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Corrosion Behaviour of Aluminium in the Presence of an Aqueous Extract of Hibiscus Rosa-sinensis

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Abstract

The inhibition efficiency (IE) of an aqueous extract of Hibiscus rosa-sinensis (white) in controlling corrosion of aluminium at pH 12 has been evaluated by weight loss method in the absence and presence of Zn^{2+}. The formulation consisting of 8 mL flower extract (FE) and 50 ppm of Zn^{2+} had 98% inhibition efficiency. Polarization study revealed that this formulation functioned as cathodic inhibitor. AC impedance spectra revealed the presence of a protective film formed on the metal surface. FTIR spectra revealed that the protective film consisted of a complex formed between the active principle of the flower extract and Al^{3+}.

***Keywords**:* corrosion inhibition, aluminium, Hibiscus Rosa-sinensis, plant extract, environmental friendly inhibitor.

Introduction

Aluminium and its alloys are very good corrosion resistant materials in neutral aqueous solution, due to the formation of passive film. It is well known that pitting corrosion occurs on metals covered with passive films. The Cl^- ions cause the passive film to break down at certain weak spots on the metal surface. During pitting corrosion, large parts of the metal surface are covered with a protective film and are in the passive state, while other small parts of the surface are in the active state.

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Corrosion behaviour of aluminium in various mediums has been studied. Several inhibitors have been used to control corrosion of aluminium. To prevent the corrosion of aluminium in acid medium, inhibitors such as imidazoline derivatives [1], Capparis decidua [2], polyethylene glycol and polyvinyl alcohol [3], delonix regia extract [4] and Sansevieria trifasciata extract [5], have been used. In alkaline medium, polyvinyl alcohol [6], gongronema latifolium extract [7], bismark brown dye [8], methyl orange [9] and onion extract [10] have been used as corrosion inhibitors to prevent corrosion of aluminium.
Corrosion inhibition of aluminium using super hydrophobic films [11], structure and stability of adhesion promoting aminopropyl phosphonate layers at polymer/aluminium oxide interfaces [12], microbially influenced corrosion of zinc and aluminium [13], corrosion inhibition of aluminium by rare earth chlorides [14], effects of inhibitors on corrosion behaviour of dissimilar aluminium alloy friction stir weld [15], a high throughput assessment of aluminium alloy corrosion using fluorometric methods [16], surface modification for aluminum pigment inhibition [17] and filiform on 6000 series aluminium [18], have been investigated. Because of the voice raised by environmental scientists, several corrosion researchers have started using environmental friendly natural products as corrosion inhibitors [19-22]. Water extracts from leaves of date palm, phoenix dactylifera, henna, Lawsonia inermis, and corn, Zea mays, were tested as corrosion inhibitors for steel, aluminium, copper and brass in acid chloride and sodium hydroxide solutions, using weight loss, solution analysis and potential measurements [23]. Priya et al. have studied the corrosion behaviour of aluminium in rain water containing garlic extract [24]. Jain et al. have investigated the electrochemical behaviour of aluminium in acidic media. The inhibitive action of the acid extracts of seeds, leaves and bank from the ficus virens plant towards hydrochloric and sulphuric acid corrosion of aluminium has been tested using mass loss and thermometric techniques. It was found that the extract acted as a good corrosion inhibitor for aluminium corrosion in all concentration of hydrochloric and sulphuric acid solutions [25]. Anuradha et al. have investigated corrosion inhibition of carbon steel in low chloride media by an aqueous extract of Hibiscus rosa-sinensis Linn. The inhibition efficiency has been evaluated by weight loss method. Various techniques such as polarization and AC impedance spectra have been used. The protective film has been analysed by FTIR and Atomic force Microscopy [26].

The present work is undertaken:

- to investigate the inhibition efficiency of Hibiscus rosa-sinensis (white) in controlling corrosion of aluminium immersed in an aqueous solution at pH 12 (NaOH), in the absence and presence of Zn^{2+} using the weight loss method;
- to examine the inhibition efficiency of the flower extract-Zn^{2+} system;
- to analyze the protective film by Fourier Transform-Infrared (FTIR) spectroscopy;
- to study the potentiodynamic polarization and AC impedance curves of the aqueous flower extract-Zn^{2+} system.

