Viability of *Eugenia Singampattiana Beddome* leaves as potential Green inhibitor on API – 5L – Grade – X52 Steel in Crude oil containing 75 %, connate water

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Abstract

Extract of different concentration of *Eugenia Singampattiana Beddome* leaves has shown potentially good inhibition performance on API – 5L – Grade – X52 line pipe Steel in Crude oil with 75 %, connate water environment. The potential and/or inhibition efficiency increased with the increase of inhibitor concentration dosage and reaches the maximum of 96.97% inhibition efficiency. The multilayer adsorption (MLA) on the metal surface may follows physisorption mechanism. Calculated values of activation energy (E_a), enthalpy of adsorption (ΔH_{ads}) and free energy changes (ΔG_{ads}) are very clearly reveals that the adsorption of naturally synthesized chemical compounds which are biodegradable derived from simple procedure of Eugenia Singampattiana Beddome leaves extract on line pipe surface follows Physisorption, endothermic and spontaneous process respectively. The inhibitor may found to obey Langmuir adsorption isotherms in different aggressive connate water environments.

Key Words:, API – 5L – Grade – X52 Steel, 75% connate water, Average Mass Loss, Adsorption isotherm.

1.0. Introduction:

API -5L Grade steel pipe series starts from API-5L-GradeB to API-5L-Grade-X65 being most familiar material widely employed almost all the Oil and Natural gas field in world wide. But the Oil and Gas industries facing a lot of problems of using this material undergoes dissolution in various concentrations of connate water environments presents in crude oil production. Use of extract of plant green leaves as an inhibitor is one of the best preventive measures of the metal dissolution is very common in different aggressive environments [1-3]. Most of the well-versatile green inhibitors are organic compounds containing polar functional groups with hetero atoms viz; S, N, O and/or P atoms in molecule, heterocyclic conjugated double bond with (π) electrons [4]. These kinds of compounds are adsorbed onto the metallic surface of API-5L-Grade –X52 and block the active corrosion surface sites. Although most of the synthetic chemicals are often expensive, toxic to both human being and the environment, and they are non-biodegradable [5]. In order to overcomes these difficulties, nowadays most of the researcher used natural products which are plenty, cheap, nontoxic and environmentally friendly as a corrosion inhibitors has become a key area, and rich source of naturally synthesized compounds present in green leaves [6-7]. Use of the extract of naturally synthesized organic compounds are either separated or extracted from aromatic herbs, spices and medicinal plants, which is regarded as one of the best practical methods in preventing the pipe line corrosion in Oil and Gas Industries. Plant extracts are an incredibly rich source of naturally synthesized chemical compounds used to prevent oil pipe line corrosion is mainly because of physical and /or chemical adsorption on pipe line surface resulting from the interaction of polar centers of green inhibitor with active sites on pipe line metal [8-11]. The plant inhibitor extract are usually rich sources of active molecules which have substantial high effective only for a particular pipes in a certain environment are highly variable: therefore, an inhibitor may works in one well may not work in another[12].Continuous substantial studies using plants containing heteroatom such as oxygen, nitrogen and sulphur *like Tithonia diversifolia,Murraya koenigii,Moringa oleifera,Vernonia Amygdalina ,Aquilaria Crassna, Cucurbita maxima,Jatropha Curcas,Prunus cerasus,Morninga oleifera, Aloe vera extract, Tamarind tea leaves, Beet root, Saponin, Terminalia bellerica, Oxandra asbeckii,Argemone mexicana, Betanin, Henna, Wheat, Ginger,Marraya koeningii, Garlic extract Ananas sativum, Artemisia Mesatlantica essential oil, spirogyraalgae, Tragacanth gum, Prunus Persic, Lemon Gross, Secang heartwood extract (Caesalpinia sappan I), Dried marjoram leaves* [13-35] have also been used for inhibition of corrosion. In continuous of our present study, *Eugenia Singampattiana Beddome* leaves extract used as a potential green inhibitor on API – 5L – Grade – X52 Steel in crude oil containing 75% connate water have been investigated with various periods of contact and temperature using the Average mass loss (AML) measurements.

