



CORROSION INHIBITION BY AN AQUEOUS EXTRACT OF *ALOE VERA* (L.) BURM F.(LILIACEAE)

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An aqueous extract of *Aloe vera* (L.) Burm f. (Liliaceae) has been used as a corrosion inhibitor in controlling corrosion of carbon steel immersed in sea water. Weight loss method reveals that 4ml of the extract provide 98% inhibition efficiency. The protective film has been analyzed using Fourier transform infrared (FTIR) spectroscopy and fluorescence spectroscopy. Electrochemical studies such as potentiodynamic polarization and alternating current impedance spectra have been used to find the mechanistic aspects of corrosion inhibition.

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aldehydes,¹² amines,^{13,14} amino acids,^{15,16} nitro compounds,^{17,18} amides,^{19,20} ester,^{21,22} thio compounds,^{23,24} phosphates,^{25,26} phosphonates,^{27,28} ketones^{29,30} and carboxylic acids.³¹⁻³³

The present work investigated the inhibition efficiency of an aqueous extract of plant material, *Aloe vera* (L.) Burm f. (Liliaceae) extract, in controlling corrosion of carbon steel (CS) immersed in sea water in the absence and presence of inhibitor, using mass loss method, analyzed the protective film by Fourier transform infrared (FTIR) spectroscopy and fluorescence spectroscopy, and proposed a suitable mechanism of corrosion inhibition, based on the results of the above studies and potentiodynamic polarization and the alternating current (AC) impedance spectra.

Introduction

Plant extracts have become important as environmentally acceptable, readily available and renewable source for wide range of inhibitors.¹ In general, the plant extracts are of inhibitors with high inhibition efficiency and of non toxicant. El-Etre et al. investigated Khillah extract² for the corrosion inhibition of SX 316 steel in acid media. Lawsonia extract³ was studied for effect against acid induced corrosion of metals. Opuntia extract⁴ was investigated for the corrosion of Aluminium in acid medium and vanillin⁵ for the corrosion of mild steel in acid media. Yan Li et al Berberine isolated an alkaloid from *Captis* studied for its anticorrosion effect for mild steel corrosion in H₂SO₄ medium⁶ Fabrizio Zucchi and Ibrahim Hashi Omar⁷ have found that *Papaia*, *Poinciana pulcherrima*, *Cassia occidentalis* and *Datura stramonium* seeds, *Calotropis procera*, *Azydracta indica* and *Auforpio turkiale* sap are useful as acid corrosion inhibitors. Sethuraman and Bothi raja⁸ have studied the acid extract of *Datura metel* as corrosion inhibitor for mild steel in acid medium. Quinine⁹ has been studied for its anticorrosive effect of carbon steel in 1 M HCl by Mohamed Ismail Awad. Anthony et al. has studied the effect of caffeine against chloride corrosion of carbon steel.¹⁰ There are many methods by which corrosion can be controlled one such method is the use of inhibitors. These inhibitors when added is small quantity, decrease the rate of corrosion. Corrosion inhibitors usually contain polar groups with atoms such as nitrogen, sulphur and oxygen. Correspondingly inhibitors include a wide list of organic and inorganic compounds¹¹ containing the functional groups such as

Experimental

Preparation of plant extract

An aqueous extract was prepared by grinding 10 g of fresh extract of aloe vera (mannose-6-phosphate) gel, filtering and making up to 100 ml using double distilled water.

Preparation of specimens

Carbon steel specimens (0.0267% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron) of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

Weight loss method

Relevant data of sea water used in the study, are given in Table1. Three mild steel specimens were immersed in 100 ml of sea water containing various concentrations of the inhibitor for one day. The weight of the specimens before and after immersion were determined using Shimadzu balance, model AY 62. The corrosion products were cleansed with Clarke's solution.³⁴

Table 1. Parameters of seawater (Cuddalore district, Tamilnadu, India)

Parameter	Value
pH	8.1
Chloride	17,600 ppm
Sulphate	3254 ppm
Total hardness	800 ppm
Calcium	160 ppm
Magnesium	100 ppm

