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Research Article

CORROSION PROTECTION OF STAINLESS STEEL IN VEGETABLES BY *ALOE VERA* JUICE

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ABSTRACT
Vegetables are very important food for human beings. People make varieties of items with vegetables. They can generally use stainless steel related container for completion of these purpose. Most of the vegetables are acidic in nature. Farmers use bulk amount of insecticides and pesticides for protection against insects and these chemicals increase acidic character of vegetables. When these vegetables kept in stainless steel utensil, after certain time it is noticed that color of the vegetables change. It happens due to formation of corrosion cell on the surface of metal. The electrochemical reaction starts and metals ions go into vegetables. In this way vegetables are contaminated. The contaminated vegetables create several types of health problems and this decrease their nutrition values. Metal ions reduce efficiency of vitamins in vegetables. The acidic vegetables produce several types of corrosion like galvanic corrosion, pitting corrosion, uniform corrosion, crevice corrosion and stress corrosion. The corrosion rate of metal studied with gravimetric and potentiostaic polarization methods. Inhibitor used for this work was *Aloe vera* . *Aloe vera* inhibition efficiency and surface coverage area studied at different concentrations and temperatures. The concentrations of *Aloe vera* selected 2ml, 4ml and 6ml and temperature maintain on these concentrations were 20^0C, 25^0C, 30^0C and 35^0C. The corrosion rate determined with and without inhibitors at different intervals of times like 24hrs, 48hrs, 72hrs and 96hrs. The surface adsorption phenomenon studied with help of Langmuir and Temkin isotherm. Activation energy increased after addition of inhibitor. It means that adsorption takes place on the surface of metal. Heat adsorption, free energy, enthalpy and entropy found to be negative so it is a sign of adsorption. Thermodynamically results indicated that *Aloe vera* bonded with metal by physical adsorption.

Key Words: *Stainless Steel, Vegetables, Aloe vera, Potentiostate and Physical Adsorption*

INTRODUCTION
Stainless steel (Holm, 1928) is a very important metal for making utensils, cookery and other items of household. It is sensitive to acid and produce chemical and corrosion reaction with metal. In this process metal lose their credibility and creates chemical and biological problems for human beings (Lewis, 1931). Chemists and corrosion specialists have tried several techniques for corrosion mitigation of metals like proper selection of shape and size, use inorganic and organic substance as inhibitors, organic and inorganic coatings, polymeric coating and nanocoating (Abiola, 2004) methods. But these chemicals release harmful substances which are not suitable for environmental and animals. To solve this problem we tried ecofriendly corrosion inhibitor, theat is *Aloe vera* juice.

Vegetables possess organic and inorganic substances. Vegetables coming in contacts with metals not only acquire a metallic taste but also corrode these metals readily. A considerable amount of information has been obtained on the effect of metals (Mobin, 2008) in foods upon animals and human beings. Many recent studies indicate that corrosion products enter into vegetables and deteriorate quality (Singh, 2010; and Alam *et al.*, 2009) of vegetables. As the metal goes into vegetables and passes from a zero charge as the metallic state is designated to positively charged ions an equivalent amount of electricity must pass from the vegetables to the metal so as to neutralize the charge. In the case of acid corrosion this may be expressed as follows:

$$M + HCl = MCl + H_2$$

Stainless steel (Wang *et al.*, 2008; Brodinov *et al.*, 2007; and Alam *et al.*, 2008) corrodes because all common structural metals form surface oxide films when exposed with vegetable but oxide formed on stainless steel is readily broke down. The other factors which affect the rate of corrosion are temperature and pH. The relative acidity of vegetables is the most important factor to be considered at low pH, the evolution of hydrogen trends to eliminate the possibility of protective film formation (Kalendova et al., 2008; Nmai, 2004; and Singh, 2011) so that steel continues to corrode.