2.0. Materials and methods

2.1 Properties of *Eugenia Singampattiana Beddome leaves*:

Eugenia singampattiana Bedd.(ESB) is a very critically endangered medicinal tree, endemic to the tail end of Southern Western Ghats, and this species is highly restricted to evergreen patches of Agasthyamalai hills also known as “Jungle Guava” or “Kaattukorandi (Tamil, Tamilnadu).Lushington called this medicinal plant as “Eugene Singampatty hills in Tinnelvelly; at present Tirunelveli District of Tamil Nadu[36]. It is proven as anticancerous, antitumerous, antioxidative, antimicrobial, antifungal, anti-inflammatory, antihyperlipidaemic and antidiabetic agents [37]. The tribal people (a group called as Kannnikkar) have enormous indigenous knowledge on this particular species which is used for food and medicinal purposes more effectively. *Ex-situ* and *in-situ* conservation strategies are to be developed for this particular species by protecting the existing natural strands and through species specific multiplication and restoration program. Compounds like flavanol glycosides, polyphenols, ellagic acids, gallic acids were reported earlier from various species of Eugenia and GC-MS analyses of leaves have proved the presence of more than eighteen compounds. The major identified compound are 5-Methoxy-2,2,6-trimethyl-1(3-methylbuta-1,3-dienyl)-7-

oxa-bicyclo heptanes followed by 1,2,3-Benzenetriol (pyrogallol), α-caryophyllene, 2-propen-1-one, 1-(2,6-dihydroxy-4-ethoxyphenyl)3-phenyl, n-Hexadecanoic acid,9,12-Octadeca dienoic acid, 2-pentanone, 1-(2,4,6-trihydroxyphenyl) α- Amyrin (β-amyrin), Squalene and limonene**.** The other compounds like alkaloids, coumarins, catechins, glycosides, flavanoids, phenols, steroids, saponins, tannins, terpenes, sugars, xanthoproteins, derivatives and fixed oils are also reported from *E. singampattiana.* Several studies have proved the significant anti-hyper proteinemia, anti-diabetic, anti-oxidant, anti-inflammatory and anti-hyper lipidaemic effects of this species. Flavonoids are also reported to regenerate the damaged pancreatic beta cells and phenols have found tube effective anti-hyperglycemic agents.

2.2 Stock solution of *Eugenia Singampattiana Leaves* Extract:

Eugenia Singampattiana Beddome leaves (ESBL) was collected from the all source were washed under running water and air-dried under shadow for about 20-25 days, crushed well using blender, then immersed in a solution of ethyl alcohol for about 48 hrs, Then it is filtered followed by evaporation technique in order to remove the alcohol solvent completely and the pure infused plant extract was collected: mass of 1g of dried mass was added to a beaker containing 100 ml of triple distilled water. From this lyophilized extract, different concentration of stock solution (10 to 1000ppm) was produced using triple distilled water and used throughout our present investigation.

2.3 Specimen preparation

Rectangular working electrode specimen of API – 5L – Grade – X52 Steel was mechanically pressed cut from pipe line into different form of coupons, each of dimension exactly 40.092 cm^2 (5.1x2.5x0.96cm) polished with silicon carbide emery paper wheel of 80,120 mesh and degreased with trichloroethylene, washed with distilled water, cleaned and dried, then stored in moisture- free desiccators prior to use as a source of mass loss determination and temperature studies.

2.4 Mass loss method

Average mass loss (AML) measurements on API – 5L – Grade – X52 Steel coupon Pre-weighed were carried out by completely immersed in 250 ml capacity beaker containing 100 ml of the test solution in the presence and absence of the inhibitor. The exposed pipe line metal specimens were withdrawn from the environment of test solutions after 24 to 360 hrs intervals at room temperature and also measured in various temperature ranges from 313K to 333K under thermostat controlled water bath. The Average Mass loss (AML) over period of exposure was taken as the basic difference in weights before and after immersion using digital balance with sensitivity of ±1 mg for pipe line coupons. The tests were performed in triplicate to guarantee the reliability of the results and the average mean value (AMV) of the mass loss is reported to check the reproducibility of results. From the Average mass loss (AML) measurements, the corrosion/inhibition rate was calculated using the following computational relationship.

