American Journal of Engineering Science and Technology Research
Vol. 3, No. 2, December 2015, pp. 1 -8, ISSN: 2327-8269 (Online)
Available online at www.ajestr.com

Research article

Study of Corrosion and Corrosion Protection of Stainless steel in Phosphate Fertilizer Industry

Rajesh Kumar Singh[1], Rajeev Kumar[2]

1. Assistant professor, Department of Chemistry, Jagdam College, J P University, Chapra, India, 841301.Email: rks_jpujc@yahoo.co.in

2. Research scholar, Department of Chemistry, Jagdam College, J P University, Chapra, India.

Abstract

Phosphate industries use bulk amount of conc. H_2SO_4 during production of phosphate fertilizers. Stainless steel is major supporting metal for completion for several processing operational works. This acid produces corrosive effect for stainless steel. It develops corrosion cell on the surface of base metal and it changes its internal morphology as well as physical, chemical, mechanical properties. H_2SO_4behaves like diabetes for this industrial metal and industries face economical. Industries expense huge money for repairing and maintenance works and sometimes production work stopped and major accident occurs. This is vital setback for industries. The eradication of corrosion problems used organic inhibitors like 1-(2-chlorophenyl)methanamine and 1-(2-bromophenyl)methanamine and its inhibition effect and surface coverage area studied at different temperatures 333^0K, 343^0K and 353^0K in presence of 15% H_2SO_4 and 15mM concentrations of inhibitors. The corrosion rate of metal determined absence and presence of inhibitors by weight loss experiment and potentiostat techniques. The surface adsorption phenomenon, surface thin film and complex formation by inhibitorswere analyzed by application of activation energy, heat of adsorption, free energy, enthalpy and entropy. Analysis of all experimental works the used inhibitors produced anticorrosive effect in H_2SO_4 acidic medium.

Keywords: Stainless steel, inhibitors, weight loss, potentiostat, surface coverage area.

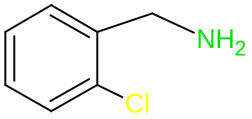
Introduction

The Corrosion of protection of metal is a bigger issue among the corrosion scientists and researchers. It is not fully control but its effect can be minimized by suitable remedies e.g. give proper design and shape of operational metals[1], take care of operating temperatures and surrounding atmosphere [2], applied different types of coatings [3], using cathodic and anodic protection [4] and addition of inhibitors[5]. Operational equipments were not designed well manner [6] then it created corrosion problems like galvanic, pitting crevice, stressed, intergranular, blistering, embritlement in presence of corrosive atmosphere. Coatings is major tools for corrosion alleviation of metal. It applied as metallic coating [7], inorganic coating [8], organic coating [9], painting coating, polymeric coating, and nanocoatings [10]. These coating did not provide good support for metal in acidic environment because porosities were developed on the surface of base metal duringcoatings and H^+ ions entered into porosities of coating materials in this ways generated corrosion cell and deteriorating coating materials. Inhibitors action can be checked corrosion in acidic medium which are inorganic, organic and mixed types inhibitors. Organic inhibitors possessed nitrogen, oxygen, sulphur, silicon, phosphorous, methyl, phenyl, primary, secondary and tertiary alkyl groups; they are highly electron rich organic compounds which produce adsorption effect on surface of metal. They can be adsorbed on the surface of base metals by physical-chemical adsorption. These organic compounds above mentioned functional groups have high electronic charge density; they received H^+ ions and suppress the attacking speed of hydrogen ions. They have capability to form thin film and complexed compound with metal and control aggressiveness of H^+ ions. Aromatic and heterocyclic organic compounds containing above mentioned functional groups produced anticorrosive effect in acidic medium. Nanocoatng of $Zn_3(PO_4)_2$[11], $Mg_3(PO_4)_2$[12] and $AlPO_4$[13]in presence of DLC (diamond like carbon) controlled high temperatures corrosion and minimize hydrogen ions attack. Plasma coating gave corrosion protection of metal in acidic environment. Composite coating materials have anticorrosive character in hostile environment. The above mentioned artificial inhibitors and coating materials are not beneficial for environment so new a day's researchers used natural organic inhibitors for corrosion control. Aloe Vera used an inhibitor for corrosion protection storage can of beverage [14], milk [15], orange juice [16] and vegetables [17].

