Review on Modification of Nanocellulose for Application in Composites

Mohammad Tajul Islam, Mohammad Mahbubul Alam, Marina Zoccola

Department of Chemical Engineering, Bharati Vidyapeeth College of Engineering, Navi Mumbai,

Maharashtra, India

ABSTRACT: Rodine Spl 213 was tested as corrosion inhibitor for mild steel in HCl & H_2SO_4 acid solution using weight loss measurements. Results obtained showed that this compound has good inhibiting properties for mild steel corrosion in HCl acid medium compared to H_2SO_4 acid medium. The results indicate that both acids showed inhibition in corrosion process by virtue of adsorption and inhibition efficiency improved with concentration. Inhibition mechanisms were deduced from the temperature dependence of the inhibition efficiency as well as from activation parameters that govern the process. Adsorption in both acids was found to obey the Langmuir adsorption isotherm. The phenomenon of physical adsorption is proposed from the obtained thermodynamic parameters.

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

I. INTRODUCTION

Corrosion inhibitor is a chemical substance which, when added in small concentrations to an environment, minimizes or prevents corrosion. Corrosion inhibitors are used to protect metals from corrosion [1]. Industries depend heavily on the metal and alloy. One of the most challenging and difficult tasks for industries is the protection of these metals and alloys from corrosion. Corrosion control of metals and alloys is an expensive process and industries spend huge amount to control this problem. The use of corrosion inhibitors is the best way to prevent destruction or degradation of metal surface in corrosive media. The use of corrosion inhibitors is the most economical and practical method for reducing corrosive attack on metals. Metal equipment must be 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.

Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Hydrochloric acid is widely used in the pickling processes of metals. Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption. In various industrial processes mild steel mostly comes in contact with acid solution and corrosion of mild steel known to occur in this environment. One of the effective methods to prevent corrosion is the use of organic inhibitors [2]. The primary reasons for chemical cleaning of boilers / heat exchangers are to prevent tube failures & improve unit availability.

Tube failures in low pressure boilers/heat exchangers are normally the results of creep which occurs when internal deposits produce excessive metal temperature. After a boiler / heat exchanger placed into service, numerous solid constituents may enter the units with the feed water & some portion of the insoluble can be expected to deposit on surfaces. Corrosion inhibitor is used with acid for general use as a de-scalent in all types of chemical de-scaling operations. It removes water hardness scales, deposits from steam and hot water, mill scales, weld scales. Corrosion inhibitors are used in de-scaling acid solution to essentially prevent the attack on metal equipment when scale is removed. There are several other advantages of inhibitors which are saving valuable metal, saving acid and reduction of acid fume [3].

Different acids are employed depending on the underground reservoir characteristics. The treatment normally involves the injection of acid at 15% concentration (sometimes from 5% up to 28%). A standard 15% acid concentration had been chosen before 1960 due to the insolubility of arsenic inhibitor, the primary inhibitor of the industry at the time, because it was not soluble in HCl concentrations higher than 17%. The most common conventional acids are HCl, HF, acetic, and formic acids. It has also been noted that mixtures of these conventional acids with sulphamic, sulphuric, phosphoric, methane sulphonic, nitric, citric, and chloroacetic acids are employed [4]. This work concerns the study into the effect of addition Rodine Spl 213 on the corrosion inhibition of mild steel in the acidic media (HCl and H_2SO_4)

using gravimetric measurements. The effect of concentration and temperature of this inhibitor on the inhibition properties was also studied with comparision of both acids.

II. RELATED WORK

The corrosion inhibition of mild steel by various organic compounds in the acidic media has been studied by several authors for azole derivatives usually are reported in the literature to be good corrosion inhibitors in the acidic solution such as azole and diazole (A. Popova et al., 2007; MZA. Rafiquee et al., 2008), triazole derivatives study are reported by (F. Bentiss et al., 1999; M. Lagrenee et al., 2002; H L. Wang et al., 2003; S. Ramesh et al., 2004; H.H. Hassan et al., 2007; Z. Tao et al., 2009), tetrazole (Kertit and Hammouti, 1996; Kertit et al., 1998; F. Bensajjay et al., 2000), pyrazole (Aouniti et al., 1996; Touham et al., 2001), oxazole (Kazaraji et al., 2000), oxadiazole (Bentiss et al., 2000; Mernari et al., 2001) and thiazole (Ajmal et al., 1994) others are alkylimidazolium ionic liquids in hydrochloric acid by (Schweifzer et al., 2007), propolis as corrosion inhibitor for carbon steel by (A. S. Fouda et al., 2013) as innovation one has even used green inhibitors like caffeic acid by (Fsde Souza et al., 2009), murraya koenigii leaves by (M. Quraishi et al., 2010) and also with marigold flower extract by (P. Mourya et al., 2014).