Corrosion Rate (mmpy) = (87.6 X W) /DAT -------------------------- (1)

[Where, mmpy = millimeter per year, W = Mass loss (mg), D = Density (gm/cm^3), A = Area of specimen (cm^2), T = time in hours]

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using the following equations.

%IE = (W1 – W2)/W1 X 100 ------------------------------- (2)

Θ = (W1-W2)/W1 ------------------------------- (3)

(Where W_1 and W_2 are the corrosion rates in the presence and absence of the inhibitor respectively)

3.0 Results and Discussion

3.1 Effect of time variation

Effect of addition of ESBL Inhibitor and its Anti-Corrosive behavior on API – 5L – Grade – X52 Steel pipe line specimen in crude oil containing 75% connate water with the presence and absence of ESBL extract at various exposure times (24hrs to 360 hrs) are shown in Table-1. Derived values were clearly reveals that in presence of ESBL extract, the corrosion rate (CR Value) moderately lowered from 0.3860 to 0.0117 mmpy for 24 hrs and 0.0226 to 0.0109 mmpy even after 360 hrs with increasing the level of inhibitor concentration (from 0 to 1000 ppm). The maximum of 99.17 % of inhibition efficiency is achieved after 24 hrs exposure time is expecting uniform coverage over the entire surface area of API-5L-Grade-X52, suggests that the adsorption and insulating/protective layer formation process occurs mainly due to the presence of main active phyto-chemical constituents atom/or molecules present in the inhibitor molecule especially hetero atom containing species and the metal ion from the surface of the metal. The stability of film formation may retained up to 120hrs exposure time. But beyond this the decrease of inhibition efficiency with increase of exposure time suggests that the stability gradually break through the insulating film formed between the inhibitor molecules and pipe line metal. Consequently,the results may conclude that the ESBL extract with >1000ppm can act as a good efficiency in corrosion prevention for API-5L-Grade-X52 pipe line steel in crude oil contains 75% connate water environment .

Table 1: Corrosion parameters of API – 5L – Grade – X52 Steel in Crude oil with 75% connate water containing various conc. of ESBL extracts with exposure time.

Conc. of inhibitors (ppm)	24 hrs		72 hrs		120 hrs		240 hrs		360 hrs	
	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E
0	0.3860	-	0.1872	-	0.0585	-	0.0246	-	0.0226	-
10	0.3041	21.21	0.0741	60.42	0.0561	40.0	0.0187	23.8	0.0187	17.24
50	0.1053	72.73	0.0711	62.50	0.0468	20.0	0.0164	33.33	0.0156	31.02
100	0.0565	84.85	0.0663	64.58	0.042	28.0	0.0129	47.82	0.0117	48.28
500	0.0351	90.91	0.0624	66.67	0.0351	40.0	0.0117	52.38	0.0109	51.72
1000	0.0117	96.97	0.0468	75.00	0.0051	92.0	0.0105	57.14	0.0109	51.72

3.2. Effect of Temperature

Dissolution behavior of API – 5L – Grade – X52 pipe steel in crude oil containing 75% connate water along with various concentration of ESBL plant extract at various thermostat controlled temperature ranges from 303to 333K was evaluated by Average weight loss (AVL) method and the observed values are summarized in Table-2. These results reveal that the decrease of corrosion rate associated with increase of inhibitor concentrations but decrease with rise in temperature from 303 to 333K.These results indicates that at lower temperature, adsorption of ESBL inhibitor on the pipe line metal surface (or at the solution interface) increased with increase of its concentration provides a wide range of insulating surface coverage. The maximum of 96.20% inhibition efficiency is reached at 313K in 1000 ppm of ESBL inhibitor concentration. However by careful examination, these results shows that the corrosion rate decreased and inhibition efficiency is increased with increase of temperature up to 313K, but beyond this the percentage of IE decreased with increase of temperature may suggests that the process is Physisorption mechanism due to the multilayer film formation on the pipe steel surface in inhibited ESBL solution environment.

