Pelagia Research Library

Der Chemica Sinica, 2012, 3(5):1252-1259

ISSN: 0976-8505
CODEN (USA) CSHIA5

Inhibition effect of vanillideneanthranilic acid on the corrosion of aluminium in 1.0 N NaOH

[1]T. Umasankareswari and [2]T. Jeyaraj

[1]P.G. and Research Department of Chemistry, Bishop Heber College (Autonomous), Trichirappalli – 620017. (INDIA)
[2]P.G. and Research Department of Chemistry, Jamal Mohamed College, Trichirappalli – 620017. (INDIA)

ABSTRACT

The inhibition effect of vanillideneanthranilic acid on the corrosion behaviour of commercial aluminium in 1.0 N NaOH as corrosion medium was investigated by mass loss , potentiodynamic polarisation and electrochemical impedance measurement methods and SEM technique . It was concluded that the inhibition efficiency increased with the increasing concentration of the inhibitor. The maximum inhibition efficiency was found to be 59.25% at 30° C. The investigation of adsorption isotherms indicate that the inhibitor fit Langmuir and Temkin isotherms, fairly well. The phenomenon of physisorption is attributed to the values of E_a, Q_{ads} *and* $\Delta G°_{ads}$ *. The potentiodynamic polarisation results reveal that the inhibitor act as a mixed type inhibitor.*

Keywords: Vanillideneanthranilic acid, tetrabutylammonium bromide, anodic control, physisorption, surface morphology.

INTRODUCTION

Amongst various types of anode materials, aluminium exhibits a high theoretical energy density (8.10W h/g) combined with a high negative standard potential (-1.67 V vs. SHE) [1]. Additional advantages are its low production cost and the existence of a large base for manufacture and distribution. Also the low atomic mass of aluminium and its ability to transfer three electrons per atom, make the metal an attractive anode material for power sources with high energy densities[2]. However it undergoes substantial self-corrosion and gasing in alkaline solution. Consequently there is coulombic loss on discharge and fuel loss during stand by[3,4]. Therefore alkaline corrosion of aluminium, corrosion has to be stopped . Although there are numerous options for controlling the corrosion of metals, the use of inhibitors , with heteroatoms such as N and O along with aromatic rings, is one of the best methods of protecting metals against corrosion [5 -7] Literature survey reveals that the Schiff bases inhibit the corrosion through their ability of getting adsorbed on the metal surface by interaction with π-electrons of the aromatic rings, and the azo methine group. Some Schiff base compound have recently been reported as effective corrosion inhibitors for mild steel [8,9] in various aqueous solutions.

MATERIALS AND METHODS

Commercially pure aluminium samples, were used for preparing aluminium coupons for mass loss and electrochemical studies . The corrosion medium, 1.0 N NaOH solution, was prepared from analytical reagent grade NaOH (MERCK) and double distilled water.Tetrabutylammonium bromide (TBAB) was used as received. The inhibitor, vanillideneanthranilic acid ,was prepared according to the procedure reported [10].

WEIGHT LOSS STUDY

Rectangular specimens of aluminium, having the dimension 2.0 x 2.0 x 0.03 cm and containing a small hole of about 1mm diameter near the upper edge, were used for studying the corrosion rate . Specimens were cleaned by buffing to produce a mirror finish and were then degreased with acetone . Initial weight of specimens were taken up to the three decimal of gm with a digital balance. The solutions of 1.0 N NaOH were prepared using double distilled water. Each specimen was suspended by Pyrex glass hooks to the same depth of 1.5 cm. below the surface of the 100 ml solution for all the experiments. Only one specimen was suspended in a Pyrex beaker of 150 ml capacity. Experiments were performed in triplicate.