Methods and materials

Preparation of flower extract

An aqueous extract of white hibiscus flower was prepared by boiling 20g of dried flower petals, with distilled water, and making up to 100 mL, after filtering the suspending impurities.

Preparation of specimens

Commercial aluminium specimens of dimensions 1.0 x 4.0 x 0.2 cm, containing 95% pure aluminium were polished to mirror finish, degreased with trichloroethylene, and used for the weight loss method and for surface examination studies.

Weight loss method

Three aluminium specimens were immersed in 100 mL of the solution containing pH = 12 and various concentrations of the inhibitor in the absence and presence of Zn^{2+}, at pH 12 (NaOH) for a period of 1 day. The weight of the specimen before and after immersion was determined using Shimadzu balance AY62. Inhibition efficiency (IE) was calculated from the relationship IE = $(1- W_2/W_1)$ x 100, where W_1 = corrosion rate in the absence of inhibitor, and W_2 = corrosion rate in the presence of the inhibitor.

Surface examination study

The aluminium specimens were immersed in various test solutions for a period of 1 day. After 1 day, the specimens were taken out and dried. The film formed on the surface of the metal specimens was analysed by surface analysis technique.

FTIR spectra

These spectra were recorded with the Perkin – Elmer - 1600 spectrophotometer. The FTIR spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr and making the pellet.

Potentiodynamic polarization study

Polarization study was carried out in an H and CH electrochemical work station Impedance Analyzer Model CHI 660A provided with *iR* compensation facility, using a three electrode cell assembly. Aluminium was used as working electrode, platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. After having done *iR* compensation, polarization study was carried out at a sweep rate of 0.01 V/s. The corrosion parameters such as Linear Polarization Resistance (LPR), corrosion potential, E_{corr}, corrosion current, I_{corr}, and Tafel slopes (b_a and b_c), were measured.

Alternating current impedance spectra

AC impedance spectra were recorded in the same instrument used for polarization study, using the same type of three electrode cell assembly. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were calculated.

Cyclic voltammetry

Cyclic voltammetry was carried out in an H and CH electrochemical work station Impedance Analyzer model CHI 660 provided with iR compensation facility, using a three electrode cell assembly. Aluminium was used as working electrode, platinum as counter electrode, and saturated calomel electrode (SCE) as reference electrode. The graph between (V) vs. current (cyclic voltammetry) was drawn.

Results and discussion

Analysis of results of weight loss method

Corrosion rates of aluminium in an aqueous solution at pH 12 (NaOH) in the absence and presence of inhibitors obtained by weight loss method are given in Table 1. The inhibition efficiencies are also given in this table.

It was observed that the white hibiscus extract (WHE) had some efficiency in controlling corrosion of aluminium at pH 12.

Table 1. Corrosion rates of aluminium immersed in NaOH solution (pH=12) and the inhibition efficiency obtained by weight loss method.

WHE (mL)	Zn^{2+} (ppm)	CR (mdd)	IE (%)
0	0	117.27	--
2	0	89.07	24
4	0	85.55	27
6	0	79.69	32
8	0	93.76	40
0	0	117.27	--
0	25	140.17	-196
2	25	77.35	-100
4	25	110.17	-88
6	25	201.58	-75
8	25	205.1	-72
0	0	117.27	--
0	50	99.68	15
2	50	90.24	23
4	50	86.73	26
6	50	63.29	46
8	50	2.34	98

Inhibitor system: White hibiscus extract (WHE) + Zn^{2+}; duration of immersion: 1 day.

When 25 ppm of Zn^{2+} were added to the flower extract, the inhibition efficiency decreased to a great extent. This may be due to the precipitation of the complex formed between Zn^{2+} and the active principle present in WHE, in the bulk of the solution. The availability of WHE near the metal surface was reduced. Hence a decrease in inhibition efficiency was observed.

Upon addition of 50 ppm of Zn^{2+} an improvement in inhibition efficiency was observed. The formulation consisting of 50 ppm of Zn^{2+} and 8 mL of the plant extract offered 98% corrosion inhibition efficiency.