The inhibition efficiency (IE , %) was then calculated using the equation

$$IE = 100 \left(1 - \frac{W_2}{W_1} \right) \quad (1)$$

where

W_1 = corrosion rate in the absence of the inhibitor

W_2 = corrosion rate in the presence of the inhibitors

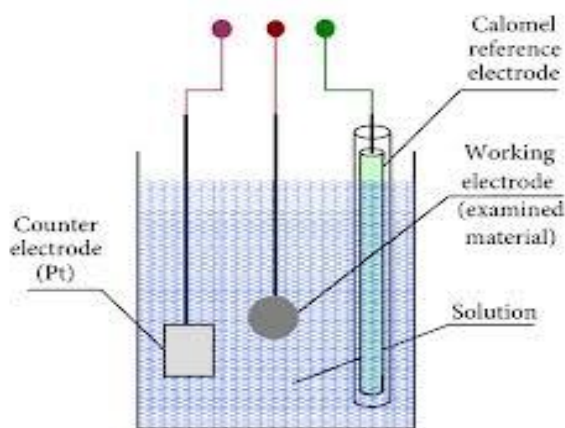
Surface Examination

The carbon steel specimens were immersed in various test solutions for a period of one day, taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by FTIR spectroscopic study.

FTIR Spectra

FTIR spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made in to pellets and FTIR spectra were recorded.

The fluorescence spectra of the film formed on the Carbon Steel samples recorded with a Hitachi F-4500 fluorescence spectrophotometer.



Scheme 1. Three electrode cell assembly. WE - working electrode, CE - counter electrode; Reference electrode - saturated calomel electrode

Potentiodynamic Polarization

The polarization studies were carried out in a three electrode cell consisting of mild steel as working electrode (WE), a platinum wire counter electrode (CE), and a saturated calomel electrode reference electrode were used for measurements³⁵. All the potential values reported here was VS SCE (Scheme1).

The working electrode was mechanically polished on various grades of emery sheet, rinsed with double distilled water, degreased with trichloroethylene. Potentiodynamic polarization curves were recorded using an H & CH electrochemical work station impedance analyzer model CHI 660A provided with iR compensation option. Polarization curve measurements were carried out at scan rate of 0.01 V s^{-1} . The exposed area (1 cm^2) was mechanically polished with a series of emery sheets of variable grade. The samples were washed thoroughly with double distilled water before insertion in the cell. During the polarization study, the scan rate was 0.01 V s^{-1} ; hold time at E_f was 0 s and quiet time was 2 s.

AC impedance measurements

The instrument used for polarization was used for AC impedance study also. The cell set up was the same as that had been used for polarization measurements. The real part and imaginary part of the cell impedance were measured in ohms at various frequencies. The values of charge transfer resistance, R_{ct} , and the double layer capacitance, C_{dl} were calculated.

$$C_{dl} = \frac{1}{2} \pi R_t f_{max} \quad (3)$$

where

R_s - Solution resistance,

f_{max} - maximum frequency.

AC impedance spectra were recorded with dc potential $E = 0 \text{ V}$, in the frequency range $1 \times 10^5 - 10 \text{ Hz}$, amplitude = 0.005 V , and quiet time = 2 s.

Result and Discussion

Weight loss studies

Table 1 shows the values of corrosion rates and inhibition efficiencies obtained from weight loss measurements of different concentrations of alo vera extract. 4 ml of the alo vera offered 98 % corrosion inhibition efficiency to carbon steel immersed in 100 ml sea water. When the concentration of alo vera was increased the inhibition efficiency decreased. This is due to the fact that when higher concentrations of alo vera are added the protective film Fe^{2+} -mannose-6-phosphate complex formed on the metal surface goes into the solution and thus destroying the protective film. It may be considered that the protective film formed may go into transpassive state, where the film is broken³⁶.

