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Corrosion and Corrosion Protection of *Unio* in Carbonic Acid Medium

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Abstract

Unio is a calciferous animal, and its outer surface is made of calcium carbonate. It usually happens in sources of sweet water. They create carbonic acid by absorbing carbon dioxide. It changes the pH of sweet water sources thus water becomes acidic. It develops corrosive environment for Unio. Carbonic acid interacts with Unio to form corrosion cells on the interface of Unio. This acid oxidizes calcium carbonate into calcium ions and slowly dissolution starts on their surface. Carbon acid produces galvanic, pitting, stress and crevice corrosion on the outer surface of calciferous animals. The corrosion rate of Unio calculated by weight loss and potentiostat techniques. Aloe vera was used as an inhibitor for the control corrosion of Unio in carbonin acid medium. It inhibits the action studied in different concentrations and temperatures. It contains electron rich organic compounds like anthraquinone, chromone, catechol, coumarin, lawsone, aloesin etc. These organic compounds formed a thin film on the surface of Unio by chemical bonding and they had capability to decrease the concentration of hydrogen ions. The inhibitor adsorption phenomenon studied by the use of Langmuir isotherm and its activation energy determined by Arrhenius equation. The bonding formation of Aloe vera on Unio interface confirmed by heat of adsorption, activation energy, free energy, enthalpy and entropy. This compound covered more surface area and produced high percentage inhibition efficiency.

Keywords: *Unio*, carbonic acid, *Aloe* vera, inhibition efficiency, thin film, chemical bonding

INTRODUCTION

Unio survives in sweet water [1] like lake, pond and river. Gases [2] like CO_2, SO_2, NO_2 absorb moist air to produce H_2CO_3, H_2SO_4 and HNO_3. These acids produce acid rain and contaminate water sources. It produces corrosive medium for calciferous animals [3]. The contaminated water [4] changes their physical, chemical and biological properties [5]. Industry effluents [6] are discharged into water sources to develop nitrate and organic compounds [7], and distilleries industry wastes produce microorganisms [8]. Paper mills effluents are acidic to alter the pH of water [9]. Sugar industries waste increases the concentration of H+ ions [10]. Densely populated areas river water is polluted due to depose suspended impurities [11], mineral salts and organic compounds. Aquatic water is contaminated due to sewage, laundries discharge and industrial wastes. They produce bacteria, algae and microorganisms which secrete acidic compounds [12]. Algae release carbon dioxide and hydrogen sulphide [13]. Carbon dioxide dissolves in water to form carbonic acid. Some microorganisms convert hydrogen sulphide into sulphuric acid [14]. Inorganic salts decompose in water to produce cations like Na^+, K^+, Ca^{2+}, Mg^{2+} and anions as Cl^-, SO_4^{2-}. HCO^{3-} etc. [15]. Aquatic water [16] contains compounds like $Ca(HCO_3)_2$,

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$Mg(HCO_3)_2$, $CaCl_2$, $MgCl_2$, $CaSO_4$. $MgSO_4$, Na_2SO_4 and NaCl. These cations and anions like Na^+, Ca^{2+}, Cl^-, SO_4^{2-}, and HCO^{3-} are present in natural waters and also contain acid ions [17] such as NO^{3-}, NO^{2-} and NH^{4+} in little amounts. Volatile organic compounds [18] diffuse into atmosphere, and they separate between air and moisture [19]. Their reactivity depends upon vapor pressure, solubility and atmospheric conditions [20]. Gases like CO_2, NO_2 and SO_2 dissolve water to form H_2CO_3 acid, HNO_3 acid and H_2SO_4 acid. These acids produce corrosive effects for calciferous animals [21]. The ocean water is components Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, HCO^{3-}, Cl^- and Br^- and in addition other compounds present 50 inorganic ions and thousands of organic molecules. The pH of ocean water is changed due to suability of CO_2, effluents, sewage, bacteria and microorganisms [22, 23]. Few toxic compounds are released during photosynthesis, respiration and chemical weathering. Corrosive substances discharge by biological reactions. Bio-wastes form macro and micro-organisms due to biological reaction [24]. Algae decrease the concentration of oxygen in water body because it is photosynthetic organisms. Bacteria and micro-organisms live in water to enhance the concentration of H+ ions. All micro-organisms excrete nutrients for other species which decrease the concentration of oxygen. Degradation of plants, animals, microbial biomass by chemical process release corrosive compounds which develop acidic medium for calciferous animals. The human made and anthropogenic sources of organic compounds are released in aquatic water to generate hostile environment. Humic compounds produce fulvic acid and dissolve in water to increase the concentration of H+ ions [25]. Degradation of plants and biopolymers yield humic compounds. Microbials dissociate proteins, carbohydrates, lignin, paraffin macromolecules, melanins and cutin into humin. Humic decomposes to produce CO_2 and H_2O.