Influence of duration of immersion on the inhibition efficiency of the Zn^{2+} - WHE system

The influence of duration of immersion on the inhibition efficiency of the Zn^{2+} - WHE system is given in Table 2. It was observed that as the duration of immersion increased, the inhibition efficiency decreased. This is due to the fact that as the duration of immersion increased, the protective film formed on the metal surface, probably Al^{3+} - active principle complex, was broken by the corrosive environment and the film was dissolved.

Table 2. Influence of duration of immersion on the inhibition efficiency of WHE – Zn^{2+} system.

Detail		1 Day	3 Day	11 Day
Corrosion rate, mdd	Without inhibitor	117.27	65.45	111.82
	With inhibitor	2.34	46.36	37.27
Inhibition efficiency, %		98	29	66

Inhibitor system : WHE 8 mL + Zn^{2+} 50 ppm; pH = 12 (NaOH).

Influence of sodium dodecyl sulphate (SDS) on the inhibition efficiency of WHE-Zn^{2+} system

When various concentrations of an anionic surfactant, SDS, were added to the inhibitor system, the inhibition efficiency decreased and reached a minimum and then increased (see Table 3). A micelle would have been formed at the minimum efficiency concentration. Afterwards the micelles would have been converted into monomer, which improved the inhibition efficiency. Further research in this direction will lead to development of very interesting new concepts.

Table 3. Influence of sodium dodecyl sulphate (SDS) on the inhibition efficiency of WHE-Zn^{2+} system.

WHE (mL)	Zn^{2+} (ppm)	SDS (ppm)	CR (mdd)	IE (%)
0	0	0	117.27	--
8	50	0	2.34	98
8	50	50	49.22	58
8	50	100	48.05	59
8	50	150	65.63	44
8	50	200	50.39	57
8	50	250	29.30	75

pH = 12 (NaOH); duration of immersion = 1 day.

Influence of N-cetyl-N,N,N-triemethylammonium bromide (CTAB) on the inhibition efficiency of WHE-Zn^{2+} systems

It is observed from Table 4 that as the concentration of CTAB increases, the IE increases and then decreases and again increases. A micelle would have been formed at the minimum efficiency concentration. Further research in this direction will lead to development of very interesting new concepts.

Table 4. Influence of CTAB on the inhibition efficiency of WHE-Zn^{2+} system.

WHE (mL)	Zn^{2+} (ppm)	CTAB (ppm)	CR (mdd)	IE (%)
0	0	0	117.27	--
8	50	0	2.34	98
8	50	50	41.04	65
8	50	100	34.01	71
8	50	150	17.59	85
8	50	200	87.95	25
8	50	250	75.05	36

pH = 12 (NaOH); duration of immersion = 1 day.

Analysis of polarization curve

The potentiodynamic polarization curves of aluminium immersed in an aqueous solution at pH 12 (NaOH) are shown in Fig. 1. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (b_a, b_c), and linear polarization resistance (LPR), are given in Table 5.

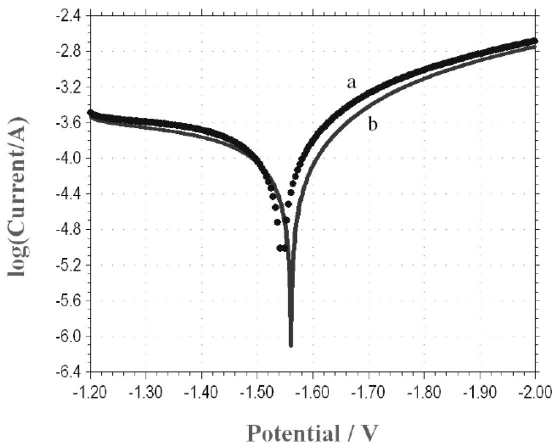


Figure 1. Polarization curves of aluminium immersed in aqueous solution at pH 12 (NaOH). (a) Aqueous solution at pH 12; (b) flower extract 8 mL + Zn^{2+} 50 ppm (pH 12).

Table 5. Corrosion parameters of aluminium immersed in NaOH solution (pH = 12) obtained by polarization study.

WHE (mL)	Zn^{2+} (ppm)	E_{corr} (mV vs SCE)	b_c (mV)	b_a (mV)	LPR (ohm cm^2)	I_{corr} (A/cm^2)
0	0	-1545	204	402	4.155×10^2	1.412×10^{-4}
8	50	-1561	192	365	5.487×10^2	0.9953×10^{-4}

Inhibitor: White hibiscus extract (WHE) + Zn^{2+}.