Oxides of metals and phosphate of metals are used as inhibitors. Sulpha drugs (Singh, 2009a, b) gave good results for corrosion control of stainless steel in sugar industry. Aromatic amine, fused aromatic amine and hetero cyclic aromatic amine worked as inhibitors in phosphate inhibitors. Cyclic amine used for corrosion inhibition of metal in pulp and paper industry. Nanocoatings of organic and inorganic on surface of metal could produce good inhibition properties and improve life of material. Several types of Nanocoatings can be done on the surface of materials like nanocomposite thin film coating, thermal barrier coating, Top layer coating, nanostructural change and conversion coating. Thiourea and its derivates worked as inhibitors in petroleum industry in various operational units like production, storage and transportation. Natural products applied for corrosion protection of metal in acidic medium and these inhibitors were found ecofriendly for environment. Metallic and nonmetallic coating mitigated affect of corrosion in corrosive environment. Organic compounds having nitrogen, oxygen and sulphur behave like anticorrosive inhibitors. Electron rich organic compounds have good inhibition capability against acid. The corrosion is controlled by the application of aliphatic and aromatic amines. It is also observed that primary, secondary, tertiary and quaternary amine is produced good inhibitive effect against acidic medium. Several workers used heterocyclic compounds as inhibitors which possessed nitrogen, oxygen and sulphur. Rubber, polymer and silicon are used as coating material for protection of metal.

MATERIALS AND METHODS

The sheets of stainless steel metal of 0.1 cm thickness were mechanically cut into coupons of sizes of 5cm length by 3cm width, perforated with hole of same diameter centrally to allow the passage of thread. These coupons were surface prepared using emery paper, ethanol and water. The tested coupons were kept into vegetables in 100ml beakers. The coupons, exposure periods were 24hrs, 48hrs, 72hrs and 96hrs. Tests were performed at different concentrations 2ml, 4ml and 6ml *Aloe vera* and at different temperatures 20^{o}C, 25^{o}C, 30^{o}C and 35^{o}C and temperature were maintained constant by keeping the solutions in a thermostat. The average corrosion rates of the in various concentrations and temperatures were determined by using weight loss method. The corrosion current measured with Potentiostatic polarization by using an EG & G Princeton Applied Research Model 173 Potentiostate. A platinum electrode used as an auxiliary electrode and a calomel electrode used as reference electrode with stainless steel coupons.

RESULTS AND DISCUSSION

The Corrosion rate of stainless steel was calculated with and without inhibitor at different concentrations and temperatures with help of equation 1.

$$K \text{ (mmpy)} = 13.56\ W / D\ A\ t \quad \ldots\ldots (1)$$

Where W = weight loss of test coupon expressed in kg, A = Area of test coupon in square meter, D = Density of the material in kg M^{-3}

The valves of corrosion rate at different concentrations expressed in Table 1, Table 2 and Table 3. Look the results of corrosion values of these tables were indicated that the corrosion rate of metal decreased after addition of inhibitor.

The inhibition efficiency and surface coverage area were calculated by using equation 2 and 3.

$$IE = (1- K / K_o)\ 100 \quad \ldots\ldots (2)$$

Where K is the corrosion rate with inhibitor and K_o is the corrosion rate without inhibitor.

The surface coverage area may be written as:

$$\theta = (1 - K / K_o) \qquad (3)$$

Where θ = Surface area, K = Corrosion rate with inhibitor, K_o = corrosion rate without inhibitor.
The inhibition efficiencies and surface coverage areas values were recorded in Table 1, Table 2 and Table 3 and Figure 1show that used inhibitor increased these values.
The corrosion rate, surface coverage areas and inhibition efficiencies were calculated at different temperatures 20^0C, 25^0C, 30^0C and 35^0C and these recorded values mention in Table 1, Table 2 and Table 3. These tables values noticed that inhibition efficiencies and surface coverage areas increased as temperatures increased. These results exhibited clearly in Figure 2.