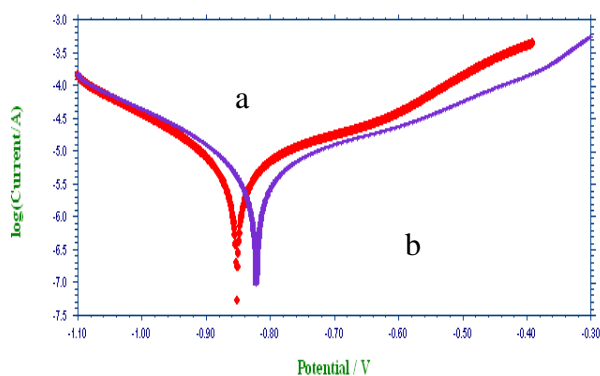
Table 2 – Corrosion rates(CR) of carbon steel immersed in sea water in the presence absence of inhibitors and the inhibition efficiencies (IE) obtained by weight loss method.

Inhibitor: Aloe vera; period of immersion: 1 day

Aloe vera extract, ml	Corrosion rate, mdd	Inhibition efficiency (IE), %
0	21.52	--
2	8.40	75
4	0.67	98
6	16.47	51
8	20.51	39

Analysis of polarization curves

The polarization study has been used to investigate the formation of protective film on metal surface³⁷⁻⁴¹. The polarization curves of carbon steel immersed in various solutions are shown in Fig 1. The corrosion parameters such as corrosion potential (E_{corr}), cathodic tafel slope and anodic tafel slope were determined from E vs $\log I$ plots Table 3. When carbon steel is immersed in sea water, the corrosion potential is -926 mV SCE. When 4 ml of aloe vera is added the corrosion potential is shifted towards the anodic side, (-882 mV SCE) indicating that the aloe vera controls the anodic reaction predominantly by forming Fe^{2+} - mannose-6-phosphate complex on the anodic sites of the metal surface. The Linear polarization resistance (LPR) value increases from 51.67×10^2 to 76.01×10^2 ohm cm^2 . This suggests that a protective film is formed on the metal surface. Further the corrosion current decreases from 7.963×10^{-6} A cm^{-2} to 5.229×10^{-6} A cm^{-2} . This suggests the inhibitive nature of this inhibitor system^{42,43}.

**Figure 1.** Polarization curves of carbon steel immersed in various test solutions: (a) Carbon steel immersed in sea water; (b) Carbon steel immersed in sea water + aloe vera 4 ml**Table 3.** Corrosion parameters of carbon steel immersed in various test solutions Inhibitor: aloe vera extract

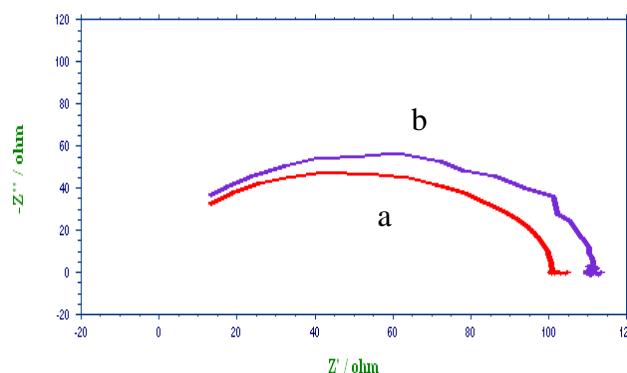
System	E_{corr} mV*	b_c mV**	b_a mV**	LPR Ohm cm^2	I_{corr} (A cm^{-2})
CS+ A	-926	153	247	51.67×10^2	7.9×10^{-6}
A + B	-882	153	226	76.01×10^2	5.2×10^{-6}

A= Sea Water, B= aloe vera 4ml,*mV vs SCE; **mV in one decade

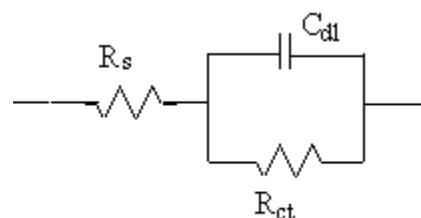
Analysis of AC Impedance spectra

AC impedance spectra have been used to detect the formation of the film formed on the metal surface. If a protective film is formed, the Charge transfer resistance increases and double layer capacitance value decreases⁴⁴⁻⁴⁶. The AC Impedance spectra of carbon steel immersed in various solutions are shown in Fig 2. The AC Impedance parameter, namely charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) are given in Table 4.

