



SAFFRON EXTRACTS AS ENVIRONMENTALLY SAFE CORROSION INHIBITORS FOR ALUMINIUM DISSOLUTION IN 2M HCl SOLUTION

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The inhibitive effect of aqueous extract of *Saffron* leaves toward the corrosion of aluminium in 2 M HCl solution has been investigated by weight loss and electrochemical polarization study. The extract functions as a good inhibitor. The inhibition efficiency increased with extract concentrations. The plant extract behaves as cathodic-type inhibitor. Surface morphology has been analysed using SEM. The adsorption of the extract components on the aluminium surface follows Temkin adsorption isotherm.

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Introduction

Pure aluminium and its alloys find a tremendous spectrum of technological and industrial applications, especially in aerospace and household industries, owing to the combination of their characteristics of low density (consequently light weight), low cost, mechanical strength, good appearance and corrosion resistance. Therefore, the economic importance of such materials has attracted many researchers to spot light on their corrosion behaviour in different corrosive environments.¹⁻⁸

Usually, a thin, compact, passive, invisible, non-porous, adherent, and instantly self-renewing film is formed on aluminium surface upon exposure to ambient atmosphere or aqueous solutions.⁹ In spite of such great walls of aluminium citadel, corrosion is the silent enemy of such metals, attacks. It is uncontested that the corrosion of aluminium is due to dissolution of such film mainly when exposed to high concentration of acids, bases, or neutral solutions containing pitting agents such as chloride ions. However, improvements in such materials, particularly in the development of suitable methods for the protection was achieved by using inhibitors.

Inorganic inhibitors, which are mainly oxidizing agents, such as chromates, iodates, and tungstates, act as anodic inhibitors and their metallic atoms are enclosed in the film improving its corrosion resistance.¹⁰⁻¹² Lanthanide salts, which have a low toxicity, were used in the inhibition of aluminium corrosion.^{13, 14} Unfortunately, these compounds are very expensive. Although many of these tested compounds have high inhibition efficiencies, the usage of them still undesired due to their adverse effects on human beings, environment, as well as their high costs.

In the recent years, there is an increasing awareness of environment and green chemistry. Therefore, many experiments were conducted to use the eco-friendly

substances as corrosion inhibitors, instead of the harmful synthetic chemicals.¹⁵⁻¹⁹ Some investigation have in recent times been made into the corrosion inhibiting properties of natural products of plant origin and have been found to generally exhibit good inhibition efficiencies.²⁰⁻⁴⁰ The significance of this area of research is primarily due to the fact that natural products are environmentally friendly and ecologically acceptable. Nevertheless, the known hazardous effects of most synthetic organic inhibitors and the need to develop cheap, non-toxic, and environmentally benign processes have now made researchers to focus on the use of natural products.

In fact, the first patented corrosion inhibitors used were either natural products, such as flour, yeast, etc.⁴¹ or by-products of food industries for restraining iron corrosion in acid media.⁴² El-Etre⁴³ studied the application of natural honey as corrosion inhibitor for copper in aqueous solution. Kliskic et al. analyzed aqueous extract of *Rosmarinus Officinalis*⁴⁴ as corrosion inhibitor for aluminium alloy corrosion in chloride solution. El-Hosary et al.¹⁹ studied the corrosion inhibition of aluminium and zinc in HCl solution using *Hibiscus Subdariffa* extract. Muller⁴⁵ investigated the effect of saccharides (reducing sugars, fructose and mannose) on the corrosion of aluminium and zinc in alkaline media. A series of reports have been highlighted on studies of natural products (exudates gums) as corrosion inhibitors of mild steel and aluminium in acidic and basic media.^{17,18,24, 46}

Available, inexpensive, non-toxic, environmentally safe and relatively high inhibition efficiency are conditions that must be satisfied by a good inhibitor. This paper will study the inhibitive effect of aqueous extract of *Saffron* plant leaves on the aluminium corrosion in 2 M HCl solution using weight loss, open circuit potential (OCP), and electrochemical polarization (Tafel, Linear polarization) measurements.