Experimental procedure

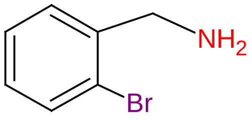
Stainless steel coupons were cut into size of (5 x 3) cm^2. Its surface was rubbed with emery paper and samples were washed with double distilled water. Finally it was rinsed with acetone and dried with air dryer and kept into desiccator. Test sample dipped into 250ml biker with support glass hook and corrosion rate metal determined absence and presence of inhibitors 1-(2-chlorophenyl)methanamine and 1-(2-bromophenyl)methanamine at different temperatures 333^0K, 343^0K and 353^0K and 15mM concentration. Thermostat used take corrosion rate results for above mention temperature. The corrosion rate was measured by gravimetric method.

The corrosion current density and corrosion rate without and with inhibitors were calculated bypotentiostatic polarization technique with help of an EG & G Princeton Applied Research Model 173 Potentiostat. A platinum electrode was used as an auxiliary electrode and a calomel electrode was used as reference electrode with stainlesssteel coupons.



1-(2-chlorophenyl)methanamine

IH(I)



1-(2-bromophenyl)methanamine

IH(II)

Results and Discussion

The corrosion rates of stainless steel without and with inhibitors 1-(2-chlorophenyl)methanamine and 1-(2-bromophenyl) methanamine were determined by equation1in 10% H_2SO_4 solution and its results were mentioned in Table1.

$$K\ (\text{mmpy}) = 87.6\ W / D\ A\ t \qquad (1)$$

where W = weight loss of test coupon expressed in gm, A = Area of test coupon in square centimeter, D = Density of the material in g/cm^3.

The surface coverage areas (θ) and the inhibitionefficiencies (IE) occupied by inhibitors were calculated equation 2 and 3 and their results were written in Table1.

$$\theta = (1 - K / K_o) \qquad (2)$$

where θ = Surface coverage area, K_o = corrosion rate without inhibitor, K = corrosion rate with inhibitor

$$IE = (1- K / K_o)\ X\ 100 \qquad (3)$$

where K_o is the corrosion rate without inhibitor, K= corrosion rate with inhibitor

The corrosion rate, surface coverage area and inhibition efficiency were calculated by equation1, equation2 and equation3 in at different temperatures and 15mM concentration of inhibitors, its values were mentioned in Table1. The results of Table1 observed corrosion rate increased in acidic medium without addition of inhibitors but its values decreased after addition of addition of inhibitors. The results of surface coverage area and inhibition efficiency with 1-(2-chlorophenyl)methanamine and 1-(2-bromophenyl)methanamine enhanced at different temperatures and it looked in figure1 (surface coverage area) versus T^0K and figure2 IE (inhibition efficiency) versus T^0K.

Table1: Corrosion of stainless steel in different temperatures without and with inhibitors in 15% H_2SO_4

Inhibitors	Temperatures	333^0K	343^0K	353^0K	C (m M)
IH(0)	K_o	391	565	836	00
	$\log K_o$	2.592	2.752	2.922	
IH(I)	K	118	192	230	15
	logK	2.071	2.283	2.518	
	$\log(\theta/1-\theta)$	0.363	0.290	0.185	
	θ	0.698	0.661	0.605	
	IE (%)	69.80	66.10	60.50	
IH(II)	K	61	155	201	15
	logK	1.785	2.191	2.303	
	$\log(\theta/1-\theta)$	0.729	0.421	0.498	
	θ	0.843	0.725	0.759	
	IE (%)	84.30	72.50	75.90	

