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Inhibition of aluminum corrosion in hydrochloric acid solution using black mulberry extract.

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Abstract

Inhibition of Aluminum corrosion in 2M hydrochloric acid solution using black mulberry (Morus nigra L.) extract has been studied by weight loss, electrochemical polarization technique and hydrogen evolution measurement. It was found that the berry extract acts as a good inhibitor for aluminum corrosion in the acid solution. The inhibition action of the extract in was discussed in view of the adsorption of its components on aluminum surface. It was found also that the adsorption is a spontaneous process and follows Langmuir adsorption isotherm. The inhibition efficiency (IE) increases as the extract concentration is increased. More over, the effect of temperature on the IE was studied. The IE decreases with increased the temperature. It was found that the presence of extract increases the activation energy of the corrosion reaction. Moreover, the thermodynamic parameters of the adsorption process were calculated. It was found also that the extract provides a good protection to aluminum against pitting corrosion in chloride ion containing solutions.

Keywords: corrosion test - electrochemical techniques – adsorption – corrosion

1-Introduction

Aluminum has an economic and industrial importance due to lightweight, high thermal and electrical conductivity. The resistance of aluminum against corrosion in aqueous media can be attributed to a rapidly formed compact, strongly adherent and continuous oxide film [1,2]. Therefore, aluminum and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries. Hydrochloric acid solutions are used for pickling, chemical and electrochemical etching of aluminum [3]. More over, the presence of aggressive ions like chloride creates extensive localized attack [4]. Because of the general aggressive acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. Most of the corrosion inhibitors are synthetic chemicals which are toxic, expensive and non-biodegradable. Therefore, it is desirable to source for environmentally safe inhibitors [4–10]. Plant extracts have become important because they are environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. Natural products were previously used as corrosion inhibitors for different metals in various environments [11–21] and their optimum concentrations were reported. The obtained data showed that plant extracts could serve as effective corrosion inhibitors.

The present work is another trial to find a cheap and environmentally safe inhibitor for aluminum corrosion in the acidic solution, where the aqueous extract of black mulberry is tested. This plant belongs to the family genotypes and has the scientific name (*Morus nigra L.*). Weight loss measurements, gasometry and potentiostatic polarization techniques are used to evaluate the inhibition efficiency of the *Morus nigra L.extract.* The effect of temperature on the corrosion reaction rates in free and inhibited acid solutions was also investigated. Moreover, the ability of the extract to provide a protection against pitting corrosion of aluminum in chloride ion containing solutions was studied using potentiodynamic polarization technique.

2. Experimental

2-1 Materials

The specimens used in this investigation were taken from aluminum with purity of 99.99% provided by provided by Aluminum Company of Egypt, Nagh Ammady.

The fresh fruits of black mulberry (*Morus nigra L.*) were washed by distilled water. It was then extracted with ethanol at 60^{o}C for 6h, then filtered [22]. The filtrate was evaporated and the sludge residue was dried at 50^{o}C. Stock solution was prepared from the collected residue and used in preparing the desired concentrations.

A solution of 2M HCl was prepared by diluting concentrated acid (37% Merck) by distilled water and used as the corrosive media.

2-2 Experimental methods

2.2.1 Gravimetric measurements

Gravimetric measurements were carried out in 50 ml of the corrosive solution. Rectangular aluminum specimens having a total surface area of 7.2cm^2 were used. The sheets were abraded successively with fine emery papers (600 – 1200 grit), rinsed with distilled water, degreased with acetone, dried before being weighed, and then hanged in the corrosive medium. The duration time of immersion was extended up to 180 min at 303K in naturally aerated solutions. At the end of each experiment, the specimens were carefully washed by distilled water, dried between two filter papers and weighed. The corrosion rate was calculated in milligrams per square centimeter per min (mg.cm^{-2}.min^{-1}).

The inhibition efficiency, *IE*, was determined according to equation:

$$IE = [1- (r / r^0)] \times 100 \qquad (1)$$

Where r and r^0 are the corrosion rates (mg.cm^{-2}.min^{-1}) of aluminum specimen in presence and absence of the *Morus* nigra *L.* extract.