SEM investigations were used to explore the morphological behaviour of aluminium in the presence of *Saffron* extract. In addition, the adsorption mode of components extract will be studied.

Experimental section

Plant classification and composition

The binomial name of *Saffron* is *Crocus Sativus* L. Its scientific classification is shown in Table 1. On the other hand, the proximate analysis of *Saffron* is presented in Table 2. In addition, chemical structures of some *Saffron* extract components are found in Table 3.

Table 1. Scientific classification of *Saffron*.

Kingdom	Plantae
(unranked)	Angiosperms
(unranked)	Monocots
Order:	Asparagales
Family:	Iridaceae
Subfamily:	Crocoideae
Genus:	<i>Crocus</i>
Species:	<i>C. sativus</i>

Table 2. Proximate analysis of *Saffron*.

Components	Mass %
Water-soluble components	53.0
(i) Gums	10.0
(ii) Pentosans	8.0
(iii) Pectins	6.0
(iv) Starch	6.0
(v) α -Crocin	2.0
Other carotenoids	1.0
Lipids	12.0
(i) Non-volatile oils	6.0
(ii) Volatile oils	1.0
Inorganic matter ("ash")	6.0
(i) HCl-soluble ash	0.5
Protein	12.0
Water	10.0
Fiber(crude)	5.0

Preparation of plant extract

A sample from crude *Saffron* leaves was soaked in triply distilled water and the plant extract was concentrated in 1 L, and found to contain 1 mg ml⁻¹ of the plant compounds (1000 ppm).


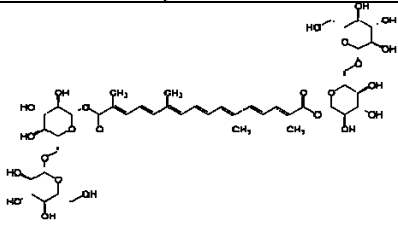
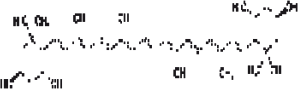
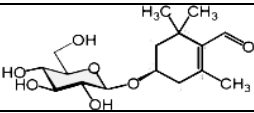
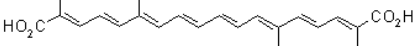
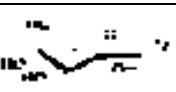
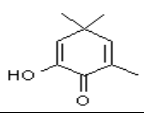

Preparation of specimens

Measurements were made on ultrapure aluminium (99.99%). The samples were polished successively using 1/0 to 6/0 emery papers, degreased with acetone and washed by distilled water before use.

Electrolyte

The solutions used were made of AR grade hydrochloric acid. Appropriate concentrations of acids were prepared by using triple distilled water.

Table 3. Chemical structures of some *Saffron* extract components.

Name	Structure
Safranal	
Crocin	
Zeaxanthin	
Picrocrocin	
Crocetin	
Decyl glucoside	
2-Hydroxy-4,4,6-trimethyl-2,5-cyclohexadien-1-one	
Lycopene	

The concentration range of the inhibitor (plant extract) employed was varied from 200 to 800 ppm and the electrolyte volume used was 100 ml, at 25 ± 1 °C.

Weight loss method

Weight loss of rectangular aluminium specimens of size (5 cm x 3 cm x 0.1 cm) in duplicate immersed in 100 ml of electrolyte with and without addition of different concentrations of plant extract was determined after 30 min at room temperature (25 ± 1 °C). The percentage inhibition efficiency (IE) was calculated from,

$$IE(\%) = \frac{W_{un} - W_{inh}}{W_{un}} 100 \quad (1)$$

where W_{un} is the weight loss of the sample in the blank solution and W_{inh} the weight loss of the sample in presence of the additive.

Table 4. Variation of polarization parameters for aluminium in 2 M HCl solution at (25 ± 1 °C) with extract addition.