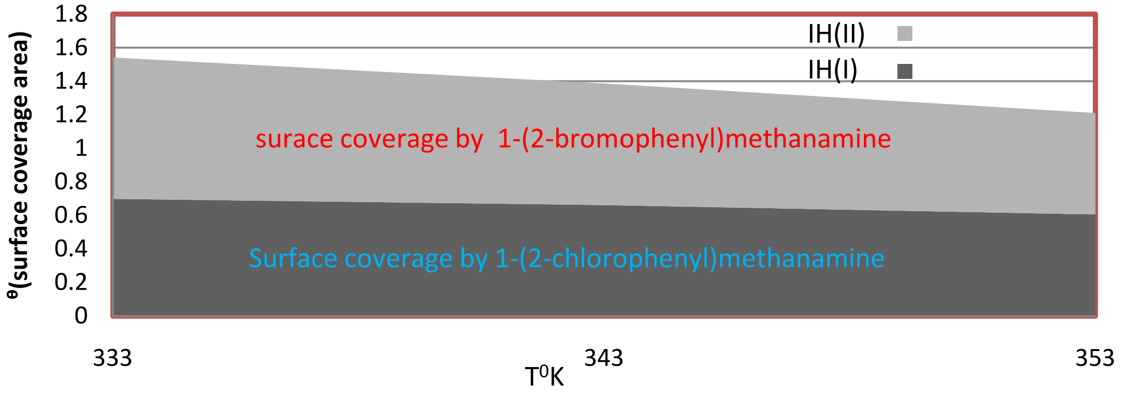


Figure1. θ (surface coverage area) versusT^0K for stainless steel at different tenpertaures

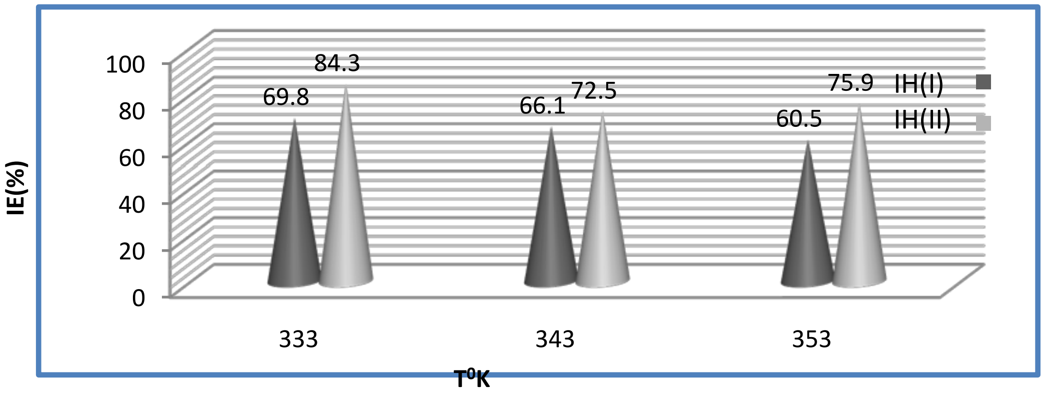


Figure2. IE(%) versus T^0K for stainless steel at different temperatures

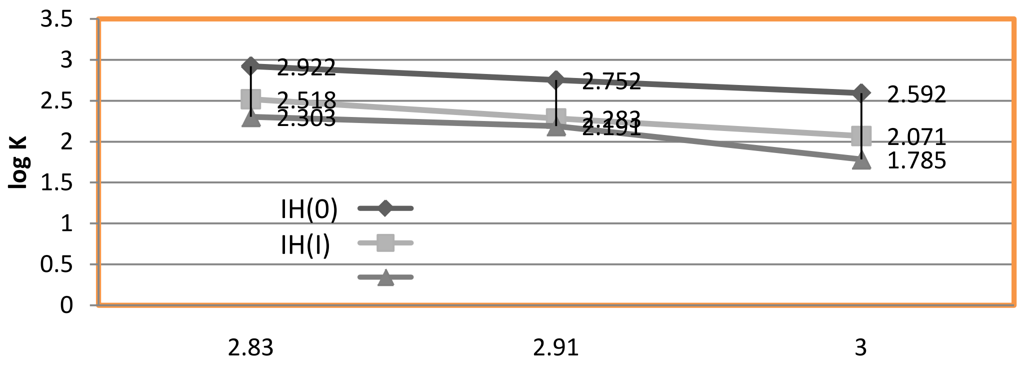


Figure3. log K versus 1/T for stainless steel at different temperatures

The activation energy, heat of adsorption, free energy, enthalpy and entropy for inhibitors 1-(2-chlorophenyl)methaneamine and 1-(2-bromophenyl)methaneamine were calculated by equation4, equation5, equation6 and equation7 and their values were recorded in Table2. The activation energy increased without inhibitors and its values decreased with inhibitors. It indicated that inhibitors bonded with base metal. Heat of adsorption negative sign noticed that inhibitors adhered with metal by physical adsorption and its plot between log($^{\theta}$/1-$^{\theta}$) versus 1/T looked in figure4. The results of free energy, enthalpy and entropy values were shown negative sign which depicted that adsorption occurred on the surface of metal and the graph of all thermodynamical values (Ea,$Q_{ads,}$ΔG,,ΔH and ΔS) versus $^{\theta}$(surface coverage area) were presented in figure5 .