2.2.2 Gasometry

The progress of the corrosion reaction was determined by volumetric measurement of the evolved hydrogen. The corrosion rate was taken as the slope of the straight line representing the variation of hydrogen volume and time of exposure. Rectangular aluminum specimens having a total surface area of (3.25cm^2) were used. The procedure was described elsewhere [23].

2.2.3 Electrochemical measurements

Potentiostatic polarization studies were carried out using Meinsberger potentiostat/ Galvanostat with software zum ps6 remote for calculating the electrochemical parameters.

Polarization experiments were carried out in a conventional three electrode cell with a platinum counter electrode and a reference saturated calomel electrode (SCE). A cylindrical electrode of the aluminum with a bottom surface area of 0.5 cm^2 was used as a working electrode. The electrode was abraded successively with fine emery papers (600 – 1200 grit), rinsed with distilled water, degreased with acetone before insert in the test solution. Before the start of each experiment, the working electrode was immersed for 10 minutes in the test solution in order to attain its steady state potential. The scan rate of polarization was 10mV/ sec. The corrosion parameters were determined by extrapolation of the cathodic and anodic Tafel lines to the corrosion potential. The inhibition efficiency (IE) and the fraction of surface coverage (θ) were calculated according to following equations:

$$IE\ \%= [1- (i_{corr} / i^0_{corr})] \times 100 \qquad (2)$$

$$\theta = 1- (i_{corr} / i^0_{corr}) \qquad (3)$$

where i_{corr} and i^0_{corr} are the corrosion current density of aluminum specimen (mA/cm^2) in presence and absence of the black mulberry extract, respectively.

All the experiments were performed in naturally aerated solutions at 298K.

3. Results and discussion.

3.1. Gravimetric measurements

Fig. 1 represents the relation between time and weight losses of aluminum coupons in solutions of 2 M HCl devoid of and containing different concentrations of black mulberry extract. Inspection of the figure reveals that the weight loss increases linearly with increasing time in all tested solutions. However, the slopes of the obtained lines, which represent the rates of weight loss, are affected by addition of extract. The presence of the extract causes a sharp decrease in the rate of weight loss.

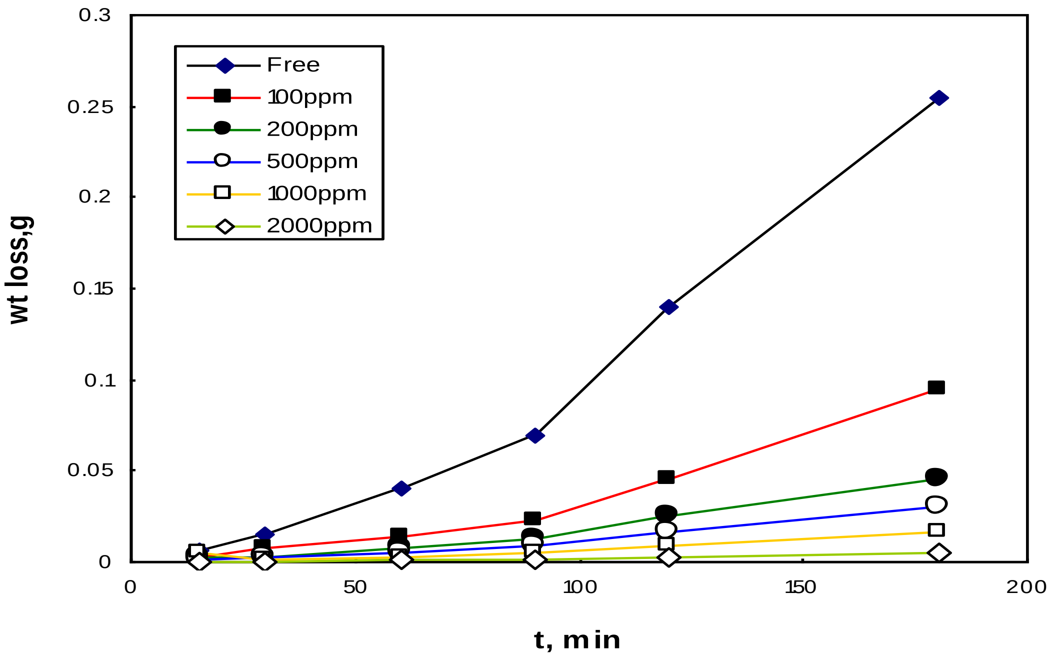

Fig. 1: Weight loss during corrosion of aluminum in free and inhibited acid solutions.

