

Understanding the Corrosion Inhibition by Rodine Spl 213 on Mild Steel Surface in HCl Acid under Different Conditions

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ABSTRACT: The inhibitive action of Rodine Spl 213 on the corrosion of mild steel in HCl was studied using weight loss measurements. Results obtained showed that this compound has better inhibiting properties for mild steel corrosion in HCl acid medium under steady condition compared to unsteady condition. The results indicate that both conditions showed inhibition in corrosion process by virtue of adsorption and inhibition efficiency improved with concentration. The adsorption of inhibitor follows Langmuir adsorption isotherm and thermodynamic functions evaluated from temperature studies results physical adsorption.

KEYWORDS: Corrosion, Inhibition, Mild steel, Acid medium, Adsorption.

I. INTRODUCTION

The corrosion control of metals is an important activity of technical, economical, environmental and aesthetical importance. Mild steel is the material of wide industrial application due to its relatively low cost compared to other metals and alloys. The study of corrosion of mild steel in acid media is both of academic and industrial concern that has received a considerable amount of attention. An important method to protect metals deployed in service in aggressive environments against corrosion is the addition of inhibitors to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate. Steel is a widely used material in various industrial sectors because of its economic and technical properties, though its resistance to corrosive attacks from its environment remains weak. Several researchers have focused their attention on the use of the most effective inhibitors that don't have harmful effects, [1–7] especially to protect steel in an acidic medium.

Acid solutions are widely used for industrial cleaning, oil well acidification and pickling. The corrosion of steel in such environments and its inhibition constitute a complex problem of process. Generally, using organic inhibitors to mitigate corrosion of mild steel in acidic media is highly cost-effective. During the past decade, the inhibition of steel in acid solutions by different types of organic inhibitors has been extensively studied. A perusal of the literature on acid corrosion inhibitors reveals that most organic substance employed as corrosion inhibitors can adsorb on the metal surface through heteroatoms such as nitrogen, oxygen, sulphur and phosphorus, multiple bonds or aromatic rings and block the active sites, decreasing the corrosion rate [9–13]. In research on organic corrosion inhibitors, attention is paid to the mechanism of adsorption and also to the relationship between inhibitor structures and their adsorption properties. It has been observed that the adsorption depends mainly on the electronic and structural properties of the inhibitor molecule such as functional groups, steric factors, aromaticity, electron density on donor atoms and p orbital character of donating electrons [8]. Acid solutions of different concentrations are widely used for pickling treatments, acid

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cleaning operations and oil well acidising. The use of corrosion inhibitors is usually required to prevent or delay corrosion of metals exposed to corrosive environments. Most corrosion inhibitors are organic compounds that contain heteroatoms such as nitrogen, oxygen, phosphorus or sulphur. Generally, the inhibiting efficiency of these inhibitors increases with the electron density.

In industry, metal equipment is cleaned from time to time to prevent damage and maintain efficiency of operation. The chemical cleaning of metals has a number of advantages over mechanical cleaning methods. Chemical cleaning is a process which primarily uses chemical solutions to remove fouling from inside plant and equipment such as heat exchanger and boilers [9-17]. It all depends on selection of corrosion inhibitors which is done based on static conditioned tests but it is important to understand the dynamic results from development and industrial safety point of view. This work concerns the study into the effect of addition Rodine spl 213 on the corrosion inhibition of mild steel in the HCl acidic media using gravimetric measurements. The effect of concentration and temperature of this inhibitor on the inhibition properties was also studied all within steady and unsteady condition of the acidic mix solution.

II. MATERIALS AND METHOD

Materials

Mild carbon steel specimens having a weight percentage composition as Carbon 0.15-0.18%, Manganese 0.70-0.90%, Phosphorus 0.040% and Sulphur 0.040% of steel were used. The specimens were of dimensions 3.9 cm x 1.2 cm and thickness 5 mm. The blank corrosive acids were 1, 2, 3 N HCl solution. Inhibitive solution - Rodine Spl 213 was used for studying inhibitive actions for different concentration of acid, inhibitive solution at different temperatures as a static condition and addition of sand, agitation effect all as dynamic condition.