When carbon steel is immersed in aqueous solution containing sea water, the R_{ct} value is 88 ohm cm^2 and C_{dl} value is 1.027×10^{-7} F cm^{-2} . When the inhibitor is added the R_{ct} value increases from 88 ohm cm^2 to 98 ohm cm^2 and C_{dl} value decreases from 1.027×10^{-7} F cm^{-2} to 0.923×10^{-8} F cm^{-2} . The equivalent circuit diagram is shown in Scheme 1. This suggests that a protective film is formed on the metal surface of the metal. Further there is increase in impedance $\log(Z / ohm)$, value from 2.02 to 2.05 (derived from Bode plot shown in Fig 3.)

**Figure 2.** AC Impedance parameter of carbon steel immersed in various test solutions (Nyquist plots): (a) Carbon steel immersed in Sea water; (b) Carbon steel immersed in Sea water+ aloe vera 4 ml**Table 3.** AC Impedance parameter of carbon steel immersed in various test solution

System	Nyquist plot		Bode plot
	$R_{ct}, \Omega cm^2$	$C_{dl}, F cm^{-2}$	Impedance, $\log(Z/ohm)$
CS + A	88	1.02×10^{-7}	2.02
A + B	101	99.23×10^{-8}	2.05

**Scheme 2.** Equivalent electrical circuit diagram, R_s = solution resistance, R_{ct} = Charge transfer Resistance C_{dl} = Double layer capacitance

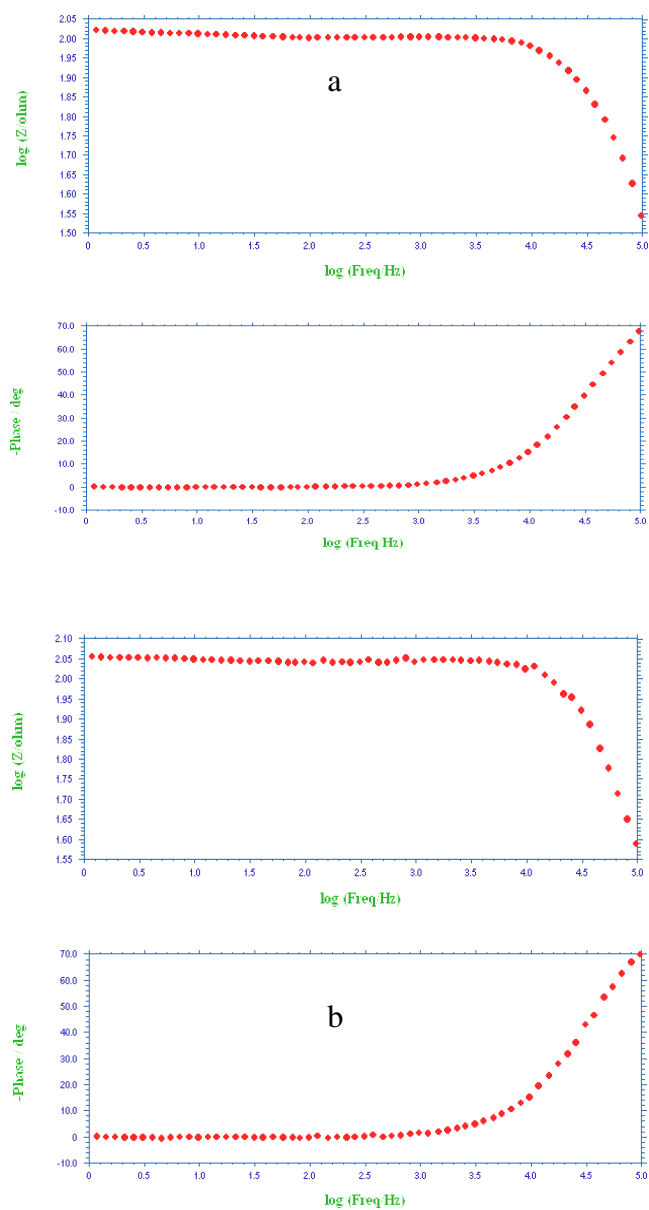
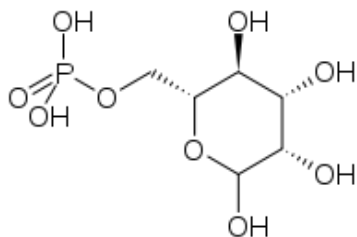


Figure 3. Bode plot of carbon steel immersed in various solutions, (a) Carbon steel immersed in sea water; (b) Carbon steel immersed in Sea water+ aloe vera 4 ml

Fourier Transfer Infrared Spectra

The main constituent of aloe vera extract is mannose-6-phosphate⁴⁷. The structure of mannose-6-phosphate is shown in Scheme 3. It contains phosphate group, hydroxyl group and ring oxygen.