METHODOLOGY

Unio's outer surface was washed with water and dried in the sun light. The test sample was rinsed in acetone and kept into desiccators. First the weight of *Unio* was measured and dipped into dissolved carbon dioxide solution. The corrosion rate of *Unio* was calculated by weight loss formula as mentioned below. The corrosion rate was determined for 1, 2, 3, 4 and 5 days and the temperature were recorded 288, 298, 303, 308 and 313K respectively. After completion of time, the sample was dried with hot air gun and weight of sample was taken. *Aloe vera* used as inhibitor for mitigation of corrosion of rate of *Unio*. 1000 ml solution carbonic was made and 50 ml of *Aloe vera* was added to it, then *Unio* sample were immersed where results calculated one days and 288K temperature. Similarly, the process was completed for 60-, 70-, 80- and 90-ml *Aloe vera* and 2,3,4 and 5 interval days where 298, 303, 308 and 313K temperatures. The corrosion rate determined formula,

$$K=534\ W/A.d.t \qquad (1)$$

Where K is corrosion rate in mpy, W is weight loss in gram, d is density and t is immersion time.

Aloe vera formed a thin film on *Unio* surface and it confirmed by activation energy, heat of adsorption, free energy, enthalpy and entropy. Their values were calculated by below mentioned equation.

Activation energy determined by Arrhenius equation,

$$K=A\ e^{-Ea/RT} \qquad (2)$$

Where K is rate constant, A is Arrhenius constant, Ea is activation energy, R is gas constant and T is absolute temperature.

Heat of adsorption calculated by formula,

$$\log(\theta /1- \theta) = \log A - q/2.303RT \qquad (3)$$

Where θ is surface coverage area, A is constant, q is heat of adsorption, R is gas constant and T is absolute temperature.
The surface coverage area calculated by formula,

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$$\theta = (1\text{-}K/Ko) \qquad (4)$$

Where Ko is corrosion rate without inhibitor and K is corrosion rate with inhibitor

The percentage inhibition efficiency determined by,

$$\theta = (1\text{-}K/Ko) \times 100 \qquad (5)$$

Free energy determined by equation,

$$\Delta G = 2.303\ R\ T\ \log(33.3\ K) \qquad (6)$$

Enthalpy and entropy calculated by transition state equation,

$$K = RT/Nh\ e^{\Delta S/R}\ e^{-\Delta H/RT} \qquad (7)$$

Where K is rate constant, R is gas constant, T is absolute temperature, N is Avogadro's number, ΔH is change in enthalpy and ΔS is change in entropy.

Potentiostat EG&G model 173 model used measured the corrosion potential, corrosion current density and corrosion current density. The corrosion current (I_c) calculated by the slope of the line by Stern-Geary equation:

$$\Delta Es/\Delta I_c = \beta_{as}\ \beta_{cs} / 2.303\ I\ (\beta_{as} + \beta_{cs}) \qquad (8)$$

Where,
$\Delta Es/\Delta I_c$ = linear polarization resistance (Rs)
$\beta_{as\ and}\ \beta_{cs}$ = anodic and cathodic Tafel slope respectively
Ij= corrosion current density in mA/cm^2.