Table-2: Corrosion parameters of API–5L–Grade–X52 pipe steel in crude oil with 75% connate water containing ESBL extract after one hour exposure time.

Conc. of inhibitor (ppm)	303 K		313 K		333 K	
	C.R	% I.E	C.R	% I.E	C.R	% I.E

	(mmpy)		(mmpy)		(mmpy)	
0	9.5445	-	9.8253	-	10.9482	-
10	8.9831	5.88	9.2638	5.714	9.8253	10.26
50	8.7024	8.82	8.7024	11.429	9.5496	12.82
100	7.5796	20.59	8.4217	14.286	8.4217	23.08
500	7.5796	20.59	8.4217	14.286	8.1409	25.64
1000	7.0786	26.47	8.1409	17.143	8.1409	25.64

3.3 Activation energy:

The activation energy (E_a) for the corrosion of API – 5L – Grade – X52 Steel in the presence and absence of ESBL extract can be determined using the following Arrhenius plot equation - 4 and its derived form - 5.

$$CR= A\exp(-E_a/RT) \quad \text{-------------- (4)}$$

$$\log (CR_2/CR_1) = E_a/2.303\, R\, (1/T_1-1/T_2) \quad \text{------------- (5)}$$

Where A is the Arrhenius pre-exponential constant, CR_1 and CR_2 are the corrosion rate at the temperature T_1 and T_2 respectively, E_a is the activation energy and R is the universal gas constant (8.314 J/molK).

It is obvious that the value of activation energy (E_a) decreased with increase of ESBL plant extract solution when compared to the blank is 3.8374kJ/mol (Table-3). This lowered observation value clearly indicates that there is a strong chemical adsorption bond between the ESBL inhibitor molecules and the pipe line steel and also the energy needed for dissolution of API pipe line increased.

3.4 Heat of adsorption:

The value of heat of adsorption (Q_{ads}) on the surface of pipe line metals in the presence of plant extract in crude oil containing 75% connate water environment is calculated by the equation - 6.

$$Q_{ads} = 2.303\, R\, [\log (\theta_2/1-\theta_2) - \log (\theta_1/1-\theta_1)] \times (T_2T_1/T_2-T_1) \quad \text{------(6)}$$

(Where R is the gas constant, θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively).

The calculated Q_{ads} values are ranged from - 63.55 to -1.20 kJ/mol (Table – 3). This negative value indicate and suggests that the adsorption of ESBL extract on the API – 5L – Grade – X52 Steel surface is follows exothermic process.

Table -3: Calculated values of Activation energy (E_a) and heat of adsorption (Q_{ads}) of ESBL extract on API – 5L – Grade – X52 Steel in crude oil with 75% connate water

S.No	Conc. of inhibitor (ppm)	% of I.E		E_a ($KJmol^{-1}$)	Q_{ads} ($KJmol^{-1}$)
		30º	60º		
1.	0	-	-	3.8374	--
2.	10	5.88	10.26	2.5063	-63.55
3.	50	8.82	12.82	2.5981	118.93
4.	100	20.59	23.08	2.9464	-45.34
5.	500	20.59	25.64	1.9980	7.97
6.	1000	26.47	25.64	1.9980	-1.20

3.5 ADSORPTION STUDIES:

Processes of adsorption are very important surface phenomenon to determine the corrosion rate of reaction mechanism. The frequently uses of isotherms are viz: Langmuir, Temkin, Frumkin, Flory- Huggins, Freundlich and the El-Awady thermodynamic-kinetic model.

