

***Juglans regia* L. extract as green inhibitor for stainless steel and aluminium in acidic media**

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Abstract Corrosion inhibition of stainless steel and aluminium with the promising green eco-friendly inhibitor *Juglans regia* L. was tested in 1 M HCl acidic solution by using various techniques such as gravimetric (weight loss), potentiodynamic polarization and electrochemical impedance spectroscopy. An increase in inhibition efficiency was identified with the increased concentration of the inhibitor, *Juglans regia* extract, both in water and in ethyl acetate solutions. The inhibition efficiency was found 88.8 % in water solvent for aluminium. For each experiment, water showed better efficiency as a solvent compared to ethyl acetate. It was also realized that the inhibitor molecule had a more positive inhibiting effect on aluminium metal. In addition, the effect of immersion time (2–8 h) was discussed and the adsorption mechanism was fitted with the Langmuir isotherm. Infrared spectra were also employed to discover the changes in functional groups of the organic molecules of the extract.

Keywords Corrosion · *Juglans regia* · Inhibition · Stainless steel · Aluminium

Introduction

Acid solutions are commonly used for the removal of undesirable scale, cleaning and pickling in industrial processes [1–3]. Aluminium metal is used in many applications because of its low atomic number, mechanical properties, high energy density and electrical conductivity [4, 5], while stainless steel is widely used due to its good corrosion and oxidation resistance in various industrial environments [6, 7].

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One of the best ways of preventing corrosion against the metals is to use an inhibitor [8]. Organic compounds like azoles [9], aminoacids [10], amines [11], anionic [12] and cationic surfactants [13] and imidazoline derivatives [14] have been reported as good corrosion inhibitors in acidic media. These organic molecules can be adsorbed on the metal surface physically or chemically. The influence of the adsorption depends on the kind of metal, the structure of the inhibitor and the type of the corrosive medium [15]. However, these organic molecules are toxic and expensive. Thus, natural plant extracts with low cost are also applied for corrosion inhibition [16, 17]. Corrosion inhibitors of the extracts of pectin [18], aloe vera [19], mango, orange and cashew peels [20], ginger [21], black pepper [22], caffeine [23], jojoba oil [24], rosemary oil [25], pennyroyal oil [26], *Garcinia mangostona* (the mangosteen) [27], *Solanum tuberosum* [28], and *Azadirachta indica* [29] have been studied as green corrosion inhibitors in acidic medium.

Walnut (*Juglans regia* L.) is a popular crop that belongs to the family Juglandaceae [30, 31]. Walnut husk and leaves are especially used in the cosmetic and medicines for treatment of cough, stomach ache [32], cancer [33], diabetes, myocardial infarction [34], skin inflammations and ulcers [35]. Several studies have shown that walnut antioxidants have an effective impact for health care [36, 37].

The oxidation of corrosion inhibitors is described as a free radical-mediated operation [38], and phenolic compounds such as polyphenols and tocopherols are bioactive materials which exist in plants. Plant phenolic molecules contain such compounds as flavonoids (flavonols, flavonons, biflavonoids, etc.) and several non-flavonoids (phenolic acids, lignins, stilbenes) in a very large range. Walnuts are especially rich in total amounts of phenolic content. Most commercial rust converters incorporate some type of polyphenolic or tannin-like compound. Tannins perform their corrosion inhibiting action by the formation of metal–tannate complexes, existing as a reticulate protective layer on the rusted steel surface [39–41]. The effect of solvents on walnut extracts has been investigated and water has shown a passable effect [42]. In this study, we focus on the inhibition effect of *Juglans regia* extract in different solvents for aluminium and stainless steel in 1 M HCl solution, and clarify the physical characterization by FT-IR spectroscopy.

Experimental

Preparation of plant extract

Two grams of dried walnut leaves were mixed with 50 mL of water and ethyl acetate solution and left in a shaker for 2 h. Then, the solution was twice filtered by Whatman filter paper No. 4. The extract was centrifuged and evaporated in a vacuum evaporator. Finally, the dried extract of the leaves was stored in the dark at $-4\text{ }^{\circ}\text{C}$ for further analysis.