Scheme 3. Mannose-6- phosphate

The aloe vera extract was evaporated to dryness to a solid mass. Its FTIR spectrum is shown in Fig 3a. The $-\text{OH}$ stretch appeared at 3410 cm^{-1} . The aliphatic $-\text{CH}$ stretching frequency appeared at 2936 cm^{-1} . The ring oxygen stretching frequency appeared at 1237 cm^{-1} . Phosphate stretching frequency appeared at 1060 cm^{-1} ⁴⁸⁻⁴⁹.

The FTIR spectrum of the protective film formed on the surface of the metal after immersion in the aqueous solution containing sea water and sea water containing 4ml of aloe vera is shown in Fig 3b. It is found that the $-\text{OH}$ stretch has shifted from 3410 cm^{-1} to 3433 cm^{-1} . The aliphatic $-\text{CH}_2$ stretching frequency shifted from 2936 cm^{-1} to 2943 cm^{-1} . Phosphate stretching frequency shifted from 1060 cm^{-1} to 1100 cm^{-1} . The ring oxygen stretching frequency shifted from 1237.20 cm^{-1} to 1237.92 cm^{-1} . It is inferred that the active principle has coordinated with through the oxygen atom of P-O groups, OH group and ring oxygen resulting in the formation of Fe^{2+} -mannose -6-phosphate complex.

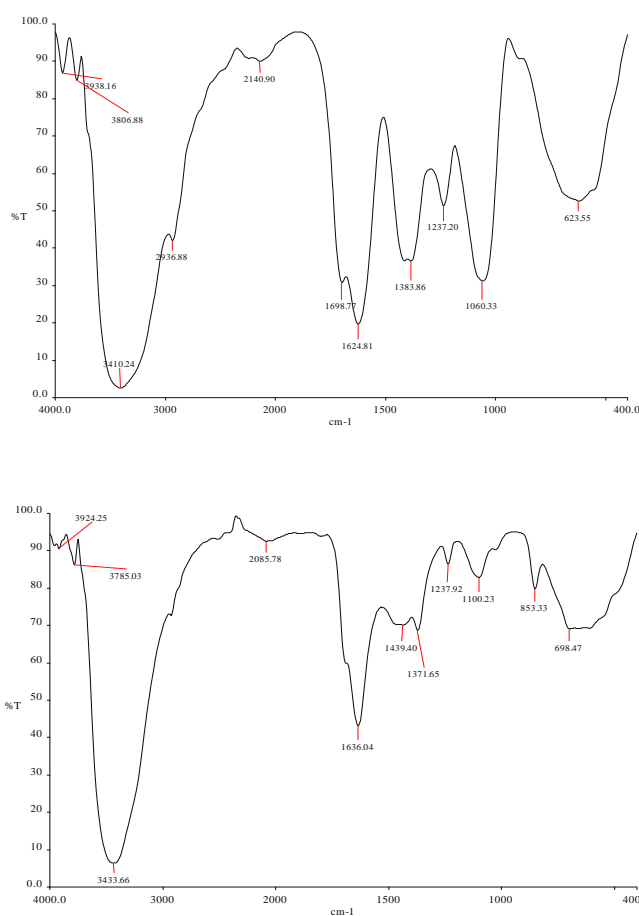


Figure 4. FTIR spectra: (a) Carbon steel immersed in Sea water (b) Carbon steel immersed in Sea water + Aloe vera 4 ml

UV-Visible adsorption spectra

The UV-Visible adsorption spectrum of aqueous solution of aloe vera is shown in Fig 5a. Peaks appear at 255 nm, 266 nm, 298 nm and 353 nm. When the Fe^{2+} (Freshly prepared $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ Solution) is added to the aqueous solution of aloe vera peak appear at 227 nm⁵⁰. This is due to Fe^{2+} - mannose-6-phosphate complex formed in solution.