Preparation of specimens

The mild steel specimen were polished mechanically using sandpaper of micro grade, washed thoroughly with distilled water, degreased with acetone and air dried before being immersed in the acid solution.

Weight loss method

In the gravimetric test, cleaned and dried specimens were weighed before immersion in their respective test solutions of 1, 2, 3 N HCl solution using CA 123 electronic weighing balance with the accuracy of ± 0.005 . The tests were conducted with different concentrations of inhibitor, acid concentration, at different temperatures as a static and for dynamic resemblance sand was added to solution on weight percent basis and agitation effect was also introduced with help of an agitator all for immersion time of 4 hrs. At the end of the tests, the specimens were carefully washed with distilled water, degreased with acetone and air dried, all to prevent further corrosion from taking place, and then reweighed.

From the initial and final weights of the specimens, the loss of weights was calculated by weight difference,

$$W_d = [W_i] - [W_f]$$

Where,

W_i = Initial Weight of Specimen in grams

W_f = Final Weight of Specimen in grams

W_d = Weight difference in grams

The Corrosion Rate (in mpy^{-1} –millimetre penetration per year) was computed from the equation below,

$$CR = \frac{87.6 \times W_d}{A \times t \times D}$$

Where,

W_d is the weight difference (gm), D is the density of the specimen (7.85 g/cm^3), A is the surface area of specimen (cm^2) and t is the immersion time (hrs).

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And the Inhibitor Efficiency Rate η (%) was computed from the equation below,

$$\eta \% = \frac{CR_{wo} - CR_w}{CR_{wo}} \times 100$$

Where,

η % = Inhibitor Efficiency (%)

CR_{wo} = Corrosion rate (without inhibitor)

CR_w = Corrosion rate (with inhibitor)

Finally, Surface Coverage (θ)

$$\text{Surface Coverage } (\theta) = \frac{CR_{wo} - CR_w}{CR_{wo}}$$

Where,

θ = Surface Coverage (θ)

III. EXPERIMENTAL RESULTS

Weight losses and Corrosion rates

The weight loss test was conducted for mild carbon steel specimens, studied by corrosion rates that were obtained at different variations in temperature and acid concentration for a clean solution of HCl acid with steady condition of the medium.

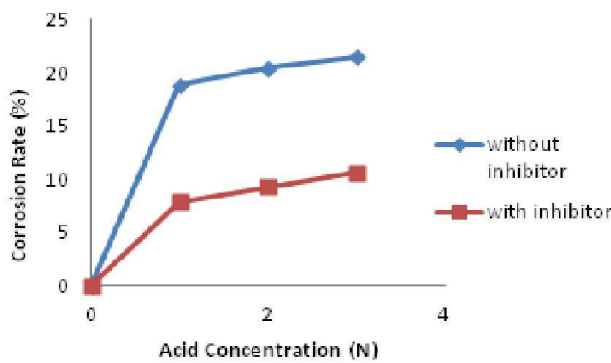


Fig. 1: Corrosion rate comparison with acid concentration at 30°C temperatures in HCl acid medium

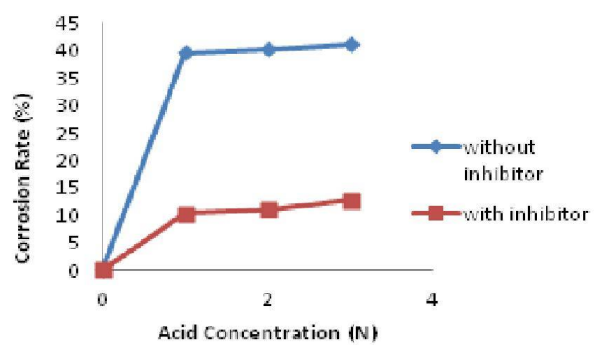


Fig. 2: Corrosion rate comparison with acid concentration at 50°C temperatures in HCl acid medium

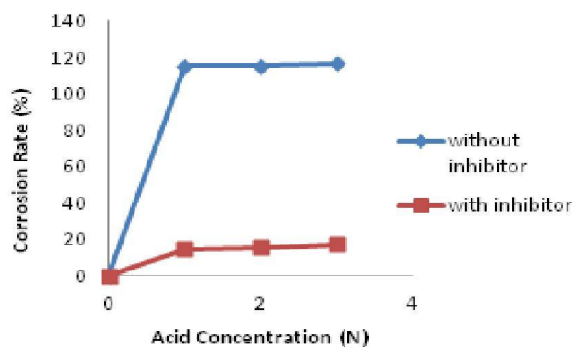


Fig. 3: Corrosion rate comparison with acid concentration at 60°C temperatures in HCl acid medium