The values of inhibition efficiencies correspond to different inhibitor concentrations are listed in Table (1). Table (1) reveals that, the black mulberry extract acts as a good corrosion inhibitor for the acid corrosion of aluminum. The corrosion inhibition increases with increasing mulberry extract concentration.

Table 1: IE different mulberry extract concentrations toward aluminum corrosion in 2 M HCl solutions, as revealed from weight loss and hydrogen evolution experiments.

Conc.,ppm	**IE%**	
	Wt. loss	**H_2 evolution**
100	75.60	62.75
200	80.00	82.35
500	90.67	88.23
1000	91.11	93.73
2000	93.33	98.04

3.3. Gasometry

The volume of hydrogen evolved during the corrosion reaction of aluminum in 2 M HCl solutions devoid of and containing different concentrations of extract is measured as a function of the reaction time, and the data are represented graphically in Fig. 2. Inspection of the figure reveals that, the hydrogen evolution starts after a certain time from the immersion aluminum coupon in the test solution. It may be expected that this time corresponds to the period needed by the acid to destruct the pre-immersion oxide film before the start of the metal attack, and it is known as the incubation period.

Further inspection of Fig. 2 reveals linear relationship between the time of reaction and the volume of hydrogen evolved, in all of the tested solutions. However, the presence of the extract decreases, markedly, the slope of the straight line. Since the slope of the line represents the corrosion reaction rate, it could be concluded that the black mulberry extract has an excellent ability to inhibit the corrosion of aluminum in the acid solution. The values of IEs of different concentrations of the extract are given in Table 1. Inspection of Table 1 reveals that the IE increases as the concentration of the extract is increased.

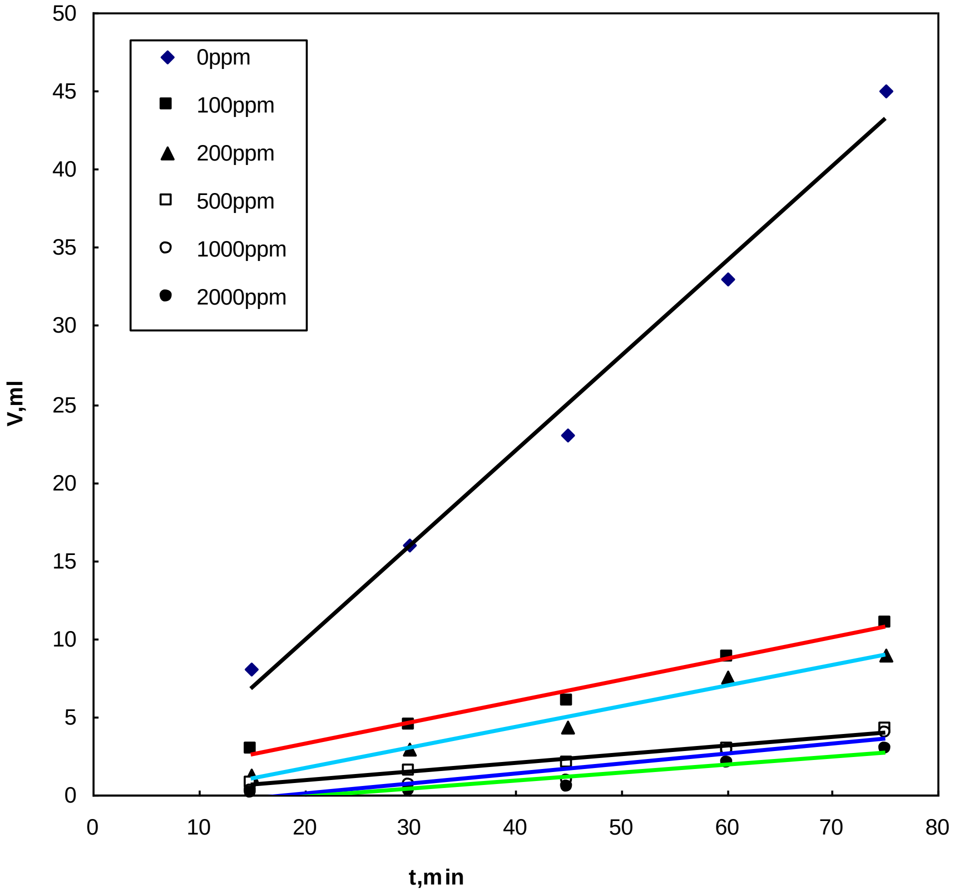

Fig.2: Hydrogen evolution during corrosion of aluminum in 2M HCl containing and devoid of different concentrations black mulberry extract.