The *Unio* corrosion rates of uncoated and coated with *Aloe vera* were determined by potentiostat techniques equation

$$K_{(mpy)} = 0.1288\ Is \times Es / \rho_s \qquad (9)$$

Where, Is (mA/cm^2) = Corrosion current density, ρ_s (g/cm^3) = density and Es = equivalent weight.

RESULTS AND DISCUSSION

Corrosion Rate and Time

The corrosion rate of *Unio* increased when it dipped into longer period dipping in carbon dioxide solution in absence of inhibitor as shown results in Table 1 and Figure 1. *Aloe vera* added in dissolved carbon dioxide solution to reduce corrosion rate of as immersion time enhanced such results looked in Table 1 and Figure 1 plotted K(mpy) versus Y(year).

Corrosion Rate and Temperature

Unio's corrosion rate recorded in absence and presence *Aloe vera* in carbonic acid medium. The results of Table 1 and Figure 2 indicated that *Unio* corrosion rate increased at low to higher temperatures, but their values were reduced by the addition of *Aloe* vera.

Table 1. Corrosion of *Unio* absence and presence of *Aloe vera* as inhibitor in H_2CO_3.

T(Yr)	K_o(mpy)	logK_o	K (mpy)	logK	C(M)	logC	T(^{0}K)	(1000X1/T)
1	99.663	1.998	29.134	1.464	50	-1.30	288	3.47
2	134.549	2.128	33.123	1.520	60	-1.22	298	3.35
3	148.865	2.172	42.484	1.628	70	-1.15	303	3.30
4	176.698	2.247	56.212	1.479	80	-1.09	308	3.24
5	187.353	2.272	61.712	1.790	90	-1.045	313	3.19

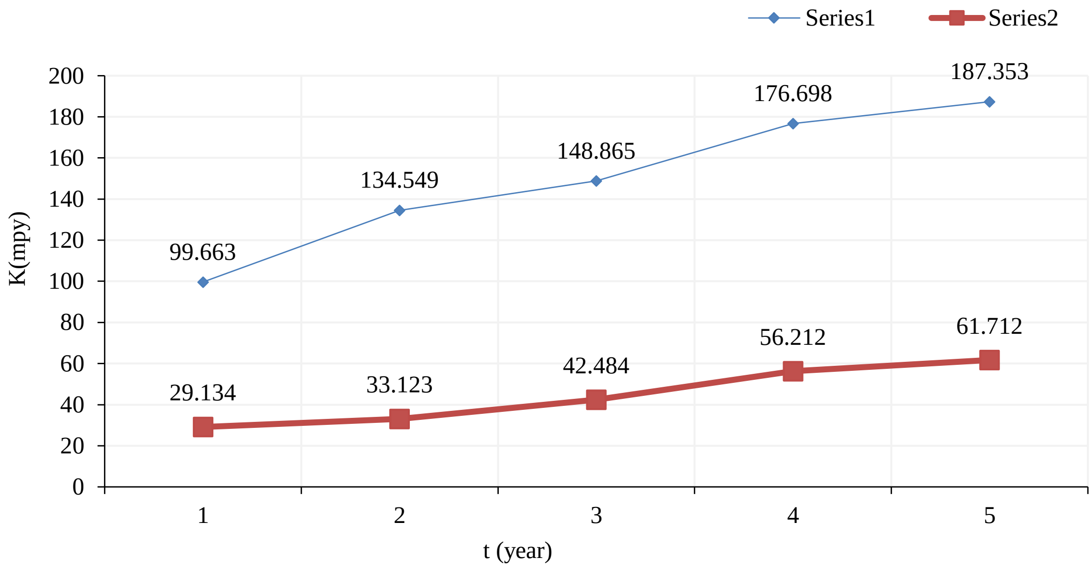

Figure 1. Plot of K (Corrosion rate) Vs t (Year).