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The weight loss of the mild steel is observed with the help of corrosion rate obtained from weight loss study. **Fig. 1, 2 & 3** shows the comparative study of corrosion rates at different temperatures. This graph is plotted at values of different HCl acid concentrations. It was observed that corrosion rate with inhibitor is less compared to corrosion rate without inhibitor that is less weight loss which shows the inhibitors effectiveness in the acid solution mixture. All these tests were carried out at static condition that is in clean solution of HCl acid with steady condition of medium.

Further, weight loss test is conducted for same mild carbon steel specimens, studied with corrosion rates that were obtained at different variations in acid concentration but for an unclean solution of HCl acid with unsteady condition of the medium which means in these tests, the medium solution was subjected to agitation at 1200 rpm with the help of an agitator where one set was clean HCl solution with agitation effect while the other was added with sand on weight percent basis which resembled the dynamic nature of the medium solution.

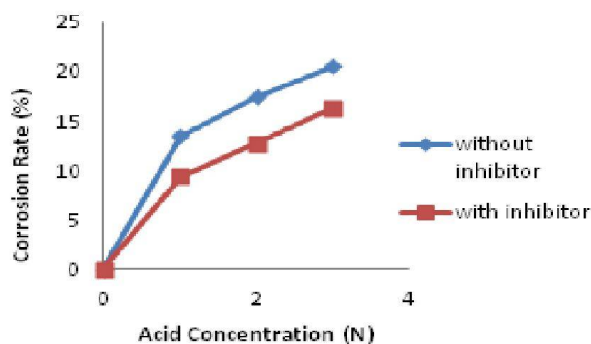


Fig. 4: Corrosion rate comparison at different acid concentration under agitation in HCl acid medium

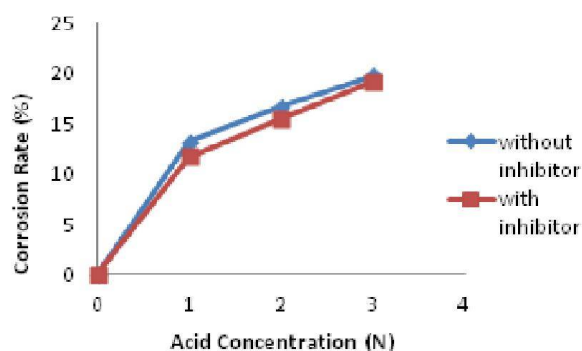


Fig. 5: Corrosion rate comparison at different acid concentration under agitation in sand + HCl acid medium

As an unsteady approach, mild steel specimens were subjected to agitation for both without sand and with sand setup of testing apparatus. **Fig. 4, 5** shows the comparative study of corrosion rates at different acid concentrations but at the temperature of 30 °C. This enabled to compare the study of specimens under the impact of clean HCl solution, agitated clean HCl solution and agitated sand added HCl solution that is of static and dynamic condition. This comparison could be understood with the help of **Fig. 1, 4 & 5** were the variation in the curve of with inhibitor is clearly noticed. The curve of with inhibitor drastically fails to maintain its effectiveness under unsteady conditions compares to steady conditions which could be further understood in Inhibitor efficiencies section.

Inhibitor efficiencies and Corrosion rates

The inhibitor efficiencies could be understood only after variations in inhibitor concentrations. The standard inhibitor concentration of Rodine Spl 213 is from (1000-3000) ppm. It is explained with first at 1000 ppm, then at different inhibitor concentrations and finally comparison with steady & unsteady conditions both at same 1000 ppm concentration.