$$d/dt\,(\log K) = E_a / R\,T^2 \qquad (4)$$

where T is temperature in Kelvin and E_a is the activation energy

$$\log(\theta/ 1-\theta) = \log(A\,.C) - (Q_{ads.}/ R\,T) \qquad (5)$$

where T is temperature in Kelvin and $Q_{ads.}$ heat of adsorption

$$\Delta G = -2.303RT\,[\log C - \log(\theta/1-\theta) + 1.72] \qquad (6)$$

where T is temperature in Kelvin and ΔG free energy

$$K = R\,T / N\,h \log(\Delta S^{\#} / R)\ X \log(-\Delta H^{\#}/ R\,T) \qquad (7)$$

where N is Avogadro's constant, h is Planck's constant, $\Delta S^{\#}$ is the change of entropy activation and $\Delta H^{\#}$ is the change of enthalpy activation.

Table2. Thermodynamical values of inhibitors in 15% H_2SO4 for stainless steel

Inhibitors	Temperatures	333^0K	343^0K	353^0K
IH(0)	E_a(o)(kJmol^{-1})	148	153	157
IH(I)	E_a(kJmol^{-1})	118	126	134
	$Q_{ads.}$ (kJmol^{-1})	-21	-16	-10
	ΔG(kJmol^{-1})	-206	-211	-216
	ΔH(kJmol^{-1})	-92	-101	-206
	ΔS(JK^{-1})	-99	-108	-117
IH(II)	E_a(kJmol^{-1})	102	117	123
	$Q_{ads.}$ (kJmol^{-1})	-42	-23	-26
	ΔG(kJmol^{-1})	-189	-205	-204
	ΔH(kJmol^{-1})	-75	-96	-99
	ΔS(JK^{-1})	-88	-104	-109

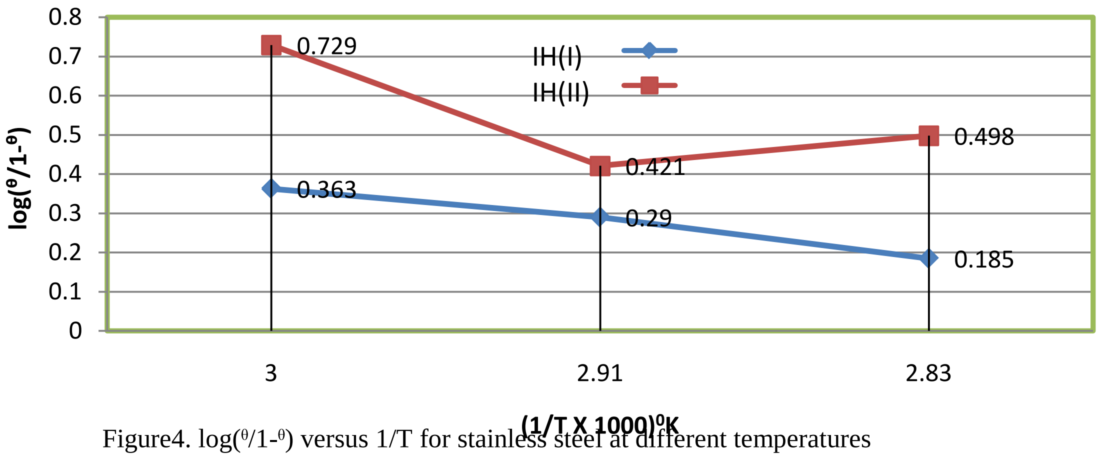


Figure4. log($^{\theta}$/1-$^{\theta}$) versus 1/T for stainless steel at different temperatures