Fluorescence spectra

The fluorescence spectrum ($\lambda_{ex} = 227$ nm) of the solution containing aloe vera extract and Fe^{2+} is shown in Fig 6a. A peak appears at 252 nm. This is due to Fe^{2+} -mannose-6-phosphate complex formed in solution. The fluorescence spectrum ($\lambda_{ex} = 227$ nm) of the film formed on the surface of the metal after immersion in the sea water and 4ml of aloe vera extract is shown in Fig 6b. The peak appeared at 252 nm confirming the presence of Fe^{2+} -aloe vera extract complex formed on the metal surface⁵¹.

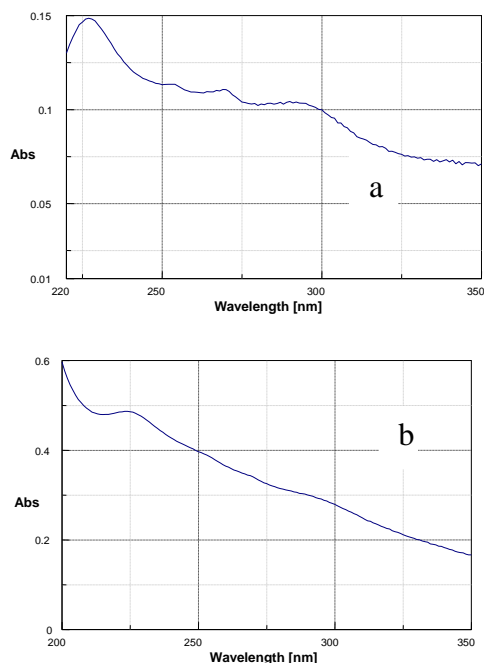


Figure 5. UV-spectra, (a) carbon steel immersed in sea water (b) film formed on metal surface after immersion solution containing sea water + aloe vera 4 ml

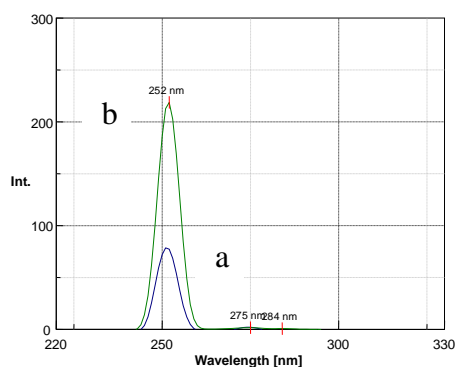


Figure 6. Fluorescence spectra, a) sea water; b) sea water + 4ml aloe vera extract

Conclusions

The main constituent of the aqueous extract of aloe vera is mannose-6-phosphate. An aqueous extract of aloe vera has excellent IE in controlling corrosion of carbon steel in aqueous solution containing sea water. The protective film consists of Fe^{2+} -aloe vera complex. It is found to be UV-fluorescent. The formulation controls the anodic reaction predominately.