Technique	Inhibitor dose, ppm	E_{corr} , mV	B_{as} , V/d	B_{cs} , V/d	I_{corr} , $\mu\text{A cm}^{-2}$	R_p , Ω	CR, mpy	IE, %
Tafel	Blank	-847	0,3879	0.2573	1114	—	1.433 x 103	—
	600	-793.6	0.3628	0.3159	171.2	—	220.3	84.6
LP	Blank	-856	0.100	0.100	740.5	14.66	952.9	—
	600	-805.2	0.100	0.100	158.8	68.37	204.4	78.5

Electrochemical measurements

A three electrode cell assembly consisting of aluminium coupon of the size (1.0 cm x 1.0 cm x 0.1 cm) embedded in specimen holder as working electrode (WE), a platinum sheet as counter electrode (CE) and saturated calomel electrode (SCE) as reference electrode (RE) containing 100 ml of electrolyte was used for electrochemical measurements at 25 ± 1 °C.

Open circuit potential (OCP) measurements

The OCP of aluminium electrode/2 M HCl and its potential in inhibited solution was followed as a function of immersion time till steady state values were reached. All potentials were measured referred to saturated calomel electrode (SCE) using EG & G (Princeton Applied Research) Model 352/352 potentiostat/galvanostat interfaced to an IBM ps/3 computer, the software is V, -5.36.

Polarization measurements

(i) Tafel

Tafel polarization curves were recorded by using computer controlled electrochemical system mentioned before. The potential increased with the speed of 5 mV s⁻¹. Experiments were carried out from -1150 to -450 mV potential ranges. Before recording the polarization curves, the (WE) was maintained at its corrosion potential for 10 min until a steady state was reached.

(ii) Linear polarization (LP)

Polarization resistance (R_p) was measured using the linear polarization method by potential scanning over the range of E_{corr} ; ±20 mV at 1 mV/s. The R_p values were obtained from the current-potential plot, for aluminium in 2 M HCl in the absence and presence of 600 ppm concentrations of the inhibitor at room temperature.

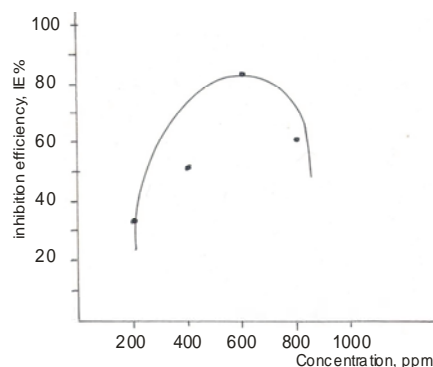
Surface analysis

The test coupons of the size 1 x 1 cm² were exposed to 100 ml of 2 M HCl having 600 ppm plant extract for 1 h at 25 ± 1 °C and washed with distilled water. After washing, specimens were dried, and examined for their topographical features using scanning electron microscope (SEM).

Results and Discussion

Weight loss measurements

The weight losses (gravimetric measurements) for aluminium in 2 M HCl containing different concentrations of the leaves of *Saffron* extract ranging from 200-800 ppm indicate that the inhibition efficiency increases as the concentration of the added extract is increased up to 600 ppm that gave 84% efficiency and then decreases after that, Fig. 1. The observed inhibition action of the *Saffron* extract could be attributed to the adsorption of its components on aluminium surface. The formed layer, of the adsorbed molecules, isolates the aluminium surface from the aggressive Cl⁻ ions medium leading to decrease in weight loss. Fig. 2 represents the variation in inhibition efficiency IE% with immersion time 30-90 min using the optimum dose (600 ppm) of *saffron* extract. Good performance behaviour of our inhibitor over 11/2 h (90 min) processing.