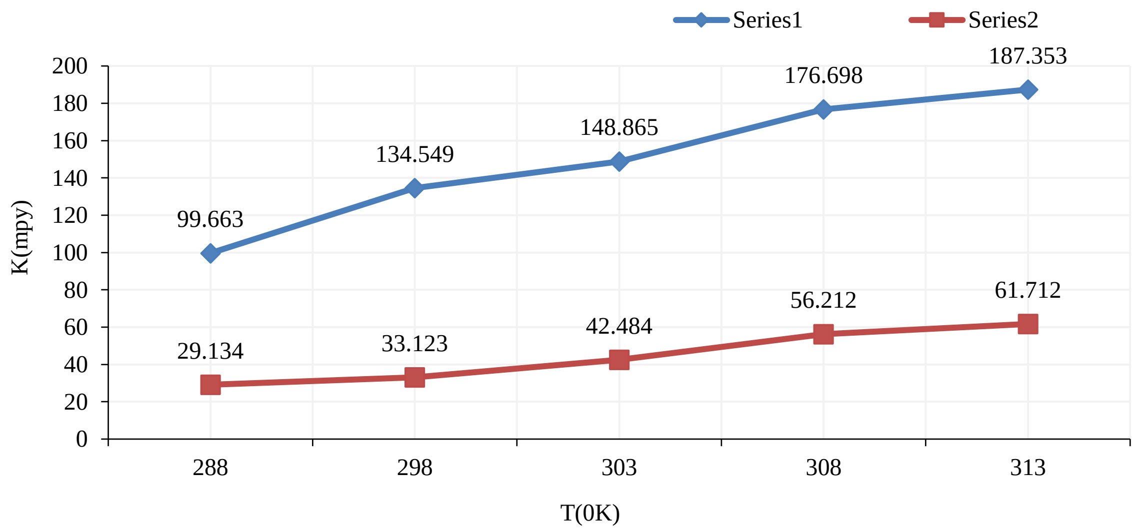

Figure 2. Plot of K (Corrosion rate) Vs T (Temperature).

Corrosion Rate and Concentration

The results of Table 1 depicated as concentration of *Aloe vera* enhanced thus corrosion *Unio* reduced. Such trends noticed in Figure 3 plotted between K(mpy) and C(M).

Corrosion Rate and Surface Coverage Area

Aloe vera reduced the corrosion of *Unio* and increased surface coverage as temperatures and dipping tine enhanced shown in Table 2 and graph K(mpy) versus θ (surface coverage) in Figure 4.

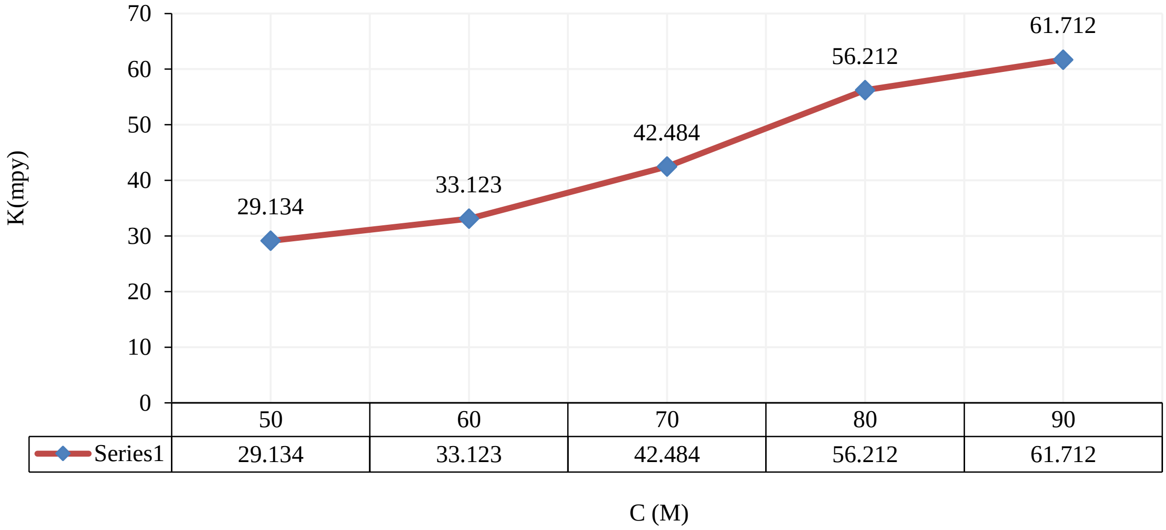

Figure 3. Plot of K(Corrosion rate) Vs C(Concentration).