References

- Tamer Soror, Y., *Eur. Chem. Bull.*, **2013**, 2(4), 150-153.
- El-Etre, A. Y., *Appl. Surf. Sci.*, **2005**, 252, 8521.
- El-Etre, A. Y., Abdallah, M., El-Tantawy Z. E., *Corros. Sci.*, **2005**, 47, 385.
- El-Etre, A.Y., *Corros. Sci.*, **2003**, 45, 2485.
- El-Etre, A.Y., *Corros. Sci.*, **2001**, 43, 1031.
- Yan Li., Peng Zhao., Qiang Liang., Baorong Hou, *Appl. Surf. Sci.*, **2005**, 252, 1245.
- Fabrizio Zucchi., Ibrahim Hashi Omar., *Surf. Tech.*, **1985**, 24, 391.
- Sethuraman, M. G., Bothi Raja, P., *Pigm. Res. Tech.*, **2005**, 34, 327.
- Mohamed Ismail Awad., *J. Appl. Electrochem.*, **2006**, 36, 1163.
- Noreen Anthony, E., Malarvizhi, P. Maheshwari, Rajendran, S., Palaniswamy, N., *Indian. J. Chem. Technol.*, **2004**, 11, 346.
- Manivannan, M., Rajendran, S., and Suriya Prabha, A., *Eur. Chem. Bull.* **2012**, 1(8), 317-29; Pandiarajan, M., Rajendran, S., Sathiyabama, J., Lydia Christy, J., Jeyasundari, J., Prabhakar, P., *Eur. Chem. Bull.* **2013**, 2(1), 1-8; Saranya, R., Rajendran, S., Krishnaveni, A., Pandiarajan, M., and Nagalakshmi, R., *Eur. Chem. Bull.*, **2013**, 2(4), 163-170; Nagalakshmi, R., Rajendran, S., Sathiyabama, J., Pandiarajan, M., and Lydia Christy, J., *Eur. Chem. Bull.*, **2013**, 2(4), 171-179; Mary Anbarasi, C., Rajendran, S., Pandiarajan, M. and Krishnaveni, A., *Eur. Chem. Bull.*, **2013**, 2(4), 197-207.
- Abdallah, M., Zaafarany, I., Fouda, A. S., *J. Mater. Eng. Perform.*, **2012**, 21(6), 995; Feng, Y., Qi, X., Jian, H.-L., Sun, R.-C., Jiang, J.-X., *Bio Resources.*, **2012**, 7(3), 3755.
- Kashkovskiy, R.V., Kuznetsov, Y., Kazansky, L. P., *Corros. Sci.*, **2012**, 64, 126.
- Hosseini, S. M. A., Salari, M., Jamalizadeh, E., Jafari, A. H., *Corros.*, **2012**, 68(7), 600.
- Gomma, G. K., Wahdan, M. H., *Mater. Chem. Phys.*, **1994**, 39(2), 142; Gowri, S., Sathiyabama, J., Rajendran, S., and Angelin Thangakani, J., *Eur. Chem. Bull.*, **2013**, 2(4), 214-219.
- Liu, P., Gao, L., Zhang, D., *J. Chin. Soc. Corros. Prot.*, **2012**, 32(2), 163; Gowri, S., Sathiyabama, J., Rajendran, S., *Eur. Chem. Bull.*, **2012**, 1(11), 470-476.
- Jayateertha, N.S., Hayavadana, N., *Res. J. Pharm. Biol. Chem. Sci.*, **2012**, 3(2), 614.
- Fernando, I. R., Daskalakis, N., Demadis, K. D., Mezei, G., *New. J. Chem.*, **2010**, 34(2), 221.
- Sliwa, A., Dive, G., Marchand-Brynaert, J., *Chem. - Asian J.*, **2012**, 7(2), 425.
- Gopiraman, M., Selvakumaran, N., Kesavan, D., Karvembu, R., *Progress Org. Coatings.*, **2012**, 73(1), 104.
- Baek, S.-Y., Kim, Y.-W., Chung, K.-W., Yoo, S.-H., *Appl. Chem. Engg.*, **2011**, 22(4), 367.
- Kalendová, A., Veselý, D., Sapurina, I., Stejskal, J., *Progress Org. Coat.*, **2008**, 63(2), 228.
- Bouklah, M., Ouassini, A., Hammouti, B., El Idrissi, A., *Appl. Surf. Sci.*, **2006**, 252(6), 2178.
- Musa, A.Y., Mohamad, A. B., Kadhum, A. A. H., Takriff, M.S., Ahmoda, W. *J. Ind. Eng. Chem.*, **2012**, 18(1), 551.
- Michael, J., Franklin, David C., White, Hugh, S., Isaacs, *Corros. Sci.*, **1992**, 33(2), 251.
- Sumanlata, Chaudhary, R. S., *Indian. J. Chem. Technol.*, **2008**, 15, 364.
- Papadaki, M., Demadis, K. D., *Comments Inorg. Chem.*, **2009**, 30(3-4), 89; Kavipriya, K., Rajendran, S., Sathiyabama, J. and Suriya Prabha, A., *Eur. Chem. Bull.*, **2012**, 1(9), 366-374.