Table 1: Inhibition of *Aloe vera* with vegetable at different temperatures and 2ml concentration

Inhibitor	Temp	20^0C	25^0C	30^0C	35^0C	C (ml)	logC
IH(0)	K_0	0.473	0.846	1.419	1.892	0.00	0.00
	$logK_0$	-0.325	-0.072	0.151	0.276		
IH(1)	K	0.315	0.671	1.121	1.596	2	-2.69
	logK	-0.501	-0.173	0.049	0.203		
	θ	0.33	0.20	0.21	0.16		
	(1- θ)	0.77	0.80	0.79	0.84		
	log(θ/1- θ)	-0.367	-0.602	-0.575	-0.720		
	(C/ θ)	-8.15	-13.45	-12.80	-16.81		
	log(C/ θ)	-0.823	-0.346	-0.096	-0.091		
	IE (%)	33	20	21	16		

Table 2: Inhibition of *Aloe vera* with vegetable at different temperatures and 4ml concentration

Inhibitor	Temp	20^0C	25^0C	30^0C	35^0C	C (ml)	logC
IH(0)	K_0	0.473	0.846	1.419	1.892	0.00	0.00
	$logK_0$	-0.325	-0.072	0.151	0.276		
IH(1)	K	0.212	0.509	0.997	1.195	4	-2.39
	logK	-0.673	-0.293	-0.001	0.077		
	θ	0.55	0.40	0.30	0.36		
	(1- θ)	0.45	0.60	0.70	0.64		
	log(θ/1- θ)	0.087	-0.176	-0.367	-0.249		
	(C/ θ)	-4.34	-5.97	-7.96	-6.63		
	log(C/ θ)	-0.468	-0.013	-0.018	-0.201		
	IE (%)	55	40	30	36		

Table 3: Inhibition of *Aloe vera* with vegetable at different temperatures and 6ml concentration

Inhibitor	Temp	20^0C	25^0C	30^0C	35^0C	C (ml)	logC
IH(0)	K_0	0.473	0.846	1.419	1.892	0.00	0.00
	$logK_0$	-0.325	-0.072	0.151	0.276		
IH(1)	K	0.198	0.359	0.721	0.898	6	-2.23
	logK	-0.703	-0.445	-0.142	-0.046		
	θ	0.58	0.57	0.49	0.52		
	(1- θ)	0.42	0.43	0.51	0.48		
	log(θ/1- θ)	0.140	0.132	-0.017	0.034		
	(C/ θ)	-3.84	-3.91	-4.55	-4.64		
	log(C/ θ)	-0.075	-0.041	-0.259	-0.193		
	IE (%)	58	57	49	52		

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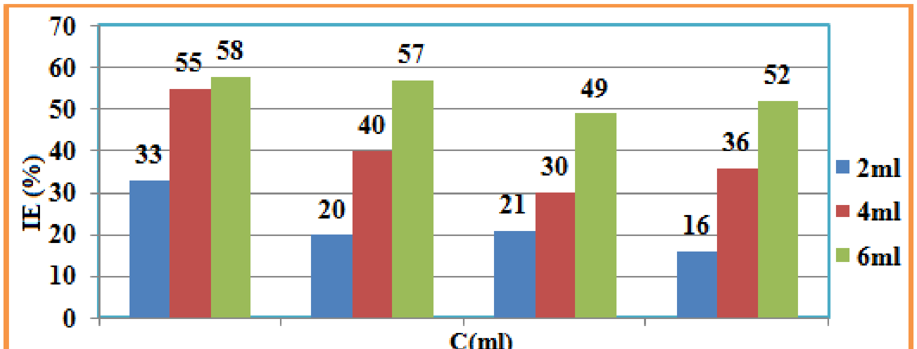

Figure 1: Plot of IE(%) Vs. C (ml) for Stainless steel at different concentrations

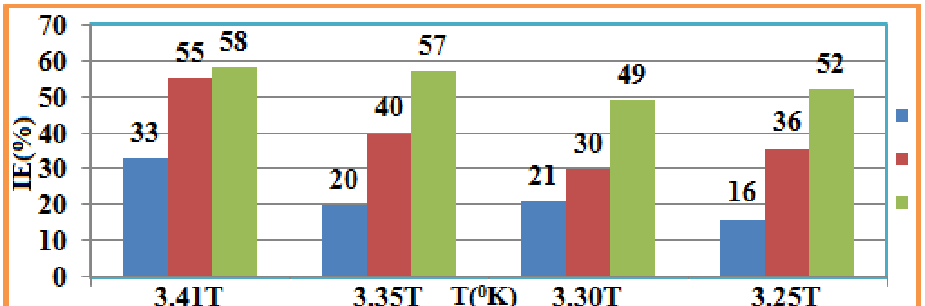

Figure 2: Plot of IE(%) Vs. T for Stainless steel at different temperatures

Activation energy was determined with help of Arrhenius equation 4

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

Where T is temperature in Kelvin and E_a is the activation energy of the reaction.