Preparation of materials and solution

The aluminium and stainless steel at 99.8 % was purchased from Aldrich. Both stainless steel and aluminium sheets were graded with thick and thin emery paper,

washed with acetone and ethanol, and dried for use. The corrosive environment of 1 M HCl solution was prepared by dilution of natural 37 % HCl (Merck) using distilled water.

Weight loss measurements

Gravimetric corrosion measurements were performed according to the method described previously [43].

In these experiments, the effects of the concentration of inhibitor and solvent and the time on weight loss measurements in 1 M HCl were investigated. Metal specimens of 1 cm² were used for weight loss experiments and degreased with acetone, rinsed in distilled water, dried in the air, and weighed accurately. The specimens were immersed in 250 mL 1 M HCl in the absence and presence of different concentration of walnut extracts. After 2–8 h immersion time, the specimens were washed in distilled water, cleaned with acetone, dried, and immediately weighed.

The corrosion rate was determined by suspending the metal specimen in the 1 M HCl solution with and without the inhibitor. Finally, the measured weight loss and the inhibition efficiency (IE %) were calculated using the formula:

$$\text{IE (\%)} = \frac{W_0 - W_i}{W_0} \times 100$$

where W_0 and W_i are the charge weight loss with and without the inhibitor, respectively.

The corrosion rate (CR) was calculated using the following formula:

$$\text{CR} = \frac{\Delta m}{At}$$

where Δm is weight loss in mg, A is the area of exposure in cm², and t is the time in hours.

Electrochemical measurements

The electrochemical experiments were carried out using a PARSTAT 2270 Potentiostat/Galvanostat. These measurements were performed in a conventional three-electrode cell. Saturated calomel electrode (SCE) and platinum (1 cm²) were used as the reference and counter electrodes, respectively. Stainless steel and aluminium with exposed areas of 1 cm² were used as working electrodes. Before measurements, the electrode potential was stabilized for 30 min. All experiments were conducted at room temperature.

Electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range of 1 kHz to 100 mHz with amplitude of 10 mV at open circuit potential. The charge transfer values were obtained from the diameter of the semicircles of the Nyquist plots. The inhibition efficiency was calculated using the following equation:

$$\text{IE (\%)} = \frac{R_t - R_t^0}{R_t} \times 100$$

where R_i^0 and R_i are the charge transfer resistances in the absence and presence of the inhibitor, respectively.

The polarization curves were carried out in the potential range from +250 to -250 mV with respect to the open circuit potential at a scan rate of 1 mV/s. Electrochemical parameters such as E_{corr} , I_{corr} and cathodic Tafel slopes (β_a , β_c) were obtained by the Tafel extrapolation method. The inhibition of efficiency was calculated by following equation [44]:

$$\text{IE (\%)} = \frac{I_{\text{corr}}^0 - I_{\text{corr}}}{I_{\text{corr}}} \times 100$$

where I_{corr} and I_{corr}^0 signify the corrosion current density in the absence and presence of the inhibitors, respectively.

FT-IR measurements

Finely powdered specimens were immersed in a saturated solution of the extract for 1 h to form the adsorption product of the extract. Fourier transform infrared (FT-IR) spectroscopy was recorded by a Perkin-Elmer BX 2 FTIR spectrophotometer at room temperature between 600 and 4,000 cm^{-1} .

Results and discussion

Weight loss measurements

Weight loss of stainless steel and aluminium in 1 M HCl was performed in the absence and presence of different concentrations of walnut extract. Inhibition efficiencies (%) in two different solvents, and the times and metal surface measurements are given in Tables 1 and 2.

The inhibition efficiency of the extract of *Juglans regia* on aluminum is higher than on stainless steel in both solvents. The inhibition efficiency values were 45 and 61 % at 0.14 mg/mL for stainless steel and reached 75 and 84 % for aluminum in ethyl acetate and water, respectively. These results indicate that the maximum inhibition efficiency is obtained in water for both metal surfaces, but the best inhibition occurs on the aluminium metal surface. The corrosion rate of aluminum is about ten times higher than stainless steel in 1 M HCl. Thus, the stainless steel is more acid-resistant than aluminium, and the inhibition effect of the molecule can be seen more clearly with aluminium, while the molecules are carried on the aluminium much better (Tables 1, 2). Also, plant phenolics including flavonoids have high antioxidant activity [45] and these plant extracts show a good ability to inhibit the corrosion of aluminium metal in acidic media [46].