Table 2. Surface coverage area and *Aloe* vera-*Unio* in dissolved carbon dioxide medium.

Ko	K	K/Ko	θ=(1-K/Ko)	T(y)	C(M)	T(^{0}K)	(1000X1/T)
99.663	29.134	0.29233	0.7076	1	50	288	3.47
134.549	33.123	0.24617	0.7538	2	60	298	3.35
148.865	42.484	0.28539	0.7146	3	70	303	3.30
176.698	56.212	0.31812	0.6818	4	80	308	3.24
187.353	61.712	0.32939	0.6706	5	90	313	3.19

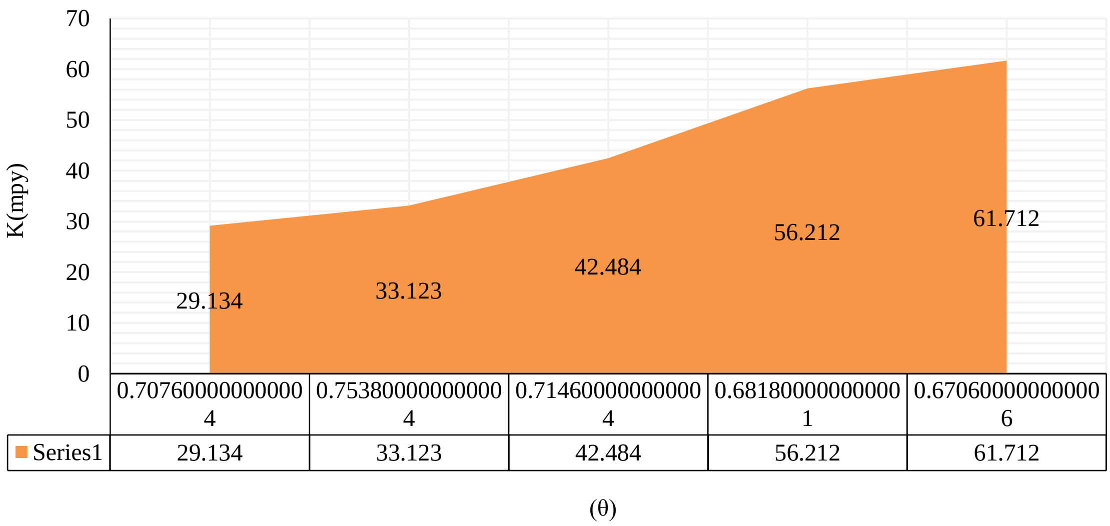

Figure 4. Plot of K(Corrosion rate) versus θ (Surface Coverage Area).

Surface Coverage and Temperature

As temperature increased, *Aloe vera* covered more surfaces on *Unio* such looked in Table 2 and Figure 5 plotted between T (temperature in Kelvin) and θ (surface coverage area).

Corrosion Rate and Percentage Efficiency

When *Aloe vera* added in dissolved in carbon dioxide medium for corrosion protection, it noticed in Table 3 and Figure 6 (plotted K Vs %E) corrosion rate reduced, and percentage efficiency increased.

Percentage Efficiency and Concentration

It observed in Table3 *Aloe vera* concentration enhanced thus percentage efficiency also increased such result noticed in Figure 7 which plotted between %E (percentage efficiency) versus concentration.

Activation Energy

The results of activation energies absence and presence of *Aloe vera* mentioned in Table 4. It observed that activation energies rose but their valued came down after addition Aloe Vera. These results confirmed that the use inhibitor adhered with *Unio* by chemical bonding.