III. EXPERIMENTAL RESULTS

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 and H_2SO_4 solution. Inhibitive solution - Rodine 213 was used for studying inhibitive actions for different concentration of both acid and inhibitive solution at different temperatures.

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 and H_2SO_4 solution using CA 123 electronic weighing balance with the accuracy of ±0.005. The tests were conducted with different concentrations of inhibitor, acid concentration and at different temperatures for an 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^3) and t is the immersion time (hrs).

And the Inhibitor Efficiency Rate ɳ (%) was computed from the equation below,
$ɳ\% = \frac{CR_{wo} - CR_w}{CR_{wo}} \times 100$
Where,

$ɳ\%$ = Inhibitor Efficiency (%)

CR_{wo} = Corrosion rate (without inhibitor)

CR_w = Corrosion rate (with inhibitor)

Finally, Surface Coverage (θ)

Surface Coverage $(\theta) = \frac{CR\ wo - CR\ w}{CR\ wo}$

Where,

θ= Surface Coverage (θ)

IV. EXPERIMENTAL RESULTS

Weight losses and Corrosion rates:
In mild carbon steel specimens, the weight loss was studied by corrosion rates that were obtained at different variations in temperature and acid concentration.
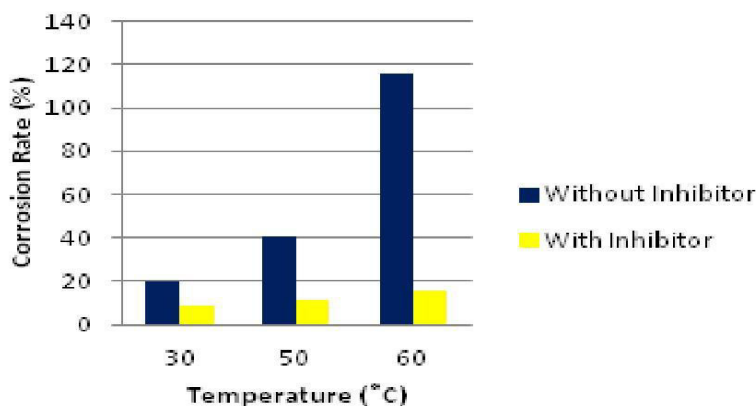

Fig. 1: Corrosion rate comparision at different temperatures in HCl acid medium

The weight loss of the mild steel is observed with the help of corrosion rate obtained from weight loss study. **Fig. 1** shows the comparative study of corrosion rates at different temperatures. This graph is plotted with the mean values of different HCl acid concentrations. So it is seen that corrosion rate with inhibitor is less compared to corrosion rate without inhibitor that is less weight loss which shows the inhibitors effectivity.
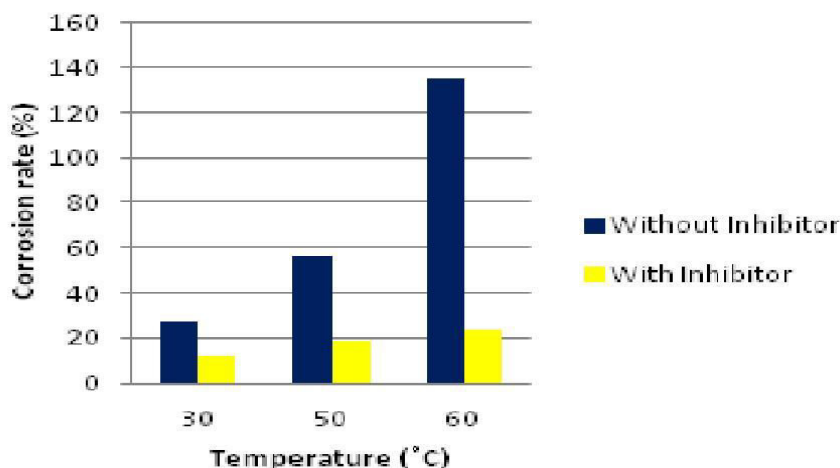

Fig. 2: Corrosion rate comparision at different temperatures in H_2SO_4 acid medium

Fig. 2 shows the comparative study of corrosion rates at different temperatures. This graph is plotted with the mean values of different H_2SO_4 acid concentrations. So it is seen that corrosion rate with inhibitor is less compared to corrosion rate without inhibitor which shows the inhibitors effectivity quite similar to HCl acid medium.