Behpour et al. [3], on the other hand, has investigated the corrosion inhibition effects of *Punica granatum* (PG) extract and its main components, ellagic acid and tannic acid, on mild steel in 2 M HCl and 1 M H_2SO_4 . They have found the highest inhibition efficiency in PG extract with 1 g/L inhibitor concentration in weight loss measurements.

Table 1 Weight loss data of stainless steel and the inhibition efficiency of *Juglans regia* extract

Solution type	Concentration of inhibitor (mg/mL)	Corrosion rate (CR)		θ		IE (%)	
		2 h	8 h	2 h	8 h	2 h	8 h
1 M HCl	Blank	0.0037	0.0013	–	–	–	–
	0.02	0.0032	0.0012	0.12	0.08	12	8
Ethyl acetate	0.06	0.0028	0.0011	0.24	0.2	24	20
	0.1	0.0023	0.0009	0.38	0.29	38	29
	0.14	0.0021	0.0008	0.45	0.39	45	39
	0.02	0.0031	0.0011	0.17	0.15	17	15
Water	0.06	0.0025	0.0010	0.32	0.29	32	29
	0.1	0.0019	0.00073	0.49	0.44	49	44
	0.14	0.0014	0.00057	0.61	0.56	61	56

Table 2 Weight loss data of aluminium and the inhibition efficiency of *Juglans regia* extract

Solution type	Concentration of inhibitor (mg/mL)	Corrosion rate (CR)		θ		IE (%)	
		2 h	8 h	2 h	8 h	2 h	8 h
1 M HCl	Blank	0.032	0.012	–	–	–	–
	0.02	0.02	0.01	0.37	0.23	37	23
Ethyl acetate	0.06	0.016	0.0084	0.49	0.3	49	30
	0.1	0.013	0.006	0.6	0.48	60	48
	0.14	0.08	0.005	0.75	0.6	75	60
	0.02	0.016	0.0071	0.48	0.41	48	41
Water	0.06	0.012	0.005	0.61	0.58	61	58
	0.1	0.09	0.0042	0.7	0.65	70	65
	0.14	0.05	0.0028	0.84	0.77	84	77

A decrease in inhibition efficiency (%IE) is also observed when the exposure time is increased, as shown in Tables 1 and 2. The effect of inhibition can be noticed even at 8 h of exposure time, indicating that the inhibitor molecule is unadulterated and shows a good inhibition effect. And for solvents and time factors with all metals, the inhibition efficiency increases with the increasing inhibitor concentration. When the concentration reaches 1.2 mg/mL, the inhibition efficiency shows excellent inhibitive properties for walnut extract, which can be as high as 84 %.

Adsorption isotherm

Adsorption isotherms can provide beneficial information on the interaction between the metal surface and the inhibitor molecule [47]. There are several adsorption isotherms, e.g., Langmuir, Frumkin, Freundlich, and Temkin. All isotherms are tested for our experimental data and the correlation coefficient, R^2 , was used to

choose the best isotherm. It was found that adsorption of the compound on the metal surface in 1 M HCl confirms the Langmuir isotherm with the strong correlation ($R^2 > 0.99$) and it can be declared as:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ad}}} + C_{\text{inh}}$$

where θ is the surface coverage, K_{ad} is the adsorption/desorption equilibrium constant, and C_{inh} is the inhibitor concentration.

Surface coverages (θ) were obtained from weight loss measurements for stainless steel at different concentrations of inhibitor in 1 M HCl. It was clear that the addition of the inhibitor increased the inhibition efficiency in the acidic media through the adsorption of the basic constituents of the inhibitors on the metal surface. This may be due to the presence of aromatic rings like phenolic acids, flavanoids, tannins, and juglone [45]. The extent of inhibition seems to depend on the nature and mode of the adsorption of the inhibitor molecules on the metal surface.

When surface coverages are plotted against the concentration of inhibitor, it was found that the solvent effect and extraction time have an important effect on the adsorption isotherms by changing the θ (Figs. 1, 2). The highest %IE and θ values for both water and ethyl acetate extracts were obtained in the concentration of 0.14 mg/mL for both aluminum and stainless steel (Tables 1, 2). These plots are linear with a slope equal to unity. This linear relationship between the concentration of inhibitor (C_{inh}) and C_{inh}/θ show that the adsorbed molecules occupy only one site and that there is no interaction with other sort of adsorbed molecules. These results also show the strong interaction of the inhibitor molecule onto the stainless steel and aluminium surfaces. This suggests that the adsorption of walnut extract on metal surfaces followed the Langmuir isotherm. All slopes are linear and the harmony of the values support the validity of the Langmuir adsorption isotherm.