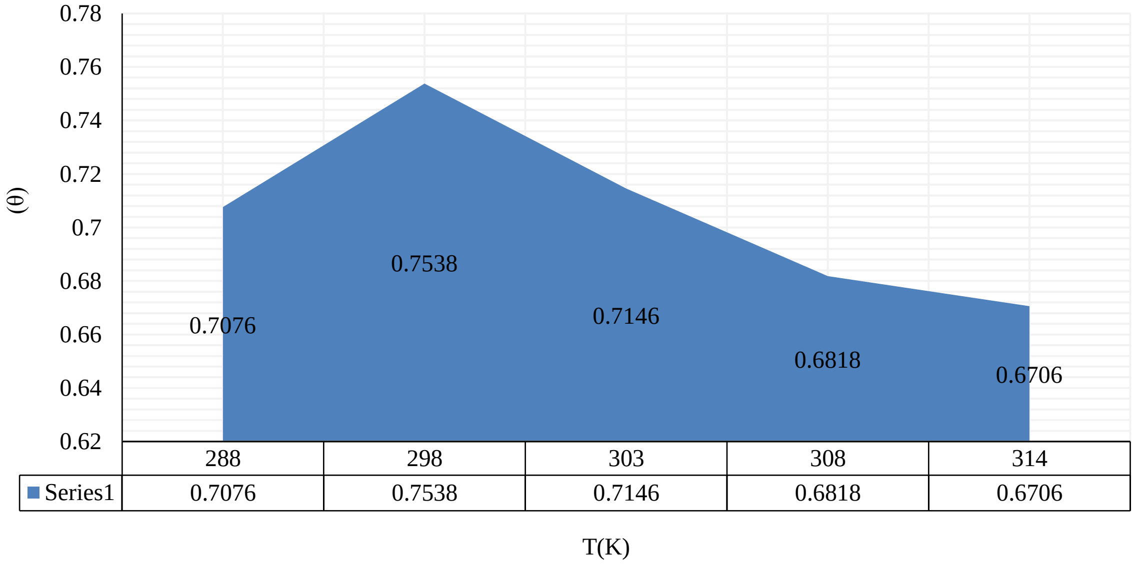

Figure 5. Plot of θ (surface coverage area) Vs. T (Temperature).

Table 3. % Inhibition Efficiency of *Aloe vera*

Ko	K	K/Ko	θ	%IH=(θX100)	T(y)	C(mM)	logC	T(0K)	1000X1/T
99.663	29.134	0.29233	0.7076	70.76	1	50	-1.30	288	3.47
134.54	33.123	0.24617	0.7538	75.38	2	60	-1.22	298	3.35
148.865	42.484	0.28539	0.7146	71.46	3	70	-1.15	303	3.30
176.698	56.212	0.31812	0.6818	68.18	4	80	-1.09	308	3.24
187.353	61.712	0.32939	0.6706	67.06	5	90	-1.04	313	3.19

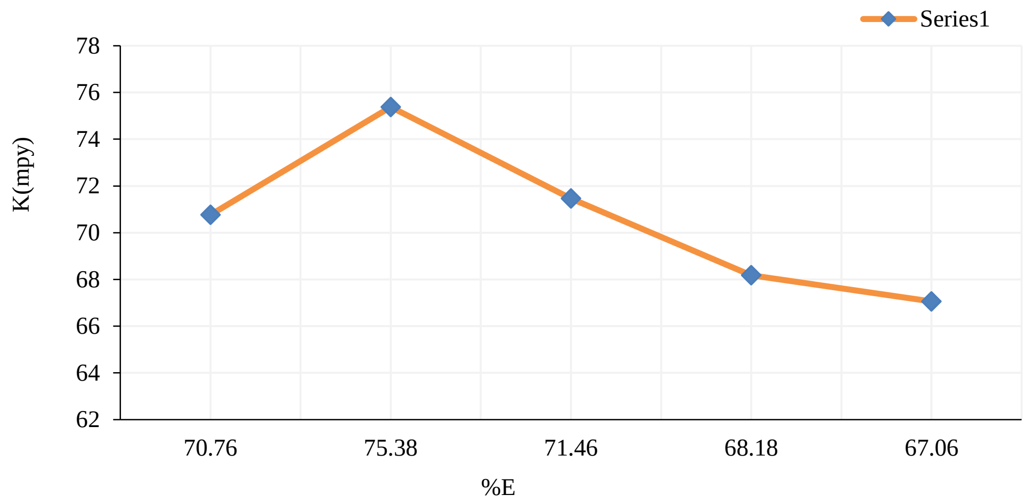

Figure 6. Plot of K (Corrosion rate) Vs. %E (Percentage efficiency).