After the sufficient exposure time the, specimen was retrieved, cleaned by running water and then dried by hot dryer and then final weight was taken. From the weight loss results, the inhibition efficiency (%IE) of the inhibitor , degree of surface coverage ,θ, and corrosion rates, CR,were calculated using equations 1,2 and 3, respectively;

$$\text{Corrosion rate, } \mathbf{CR\ (gcm^{-2}\ min^{-1})} = \frac{\Delta m}{At} \text{ -------------------------(1)}$$

$$\mathbf{\%\ I = \left(1 - \frac{C_{Ro}}{C_{Ri}}\right)\ x\ 100} \text{ --(2)}$$

$$\boldsymbol{\theta} = \left(1 - \frac{C_{Ro}}{C_{Ri}}\right) \text{ -- (3)}$$

where CR_0 and CR_i are the corrosion rates for aluminium in the presence and in the absence of inhibitor in 1.0 N NaOH solution, respectively , θ is the degree of surface coverage by the inhibitor , A is the surface area of the aluminium coupon (in cm^2) , t is the time of immersion and Δm is the weight loss of aluminium after time t.

Electrochemical measurements

The aluminium coupons, with an exposed area of $1cm^2$ was used as working electrode. It was polished with sand paper to a metallic shine,. washed with distilled water, degreased with ethanol, and dried. The electrochemical measurements were carried out in a three electrode glass cell, consisting of aluminium as the working electrode (WE), platinum as the counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode. The electrode potential was allowed to stabilize in a period of 60 minutes before starting the measurements.

Measurements were carried out with Princeton Applied Research Electrochemical Analyser (model K0264 Micro cell kit) along with electrochemical analyser software for plotting, graphing and fitting data. Tafel polarisation curves were obtained by automatically changing the electrode potential from +300 to -300 mV about the open circuit potential. The scan rate was 10 mV/sec. Impedance measurements were performed out in the frequency range from 100 kHz to 1Hz using ac signal with an amplitude of 27 mV peak to peak at open circuit potential.

SEM Analysis

Scanning Electron Microscope (SEM) images were taken in order to study the changes that occur during the corrosion of aluminium in the presence and in the absence of the inhibitor .The aluminium specimens used for surface morphological studies were immersed in 1.0 N NaOH containing optimum concentration of inhibitor and blank for 1h. Then, they were removed , rinsed quickly with rectified spirit and dried . The analysis was performed on HITACHI - model S-3000 H Scanning electron microscope.

Table 1: Inhibition of corrosion of aluminium in 1.0 N NaOH by vanillideneanthranilic acid at 30^0C (weight loss method)

[vanillideneanthranilic acid], M	rate of corrosion x 10^{-4}, g $cm^{-2}min^{-1}$	% inhibition efficiency
0	2.6315	---
0.001	1.852	29.62
0.002	1.7641	32.96
0.003	1.7543	33.33
0.004	1.667	36.66
0.005	1.657	37.03
0.006	1.462	44.44
0.007	1.315	50.00
0.008	1.204	54.25
0.009	1.167	55.65
0.010	1.0721	59.25

RESULTS AND DISCUSSION

The weight loss of aluminium in 1.0 N NaOH decreases with increase in the concentration of inhibitor . At 323 K , the values obtained from weight loss were relatively higher than the values obtained at 303 K , indicating that the rate of corrosion of aluminium in NaOH increased with increase in temperature. Values of the corrosion rates of aluminium (in the absence and in the presence of the inhibitor) and inhibition efficiencies are recorded (Table 1 and 3).

Alkaline solution, the aluminium surface is negatively charged[11]. The TBA^+ cations, on the metal surface provide a better electrostatic condition, which promotes a direct adsorption of inhibitor anions, R^{--} on the metal surface as depicted in model given below. A similar model was proposed for the adsorption of some organic compounds , on the mild steel in acid electrolyte[12].