Inhibitor efficiencies and Corrosion rates:
The inhibitor efficiencies could be understood only after variations in inhibitor concentrations. The standard inhibitor concentration that is of rodine spl 213 is from (1000-3000) ppm.
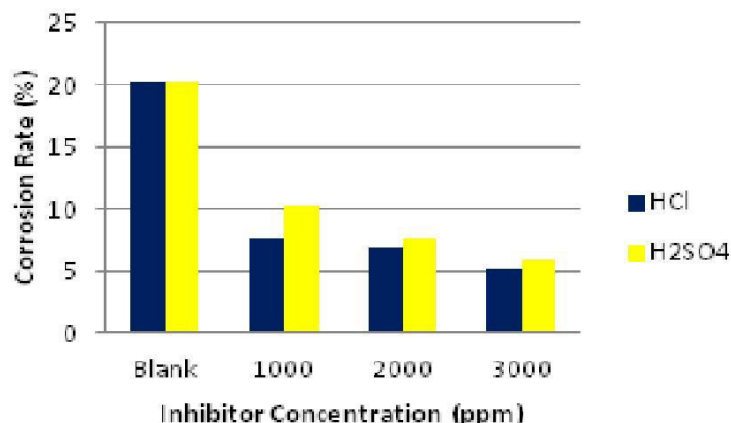
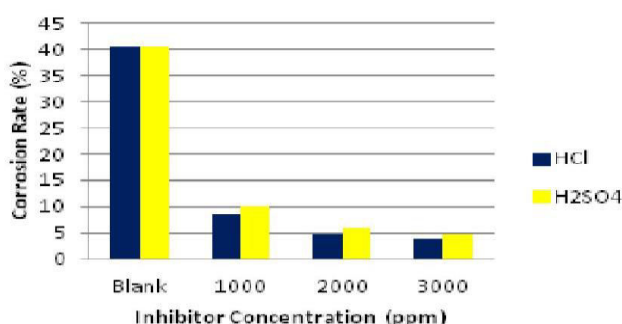**Fig. 3:** Corrosion rate comparision at different inhibitor concentration in both HCl & H_2SO_4 acid medium of 1 N

Fig. 4: Corrosion rate comparision at different inhibitor concentration in both HCl & H_2SO_4 acid medium of 2 N
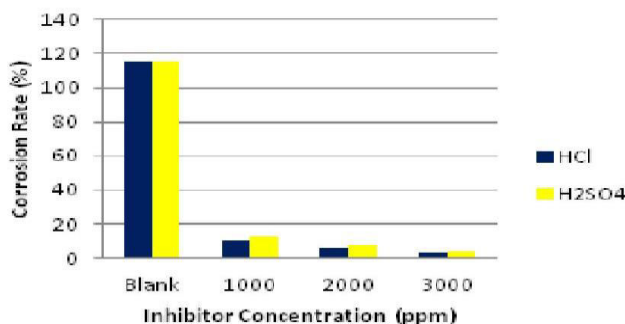

Fig. 5: Corrosion rate comparision at different inhibitor concentration in both HCl & H_2SO_4 acid medium of 3 N

The weight loss of the mild steel in 1, 2, 3 N HCl and H_2SO_4 with various concentrations of inhibitor is determined after 4h of immersion at 30°C. The corrosion rate values were evaluated as shown in **Fig. 3** were for 1N HCl & H_2SO_4 acid medium, corrosion rates were measured with different inhibitor concentrations, in **Fig. 4** Corrosion rate at different inhibitor concentration in both HCl & H_2SO_4 acid medium of 2 N and **Fig. 5** shows the same for 3 N. Corrosion rate values of mild steel without inhibitor that is the blank one shows the highest corrosion rate whereas the ones with inhibitor shows decrease in corrosion rate when the inhibitor concentration increases. In this way from **Fig. 3, 4 & 5** it was observed that with increase in acid concentration there is increase in rate of corrosion and with increase in inhibitor concentration there is fall in corrosion rate that is less weight loss.
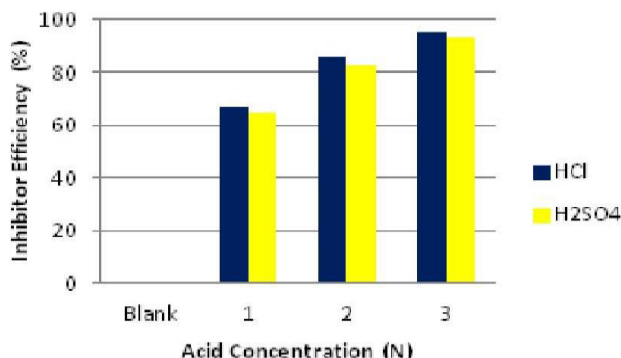
Fig. 6: Inhibitor efficiency with respect to HCl & H_2SO_4 acid medium at different concentration\

