotherms fitted for Hibiscus extracts for 4 days of study.

are in the range of –1.484 to –1.818 kJ/mol which is also in good agreement with the earlier reported values of –1.36 to –1.48 kJ/mol for other green corrosion inhibitors[3].

Probable mechanism of corrosion inhibition:

Visual observation indicated occurrence of lesser number of pits and cracks in presence of Hibiscus leaves extract compared to only acidic medium without any corrosion inhibitors. This suggests probable formation of some protective film over the surface of mild steel which may be responsible for the reduction in corrosion rate. To validate the hy-

Table 3. Equilibrium constant and standard Gibb's free energy for Hibiscus leaves extracts

No. of days	*Y*-intercept $1/K_{ads}$ (g/L)	K_{ads} (L/g)	ΔG°_{ads} (kJ/mol)
1	0.48	2.08	–1.818
2	0.5	2	–1.717
3	0.55	1.82	–1.484
4	0.55	1.82	–1.484

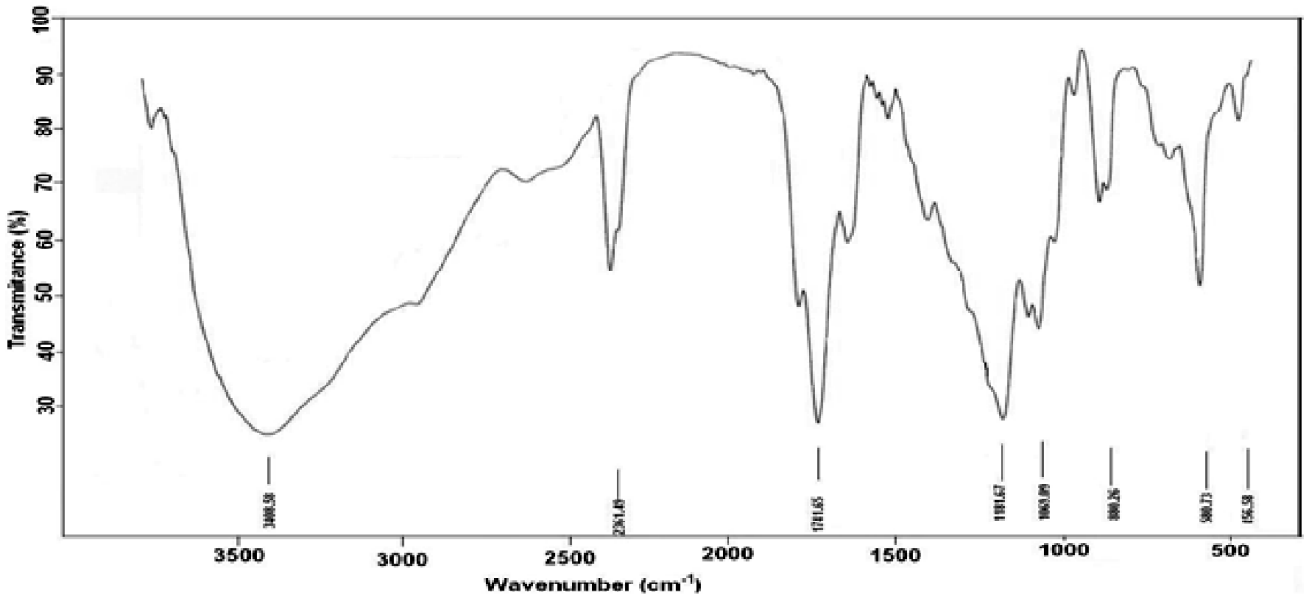

Fig. 6. FTIR spectra of Hibiscus leaves extract.

pothesis an FTIR analysis of the Hibiscus leaves extract was conducted and the results are reported in Fig. 6. A width signal at wave number 3408.58 cm^{-1} is for the O-H bond, aromatic ring C=C double bonds were at 1181.67 cm^{-1}, the aromatic ring C-H bond observed at 2361.49 cm^{-1} and 1741.65 cm^{-1} is for the carbonyl group (C=O). Published literature reported that Hibiscus leaves extracts contain flavonoid compounds[4,6]. The corrosion inhibition of mild steel in presence of Hibiscus leaves extracts may be due to formation of a protective layer of $Fe(OH)_2$ or $Fe(OH)_3$ possible in presence of functional group -OH as evident from FTIR analysis. Further investigation and scanning electron microscopic analysis (SEM) needed for the metal pieces to conclusively infer on protective layer formation of iron hydroxides.

Conclusions

The results for inhibition efficiencies fairly justify potential of Hibiscus leaves extract as a green corrosion inhibitor at room temperature. Experimentation indicated that inhibition efficiency is about 89% for first two days, which is reduced to about 80% in 4th day. The Langmuir adsorption isotherm fitted well to the data clearly indicated the nature of adsorption to be physical one. The negative values of ΔG°_{ads} supplemented the above statement and hence proved the spontaneity of the adsorption process. The values of equilibrium adsorption constant K_{ads} matched well with earlier published data. A probable mechanism of iron hydroxides formation as the protective layer on surface of the mild steel may lead to corrosion inhibition effect for the Hibiscus leaves extract.

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