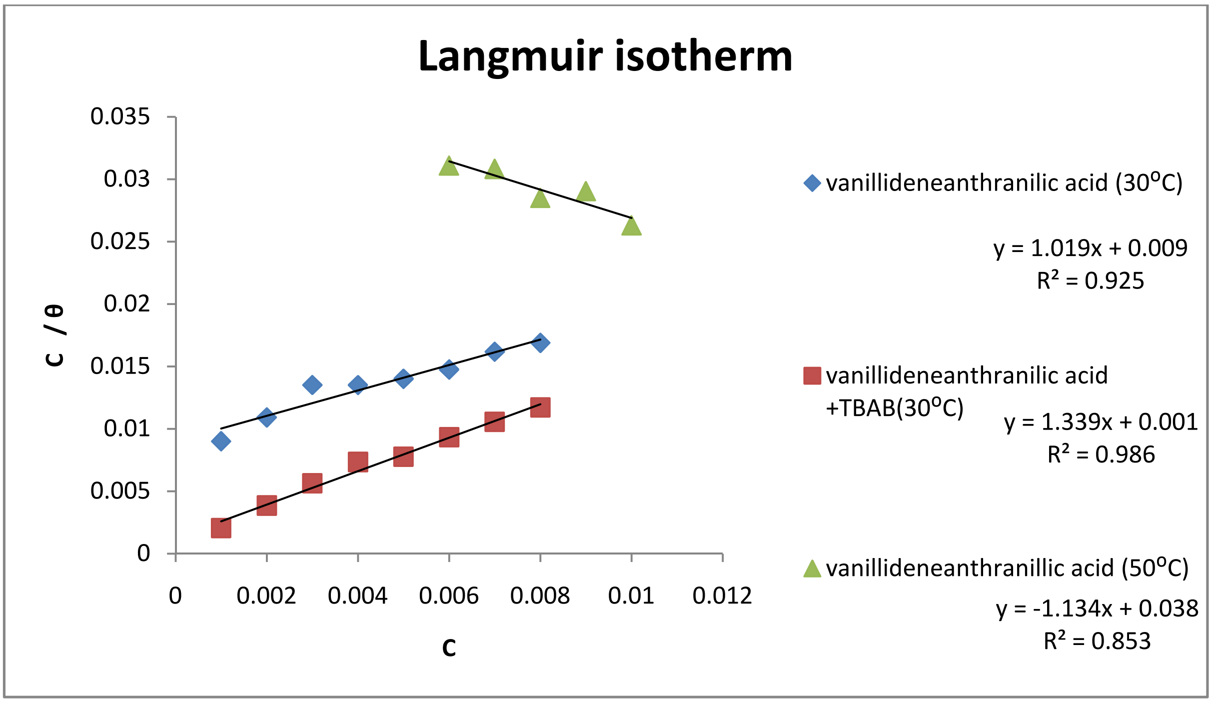
Table 2 : Inhibition of corrosion of aluminium by tetrabutylammonium bromide(TBAB) at 30^{0}C

[TBAB}, M	Rate of corrosion x 10^{-4}, gcm^{-2} min^{-1}	% inhibition
Blank	4.449	--
0.0002	4.359	2.0
0.0004	4.270	4.0
0.0006	4.049	9.0

Table3: Inhibition of corrosion of aluminium by 1.0 N NaOH by vanillideneanthranilic acid along with TBAB at 30° and 50° *C*
[TBAB} = 0.0006 M

[vanillideneanthranilicacid] M	% inhibition		$E_{a\ kJmol}^{-1}$	Q_{ads} kJ mol^{-1}
	33±0.5^{0}C	50±0.5^{0}C		
0	---	---	--	--
0.006	44.44	19.30	80.23	-49.09
0.007	50.00	22.71	82.82	-49.83
0.008	54.25	28.07	89.40	-45.21
0.009	55.66	30.99	85.12	-50.2
0.010	59.25	38.01	84.18	-35.14

Fig.1 Langmuir adsorption isotherm



Temperature ° C inside paranthesis

Several isotherms like Langmuir isotherm, El-Awady et al. isotherm , Temkin isotherm, Freundlich isotherm, Frumkin isotherm and Flory-Huggins isotherm, etc., were studied with the θ, surface coverage values determined from weight loss studies. Among all these isotherms, the best -fit adsorption isotherm is the Langmuir adsorption isotherm for adsorption of vanillideneanthranilic acid on aluminium surface with the mean R^2 value greater than 0.85.