When aluminium is immersed in a pH 12 aqueous solution (NaOH), the corrosion potential is -1545 mV vs. SCE. When the inhibitors are added (8 mL of extract WHE and 50 ppm of Zn^{2+}), the corrosion potential shifts to cathodic side (-1561 mV vs. SCE). Further LPR value increases from 4.155 x 10^2 to 5.487 x 10^2 and corrosion current decreases from 1.412 x 10^{-4} to 0.9953 x 10^{-4}

A/cm^2. These results suggest that a protective film is formed on the metal surface. This protects the metal from corrosion.

Analysis of AC impedance spectra

The AC impedance spectra of aluminium immersed in an aqueous solution at pH 12 (NaOH) are shown in Fig. 2. The AC impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}) [derived from Nyquist plots (Fig.2a and b)], and impedance, log(z/ohm), values derived from Bode plots (Fig.2c and d), are given in Table 6.

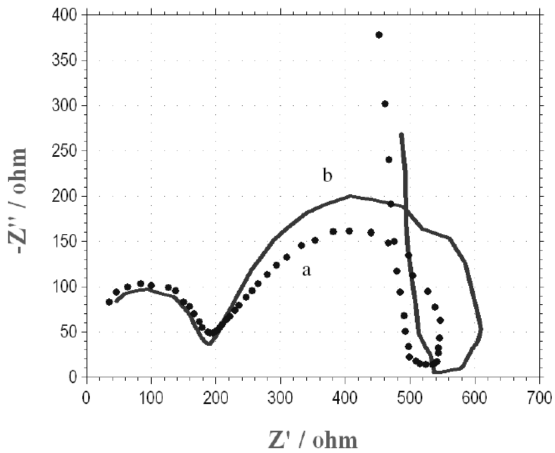


Figure 2 (a and b). AC impedance spectra of aluminium immersed in aqueous solution at pH 12 (NaOH). Nyquist plots: (a) aqueous solution at pH 12; (b) flower extract 8 mL + Zn^{2+} 50 ppm (pH 12).

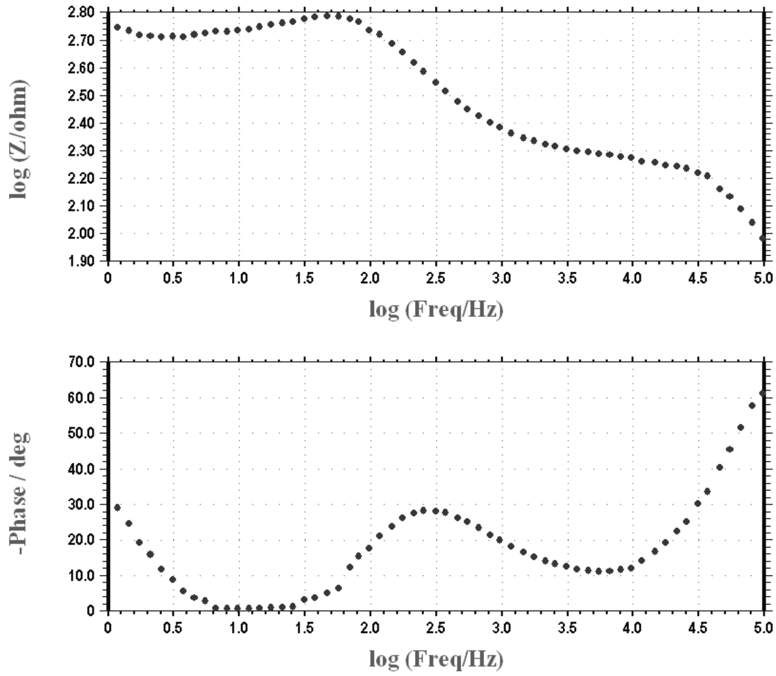


Figure 2c. AC impedance spectra of aluminium immersed in aqueous solution at pH 12 (NaOH). Bode plots: (c) aqueous solution at pH 12.