Electrochemical measurements

Polarization measurements

Polarization curves of stainless steel and aluminium in 1 M HCl in the absence and presence of inhibitors are shown in Figs. 3 and 4, respectively. The values of E_{corr} , I_{corr} and cathodic Tafel slopes (β_a , β_c) of the polarization curves with the concentrations of inhibitor are given in Tables 3 and 4. Clear reductions of anodic and cathodic currents are shown in the potentiodynamic curves, and the Tafel plots indicate the cathodic reduction (H^+ evolution) and the anodic reduction (metal dissolution). The inhibitor molecules are adsorbed onto the metal surface and decrease the surface area of corrosion by blocking the reaction site of the surface area [48].

Juglans regia L, which is a green inhibitor, plays an important role on both aluminium and stainless steel. I_{corr} values decrease with the increase in inhibitor concentration. By comparing the polarization curves, the results reveal that the inhibition efficiency of *Juglans regia* in water is better than in ethyl acetate for both

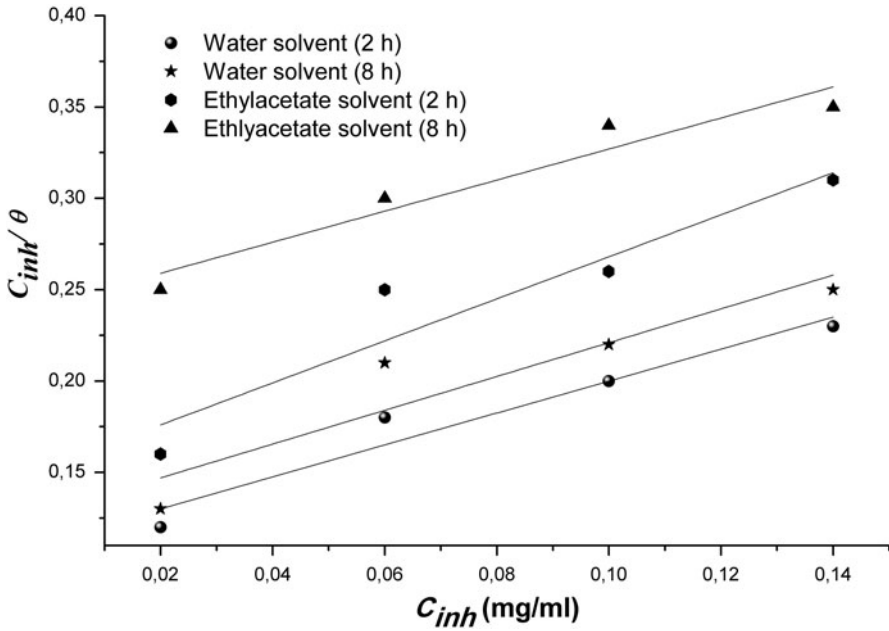


Fig. 1 Adsorption isotherm model of *Juglans regia* extract in ethyl acetate and water for stainless steel at different exposure times