The Langmuir isotherm equation is of the form:

$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$ ----------------------------(4)

The plot of $\frac{C}{\theta}$ against C, is a straight line graph.

The values of $\Delta G°_{ads}$ for the adsorption process, were calculated at each θ value, using Langmuir isotherm .

$K = \frac{\theta}{C(1-\theta)}$ ----------------------------------(5)

Table 4: values of $\Delta G°_{ads}$ for corrosion inhibition by vanillideneanthranilic acid

[vanillideneanthranilic acid] **M**	Surface coverage θ	$\Delta G°_{ads,}$ k J mol^{-1}
0.001	0.2963	-25.59
0.002	0.3297	-24.42
0.003	0.3333	-23.39
0.004	0.3666	-22.80
0.005	0.3703	-22.35
0.006	0.4444	-22.67
0.007	0.5000	-22.84
0.008	0.5425	-22.93
0.009	0.5566	-22.78
0.010	0.5925	-22.89

The equilibrium constant of adsorption is related to the free energy of adsorption (ΔG_{ads}) according to equation.(6) [13,14].

$\Delta G_{ads} = -2.303RT \log (55.5\ K)$ --------------------(6)

where R is the gas constant , T is the temperature, K is the equilibrium constant of adsorption and 55.5 is the molar concentration of H_2O. The values of $\Delta G°_{ads}$ are negatively lower than the threshold values of -40 kJ mol^{-1} required for chemical adsorption. The negative values of $\Delta G°_{ads}$ show that the adsorption of inhibitor on aluminium surface is spontaneous and favours the mechanism of physical adsorption[15].

The presence of TBAB increases the inhibition efficiency of the inhibitors, (Table5). This behaviour is due to the synergistic effects, according to Schmitt and Bedbur [16], who proposed cooperative adsorption, namely competitive and cooperative. The synergistic inhibition effect was evaluated using S_θ parameter.

Table 5 : Effect of TBAB on the inhibition of corrosion of aluminium in 1.0 N NaOH by vanillideneanthranilic acid

[TBAB] = 0.0006 M

[vanillideneanthranilic acid], M	**% Inhibiton**	**[vanillideneanthranilic acid], M +TBAB**	**% Inhibiton**	**Synergism parameter S_θ**
0.001	0.2963	0.001	48.50	1.192
0.002	0.3297	0.002	51.78	1.205
0.003	0.3333	0.003	53.17	1.233
0.004	0.3666	0.004	54.44	1.197
0.005	0.3703	0.005	64.33	1.513
0.006	0.4444	0.006	64.33	1.305
0.007	0.5000	0.007	66.31	1.217
0.008	0.5425	0.008	68.30	1.158

Aramaki and Hackerman [17,18] calculated the synergism parameter, S_θ by the equation :

$$S_\theta = \frac{1 - \theta_{1,2}}{1 - \theta'_{1\,2}} \qquad \text{--------------------------(7)}$$

where $\theta_{1,2} = (\theta_1 + \theta_2)$,
θ_1 = surface coverage by Schiff anion ,
θ_2 = surface coverage by TBA cations , and

θ'_{12} = surface coverage measured for the combination of the Schiff anion and the TBA^+ present together in the solutions.

The S_θ values are greater than unity(Table 5) , suggesting that the enhanced inhibition efficiency caused by the addition of TBAB to the Schiff base is mainly due to the synergistic effect, since the S_θ values are independent of the concentration of additives. It can be concluded that the inhibitors are preferentially adsorbed in anionic form by columbic attraction on the negatively charged metal surface[11], where the TAB^+ cation is already chemisorbed and suppresses the corrosion rate by the stabilization of adsorbed anion and by the increase of surface coverage.
The activation energies for the corrosion processes were calculated using the Arrhenius equation :

$$CR = A \exp\left(\frac{-Ea}{RT}\right) \quad \text{------------------} \quad (8)$$