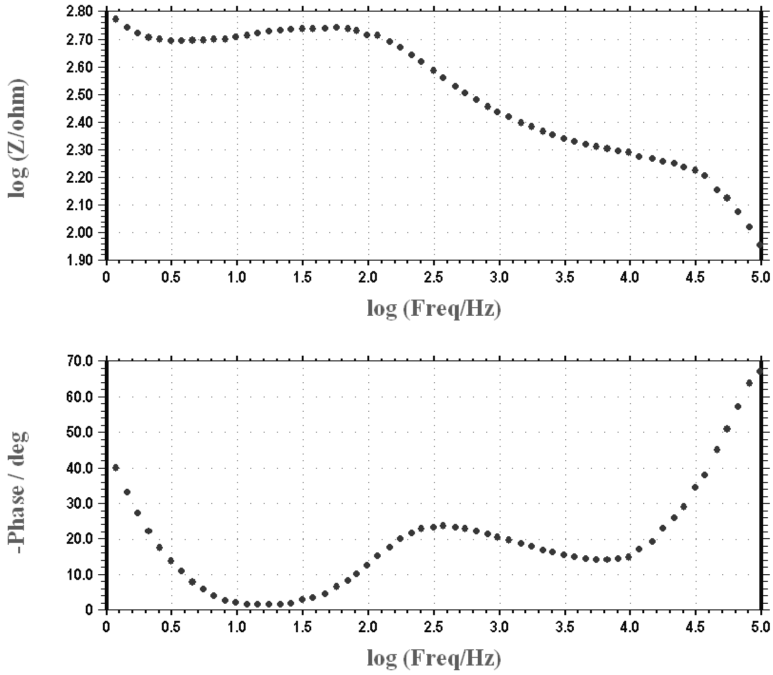


Figure 2d. AC impedance spectra of aluminium immersed in aqueous solution at pH 12 (NaOH). Bode plots: (d) flower extract 8 mL + Zn^{2+} 50 ppm (pH 12).

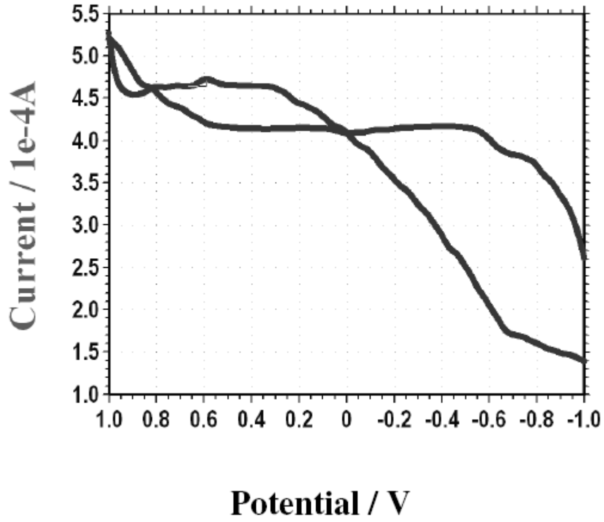
Table 6. AC impedance parameters of aluminium immersed in NaOH solution (pH = 12) obtained by AC impedance spectra.

WHE (mL)	Zn^{2+} (ppm)	R_t (ohm cm^2)		C_{dl} ($\mu F/cm^2$)		Impedance log (z/ohm)
		R_{t1}	R_{t2}	C_{dl1}	C_{dl2}	
0	0	159.22	353.2	1.8286×10^{-8}	2.098×10^{-6}	2.76
8	50	144.31	420.7	2.0171×10^{-8}	2.1530×10^{-6}	2.78