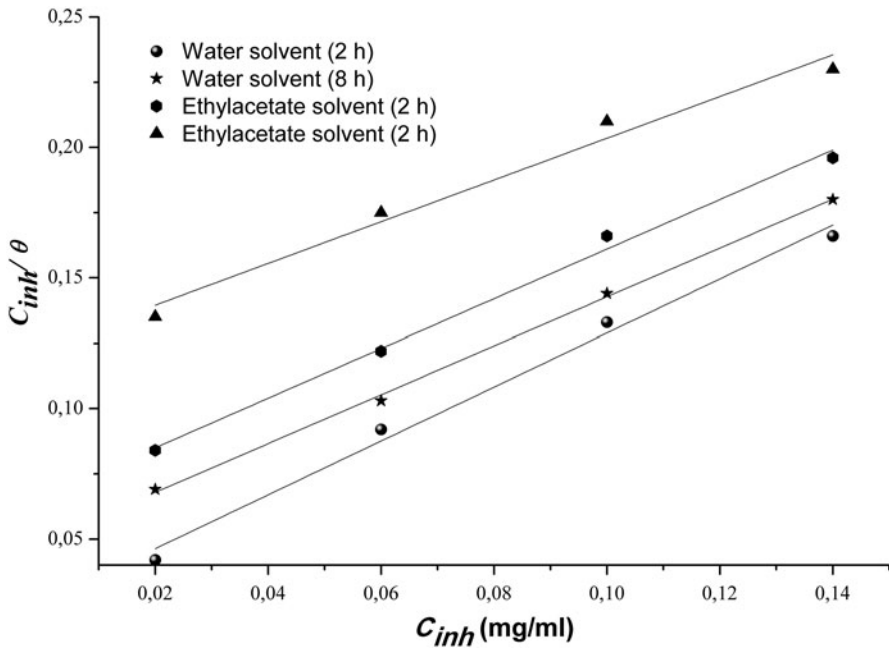


Fig. 2 Adsorption isotherm model of *Juglans regia* extract in ethyl acetate and water for aluminium at different exposure times

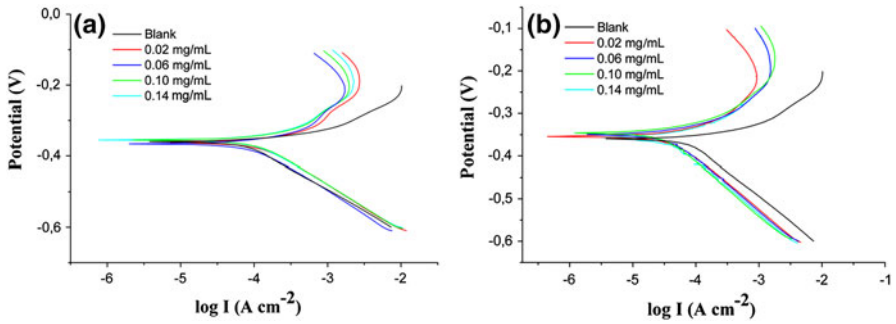


Fig. 3 **a** Polarization curves of stainless steel in 1 M HCl for various concentrations of *Juglans regia* extract in ethyl acetate. **b** Polarization curves of stainless steel in 1 M HCl for various concentrations of *Juglans regia* extract in water

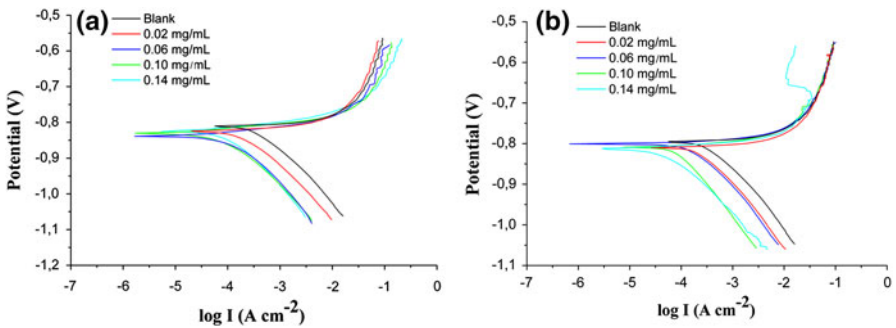


Fig. 4 **a** Polarization curves of aluminium in 1 M HCl for various concentrations of *Juglans regia* extract in ethyl acetate. **b** Polarization curves of aluminium in 1 M HCl for various concentrations of *Juglans regia* extract in water

Table 3 Effect of *Juglans regia* extract on stainless steel in 1 M HCl

Solution type	Concentration of inhibitors (mg/mL)	E_{corr} (mV)	I_{corr} (μA)	β_a (mV)	β_c (mV)	IE (%)
1 M HCl	Blank	-354.32	41.31	47.49	127.07	–
	0.02	-349.85	32.96	46.32	126.88	20.21
	0.06	-357.36	30.51	48.23	124.807	26.14
Ethyl acetate	0.1	-345.74	25.79	43.03	133.135	37.57
	0.14	-351.61	20.58	44.31	130.587	50.18
Water	0.02	-356.26	17.36	74.53	194.931	57.98
	0.06	-360.54	16.02	60.195	168.206	61.22
	0.1	-355.71	15.52	73.535	180.698	62.43
	0.14	-355.14	14.3	73.186	168.206	65.4