The characterization of the corrosion rate of mild steel in the different inhibitor/corrodent solutions was carried out by an assessment of the inhibition efficiency at different acid concentrations.

Fig. 6 shows the plot of inhibitor efficiency at different acidic concentration of HCl & H_2SO_4. Initially it shows the blank plot with 0% efficiency then for 1, 2, 3 N. The inhibition efficiency increases with increasing acid concentration, reaching optimum value of 96-98% at 3 N concentrations of both acids. It was observed that inhibitor efficiency (%) of HCl was always high compared to H_2SO_4 which shows that inhibitor in HCl acid medium is more effective compared to the inhibitor in H_2SO_4 acid medium.

Langmuir adsorption isotherms:
The elucidation of adsorption mechanism was done from the experimental data that requires estimation of the adsorption modes of the inhibiting species (whether molecular or ionic). The predominant adsorption mode will be dependent on factors such as the inhibitor concentration, chemical changes to the mixture solution and the nature of the surface charge on metal. A negative surface charge will favour the adsorption of cations whereas anion adsorption is favoured by a positive surface charge. The ability of Cl^- ions in hydrochloric acid to be strongly adsorbed on the metal surface and hence facilitate physical adsorption of inhibitor cations is an important consideration compared to sulphuric acid. The plot of the ratio of concentration to surface coverage (C/θ) against concentration (C) displayed a straight line for tested inhibitor (**Fig. 7** & **8**).
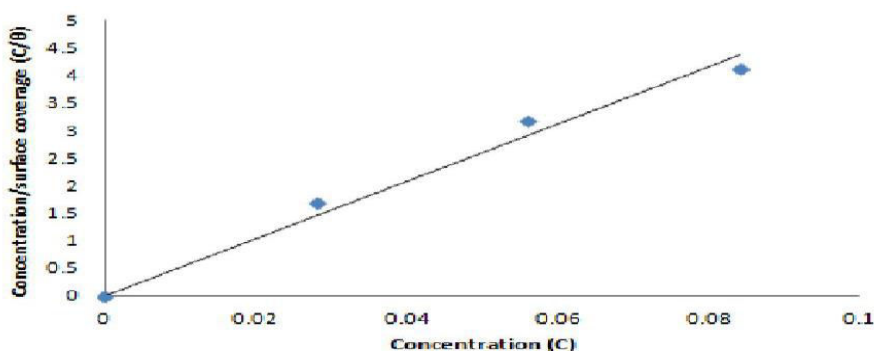

Fig. 7: Langmuir adsorption isotherm for corrosion inhibitor in 1 N HCl acid medium
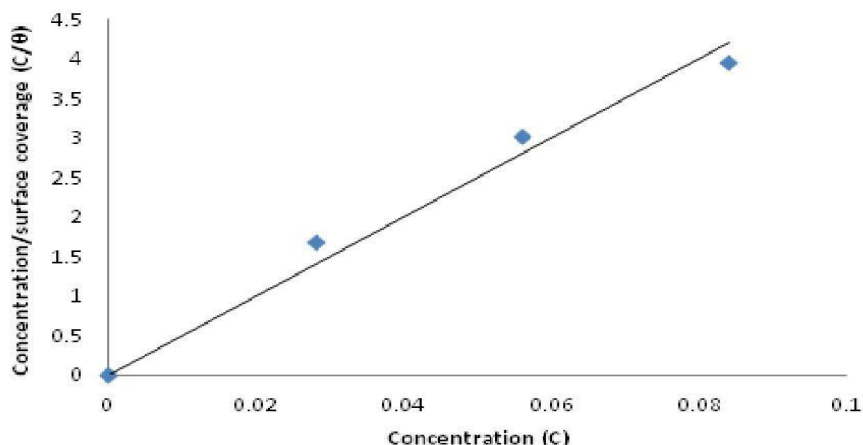
Fig. 8: Langmuir adsorption isotherm for corrosion inhibitor in 1 N H_2SO_4 acid medium