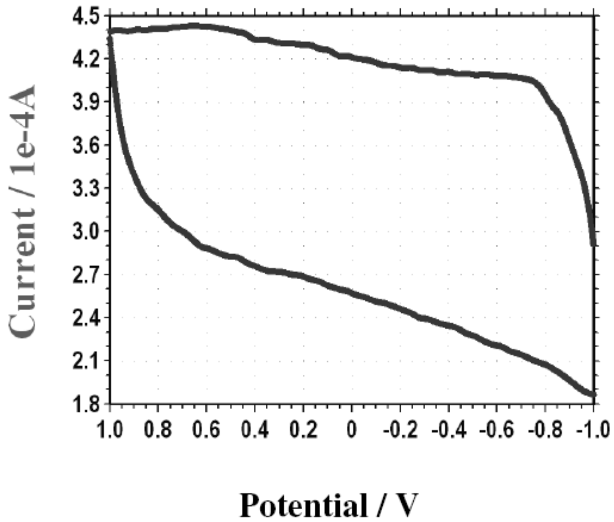
When Al was immersed in NaOH solution at pH 12, two semicircles were observed. The one at high frequency region corresponds to corrosion process; the other at low frequency region corresponds to protective nature of the film formed on the metal surface. It was observed that there was increase in charge transfer resistance and decrease in double layer capacitance values. These observations suggested that, a protective film was formed on the metal surface in the presence of inhibitors, namely, 50 ppm of Zn^{2+} and 8 mL of flower extract. This fact was further confirmed by the evidence that, there was increase in the value of impedance, log(z/ohm), when inhibitors were added.

Analysis of cyclic voltammograms

The cyclic voltammogram of aluminium immersed in an aqueous solution at pH 12 is shown in Fig. 3a. The E_p is found to be 0.589 V and the iP is found to be 7.915 x 10^{-6} A/cm^2. The Ah value is 2.9720 x 10^{-6} C. These values correspond to corrosion of aluminium at pH 12. The potential 0.589 V may be due to formation of Al^{3+} at pH 12. When Al is immersed in the inhibitor solution (Fig. 3b), the peak has disappeared, indicating protective nature of the film formed on the metal surface, in the presence of inhibitor system. Further the bulging out appearance of the cyclic voltammogram suggests the capacitance behaviour of the film formed on the metal surface. Corrosion of metal by release of electron is prevented.



a)



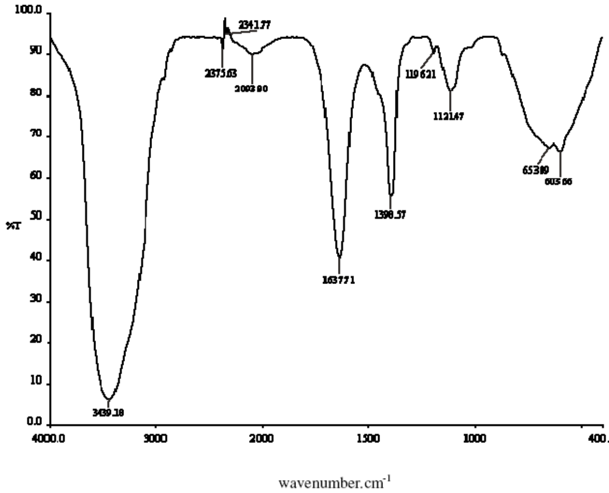
b)

Figure 3. Cyclic voltammograms of aluminium immersed in aqueous solution at pH 12 (NaOH). (a) Aqueous solution at pH 12; (b) (b) Flower extract 8 mL + Zn^{2+} 50 ppm (pH 12).

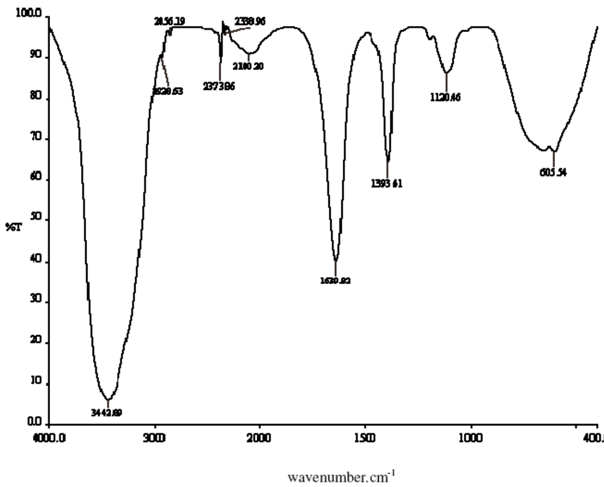
Analysis of FTIR spectra

A few drops of an aqueous extract of flower were placed on a glass plate and evaporated to dryness. A solid was obtained. Its FTIR spectrum (KBr) is shown in Fig.4. The peak at 3439 cm^{-1} corresponds to –OH stretching frequency; the peak at 1638 cm^{-1} corresponds to –C = O stretching frequency; the peak at 1122 cm^{-1} is due to ring oxygen atom. Thus the active principle in aqueous extract of the flower, quercetin–3–O–glucoside (Fig. 5) [26] is confirmed by FTIR.