Table 4 Effect of *Juglans regia* extract on aluminium in 1 M HCl

Solution type	Concentration of inhibitors (mg/mL)	E_{corr} (mV)	I_{corr} (μ A)	β_a (mV)	β_c (mV)	IE (%)
1 M HCl	Blank	-794.70	314.46	109.04	116.79	-
	0.02	-811.01	249.9	113.995	126.461	20.54
	0.06	-803.91	184	153.419	139.417	41.49
Ethyl acetate	0.1	-805.56	86.99	139.417	153.419	72.33
	0.14	-814.77	71.91	122.356	128.701	77.13
	0.02	-800.76	147	101.419	108.219	53.25
Water	0.06	-812.78	83.94	16.914	78.55	73.31
	0.1	-830.53	51.38	35.711	104.572	83.66
	0.14	-838.47	35.25	22.518	74.749	88.78

stainless steel and aluminium. While the inhibition efficiency in water reaches 65.4 % at 0.12 mg/mL for stainless steel, that value is only 50.2 % in ethyl acetate. The inhibition efficiency of the extraction of *Juglans regia* in water reaches 88.8 % for aluminium and this is passable for a corrosion inhibitor.

EIS measurements

The effect of inhibitor concentration in water and ethyl acetate on the impedance behavior of stainless steel and aluminium in 1 M HCl is presented in Figs. 5 and 6. The equivalent Randles circuit model is shown in Fig. 7, where R_{Ω} represents the solution and corrosion product resistance, and R_t and C_{dl} represent corroding interfaces. The double-layer capacitance (C_{dl}) was calculated as follows:

$$C_{dl} = \frac{1}{2\Pi f_{max} R_t}$$

Nyquist plots show that the diameter of the semicircles increase with the addition of inhibitor. Tables 5 and 6 show that the value of R_t increases from 137.4 to

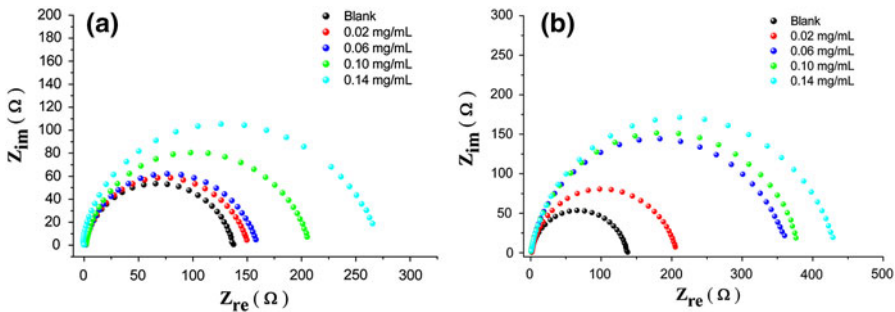


Fig. 5 a Nyquist plots for stainless steel in the absence and presence of different concentrations of *Juglans regia* extract in ethyl acetate. b Nyquist plots for stainless steel in the absence and presence of different concentrations of *Juglans regia* extract in water

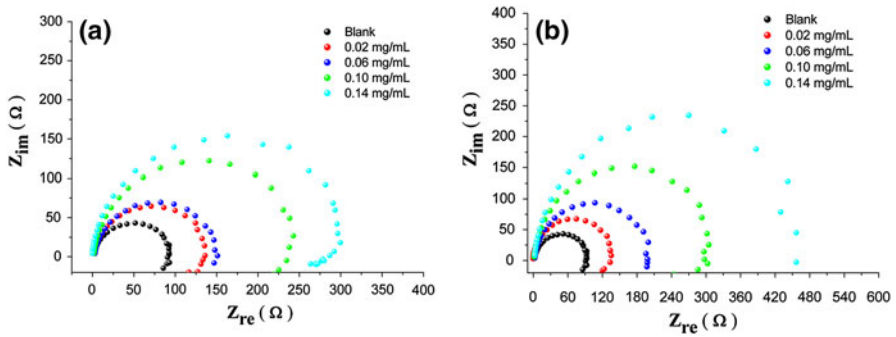


Fig. 6 **a** Nyquist plots for aluminium in the absence and presence of different concentrations of *Juglans regia* extract in ethyl acetate. **b** Nyquist plots for aluminium in the absence and presence of different concentrations of *Juglans regia* extract in water