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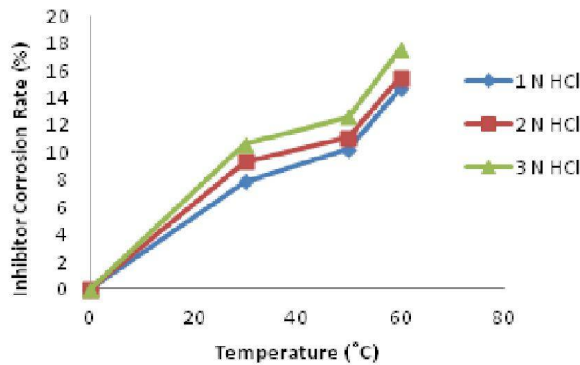


Fig. 6: Inhibitor corrosion rate comparison at different temperatures in HCl acid medium with 1000 ppm inhibitor concentration

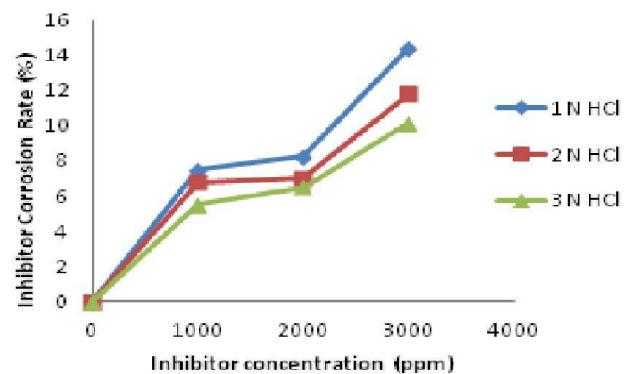


Fig. 7: Inhibitor corrosion rate comparison at different inhibitor concentration in HCl acid medium

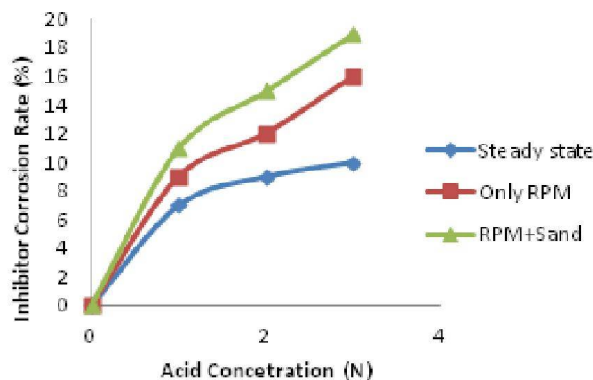


Fig. 8: Inhibitor corrosion rate comparison at different acid concentration under steady & unsteady conditions in HCl acid medium

The weight loss results obtained for mild steel in 1, 2 & 3 N HCl acid in the presence and absence of different concentration of Rodine Spl 213 in solution mixture with sand are summarized as shown in **Fig. 6, 7 & 8** were first the inhibitor corrosion rate is varied with different medium temperature, then it is ideally compared with the different concentrations of inhibitor for its effective study and finally inhibitor corrosion rate with different acid concentrations which is prior because its comparison includes with steady and unsteady conditions where steady condition includes tests with clean acid solution without any motion whereas in unsteady condition sand was added to solution on weight percent basis and agitation effect was also introduced with help of an agitator.

So due to sand particles the erosion of the specimen takes place more as compare to clean solution. The corrosion rate values of carbon mild steel in 1, 2 & 3 N HCl decreases as the concentration of inhibitor increases i.e. the inhibition efficiency increases as the concentration of inhibitor is raised as seen in **Fig. 9** and the temperature of solution is maintained at the 30°C for this set.

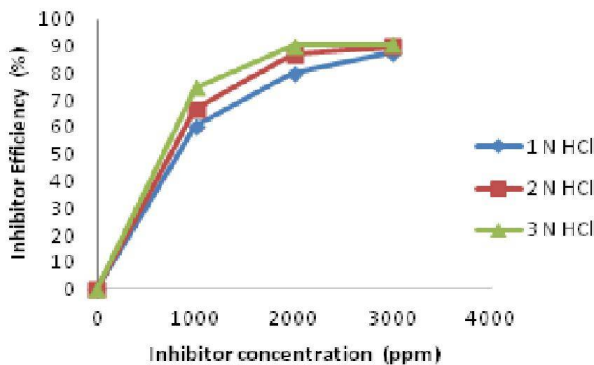


Fig. 9: Inhibitor efficiency comparison at different inhibitor concentration in HCl acid medium at different concentrations