3.3. Potentiostatic polarization

The effect of addition of different concentrations of black mulberry on the cathodic and anodic polarization curves of Al in 2M HCl solution at 303K was studied. The corrosion parameters extracted from the polarization curves such as, the values of the corrosion current densities (i_{corr}), together with the corrosion potential (E_{corr}), the cathodic and anodic Tafel slopes, and the surface coverage (θ) are listed in Table (2). Inspection of Table (2) reveals that increasing concentration of the black mulberry give rise to a consistent decrease in the anodic and cathodic current densities without remarked change in the corrosion potential (E_{corr}). Furthermore, the addition of the extract decreases the values of both anodic and cathodic Tafel constants. These findings suggest that the extract works as mixed inhibitors.

Further inspection of Table 2 reveals that the value of θ increases with increasing inhibitor concentration. The observed inhibition efficiency of black mulberry could be attributed to the adsorption of its components on the aluminum surface. The adsorbed molecules isolate the metal surface from the aggressive medium leading to decreasing the corrosion rate.

Table 2: Corrosion parameters of Al/2M HCl without and with different concentrations of black mulberry

Conc., ppm	**β_a (mV/decade)**	**β_C (mV/decade)**	**E_{Corr} (mV)**	**I_{Corr} (mA)**	**IE (%)**	**θ**
0	376	- 370	- 848	41.12	----	----
100	267	-377	-861	25.36	38.33	0.38
200	246	-337	-867	14.13	65.64	0.66
500	209	-300	-873	9.98	75.73	0.76
1000	136	-298	-868	7.934	80.71	0.81
1500	106	-273	-857	6.94	83.12	0.83
2000	85	-212	-855	2.90	92.95	0.93

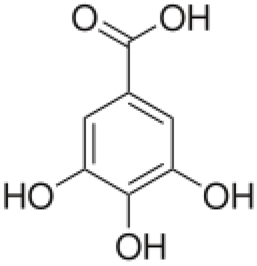

Fig 3: Gallic acid

The chemical components of the black mulberry extract were identified [22]. The black mulberry belongs to genotypes and has antioxidant activity between 63% and 76%. It was reported that the extract contain gallic acid, together with ascorbic, malic and citric acids. In addition, black mulberry extract contain six fatty acids (linoleic, palmitic, oleic, stearic, myristic, nonadecenoic acids). The extract is considered as antioxidant phenotypes due to the presence of gallic acid (Fig 3) as a major component. In this study, the concentration of extract was calculated with respect to its major component gallic acid. It is necessary to emphasize that the inhibition action of the extract is not attributed to gallic acid only, but the other components present in the extract contribute in the process also. Moreover, it was reported that Aluminum(III) form chelates with ascorbic acid [24–26]. This indicates that all the components of black mulberry extract act in synergism in corrosion inhibition process.

3.4. Isotherm adsorption

The adsorption of these compounds on the electrode surface makes a barrier for mass and charge transfers. This situation leads to a protection of the metal surface from the attack of the aggressive anions of the acid.

The Dependence of the fraction of the surface occupied by the adsorbed molecules on the inhibitor concentration is presented in Fig 4. A plot of C/ θ versus C gives a straight line with approximately unit slope. This result suggests that the adsorption of inhibitor molecules on the aluminum surface follow Langmuir isotherm. Thus, this result suggests that there are no interaction or repulsion forces between the adsorbed molecules. It is of interest to mention here that, the θ values obtained from the other used techniques obey also the Langmuir adsorption isotherm.