- ²⁸Benabdellah, M., Dafali, A., Hammouti, B., Aouniti, A., Rhomari, M., Raada, A., Senhaji, O., Robin, J. J., *Chem. Eng. Commun.*, **2007**, *194*(10), 1328.
- ²⁹Ateş, E., Kizilcan, N., *Pigment Resin Technol.*, **2012**, *41*(4), 210.
- ³⁰Sherif, E. M., Park, S.-M., *Electrochim. Acta.*, **2006**, *51*(7), 1313.
- ³¹Herrag, L., Chetouani, A., Elkadiri, S., Hammouti, B., Aouniti, A., *Port. Electrochim. Acta.*, **2008**, *26*(2), 211.
- ³²Quartarone, G., Battilana, M., Bonaldo, L., Tortato, T., *Corros. Sci.*, **2008**, *50*(12), 3467.
- ³³Eddy, N. O., Abasiokong, B.O., *J. Corros. Sci. Engg.*, **2006**, 10.
- ³⁴Wranglen, G., *Introduction to corrosion and protection of metals, London: Chapman & Hall* **1985**, 236.
- ³⁵Vijaya, N., Peter Pascal Regis, A., Rajendran, S., Pandiarajan, M., and Nagalakshmi, R., *Eur. Chem. Bull.* **2013**, *2*(5), 275-278.
- ³⁶Sathyabama, J., Susai R., Arokia, S. J., John, A. A., *Indian. J. Chem. Technol.*, **2008**, *15*, 462.
- ³⁷Nagalakshmi, R., Rajendran, S., Sathiyabama, J., Pandiarajan, M., Lydia Christy, J., *Eur. Chem. Bull.*, **2012**, *1*(17), 238.
- ³⁸Sahayaraja, A., Nagalakshmi, R., Rajendran, S., Angelin Thangakani, J., Pandiarajan, M., *Eur. Chem. Bull.*, **2012**, *1*(3), 130.
- ³⁹AgilaDevi, S., Rajendran, S., Jeyasundari, J., Pandiarajan, M., *Eur. Chem. Bull.*, **2013**, *2*(2), 503.
- ⁴⁰Rajendran, S., Sridevi S. P., Anthony, N., John Amalraj, A., Sundaravadevelu, N., *Anti Corros. Methods Mater.*, **2005**, *52*, 102.
- ⁴¹Felicia Rajammal Selvarani, Santhanalakshmi, S., Wilson sahayaraja, J., John Amalraj, A., and Rajendran, S., *Bull. Electrochem.*, **2004**, *20*, 561.
- ⁴²Agnesia Kanimozhi, S., Rajendran, S., *Int. J. Electrochem. Sci.*, **2009**, *4*, 353.
- ⁴³Shymala Devi, B., Rajendran, S., *Eur. Chem. Bull.*, **2012**, *1*(5), 150.
- ⁴⁴Pandiarajan, M., Prabhakaran, P., Rajendran, S., *Eur. Chem. Bull.*, **2012**, *1*(7), 238.
- ⁴⁵Rajendran, S., Mary Reenkala., Noreen Anthony., and Ramaraj, R., *Corros.Sci.*, **2002**, *44*(10), 243.
- ⁴⁶Mary anbarasi, C., Rajendran, S., *J. Electrochem. Sci. Eng*, **2012**, *2*(1), 1.
- ⁴⁷www.nature4science.com/AloeVera/1_DescriptionofAloeVera.pdf
- ⁴⁸Silverstein, R. M., Bassler, G. C., Morrill, T. C., *Spectroscopic Identification of organic compound, New York, NY, John Wiley and Sons* **1986**, 95.
- ⁴⁹Vinothkumar, K. P., Sankaranarayanan, M., Rexin Thusnavis, G., *J. Mater. Environ. Sci*, **2010**, *1*(2), 1.
- ⁵⁰Rajendran, S., Shanmugapriya, S., Rajalakshmi, T., and Amal Raj, A. J., *Corros.*, **2005**, *61*, 685.
- ⁵¹Yesu Thangam, Y., Kalanithi, M., Mary Anbarasi, C., Rajendran, S., *Arab. J. Sci. Eng.*, **2009**, *34*(2C), 49.

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