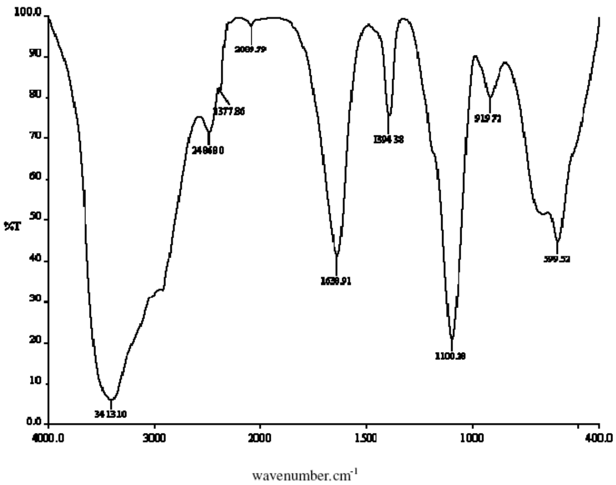
A few drops of freshly prepared aluminium sulphate solution were mixed with the aqueous flower extract; aluminium – flower extract complex was formed. It was evaporated to dryness, and the FTIR spectrum (KBr) was recorded (Fig. 4b). The –OH stretching frequency has shifted from 3439 to 3443 cm^{-1}; the –C=O stretching frequency has shifted from 1638 to 1640 cm^{-1}, and the ring oxygen atom – frequency has shifted from 1122 to 1120 cm^{-1}. These evidences indicate that during the formation of aluminium complex, there is coordination between Al^{3+} and the oxygen atoms of –OH group, -C=O group and ring oxygen atom.



a)



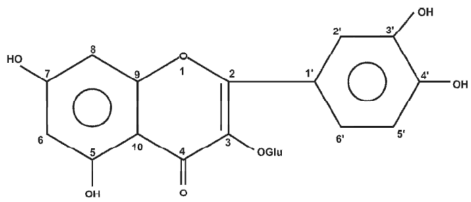
b)



c)

Figure 4. FTIR spectra (KBr). (a) Flower extract dried to solid mass; (b) Flower extract Al^{3+} complex; (c) Film formed on aluminium metal surface after immersion in the aqueous solution (pH 12) containing 8 mL of flower extract + 50 ppm of Zn^{2+}.

The FTIR spectrum of the protective film formed on the surface of the metal after immersion in the solution containing 8 mL of flower extract and 50 ppm of Zn^{2+}, is shown in Fig. 4c.
The –OH stretching frequency has shifted from 3439 to 3413 cm^{-1}; the –C=O stretching frequency has shifted from 1638 to 1640 cm^{-1}; and ring oxygen atom stretching frequency has shifted from 1122 to 1100 cm^{-1}.
This confirms the presence of Al^{3+} - flower extract complex on the metal surface. Al^{3+} has coordinated with the O-atom of the –OH group, -C=O group and the ring oxygen atom. Similar observation has been made by Anuradha et al., who reported the formation of Fe^{2+} - flower extract complex, while studying the inhibition of corrosion of carbon steel by the flower extract [26].



Quercetin - 3 - 0 - glucoside
(Active principle)

Figure 5. Quercetin – 3 – 0 – glucoside.

Conclusions

The inhibition efficiency (IE) of an aqueous extract of Hibiscus rosa-sinensis (white) in controlling corrosion of aluminium at pH 12 has been evaluated by

- weight loss method in the absence and presence of Zn^{2+};
- the formulation consisting of 8 mL flower extract (FE) and 50 ppm of Zn^{2+} had 98% inhibition efficiency;
- polarization study revealed that this formulation functioned as cathodic inhibitor;
- AC impedance spectra revealed the presence of a protective film formed on the metal surface;
- FTIR spectra revealed that the protective film consisted of a complex formed between the active principle of the flower extract and Al^{3+}.

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