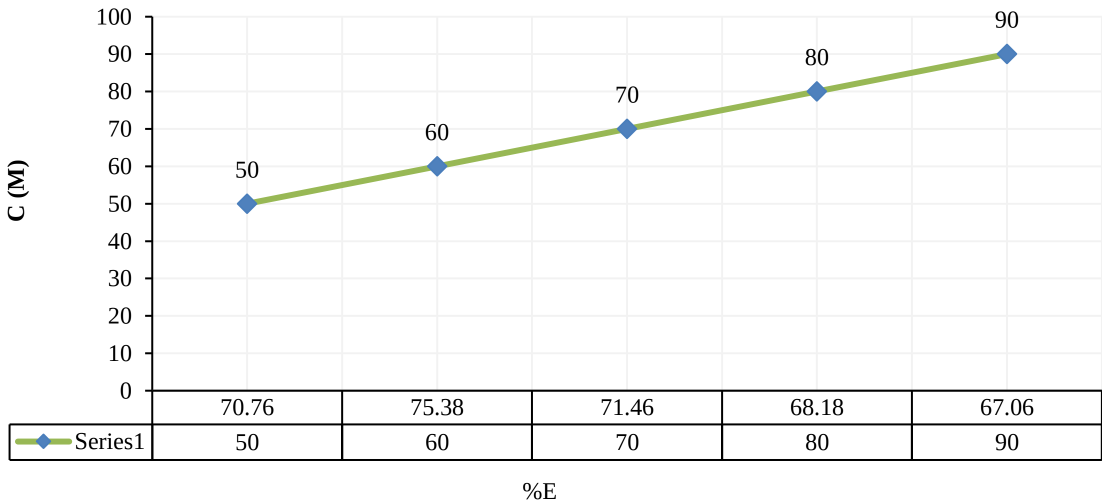

Figure 7. Plot of C (Concentration) Vs %E (Percentage efficiency).

Table 4. Thermal parameters of *Aloe vera*.

T(^{0}K)	288	298	303	308	313
C(M)	50	60	70	80	90
Eao	132.80	136.71	137.23	139.63	138.95
Ea	97.311	97.624	102.841	108.728	109.469-
q	-25.313	-31.212	-25.177	-20.575	-18.278
ΔG	-198.48	-195.398	-199.002	-203.327	-202.557
ΔH	-148.348	-187.837	-273.381	-410.333	-475.361
ΔS	-99.886	-114.204	-143.132	-189.007	-212.188
θ	0.7076	0.7538	0.7146	0.6818	0.6706

Heat of Adsorption

Aloe vera produced negative heat of adsorption such results mentioned in Table 4. It depicted that inhibitor formed chemical bonding with *Unio*.

Free Energy

The negative sign of free energy exhibited that *Aloe vera* attached with *Unio* through chemical bonding. During adsorption of inhibitor exothermic reaction occurred.

Enthalpy

Aloe vera used for corrosion mitigation of *Unio* in carbon dioxide solution. Its enthalpy values are found to be as shown in Table 4. When *Unio* dipped into *Aloe vera* solution, it produced an exothermic reaction. The results of Table 4 indicated that *Aloe vera* formed chemical bonding with *Unio* and stop its dissolution.

Entropy

The negative values of entropy confirmed that *Aloe vera* exhibited exothermic reaction. It boned with *Unio* by chemical bonding in an order matrix.