3.5.1. LANGMUIR ISOTHERM,TEMKIN,FLORRY-HUGGINS ETC.,

An adsorption isotherm gives more informative in understanding the mechanism of interaction between the inhibitor molecules and pipe line surface. To attempt various isotherms of the following viz: Langmuir, Temkin, Florry- Huggins, Frumkin, Freundlich adsorption, and El-Awady thermodynamic – kinetic model according to the following general form,

$$Log\ C/\theta = \log C - \log K \text{ --- } (8)$$

$$Exp(-2a\ \theta) = K_{ads}C \text{ -- } (9)$$

$$\Theta = (-2.303\log k/2a) - (2.303\log C/2a) \text{ --------------------------------------- } (10)$$

$$Log(\theta/C) = \log K + x\log(1-\theta) \text{ -- } (11)$$

$$\log\{[C]*(\theta/1-\theta)\} = 2.303\log K + 2\alpha\theta \text{ ----------------------- } (12)$$

$$\Theta = Kc^n \text{ -- } (13)$$

$$Log\ \theta = \log K + n\log C \text{ --------------------------------- } (14)$$

$$Log(\theta/1-\theta) = \log K + y\log C \text{ ------------------------------------ } (15)$$

Plotting of these isotherm and its related parameters are listed out in Table – 4.The observed results indicates that the average regression Co-efficient value (R2) is 0.9950 for Languimer isotherm,0.9275 for Temkin,0.9072 for Florry-Huggins,0.9463 for Frumkin,0.9156 for Freundlich and 0.9183 for El-Awady.When compare to all the isotherm, the regression Co-efficient value (R2) is very close to unity and obeyed Langmuir adsorption isotherm. Since remaining other isotherms are for away to the unity.

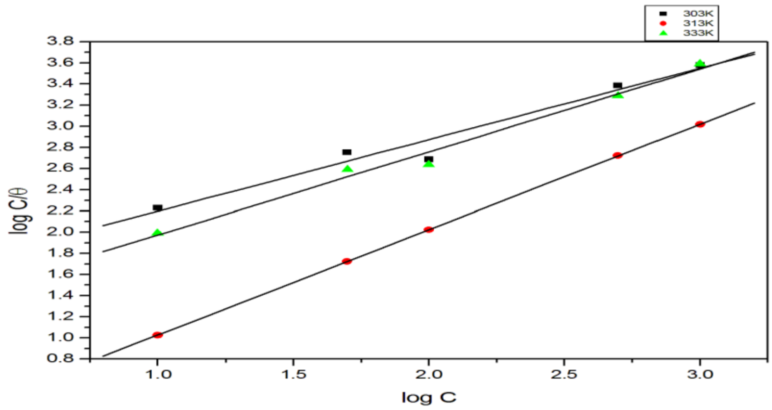

Figure -1.Langmuir isotherm for adsorption of ethanol extract of ESBL on API-5L- Grade – X52 Steel surface.

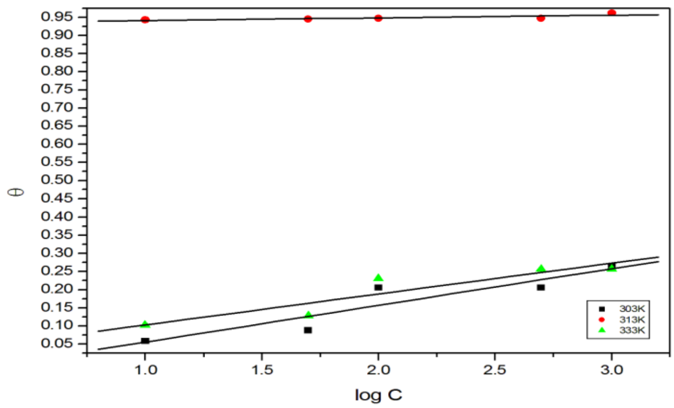

Figure-2.Temkin isotherm for adsorption of ethanol extract of ESBL on API – 5L – Grade – X52 Steel surface.