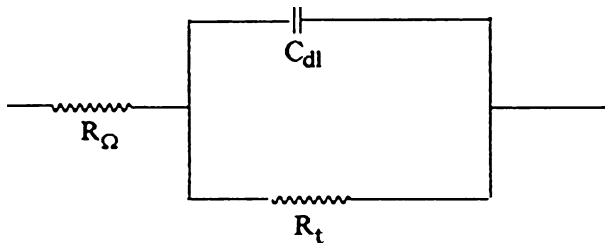


Fig. 7 Prescribed equivalent circuit schematic by Randles

444.5 Ω with the addition of *Juglans regia* extract in water, while the value of R_t increased from 137.4 to 210.0 Ω with the addition of *Juglans regia* extract in ethyl acetate, for stainless steel. On the other hand, C_{dl} values decrease with the increase in inhibitor concentration. This can be explained by the decrease in the local dielectric constant and/or with the increase in the thickness of the electrical double layer, suggesting that the inhibitor molecules show adsorption on the metal surface [49, 50]. Consequently, the inhibitor in water shows better corrosion efficiency and the results for aluminium are similar to those for stainless steel. As seen from Tables 5 and 6, the charge transfer resistance and the inhibition efficiency values increase while the C_{dl} values decrease with the increasing concentration of the inhibitor for both metals and solvents. These results indicate that a passive layer is formed on the metal surface with increasing inhibitor concentration. This layer increases the charge transfer resistance and decreases the double-layer capacitance (C_{dl}) on the metal surface. The inhibition effect was observed on both metals in water and ethyl acetate. Inhibition efficiency values of the inhibitor *Juglans regia* in water are higher than those of in ethyl acetate on aluminium and stainless steel. These results clarify that the extract of *Juglans regia* in water shows more effective antioxidant properties. As can be seen in the results, the inhibitor molecule has more

Table 5 Impedance parameters of *Juglans regia* on stainless steel in 1 M HCl

Solution type	Concentration of inhibitors (mg/mL)	R_t (Ω)	f_{max} (Hz)	C_{dl} ($\mu\text{F cm}^2$)	IE (%)
1 M HCl	Blank	137.45	2.728	424.7	–
Ethyl acetate	0.02	150.5	2.728	387.8	8.67
	0.06	161.5	2.728	361.4	14.89
	0.1	210	2.728	278	34.55
	0.14	277.1	2.728	210.6	50.4
Water	0.02	205.2	4.25	182.6	33.02
	0.06	373.3	4.25	100.4	63.18
	0.1	392.2	4.25	95.5	64.95
	0.14	444.5	4.25	84.3	69.08

Table 6 Impedance parameters of *Juglans regia* extract on aluminium in 1 M HCl

Solution type	Concentration of inhibitors (mg/mL)	R_t ($\Omega \text{ cm}^2$)	f_{max} (Hz)	C_{dl} ($\mu\text{F cm}^2$)	IE (%)
1 M HCl	Blank	92.5	21.13	81.5	–
Ethyl acetate	0.02	135.8	18.05	64.9	31.88
	0.06	149.5	18.05	59	38.13
	0.1	251	18.05	35.1	63.15
	0.14	305	18.05	28.9	69.67
Water	0.02	150	36.65	29	38.3
	0.06	210	36.65	20.7	55.95
	0.1	307.1	36.65	18.9	69.88
	0.14	450.5	36.65	12.9	79.47

effect on aluminium metal because the stainless steel is more acid-resistant than the aluminium.

FT-IR analysis

Since the best results are obtained in water with aluminium, IR spectra were analyzed in this solvent with this metal. The infrared spectra of *Juglans regia* extract in water and the product of adsorption between the extract and aluminium powder are given in Figs. 8 and 9, respectively. From the spectra in Fig. 8, the broad peak centered at $3,275 \text{ cm}^{-1}$ can be attributed to phenolic hydroxyl (OH) groups. The bands at $1,596$ and $1,032 \text{ cm}^{-1}$ are assigned to the (C=O) and carboxylic acid groups, respectively. The dried adsorption product of the extract with aluminium powder (Fig. 9) has IR spectral bands at different wave numbers, corresponding to phenolic hydroxyl groups ($3,292 \text{ cm}^{-1}$), carbonyl groups ($1,542 \text{ cm}^{-1}$), and carboxylic acid groups ($1,017 \text{ cm}^{-1}$), thus confirming the adsorption on the metal surface.