The reduction of inhibition efficiency with rise in temperature (Table 3), is suggestive of the physical adsorption mechanism on the metal surface[19]. Within the temperature range of 303(T_1) to 323 K(T_2), equation(8) can be written as

$$\log\left(\frac{CR_2}{CR_1}\right) = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{--------------} \quad (9)$$

where E_a is the activation energy , CR_2 and CR_1 are the corrosion rates at the temperature T_1(303 K) and T_2 (323 K) , respectively , Values of E_a calculated from the equation (9) are recorded .The values (Table 3) are less than -80 kJ mol^{-1} indicating physisorption[20-22].The activation energies E_a were also observed to increase with increasing in the concentration of inhibitor, indicating that there is decreasing the adsorption of the inhibitor with increasing concentration. The heat of adsorption (Q_{ads}) was calculated using equation[12].

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left(\frac{T_1 \times T_2}{T_2 - T_1}\right) \text{kJ mol}^{-1} \quad \text{------} \quad (10)$$

where θ_1 and θ_2 are the degrees of surface coverage at the temperatures T_1 (303 K) and T_2 (323 K), respectively.

Values of Q_{ads} calculated from equation (10) are recorded.(Table 3) These values are negative, indicating that the adsorption is exothermic[23].

Electrochemical Polarisation studies

The addition of the investigated inhibitors increases both the cathodic and the anodic overvoltage. The corrosion current density (I_{corr}) decreases with the increasing the concentration of the additives, which indicates that these compounds retard the dissolution of metal in 1.0 N NaOH. The additives influence both cathodic and anodic processes in NaOH solution. This indicates that the additives act as mixed -type inhibitor. But the anode is more polarized than the cathode when external current was applied.

The corrosion potential (E_{corr}) values are shifted to less negative values by increasing the concentration of the compound , which confirms that the inhibitors are mainly of the anodic type.

Table 6 . Anodic and cathodic polarization of aluminium in 1.0 N NaOH without and with vanillideneanthranilic acid

[vanillideneanthranilic acid] ,M	OCP , V	E_{corr}, V	I_{corr}, mA cm^{-2}	βc mV/dec	βa mV/dec	Percentage Inhibition
Blank	1.26	-1.343	18.037	280	420	-
0.003	1.229	-1.303	12.073	257	425	33.1
0.005	1.180	-1.333	10.086	252	440	44.1
0.009	1.255	-1.380	9.149.5	248.2	446	49.27

Impedance measurements

Furthermore , corrosion behaviour of aluminium in 1.0 N NaOH with and without addition of inhibitor was investigated by electrochemical impedance spectroscopy (EIS) measurement at corrosion potential E_{corr} after 30 min of immersion (at 30°C) . The corresponding Nyquist diagrams are shown Fig.2.

Fig.2 Nyquist plots for Al in 1.0 N NaOH with different concentrations of vanillideneanthranilic acid