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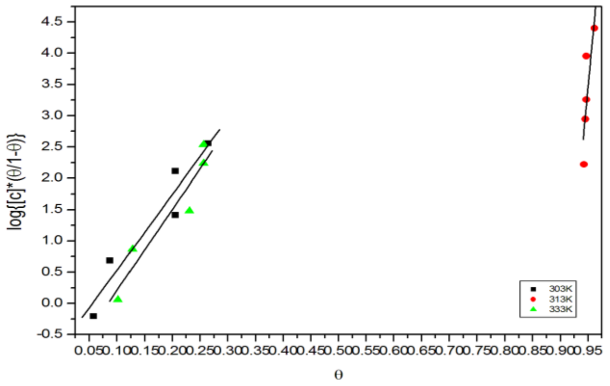

Figure -3. Frumkin isotherm for adsorption of ethanol extract of ESBL on API – 5L – Grade – X52 Steel surface .

3.6. FREE ENERGY OF ADSORPTION

The equilibrium constant of adsorption of ethanol extract of ESBL on the surface of API – 5L – Grade – X52 Steel is related to the free energy of adsorption (ΔG) according to equation - 16

$$\Delta G = -2.303RT \log (55.5K) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

Where R is gas constant and T is the temperature.

The free energy of adsorption was calculated from values of 'k' obtained from Langmuir, Temkin, Florry – Huggins, Frumkin, Freundlich and El-Awady according to equation (16) and is recorded in Table-4. The results show that the free energy of adsorption 'ΔG' are negative and less than the threshold value on 40kJ/mol required for chemical adsorption, indicating that adsorption of ethanol extract of CRL on API – 5L – Grade – X52 Steel surface is spontaneous and occurred according to the mechanism of physisorption. Since this phenomenon is attributed to electrostatic interactions between the charged metal ions and charged molecules present in the phyto-chemical constituents.

Table: 4. Adsorption parameters for adsorption of ethanol extract of ESBL on API – 5L – Grade – X52 Steel surface.

Isotherm	Temperature	R^2	K	ΔG_{ads} kJ/mol	Slope value
Langmuir	303K	0.9995	33.3426	-18.9554	
	313K	0.9962	18.3216	-18.9121	

	333K	0.9894	15.3780	-18.6892	
					a
Temkin	303K	0.9251	0.0025	-5.2360	-11.38
	313K	0.9377	0.0032	-4.2325	-35.10
	333K	0.9198	0.0052	-3.6056	-64.69
					x
Florry-Huggins	303K	0.9021	0.0078	2.1030	10.24
	313K	0.9121	0.0126	-1.8324	11.42
	333K	0.9068	0.0326	-1.6486	13.96
					α
Frumkin	303K	0.9588	0.2046	-6.1218	6.07
	313K	0.9316	0.1961	-5.1261	5.12
	333K	0.9485	0.0798	-4.1220	6.49
					n
Freundlich	303K	0.9251	0.0299	-1.2838	0.3251
	313K	0.9049	0.0321	-2.1921	0.2152
	333K	0.9168	0.0650	-3.5532	0.2150
					1/y
El-Awady	303K	0.9269	0.0280	13.7781	2.64
	313K	0.9097	0.0342	14.6234	2.19
	333K	0.9182	0.0652	14.9271	3.84

4.CONCLUSIONS

Eugenia Singampattiana Beddome leaves (ESBL) has shown excellent inhibition performance for API – 5L – Grade – X52 pipe line steel in Crude oil with 75%, connate water environment. The inhibition efficiency increased with the increase of ESBL inhibitor concentration. The maximum inhibition efficiency was achieved 96.97% up to 313K.However inhibition efficiency gradually decreased beyond 333K.It follows physical adsorption process. The value of activation energy (E_a), enthalpy of adsorption (ΔH_{ads}) and free energy changes (ΔG_{ads}) indicates that the adsorption of inhibitor on metal surface follows physical, exothermic and spontaneous process respectively. The inhibitor is found to obey Langmuir adsorption isotherm. Since the average regression coefficient value (R) is very close to unity(0.9913)

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