Langmuir adsorption isotherm could be represented using the following equations [27, 28]:

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \qquad (4)$$
$$\text{And } K_{ads} = 1/55.5\ e^{-\Delta G_{ads}/RT} \qquad (5)$$

where ΔG^o_{ads} is the standard free energy of adsorption where one molecule of water is replaced by one molecule of inhibitor [29] and the numerical value (1/55.5) in the equation stands for the molarity of water. The calculated value of the standard free energy of adsorption was found to be -27 kJ mol^{-1}.
The negative sign indicates that the adsorption of black mulberry components on aluminum surface is a spontaneous process.

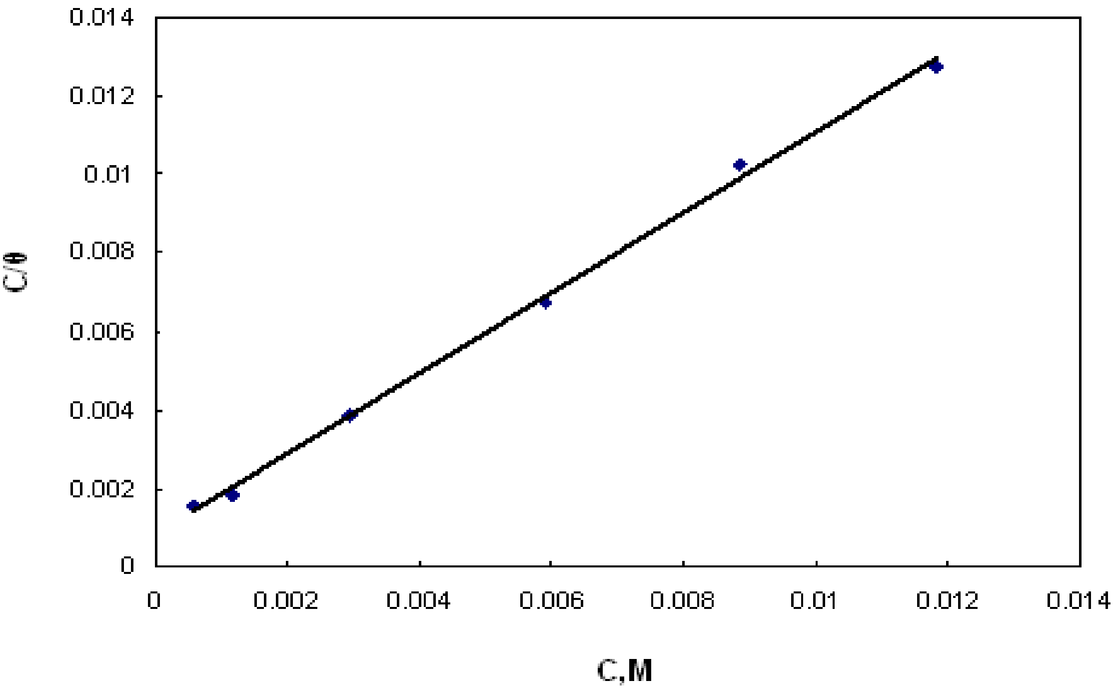

Fig. 4: Langmuir adsorption isotherm for Aluminum.

3.5 Effect of Temperature

The current densities of Al corrosion, in the acidic medium in absence and presence of 2000 ppm of black mulberry extract were traced in temperature range of 303 - 343 K. It was found that the rates of aluminum corrosion, in both free and inhibited acid solutions, increase with increasing temperature. The aluminum corrosion rates in inhibited solutions are affected by the rise of temperature more than that in free acid solution. Consequently, the IE of the extract decreases with increasing temperature. This result suggests a physical adsorption of the extract components on the aluminum surface. The plot of logarithm of the corrosion rate versus the reciprocal absolute temperature gives straight lines (Fig. 5) according to Arrhenius equation is represented as:

$$\ln r = A - E_a/RT \qquad (6)$$

where r is the corrosion rate (mA/cm^2), A is the frequency factor and E_a is the apparent activation energy. The values of E_a were obtained from the slopes of the straight lines and found to be 11.0 and 23.5 kJ mol^{-1} mass concentration for corrosion reactions in absence and inhibited acid, respectively. It is clear that, the corrosion process is inhibited via increasing the activation energy of the reaction. The increase in activation energy is achieved via formation of an adsorbed film on the metal surface leading to retarding the energy and mass transfer. However, increasing temperature retards this effect by enhancing the desorption process and thus the inhibition efficiency of the black mulberry is decreased.