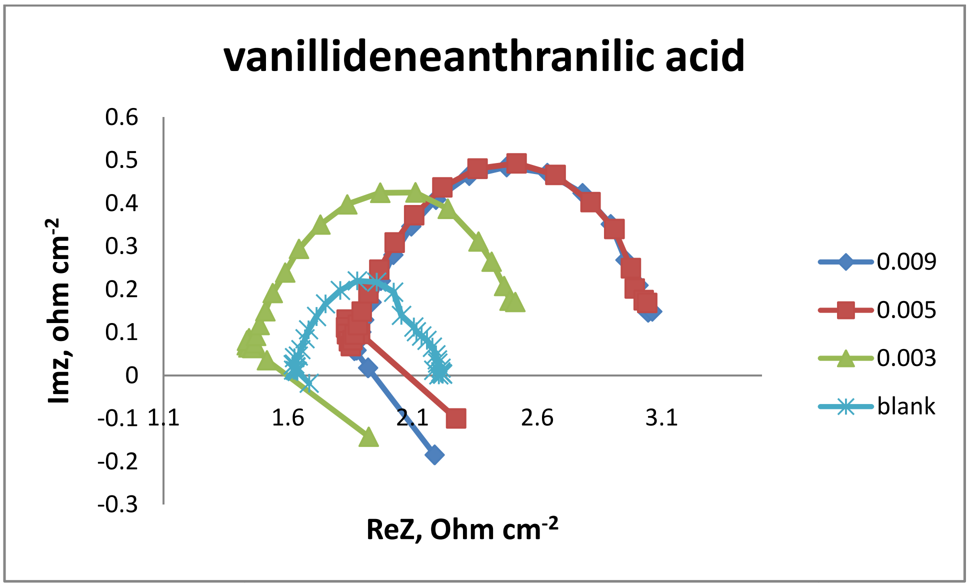


Table 7 : Values of C_{dl} and R_p for Al in 1.0 N NaOH solution in the absence and presence of various concentration of the vanillideneanthranilic acid or at ocp and at (30±0.5°C.)

[vanillideneanthranilic acid],M	R_s, ohm cm^{-2}	R_{ct}, ohm cm^{-2}	C_{dl}, F cm^{-2}
Blank	1.626	0.579	2.252
0.003	1.477	0.9963	1.60
0.005	1.899	1.148	0.948
0.009	1.899	1.148	0.644

The Nyquist plots of the impedance behaviour of aluminium in 1.0 N NaOH and in the presence of various concentrations of the inhibitor is shown in (fig. 2). The existence of a single semicircle shows the presence of single charge transfer process during dissolution [23]. The charge transfer resistance (R_{ct}) and the interfacial double layer (C_{dl}) values derived from these curves are listed .It is obvious that the R_{ct} values (Table7) increase with the inhibitor concentration while C_{dl} value decreases . IE was calculated from the charge transfer resistance (R_{ct}) values from the following equation [1].

$$IE = \frac{Rct_{(i)} --- Rct_{(b)}}{Rct_{(i)}} \qquad \text{--------------------------}(11)$$

where , $R_{ct(i)}$ and $R_{ct(b)}$ were the inhibited and uninhibited charge transfer resistance values .

The increase of the concentration of the inhibitor causes the diameter of the semi-circles to increase.

Microscopic study

Microphotograph's (Fig. 3a, 3b, and 3c) for aluminium in 1.0 N NaOH without and with vanillideneanthranilic acid at 200 x magnification are shown. Comparison micrographs seem to indicate that in the presence of the inhibitor, the surface of aluminium sample has improved considerably regarding its smoothness. The smoothening of the metal surface would have probably, resulted from the inhibitor adsorption on the metal surface [24,25].

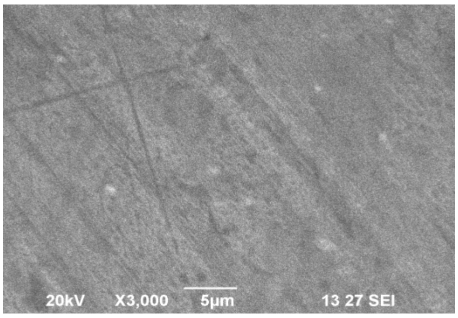


Fig . 3a

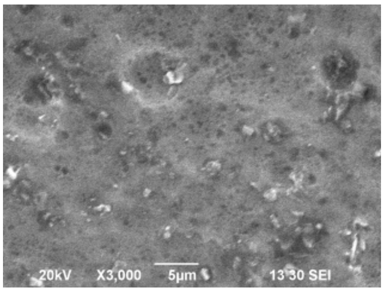


Fig.3b

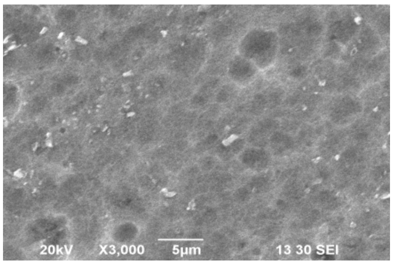


Fig. 3c

CONCLUSION

The corrosion of aluminium in 1.0 N NaOH was found to decrease with the increasing concentration of the inhibitor, vanillideneanthranilic acid. The inhibition efficiency values, obtained from mass loss studies and polarization measurements, showed, the same trend. The type of corrosion was shown to be physisorption The electrochemical polarisation shows that the corrosion inhibition is mixed type . The results of SEM study show that corrosion inhibition is through adsorption process.