**Figure 1.** Variation of inhibition efficiency IE% with inhibitor concentration

To study the adsorption behaviour of *Saffron* extract on aluminium surface in 2 M HCl medium, the adsorption isotherm must be defined. The nature of corrosion inhibition has been deduced in terms of the adsorption characteristics of the inhibitor.⁴⁷ The metal surface in aqueous solution is always covered with adsorbed water dipoles. Therefore, the adsorption of the inhibitor molecules from aqueous solution is a quasi substitution process.^{48,49} Therefore, the relation between the concentration of the extract (c) and the fraction of aluminium surface covered by adsorbed components (θ) was obtained. Because the inhibition action is postulated as a result of the adsorption, (θ) is directly related with the inhibition efficiency (IE) and was calculated using the equation: (θ) = IE/100.

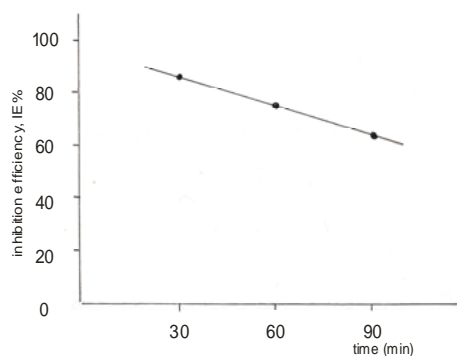


Figure 2. Effect of exposure time

Adsorption isotherm analysis

A graphic representation of the relationship between logarithm (extract concentration) and surface coverage (θ) is given in Fig. 3. Inspection of Fig. 3 reveals that a straight line was obtained fitting Temkin adsorption isotherm.

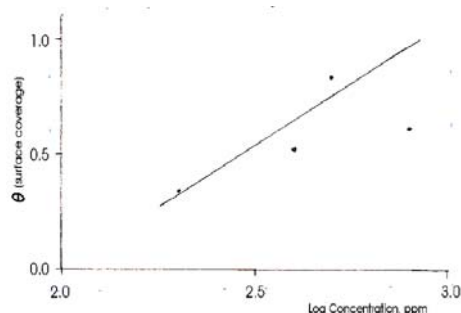


Figure 3. Temkin adsorption isotherm (θ) vs. $\log C$.

Open circuit potential studies

Potential Vs time plots for aluminium in 2 M HCl in absence and presence of (600 ppm) *Saffron* extract at room temperature (25 ± 1 °C) are shown in Fig. 4, curves (a) and (b) respectively. The curves indicated that in the presence of 600 ppm inhibitor, curve (b), the potential was shifted to less negative values. Whereas, the potential of a blank solution curve (a) was noticed to have more negative magnitudes.

Polarization measurements

Fig. 5 represents the anodic and cathodic Tafel polarization curves of aluminium electrode in solution of 2 M HCl alone and in the presence of 600 ppm inhibitor extracts concentration. Inspection of Fig. 5 reveals that the polarization curves are shifted towards less negative potentials and less current densities with inhibitor addition, curve (b). This behaviour indicates the inhibitive action of the added extract on aluminium corrosion in the acid solution. Various kinetic parameters, such as corrosion current (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a) and inhibition efficiency (IE %) are given in Table 4.

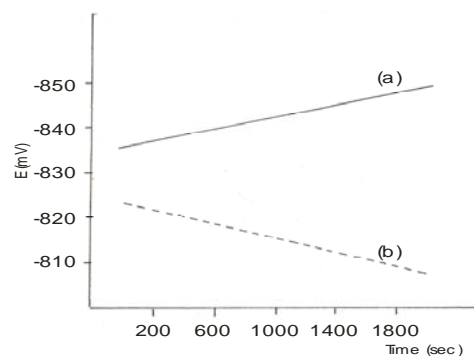


Figure 4. Potential vs. time plots for aluminum in 2 M HCl solution at (25 ± 1 °C): (a) blank, (b) 600 ppm inhibitor

The addition of plant extract does not change the value of anodic Tafel slope (β_a) significantly. Corrosion current of aluminium decreases much in the presence of 600 ppm inhibitor addition. Increase in cathodic Tafel slope (β_c) with plant extract dose applied indicates that *Saffron* inhibitor inhibits corrosion by inhibiting cathodic reaction by simply blocking the available surface area. The inhibitor molecules decrease the surface area of corrosion and cause only inactivation of the part of the surface with respect to the corrosion medium.