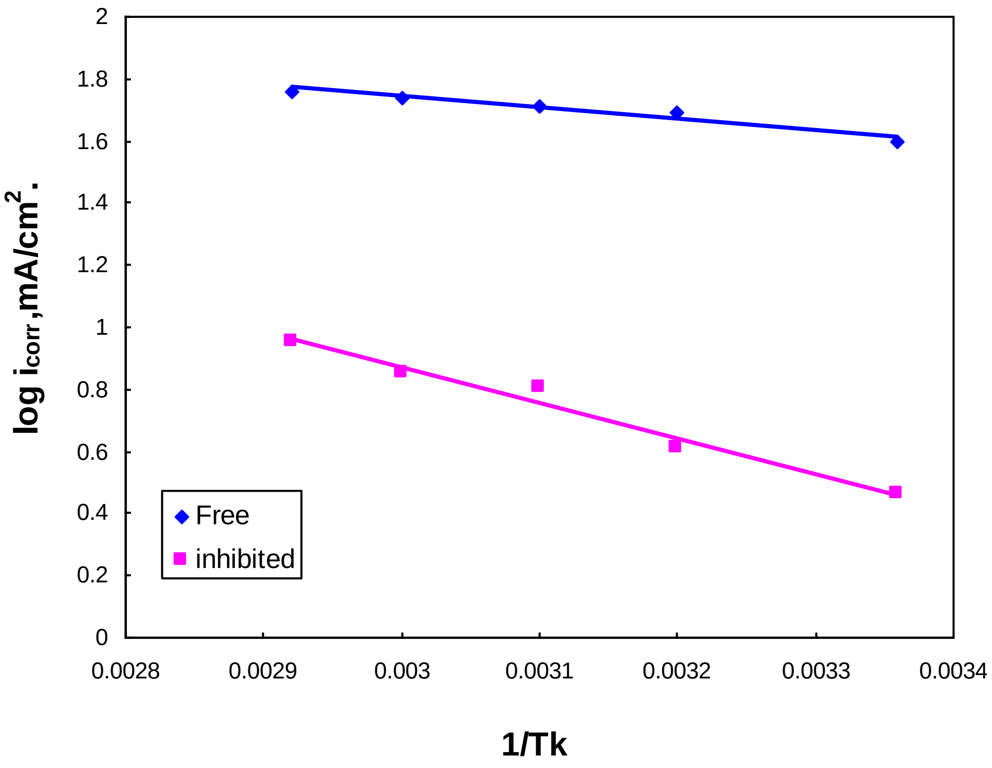

Fig. 5: Effect of temperature on aluminum corrosion rates in absence and inhibited acid**.**

3.5. Pitting corrosion

Potentiodynamic curves of aluminum electrode were traced in solutions of 3.5% NaCl devoid of and containing different concentrations of black mulberry extract. The aluminum potential was swept from hydrogen evolution potential toward anodic direction up to the pitting potential, at scanning rate of 1.0 mV/sec. No anodic oxidation peaks or any fine structures could be observed in the anodic scan. The pitting potential was taken as the potential at which the current increases sharply to a very high value. The pitting potential values are given in Table 3. Inspection of the data of the table reveals that the presence of *Morus nigra L.* extract shifts the pitting potential of aluminum to less negative potential. This result suggests that the extract increases the resistance of aluminum toward pitting corrosion. The shift in the pitting potential increases as the inhibitor concentration is increased.

Table 3: Values of pitting potential E_{pit} of aluminum in free and inhibited in 3.5% NaCl solutions

Con, ppm	**0**	**200**	**500**	**1000**	**2000**
E_{pit}, mV	-752	-650	-533	-500	-450

Conclusion

1. The Morus nigra L. extract acts as a good inhibitor for corrosion of aluminum in 2.0M HCl solution. The IE increases with increasing extract concentration.
2. The inhibition action is performed via adsorption of the extract compounds on aluminum surface. The adsorption process is spontaneous and follows Langmuir adsorption isotherm.
3. The presence of the Morus nigra L. extract increases the activation energy of the corrosion reaction.
4. The adsorption process is physical in nature.
5. The Morus nigra L. provide some protection against pitting corrosion of aluminum in presence of chloride ions. The degree of protection increases with increasing extract concentration.

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