Table 1. Values of Langmuir Parameters for mild steel in different acidic media

Acid medium	Slope	K	R^2
HCl	47.32	13.57	0.98
H_2SO_4	49.46	29.46	0.94

Table 1 shows the correlation coefficient of the Langmuir adsorption isotherm. The linear plot with high correlation coefficient (0.98) and slope of about unity (0.94) clearly reveals that the surface adsorption process of rodine inhibitor in both acidic medium on the mild steel surface, obey the Langmuir adsorption isotherm. Therefore, one can infer that physisorption occurred.

Table 2. Calculated values of corrosion rate and inhibition efficiency ($\eta\%$), activation energy (E_a) and heat of adsorption (Q_{ads}) of *Rodine spl 213* on mild steel in 1 N HCl at different temperatures.

Concentration (ppm)	Corrosion rate (mm/yr)		Inhibition efficiency ($\eta\%$)		E_a (KJmol^{-1})	Q_a (KJmol^{-1})
	30 ˚C	60 ˚C	30 ˚C	60 ˚C		
1000	0.076	0.147	59.494	87.267	42.05	-2.477
2000	0.069	0.122	66.082	89.463	36.4	-2.482
3000	0.053	0.104	75.556	90.034	43.83	-2.475

Table 3. Calculated values of corrosion rate and inhibition efficiency ($\eta\%$), activation energy (E_a) and heat of adsorption (Q_{ads}) of *Rodine spl 213* on mild steel in 1 N H_2SO_4 at different temperatures

Concentration (ppm)	Corrosion rate (mm/yr)		Inhibition efficiency ($\eta\%$)		E_a (KJmol^{-1})	Q_a (KJmol^{-1})
	30 ˚C	60 ˚C	30 ˚C	60 ˚C		
1000	0.103	0.223	58.851	83.122	50.03	-2.470
2000	0.076	0.177	62.574	84.710	54.01	-2.465
3000	0.058	0.117	72.783	85.528	44.64	-2.474

Effect of temperature:

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.

$$log\left(\frac{\rho 2}{\rho 1}\right) = \frac{Ea}{2.303R}\left(\frac{1}{T1} - \frac{1}{T2}\right)$$

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

$$Qads = 2.303R\left(log\left(\frac{\theta 2}{1-\theta 2}\right) - log\left(\frac{\theta 1}{1-\theta 1}\right)\right) \times \frac{T1 \times T2}{T2 - T1}$$

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.

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

The standard free energy of adsorption, $\Delta G°_{ads}$, which can characterize the interaction of adsorption molecules and metal surface, was calculated by equation of K. The negative values of $\Delta G°_{ads}$ ensure the spontaneity of adsorption process and stability of the adsorbed layer on the mild steel surface. Generally, the values of $\Delta G°_{ads}$ around -20 kJ/mol or lower are consistent with physisorption, while those around -40 kJ/mol or higher involve chemisorptions. The values of free energy, $\Delta G°_{ads}$, are -16.69 and -18.64 kJmol^{-1} for both hydrochloric acid & sulphuric acid medium respectively which 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. The calculated values of E_a and Q_{ads} are given in **Table 2 & 3**.

Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in the presence of inhibitor gives some insight into the possible mechanism of inhibitor adsorption. A decrease in inhibition efficiency with rise in temperature, with analogous increase in corrosion activation energy in the presence of inhibitor compared to its absence, is frequently interpreted as being suggestive of formation of an adsorption film of physical (electrostatic) nature. The effect, corresponding to an increase in inhibition efficiency with rise in temperature and lower activation energy in the presence of inhibitor, suggests a chemisorption mechanism.

V. CONCLUSION

The corrosion inhibitor Rodine Spl 213 found to be effective acid inhibitors of mild steel in various concentration of hydrochloric acid and sulphuric 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 exhibited better inhibition efficiency than the sulphuric acid medium because sulphuric acid had a greater base metal loss of mild steel compared to hydrochloric acid. The thermodynamic parameters indicated that the inhibitor is physisorbed on the metal surface and that its adsorption obeys the Langmuir adsorption isotherm.

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