The corrosion rate (CR) is directly related to the R_p and can be calculated from it.⁵⁰ The R_p value can help us to assess the relative ability of a material to resist corrosion. Since R_p is inversely proportional to I_{corr} , so the materials with highest R_p (and thus the lowest I_{corr}) have the highest corrosion resistance. From all these facts, we can discuss and correlate between the data obtained from R_p and those computed from Tafel plots. Polarization parameters for aluminium corrosion in 2 M HCl and the presence of 600 ppm *Saffron* extract are shown in Table 3. It is observed that, in the presence of inhibitor, E_{corr} shifts to more positive values. Furthermore, the value of R_p increases, while the value of I_{corr} decreases with additive. From the data depicted in Table 4, it has been found that the addition of *Saffron* to aluminium in 2 M HCl enhances the corrosion inhibition efficiency (IE %).

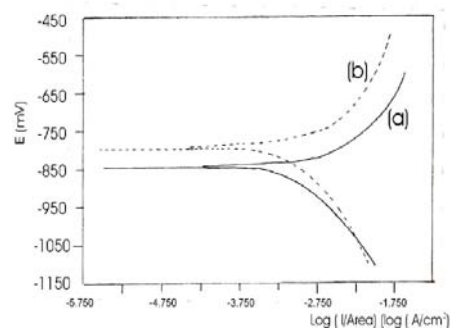


Figure 5. Polarization curves for aluminum in 2 M HCl solution: (a) blank, (b) 600 ppm inhibitor

SEM investigation

Scanning electron micrographs (SEM) of aluminium surface immersed in 2 M HCl (blank) and 2 M HCl containing 600 ppm plant extract are shown in Fig. 6.

A rough surface was noticed for aluminium immersed in 2 M HCl solution. In case of aluminium immersed in 2 M HCl with 600 ppm *Saffron* extract, a smooth surface was noticed and it is easily comparable with the polished surface. This shows that, this plant extract inhibits corrosion of aluminium in 2 M HCl solution.

Inhibition mechanism

The existing data show that most organic inhibitors get adsorbed on the metal surface by displacing water molecules and form compact barrier film.⁵¹ Availability of lone pairs and π (π) electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal, forming a coordinative covalent bond.⁵² The strength of chemisorption bond depends on the electron density on the donor atom of the functional group and also the polarizability of the group. Observation of the chemical structures of *Saffron* reveals that these compounds can adsorb on aluminium surface via the lone pairs of electrons present on their oxygen atoms.



Figure 6 (a)

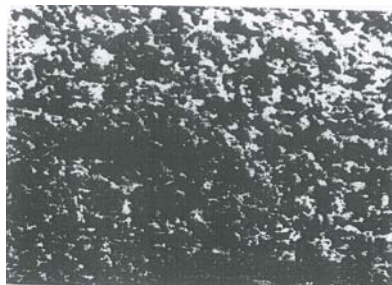


Figure 6 (b)

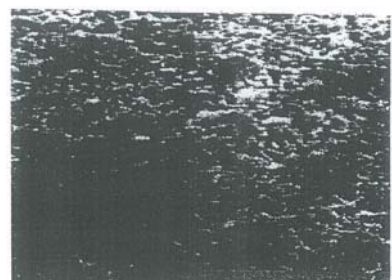


Figure 6 (c)

Figure 6. SEM graphs of aluminium (a) polished clean surface, (b) immersed in 2 M HCl solution, (c) immersed in 2 M HCl with 600 ppm of plant extract.

The adsorption of such compounds on the aluminium surface make a barrier for charge and mass transfer leading to decrease the interaction of the metal with the corrosive environment (2 M HCl). As a result, the corrosion rate of aluminium is decreased.

Conclusions

From the overall experimental results the following conclusions can be deduced:

The aqueous extract of *Saffron* (LV) acts as a good inhibitor for corrosion of aluminium in 2 M HCl solution.