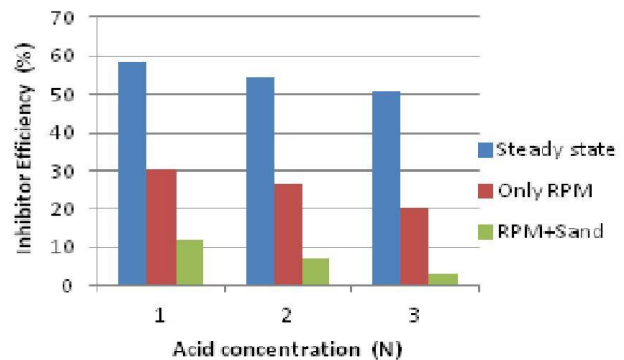


Fig. 10: Inhibitor efficiency comparison at different acid concentration under steady & unsteady conditions in HCl acid medium

And finally with the help of **Fig. 8 & 10** it is observed that there is fall in inhibitor efficiency which is due to static and dynamic nature of the medium. In steady conditions, the action of inhibitor over the carbon mild steel specimen is providing a worth satisfactory results but when subjected to unsteadiness that is introduction of sand in one set and another without sand but both under constant agitation resulted a critical fall in the inhibitor effect to prevent weight loss of the specimens.

Langmuir adsorption isotherms

The inhibitive action of Rodine Spl 213 toward the acid corrosion of mild carbon steel could be attributed to the adsorption of its components onto the mild steel surface. The basic information of the interaction between the surface of mild steel and inhibitor can be determined from several adsorption isotherms. The common used adsorption isotherms are the Temkin, Frumkin and Langmuir isotherm.

According to the Langmuir adsorption isotherm, the surface coverage (θ) is related to inhibitor concentration (C_{inh}) by equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh}$$

Where,

K = the adsorption equilibrium constant.

K is related to the standard free energy of adsorption (ΔG°_{ads}) by equation:

$$K = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right)$$

Where,

$C_{solvent}$ = molar concentration of the solvent, which in the case of water is 55.5 mol L⁻¹.

R = the gas constant

T = the absolute temperature.

The degree of surface coverage (θ) for different concentrations of the inhibitor (C) has been evaluated. The data were tested graphically to determine a suitable adsorption isotherm. When a straight line is obtained with a linear correlation coefficient (R^2) almost equal to 1.0 then Langmuir adsorption method is success.

The plot of the ratio of concentration to surface coverage (C/θ) against concentration (C) displayed a straight line for tested inhibitor (**Fig. 11**).

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Table 1. Values of Langmuir Parameters for mild steel in HCl acid medium

Acid medium	Slope	K	R ²
HCl	1.342	25	0.97

Table 1 shows the correlation coefficient of the Langmuir adsorption isotherm. The linear plot with high correlation coefficient (0.97) and slope of about unity clearly reveals that the surface adsorption process of rodine inhibitor in acid medium on the mild steel surface, obey the Langmuir adsorption isotherm. Therefore one can infer that physisorption occurred.

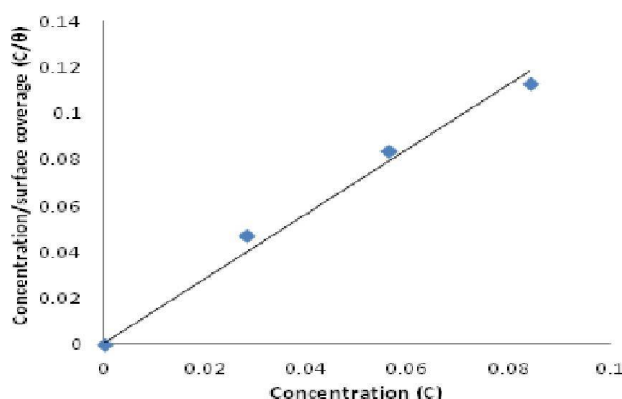


Fig. 11: Langmuir adsorption isotherm for corrosion inhibitor in 1 N HCl acid medium

The slopes of straight lines (**Fig. 11**) were found to be very close to unity. This means that, adsorbed molecule occupies only one site and it does not interact with other adsorbed species.