Surface Coverage Area

Thermal results of activation energy, heat of adsorption, free energy, enthalpy and entropy mentioned in Table 4. The surface coverage areas developed by *Aloe vera* and thermal values noticed that chemisorptions occurred on *Unio* surface.

Table 5. Potentiostat Polarization of *Aloe vera*.

IH	ΔE(mV)	I(mA)	Ba(mV)	Bc(mV)	Ic(mA)	logIC	C(mm)	K(mpy)
IH(o)	-500	450	260	130	34	1.53	00	208
K (50)	-415	371	188	165	31	1.49	50	190
K (60)	-390	320	140	185	28	1.44	60	171
K (70)	-370	290	130	190	26	1.41	70	159
K (80)	-350	270	110	195	23	1.36	80	141
K (90)	-310	250	95	200	22	1.34	90	135

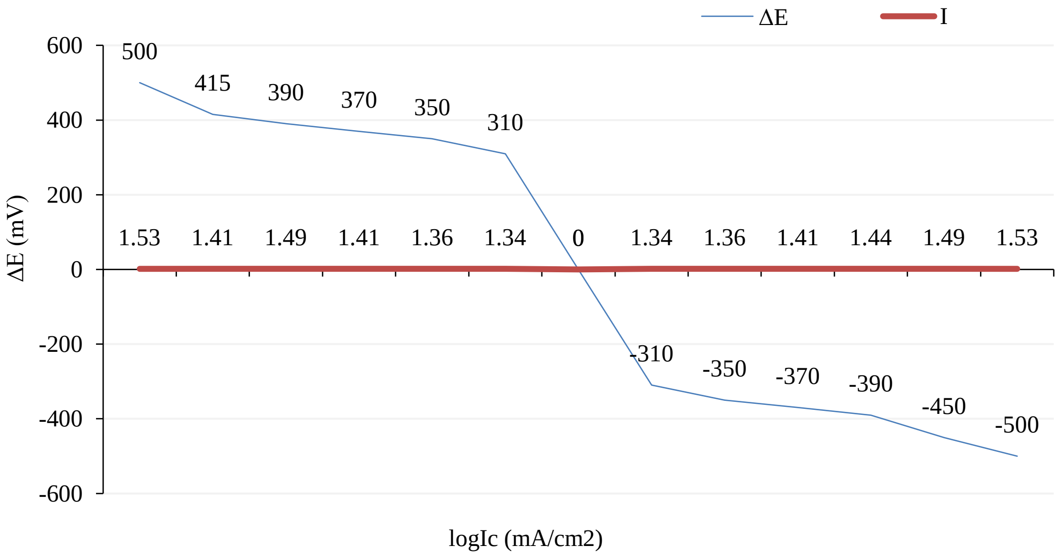

Figure 8. Plot of ΔE (Electrode potential) Vs log Ic (Current density).

Corrosion Potential

The absence of Aloe *vera* corrosion potential increased but its values decreased after addition of *Aloe vera* such results recorded in Table 5 and Figure 8.

Corrosion Current

It observed that without use of *Aloe vera* corrosion current enhanced, but its values reduced when *Aloe vera* added as shown in Table 5.

Current Density

It produced low current density annihilation of inhibitor and it developed high current density when *Aloe vera* added for corrosion control of *Unio* such as seen in Table 5.

Corrosion Rate

The results of Table 5 depicted corrosion rate *Unio* going up in absence of *Aloe vera* when *Aloe vera* added its values going down.

CONCLUSION

Unio are a calciferous animal and they survive in river water. Corrosive substances are discharged into river by different sources so its pH values of water reduce. Acidic water produces adverse environment for *Unio* and it accelerates corrosion reaction. *Aloe vera* used to check the corrosion of *Unio*. *Aloe vera* contains aromatic and aliphatic amines and these compounds formed thin film on *Unio* interface. *Aloe vera* suppressed the attack of hydrogen ions. It increased surface coverage area and inhibition efficiency. *Aloe vera* boned with *Unio* by chemical bonding, as demonstrated by the results of activation energy, heat of adsorption, free energy, enthalpy, and entropy.

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