The values of activation energies were represented in Table4, Table5 and Table6 absence and presence inhibitor. It observed that without inhibitor activation energies decreased and with inhibitor activation energies increased. The plot between log K Vs. 1/T in Figure 3 and log $(^{\theta}/1-{}^{\theta})$ vs. 1/T in Figure 4 are found to be straight line. It indicated that inhibitor bonded with metal by physical adsorption.

The heat of adsorption was calculated by Langmuir adsorption isotherm equation and it values recorded in Table 4, Table 5 and Table 6.

$$\log(\theta/1-\theta) = \log(A.C) - (Q_{ads}/RT) \quad \ldots\ldots (5)$$

Where T is temperature in Kelvin and Q_{ads} heat of adsorption

The heat of adsorption found to be negative so it indicated that adsorption occurred on the metal surface. The values of heat of adsorption were shown that inhibitors were bonded with metal by physical adsorption. The plot between log $(^{\theta}/1-{}^{\theta})$ vs. log C found to be straight line in figure 5 which indicates Langmuir adsorption isotherm. It is a sign of adsorption.

Temkin equation of isotherm for adsorption expressed as:

$$\log(C/{}^{\theta}) = \log C - \log K \quad \ldots\ldots (6)$$

Where C is concentration of inhibitor, θ is surface coverage area and K is constant.

The values of log $(C/{}^{\theta})$ are mentioned in Table1, Table 2 and Table 3. The plot against log $(C/{}^{\theta})$ vs. log C was shown a straight line in figure 6 which indicates sign of adsorption.

Free energy was determined by equation 7 and it values recorded in Table 4, Table 5 and Table 6 at different concentrations.

$$\Delta G = -2.303RT[\log C - \log(\theta/1-\theta) + 1.72] \quad \ldots\ldots (7)$$

Free energy results show that use inhibitor produces an exothermic reaction so it indicates sign of adsorption.

The energy of enthalpy and entropy were determined by transition state equation 8 and it values mentioned in Table 2.

$$K = R\,T / N\,h \log (\Delta S^{\#} / R) \times \log (-\Delta H^{\#} / R\,T) \quad \ldots\ldots\ldots\ldots (8)$$

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.

Enthalpy and entropy values are mentioned in Table 4, Table 5 and Table 6 which are found to be negative, it exhibits an exothermic reaction. The negative values of entropy indicate that inhibitors stable on surface adsorption of metal.

Table 4: Thermodynamically parameters for *Aloe vera* at different temperatures and 2ml Concentration

Thermodynamically Parameters	20^0C	25^0C	30^0C	35^0C
$E_{a(0)}$	26.87	7.11	4.04	11.75
E_a	32.68	11.08	3.09	12.81
Q_{ads}	-23.94	-38.57	-36.29	-44.76
ΔG	-26.63	-41.24	-38.98	-47.45
ΔH	-67.19	-44.21	-29.03	-18.65
ΔS	-39.40	-26.39	-17.59	-11.47

Table 5: Thermodynamically parameters for *Aloe vera* at different temperatures and 4ml Concentration

Thermodynamically Parameters	20^0C	25^0C	30^0C	35^0C
$E_{a(0)}$	26.87	7.11	4.04	11.75
E_a	43.90	18.77	6.09	4.78
Q_{ads}	-5.67	-11.27	-23.16	-15.48
ΔG	-8.06	-13.66	-25.55	-17.87
ΔH	-78.93	-52.55	-32.82	-26.73
ΔS	-46.29	-31.37	-19.89	-16.44

The corrosion current density determined absence and presence of inhibitor with help of equation 9 and values recorded in Table 7.

$$\Delta E/\Delta I = \beta_a\, \beta c / 2.303\, I_{corr} (\beta_a + \beta_c) \quad \ldots\ldots\ldots\ldots (9)$$

Where $\Delta E/\Delta I$ is the slope which linear polarization resistance (Rp), β_a and β_c are anodic and cathodic Tafel slope respectively and I_{corr} is the corrosion current density in mA/cm^2.