The inhibition efficiency increases with increasing extract concentration and attain a maximum value of 84.6 % at 600 ppm.

Saffron acts as a cathodic inhibitor with modifying the hydrogen reduction mechanism.

The inhibitive action of extract was attributed to the adsorption of its components on aluminium surface.

The adsorption of extract components follows Temkin adsorption isotherm.

References

- Rozenfeld, I. L. , *Corrosion Inhibitors*, McGraw-Hill, New York, **1981**
- Tomcsanyi, L., Varga, K., Bartik, I., Horanyi G. and Maleczki, E., *Electrochim. Acta*, **1989**, *34*, 855.
- Stevanovic, R. M., Despic, A. R. and Drazic, D. M., *Electrochim. Acta*, **1988**, *33*, 397.
- Frers, S. E., Stefenel, M. M., Mayer, C. and Chierchie, T., *J. Appl. Electrochem.*, **1990**, *20*, 996.
- Maayta, A. K. and Al-Rawashdeh, N. A. F., *Corros. Sci.*, **2004**, *46*, 1129.
- Ovari, F., Tomcsanyi, L. and Turmezey, T., *Electrochim. Acta* **1988**, *33*, 323.
- Young, L., *Anodic Oxide Films*, Academic Press, New York, **1961**, p. 4-10.
- Saleh, M. R. and Shams El Din, A. M., *Corros. Sci.* **1981**, *12*, 688.
- Telegdi, J., Kalman, E. and H. Karman, H., *Corros. Sci.* **1992**, *33*, 199.
- Mahmoud, S. S., *Bull. Electrochem.* **1995**, *11*, 366.
- Hiuton, B. R.W., Arnott, D. R. and T. Ryan, *Mater. Forum* **1986**, *9*, 162 .
- Bazzi, L., Kertit, S. and Hamani, M., *Bull. Electrochem.* **1998**, *14*, 34
- Mansfeld, F., Lin, S., Kim, S. and Shih, H., *Corros. Sci.* **1987**, *27*, 997.
- Macdonald, D. D., *Electrochem. Soc.* **1993**, *138*, L 27.
- El-Etre, A.Y., *Corros. Sci.* **1998**, *40*, 1845.
- Bouyanzer, A., Hammouti, B. and Majidi, L., *Mater. Lett.* **2006**, *60*, 2840.
- El-Etre, A.Y., *Corros. Sci.* **2001**, *43*, 1031.
- El-Etre, A.Y., *Corros. Sci.* **2003**, *45*, 2485.
- El Hosary, A. A., Saleh, R. M. and Shams El-Din, A. M., *Corros. Sci.* **1972**, *12*, 897.