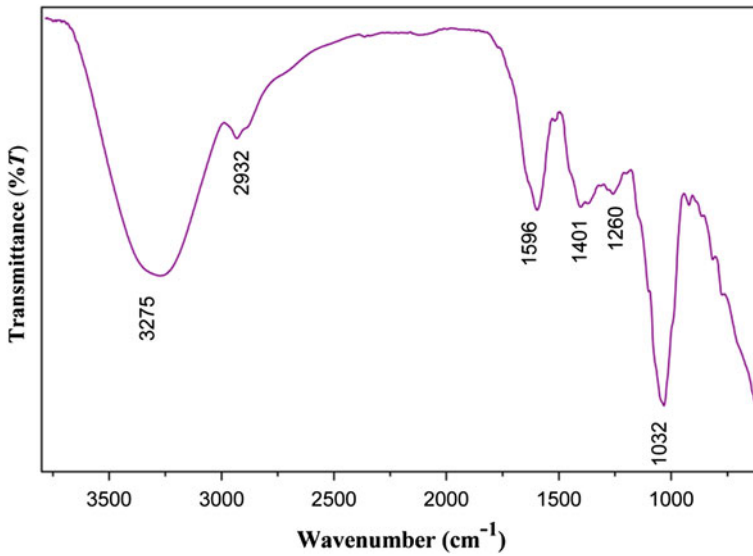


Fig. 8 IR spectra of *Juglans regia* extract in water solvent

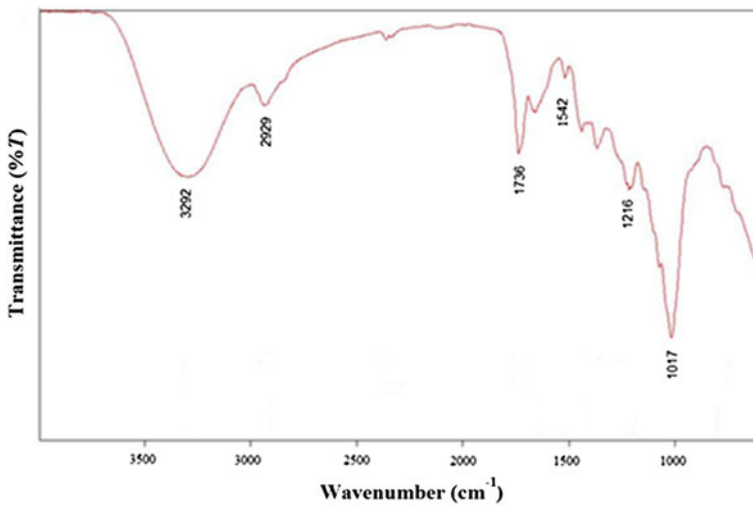


Fig. 9 IR spectra of the reaction product between *Juglans regia* extract in water solvent and aluminium powder

Conclusion

Juglans regia acts as an efficient green corrosion inhibitor in 1 M HCl for aluminium and stainless steel, showing a better performance in the case of aluminium. The inhibition efficiency increases with the increased inhibitor

concentration. A remarkable reduction in the corrosion rate for aluminium is seen from weight loss measurements: 84 % in 2 h. For all experiments, inhibition efficiency is observed even at 8 h. Polarization curves and EIS measurements also indicate that *Juglans regia* extract in water and ethyl acetate acts as a corrosion inhibitor, and the extract in water shows the better performance. The adsorption of the extract on the aluminium and stainless steel surfaces in an acidic medium obey the Langmuir adsorption isotherm. FT-IR analysis also supports the adsorption of inhibitor molecules seen in the study. The inhibition efficiency of *Juglans regia* extract can be explained by its antioxidant effect. All these results indicate that *Juglans regia* extract can be used as an impressive eco-friendly corrosion inhibitor for aluminium and stainless steel in 1 M HCl with the maximal importance of this compound being its accessibility in nature and in trade sales.

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