Acknowledgement
The authors are thankful to the Principal, Management and the HOD of Chemistry, Bishop Heber College (Autonomous), Trichirappalli for providing facilities.

REFERENCES

[1] Mohammed A. Amin , Syed S. Abd El- Rehim , Essam EF. El - Sherbini, Omar A. Hazzazi , Mohsen N. Abbas , *Corros. Sci*., **2009**, 51, 658-667.
[2] Abdel-Gaber AM , .Khamis E, Abo-ElDahab H Sh .Adeel , *Mater. Chem. Phys.*, **2008**,109, 297-305.
[3] Doche ML, Novell-Cattin F, Durand R Rameau JJ, *J. Power Sources*, **1997**,65,197-205.
[4] Draziica DM, Popic JP, *J.Appl. Electrochem*, **1999**, 29 ,43-50.
[5] Shaker NO, Badr e e, Kandeel EM. *Der Chemica Sinica*, **2011**, 2 (4), 26.
[6]El-Sadek BM , *Der Chemica Sinica*, **2011**, 2(3),125.
[7] Adul Nasser JA, RathunaGiri V, Karthikeyan S, Srinivasan NK, Karthikeyaan R, *Der Chemica Sinica*, **2012 ,** 3(2) ,402-412.
[8] Rammelt U, Reinhar G, *Electrochim. Acta*, **1994**, 40(4), 505.
[9] Zhang SH , Lyon SB, *Corros. Sci.*, **1994**, 36(8), 309.
[10] Mosad FM, EL.Ajaily MM Ben Gweirif S , *Journal of Science and its application*, **2007** , 1 (1), 72-78.
[11] Mazhar AA, Arab ST, Noor AE, *Corros*, **2002**, 58,3, 1.
[12] Eddy NO, Mamza AP, *Port. Electrochim. Acta*, **2009**, 27, 443-456.
[13] El-Etre AY, Abdullah M El-Tantaway Z E, *Corros. Sci*., **2005**, 47, 385.
[14] Odoemelam SA, Eddy NO, *J.Surface Sci. Technol*., **2008**, 24, 1.
[15] Rosaline Vimala J , Leena Rose A, Raja S, *Der Chemica Sinica*, **2012**,3(3), 602-612.
[16] Schmitt G, Bedbur K, Werkst, U *Corros*., **1985**, 361, 273.
[17] Umoren SA, Ebenso EE, *Mater Chem. Phys*. **2007**, 106, 387.
[18] Gomma GK, *Mater. Chem. Phys.*, **1998**, 54, 24.
[19] Ferrreia ES, Giacomelli C, Gicomelli FC, Spinelli A, *Mater. Chem. Phys*., **2004**, 83(1) 129.
[20] Umoren SA, Obot IB, Ebenso EE, *E.Journal of chemistry*, **2008**, 5, 355.
[21] Rajappa SK, Venkatesha TV, Peaveen BM, Bull. *Mater. Sci* ., **2008**, 31, 37.

[22] Irohaa BN, Akaranta O, James OA, *Der Chemica Sinica*,**2012**, 3(4), 995-1001.
[23] Shahrabi T, Yazdzad A, Hosseini M, *J. Mater, Sci. Technol.,* **2008**,24 (3), 427- 432.
[24] Sing MM, Rastogi BR, Yadav M, *J. Eng. & Mater. Sci.*, **2003**,10,155.
[25] Yadav M, Behera D, Sharma U, *Der Chemica Sinica*, **2012**, 3(1), 262-269.