Effect of temperature

There are two main types of interaction often describe adsorption of inhibitor on a corroding system viz: chemical adsorption and physical adsorption. It has been suggested that physisorbed molecules are attached to the metal at the cathodes and essentially retard metal dissolution by stifling the cathodic reaction whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached. The apparent activation energies (E_a) for the corrosion process in absence and presence of inhibitor were evaluated from Arrhenius equation.

$$\log \left(\frac{\rho_2}{\rho_1} \right) = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Whereas estimates of the heats of adsorption (Q_{ads}) were obtained from the trend of surface coverage with temperature as follows;

$$Q_{ads} = 2.303R \left(\log \left(\frac{\theta_2}{1 - \theta_2} \right) - \log \left(\frac{\theta_1}{1 - \theta_1} \right) \right) \times \frac{T_1 \times T_2}{T_2 - T_1}$$

ρ_1 and ρ_2 are the corrosion rates in temperatures T_1 and T_2 , respectively while θ_1 and θ_2 are the degrees of surface coverage at temperature T_1 and T_2 and R is the gas constant.

$$K = \frac{1}{55.5} \exp \left(\frac{-\Delta G^\circ_{ads}}{RT} \right)$$

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The standard free energy of adsorption, ΔG°_{ads} , which can characterize the interaction of adsorption molecules and metal surface, was calculated by equation of K. The negative values of ΔG°_{ads} ensure the spontaneity of adsorption process and stability of the adsorbed layer on the mild steel surface. Generally, the values of ΔG°_{ads} around -20 kJ/mol or lower are consistent with physisorption, while those around -40 kJ/mol or higher involve chemisorptions. The calculated values of E_a and Q_{ads} are given in **Table 2**

Table 2. Values of Langmuir Parameters for mild steel in HCl acid medium

Concentration (ppm)	E_a (KJmol ⁻¹)	Q_{ads} (KJmol ⁻¹)
1000	42.02	-2.486
2000	35.49	-2.484
3000	39.14	-2.480

The value of free energy, ΔG°_{ads} , is -18.23 kJ/mol for hydrochloric acid is consistent with literature survey and therefore authenticates physical adsorption. This implies that the rodine adheres on the surface of the corroding system and so gives a very strong inhibitor.

IV. CONCLUSION

Rodine Spl 213 corrosion inhibitor found to be effective HCl acid inhibitors of mild steel in various concentration of hydrochloric acid. So based on above study it was found that rate of corrosion increases with acid concentration, efficiency of corrosion inhibitor steadily falls with increase in acid concentration and temperature followed by surface coverage which decreases with increase in acid concentration but corrosion rate immediately drops with increase in inhibitor concentration. However, hydrochloric acid medium in steady conditions exhibited better inhibition efficiency than in the unsteady condition because unsteady conditions to acid medium had a greater base metal loss of mild steel compared because of vigorous turbulence. This result clearly shows whether there is still the need for industries to rely over the static conditioned tests for selection of corrosion inhibitors for their process equipments cleaning and maintenances purposes or need to work with dynamic conditioned tests. The thermodynamic parameters indicated that the inhibitor is physisorbed on the metal surface and that its adsorption obeys the Langmuir adsorption isotherm.