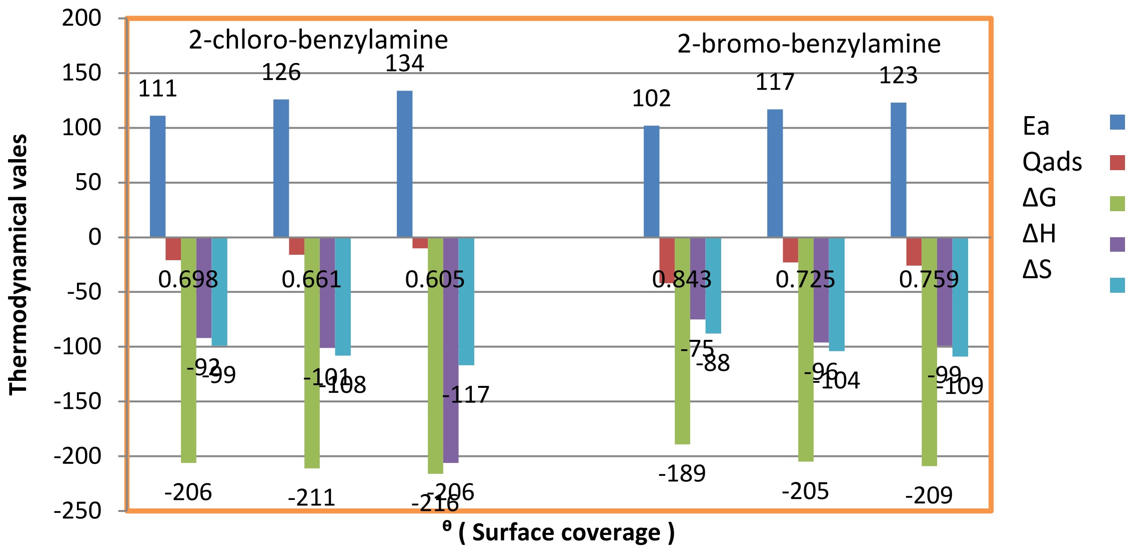


Figure5. Thermodynamical values of different inhibitors versus θ(surface coverage area) at different temperatures

The corrosion current densitydetermined in the absence and presence of inhibitor with the help of equation 8 and their values were recorded in Table3.

$$\Delta E/\Delta I = \beta_a \beta_c / 2.303 I_{corr} (\beta_a + \beta_c) \qquad (8)$$

where ΔE/ΔI is the slope which linear polarization resistance (R_{p}), β_a and β_c are anodic and cathodic Tafel slope respectively and I_{corr} is thecorrosion current density in mA/cm^2.

The metal penetration rate (mmpy) was determined by equation9 in absence and presence of inhibitors.

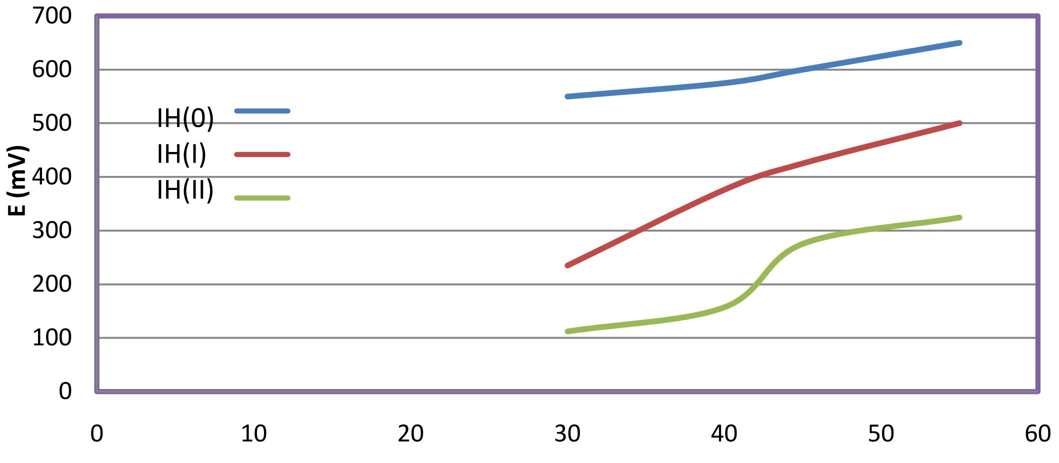
$$C.R\ (mmpy) = 0.327\ I_{corr}\ (mA/cm^2) \times Eq.Wt\ (g) / \rho\ (g/cm^3) \qquad (9)$$

where I_{corr} is the corrosion current density ρ is specimen density and Eq.Wt is specimen equivalent weight.

The results of Table3 indicatedthat corrosion current increase without inhibitors and its values reduced after addition of inhibitors because these inhibitors enhanced cathodic current so corrosion current and corrosion rate minimized. Tafel graph was plotted in Figure6between electrode potential and corrosion current density in the absence and presence of inhibitors.