Looks the results of Table 7, it is noticed that corrosion current increases without inhibitor and its values reduce after addition of inhibitor.

The metal penetration rate (mmpy) is determined by

$$C.\,R\,(mmpy) = 0.1288\, I_{corr}\,(mA/cm^2) \times Eq.Wt\,(g) / \rho\,(g/cm^3) \quad \ldots\ldots\ldots (10)$$

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

Table 6: Thermodynamically parameters for *Aloe vera* at different temperatures and 6ml Concentration

Thermodynamical Parameters	20^0C	25^0C	30^0C	35^0C
$E_{a(0)}$	26.87	7.11	4.04	11.75
E_a	45.85	28.08	8.96	2.85
Q_{ads}	-9.13	-8.45	-1.07	-2.11
ΔG	-11.36	-10.68	-3.30	-4.34
ΔH	-80.23	-61.52	-41.66	-34.19
ΔS	-47.05	-36.72	-25.24	-21.04

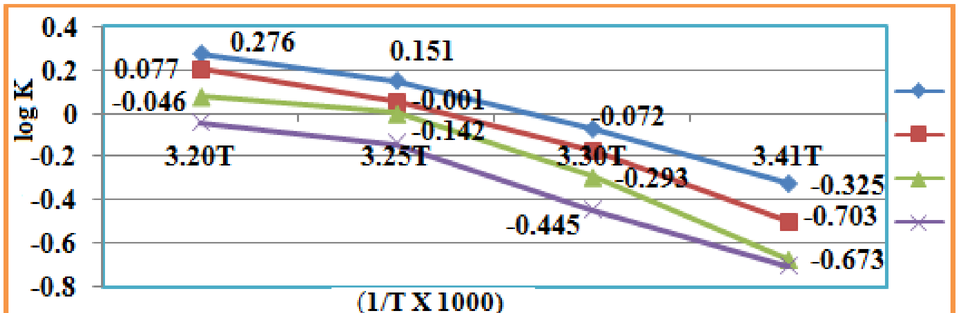

Figure 3: Plot of logK Vs. 1/T for Stainless steel at different temperatures

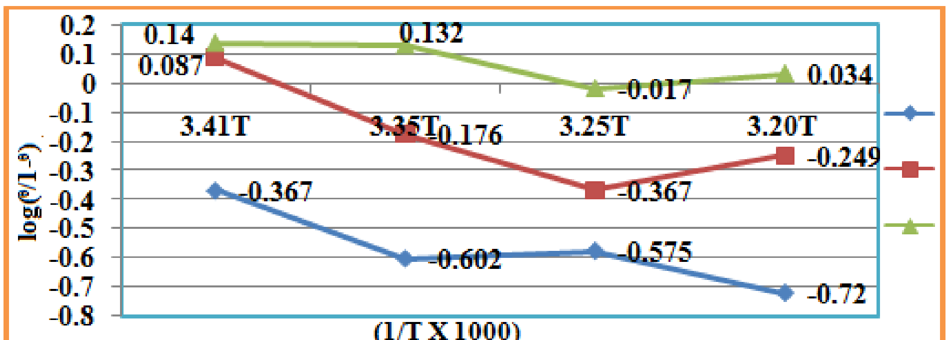

Figure 4: log(θ/1-θ) Vs. 1/T for Stainless steel at different temperatures

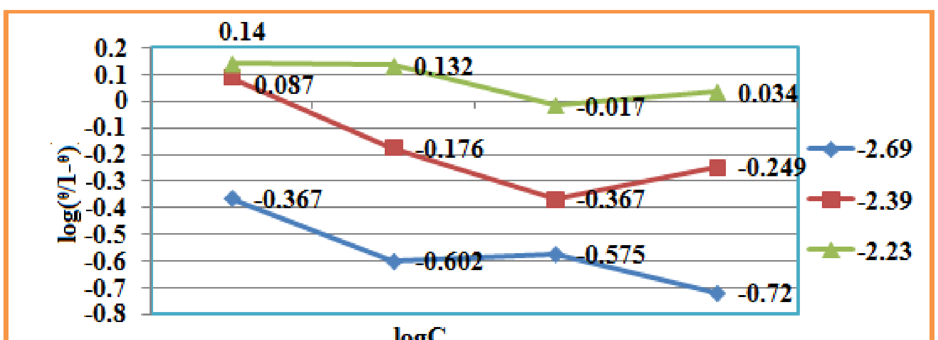

Figure 5: plot of log(θ/1-θ) Vs. logC for Stainless steel at different concentrations