REFERENCES

- [1]. F. Bensajjay, S. Alehyen, M. El Achouri, S. Kertit (2016), "Corrosion inhibition of steel by 1-phenyl 5 mercapto 1,2,3,4-tetrazole in acidic environments (0.5M H₂SO₄ and 1/3 M H₃PO₄), Anti-Corrosion Methods and Materials, Vol. 50, pg no 402-409, 2016.
- [2]. Viswanathan S. Saji, "A Review on Recent Patents in Corrosion Inhibitors", Recent Patents on Corrosion Science, Vol. 2, pg no 6-12, 2010.
- [3]. Abdulghani A. Jarallal, Muhannad M. Al-Darbi, "Developing New Innovative Descaling and Corrosion Inhibiting Solutions to Protect Steel Equipment in the Oil and Gas Industry", International Conference, china, 2013.
- [4]. Nutan Kumpawat, Alok Chaturvedi, Rajesh Kumar Upadhyay, "Comparative Study of Corrosion Inhibition Efficiency of Naturally Occurring Ecofriendly Varieties of Holy Basil (Tulsi) for Tin in HNO₃ Solution", Open Journal of Metal, Vol. 2, pg no 68-73, 2012.
- [5]. Forsal, L. Lakhrissi, K. Naji, S. Abirou, M. Ebn Touhami, B. Lakhrissi, and M. Addou, "The Efficiency of Corrosion Inhibitor as Given by Electrochemical Impedance Spectroscopy Tafel Polarization and Weight-Loss Measurements", Spectroscopy Letters: An International Journal for Rapid Communication, Vol. 43, pg no 136-143, 2010.
- [6]. Y. El-Etre, "Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves", Journal of Colloid and Interface Science, Vol. 314, pg no 578-583, 2007.
- [7]. S. Ananth Kumar, A. Sankar, S. Rameshkumar, "Oxystelma Esculentum Leaves Extracts As Corrosion Inhibitor For Mild Steel In Acid Medium", International Journal of Scientific & Technology Research, Vol. 2, Issue 9, pg no 55-58, 2013.
- [8]. F. Bentiss, M. Bouanis, B. Mernari, M. Traisnel, H. Vezin, M. Lagrene'e, "Understanding the adsorption of 4H-1,2,4-triazole derivatives on mild steel surface in molar hydrochloric acid", Applied Surface Science, Vol. 253, pg no 3696-3704, 2007.
- [9]. Aisha Al-Turkustani, "Corrosion inhibition of steel in sulphuric acid by aqueous extracts of Rose and Rose water", Indian journal of Chemical Technology, Vol. 23, pg no 131-138, 2016.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

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- [10]. Ebenso, E. E., Eddy, N. O. and Odiongenyi, A. O. "Corrosion inhibitive properties and adsorption behaviour of ethanol extract of Piper guinensis as a green corrosion inhibitor for mild steel in H₂SO₄, African Journal of Pure and Applied Chemistry, Vol.2, pg no 107-115, 2008.
- [11]. Emeka E. Oguzie, "Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel", Corrosion Science, Vol. 50, pg no 2993-2998, 2008.
- [12]. E.E. Ebenso, N.O. Eddy, A.O. Odiongenyi, "Corrosion Inhibition and Adsorption Properties of Methocarbamol on Mild Steel in Acidic Medium. Portugaliae Electrochimica Acta", Vol .27, pg no 13-22, 2009.
- [13]. L. A. Nnanna, O. C. Nwadiuko, N. D. Ekekwe, E. P. Eti, K. B. Okeoma, "The effect of inhibitor on the corrosion of aluminium alloy in acidic solutions", Archives of Applied Science Research, Vol. 3, pg no 68-74, 2011.
- [14]. A.Y. El-Etre, "Inhibition of aluminum corrosion using Opuntia extracts. Corrosion science", Vol .45, pg no 2485-2495, 2003.
- [15]. EE Abd El Aal, W Zakria, A Diab and SM Abd El Haleem, "Aniline and some of its derivatives as corrosion inhibitors for nickel in 1M HCl solution ", Journal of Chemical Technology and Biotechnology, Vol .74, pg no 1061-1068, 1999.
- [16]. Adriana Samide, "A pharmaceutical product as corrosion inhibitor for carbon steel in acidic environments", Journal of Environmental Science and Health. Part A, Vol .48, pg no 159-165, 2013.
- [17]. Gajanan Kumbhar, S.V. Ranade, "Effectiveness of corrosion inhibitors on mild steel in acidic medium", International Journal of Advanced Technology in Engineering and Science, Vol 3, pg no 88-93, 2015.
- [18]. Boleslaw Ludwik Dunks, "Surface Area of Activated Charcoal by Langmuir Adsorption Isotherm", Journal of Chemical Education, Vol. 38. pg no 357-358, 1961.
- [19]. Keith J. Laidler, "The Development of the Arrhenius Equation. Journal of Chemical Education", Vol. 61, pg no 494-498, 1984.
- [20]. DK Chattoraj, "Thermodynamics of Adsorption at Interfaces and the Gibbs Surface Excess", Proceedings of the Indian National Science Academy, Vol. 67, pg no 663-685, 2001.