Table3. Potentiostatic polarization of inhibitors in 15mM concentration and 15% of H_2SO_4

ΔE(mV)	ΔI	β_a	β_c	$I_{corr.}$(mA/cm^2)	K(mmpy)	C(mM)
-650	550	350	250	55.79	4.379	0.00
-600	475	225	315	45.17	0.354	15
-575	350	175	325	30.10	0.236	



Fiigture6. Plot of E(mV) Vs. I(mA) for stainless steel with 15mM concentration of inhibitors

Conclusion:

These inhibitors possessed electron releasing functional which has capability to enhance electron charge density towards corred metal and protected base metal. The results of surface coverage area and inhibition efficiency with both inhibitors indicated that a protective layer developed on the surface of metal. The results of activation energy, heat of adsorption, free energy, enthalpy and entropy were shown both inhibitors bonded with base metal physical-chemical adsorption.

Acknowledgement:

I am thankful to UGC, New Delhi for providing me financial support for this work. The author is thankful to Professor Sanjoy Misra, Department of chemistry, Ranchi University, Ranchi who provide me suggestion and guidance. I am also thankful to the department of chemistry, Ranchi University, Ranchi and the department of applied Chemistry Indian school of Mines, Dhanbad for providing laboratory facilities.

References:

1. Khramov AN, Voevodin NN (2004), Hybrid organo-ceramic corrosion protection coating with encapsulated organic corrosion inhibitors. Thin solid films, 447, 549-557.
2. Seth A, van Ooij (2004), Novel water based high-performance primers that can replace metal pretreatments and chromate-containing primers. J. Mater.Eng. Perform. 13, 468-474.
3. Ianmuzzi M, Frankel GS, (2007) Mechanisms of corrosion inhibition of AA 2024-T3 by vanadates. Corros. Sci., 49, 2371-2391.
4. Moutarlier V, Neveu B, Gigandet MP (2008), Evaluation of corrosion protection for sol-gel coatings doped with inorganic inhibitors. Surf Coat Technol, 202, 2052.
5. Code A, Arenas M A, de Frutos (2008), Effective corrosion protection of 8090 alloy by cerium conversion coatings. Electrochim Acta, 53, 7760-68.
6. Shem M, Schmidt T, Gerwann J et al (2009), CeO2-filled sol-gel coatings for corrosion protection of AA2024-T3 aluminium alloy, Corrosion Sci. 51, 2304.
7. Pulvirenti A L, Bishop E J, Adel-Hadai M A, Barkatt A, (2009), Solubilisation of nickel from powders at near-neutral pH and the role of oxide layers. Corros. Sci. 51, 2043-2054.
8. Glezakou V A, Dang LX, Mc Grail BP,(2009) Spontaneous activation of CO2 and possible corrosion pathways on the Low-index iron surface Fe (100), J. Phys. Chem. 113, 3691-3696.

9. Farias MCM, Santos CAL, (2009) Friction behavior of lubricated zinc phosphate coating, Wear, 266, 873-877.
10. Cuevas-Arteaga C, (2008) Corrosion study of HK-40m alloy exposed to molten sulphate|vandate mixtures using the electrochemical noise technique, Corros. Sci. 50, 650-663.
11. Singh R K, Misra Sanjoy,(2013) Corrosion protection of stainless steel in CO2 environment by nanocoating of zinc phosphate with DLC filler, Journal of Metallurgy & Materials Science, 55, 149-156.
12. Singh R K, Misra Sanjoy,(2013) Corrosion protection of rebar steel in marine atmosphere by nanocoating, Journal of Metallurgy & Materials Science, 55, 313-321.
13. Singh R K, Misra Sanjoy,(2013) Corrosion protection of mild steel in SO2 environment by nanocoating with DLC filler, Journal of Metallurgy & Materials Science, 55, 227-234.
14. Singh R K, Kumar Vikas (2014), Use of Aloe Vera as corrosion inhibitor for protection of stainless steel, Journal der Pharmazie Forschung, 2, 110-120.
15. Singh R K (2014), Corrosion mitigation of milk by Aloe Vera, Journal of food and technology, 2,25-32.
16. Singh R K, Kumar Vikas, (2014), Inhibition of metallic can in organic juice by Aloe Vera, International journal on environment science, 5, 11-20.
17. Singh R K, Kumar Vikas, (2014), Aloe Vera used as inhibitor for corrosion protection of vegetables' utensils, International journal of green and Herbal chemistry, 3, 211-220.