- ²⁰Ekpe, U. J., Ebenso, E. E., Ibok, U. J. and Afri, W., *Sci. Assoc.* **1994**, *37*, 13.
- ²¹Ebenso, E. E., Ekpe, U. J. and Afri, W., *J. Bio. Appl. Chem.* **1996**, *41*, 21.
- ²²Avwiri, G. O. and Igho, F. O., *Matter. Lett.* **2001**, *57*, 3705.
- ²³Ebenso, E. E., Ibok, U. J., Ekpe, U. J., Umoren, S., Jackson, E., Abiola, O. A., Oporka, N. C. and Martinez, S., *Trans. SAEST* **2004**, *39*, 117.
- ²⁴El-Etre, A. Y., Abdallah, M. and El-Tantawy, Z. E., *Corros. Sci.* **2005**, *47*, 385.
- ²⁵El-Etre, A. Y. and El-Tantawy, Z. E., *Port. Electrochem. Acta* **2006**, *24*, 347.
- ²⁶Umoren, S. A., Obot, I. B., Ebenso, E. E., Okafor, P. C., Ogbobe, O. and Oguzie, V., *Anti. Corros. Meth. Mater.* **2006**, *53*, 277.
- ²⁷Oguzie, E. E., Onuchukwu, A. I., Okafor, P. C. and Ebenso, E. E., *Pigm. Res. Technol.* **2006**, *35*, 63.
- ²⁸Oguzie, E. E., *Mater. Chem. Phys.* **2006**, *99*, 441.
- ²⁹Oguzie, E. E., *Corros. Sci.* **2007**, *49*, 1527.
- ³⁰Okafor, P. C., Ekpe, U. J., Ebenso, E. E., Umoren, E. M. and Leizou, K. E., *Bull. Electrochem.* **2005**, *21*, 347.
- ³¹Okafor, P. C., Ekpe, U. J., Ebenso, E. E., Oguzie, E. E., Umo, N. S. and Etor, A. R., *Trans. SAEST* **2006**, *21*, 82.
- ³²Okafor, P. C., Osabor, V. I. and Ebenso, E. E., *Pigm. Res. Technol.* **2007**, *35*, 299.
- ³³Okafor, P. C. and Ebenso, E. E., *Pigm. Res. Technol.* **2007**, *36*, 134.
- ³⁴Umoren, S. A., Obot, I. B., Ebenso, E. E., Okafor, P. C., Ogbobe, O., and Oguzie, E. E., *Anti. Corros. Methods Mater.* **2006**, *53*, 277.
- ³⁵Khuzaeu, V. U. and Aripova, S. F., *Chem. Nat. Compound* **2000**, *36*, 418.
- ³⁶Sangeetha, M., Rajendran, S., Sathiyabama, J., Krishnaveni A., Santhy, P., Manimaran, N., Shyamaladevi, B., *Port. Electrochim. Acta*, **2011**, *29*, 429.
- ³⁷Sirbharathy, V., Rajendran, S., Sathiyabama, J., *Int. J. Chem. Sci. Technol.*, **2011**, *3*, 108.
- ³⁸Syamala Devi, B., Rajendran, S., *Int. J. Chem. Sci. Technol.*, **2011**, *1*, 79.
- ³⁹Sangeetha, M., Rajendran, S., Muthu Megala T. S., and Krishnaveni, K., *Zast. Mater.*, **2011**, *52*, 35.
- ⁴⁰Antony, N., Benita Sherina, H., and Rajendran, S., *Int. J. Eng. Sci. Technol.*, **2010**, *2*, 2774
- ⁴¹Bablwin, J., *British Patent* 2327, **1895**.
- ⁴²Putilova, N., Balezin, S. A. and Barannik, V. P., *Metallic Corrosion Inhibitors* **1960**, (Pergamon Press, Oxford, London).
- ⁴³El-Etre, A. Y. and Abdallah, M., *Corros. Sci.* **2000**, *42*, 731.
- ⁴⁴Kliskic, M., Radosevic, J., Gudic, S. and Katolinic, V., *J. Appl. Electrochem.* **2000**, *30*, 823.
- ⁴⁵Muller, B., *Corros. Sci.* **2002**, *44*, 1583.
- ⁴⁶El-Etre, A. Y., *Appl. Surf. Sci.* **2005**, *252*, 8521.
- ⁴⁷Bentiss, F., Lagrenee, M., Traisnel, M., Mernari, B. and El-Attari, H., *J. Appl. Electrochem.* **1999**, *29*, 1073.
- ⁴⁸Rudresh, H. B. and Mayanna, S. M., *J. Electrochem. Soc.* **1977**, *124*, 340.
- ⁴⁹Bockris, J. O., Devanathan, M. A. V. and Muller, K., *Proc. Roy. Soc. London A* **1963**, *274*, 55.
- ⁵⁰Uhling, H. H. and Revie, R. W., *Corrosion and Corrosion control*, 3rd edition, Wiley, New York, **1985**.
- ⁵¹Muralidharan, S., Phani, K. L. N., Pitchumani, S., Ravichandran, S. and Iyer, S. V. K., *J. Electrochem. Soc.* **1995**, *142*, 1478.
- ⁵²Hackerman, N. and Hard, R. M., *Proc. Int. Congress. of Metallic Corrosion*, Butterworth, London, **1962**.

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