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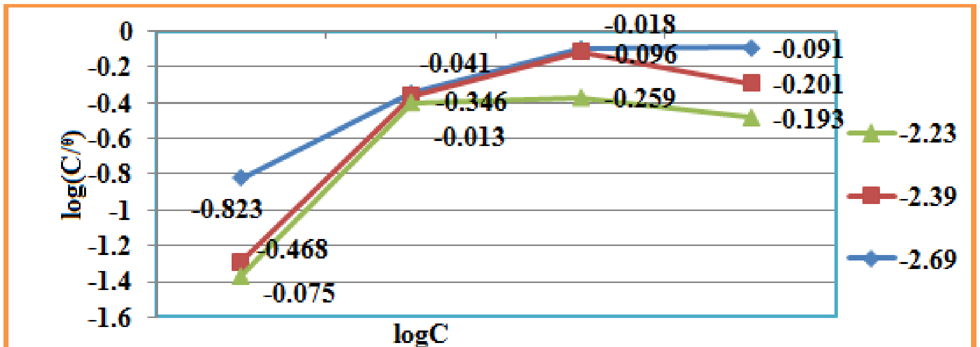

Figure 6: Plot of log(C/θ) Vs. log C for Stainless steel at different concentrations

Figure 7 indicates that Table graph has plotted between electrode potential and current density and absence and presence of inhibitors. Anodic potential, current density and corrosion rate increased without inhibitors but addition of inhibitors these values decreased and inhibition efficiency increased.

Table 9: Potentiostatic Polarization values of *Aloe vera* inhibitor with different concentration at 30^{0}C

Inhibitor	ΔE	ΔI	βa	βc	Icorr	K(mmpy)	IE(%)	C(ml)
	-800	350	250	230	28.81	0.875	0.00	0
IH(0)	-510	215	130	150	12.76	0.387	55.77	2
IH (1)	-500	205	125	145	12.01	0.365	58.28	4
	-490	200	120	140	11.45	0.348	60.57	6

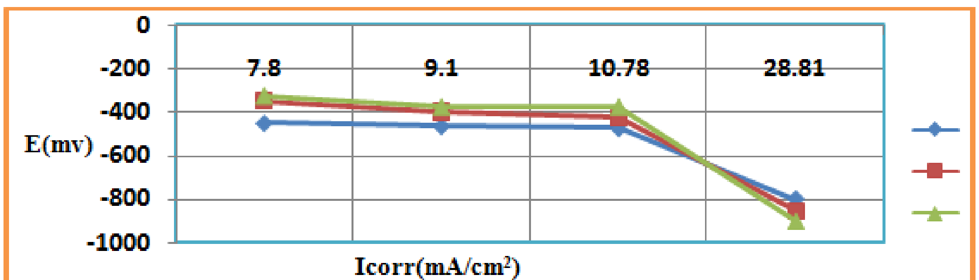

Figure 7: Plot of E (mV) Vs. Icorr(mA/cm^2) for Stainlees teel at different concentrations

CONCLUSION

Aloe vera is a medicinal natural plant. It is ecofriendly and it has no any side effect. Due to this character it is used as inhibitor in vegetables for protection of stainless steel. Its inhibition efficiency is low at lower concentration and its inhibition efficiency is high at higher concentration. The inhibition efficiency lies between 22 to 73% at different concentrations. It also produces good inhibitive effect at different temperatures. The results of activation energy, heat of adsorption, free energy, enthalpy and entropy show that *Aloe vera* bonded with metal surface physical adsorption. Potentiostatic polarization study results indicate that corrosion current decrease after addition of inhibitor.

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