MODELING OF CORROSION KINETICS OF MILD STEEL IN HYDROCHLORIC ACID IN THE PRESENCE AND ABSENCE OF A NATURAL INHIBITOR

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ABSTRACT

Nyctanthes arbor-tristis (Naf) (Night flowering jasmine or Parijat) was investigated as a corrosion inhibitor for mild steel in an hydrochloric acid solution. The results revealed that the order of reaction is 0.374, with activation energy found to be 10.27 kJ/mol. Nyctanthes arbor-tristis (Naf) was effective in increasing the inhibition efficiency for all inhibition concentrations. The corrosion rate profile was found to be second- order kinetics with respect to corrosion activity.

Keywords: Mild Steel; Hydrochloric Acid; Corrosion; Nyctanthes arbor-tristis (Naf); Kinetics.

INTRODUCTION

Corrosion is the major problem in application of metal services. Acid solutions specifically, hydrochloric acid , Sulphuric Acid,etc are used for the removal of rust and scale in industrial processes [1]. The contact of acid solutions and metals causes metal dissolution and corrosion. Due to these Corrosion causes plant shutdowns, costly maintenance and expensive overdesign waste of valuable resources, loss or contamination of product, reduction in efficiency, [2]. The iron and steel are the backbone of industrial constructions, many precaution have been made to find methods of reducing the corrosion and wear costs of these metals. The most important methods in the corrosion protection of these metals is by using inhibitors. Corrosion inhibitor is a chemical substance that is effective when added to a corrosive environment in very small amounts or as per requirement, to decrease the corrosion rate of the exposed metallic material [3]. Heterocyclic compounds containing both nitrogen and sulfur are of particular importance, as they often provide excellent inhibition [4-10]. The synthetic and as well as naturally-occurring materials have been proposed as inhibitors for metal corrosion [11-13]. There are many methods have been proposed to evaluate the inhibition efficiency. The widely used method is based on comparing the rate of corrosion under inhibition with and without inhibition. The calculated rates of corrosion with and without inhibitor use are based on fixed immersion time. The reported inhibition efficiency is based on fixed values of corrosion rates. It is not guaranteed that the rate of corrosion is constant with time. It is established that the inhibitor will progressively be adsorbed on the surface of the metal, thereby, simultaneously reducing the rate of corrosion. The calculations for the inhibition efficiency be based on intrinsic corrosion rate parameters. Another most important method to find the inhibition efficiency is based on comparing the activation energy for inhibited and uninhibited corrosion processes. The Arrhenius relation is used to calculate the activation energy. The numerous reported results regarding the calculation of activation energy are based on the assumption that the rate of corrosion is zero order kinetics. No attempts have been made to verify the zero- order kinetic assumption.

In this study, the intrinsic kinetics of corrosion is investigated. The objectives of this research are to determine specific corrosion reaction rate constant, the corrosion reaction order, and the activation energy for the corrosion of mild steel in 0.25M Hydrochloric acid solution. In addition, the research involved studying the inhibition efficiency of a drug inhibitor called Nyctanthes arbor-tristis (Naf) on the corrosion process of mild steel. Finally, modeling the rate of corrosion profile and its kinetics under different operating conditions is accomplished.

EXPERIMENTAL:-"NYCTANTHES ARBOR-TRISTIS"

Nyctanthes arbor-tristis is a tree which is called as Night flowering jasmine or Parijat, found commonly in parts of Maharashtra which is a night flowering tree. The tree grows around 10 meters in height and it spreads widely through its branches with a bark. The bark is flaky grey in colour. The Leaves of Na are simple and contains entire margin. The flowers of Nyctanthes arbor-tristis (Na) are white in colour and consist of eight lobed white corollas and have an orange holed centre.

The flowers are having pleasant fragrance and are found in clusters of seven. They blossom in the morning and close at the evening period. The flowers are found in plenty in a single tree. Lot of flowers are blossomed and is collected in bunches every morning of the day. The leaves extract contains D-mannitol,Oleanolic acid,nyctanthic acid and flavanols.The flowers contain D-mannitol,oils,tannins and glucose

Fig No.1 Flowers of Nyctanthes arbor- tristis plant.

Classification of Nyctanthes arbor-tristis:

Table No.1 Classification of Naf plant

Sr. No.	Classification	Type
01	Kingdom	Plantae
02	Order	Lamiales
03	Family	Oleaceae
04	Genus	Nyctanthes
05	Species	N. arbor-tristis
06	Binomial name	Nycanthes arbor-tristis

SPECIMEN PREPARATION

The test specimens were metal plate made of mild steel alloy. The dead mild steel has a carbon content of 0.1-0.17 wt %, and it is widely used in the production of wires, plain sheet, nails, rivets, tubes and rolled sheets for the production of pressings. The test specimens were 2cm length x 4 cm width and 1mm thickness. The specimens were first mechanically polished with 400,600, 800, 1000, and 1200 grade of emery paper, in order to obtain a smooth & clean surface of metal plate, afterwards the metal plate were degreased in acetone, then it should be rinsed in a distilled water, and finally it was dried s in oven and weighed. The weights of the specimens of metal plate before and after corrosion were determined by using an analytical balance with a linearity ± 0.0002 g.

COROSION EXPERIMENTS

After accurately weighting, the specimens of metal plate were immersed in solution in a beaker containing 500 mL HCl, with and without addition of different concentrations of Nyctanthes arbor-tristis (Naf). The concentrations of HCl used were 0.25M, 0.5M and 0.75M, while the concentrations of the inhibitor were: 50, 100, 200, & 300 50 ppm. The acid solutions were made from analytical grade 38% HCl and deionized water. All experimental were carried out at 296 K (except experiments for the effect of temperature). The temperature was controlled by a thermostat bath. After the required time of immersion of metal plate, a triplicate of specimens of metal plate was periodically taken out, dried and mechanically polished with a 600,800,1000 1200 grade of emery paper, in order to remove all corrosion products and to obtain a smooth surface. The polished specimens of metal plate were degreased in acetone solution, then rinsed in distilled water, and finally dried and weighted (W). The rate of corrosion (g/cm2hr) is calculated based on the difference in weights of the specimen, and using the relation:

$$r_c = \frac{(W_0 - W)}{t.A} \qquad (1)$$

where (W) - weight of specimen before corrosion, (Wi) - weight of specimen after being subjected to corrosion and polished to remove all the corrosion product, (t) - time of immersion in (h) and (A) is the surface area of the metal specimen in cm2.

THEORETICAL CONSIDERATIONS: - KINETICS OF THE CORROSIONPROCESS

The use of differential and integral methods to determine the reaction order and specific reaction constant for corrosion process is difficult, because it requires the concentration-time profile. The complex chemistry of corrosion could render the differential methods ineffective. In this case, the method of initial rates could be employed to determine the reaction order and the specific reaction constant. In this research, a series of experiments is carried out at different initial acid concentrations, (C_{HCl_0}) and the initial rate of corrosion (rc)0 is determined for each run.

The rate law is consider to be as,

$$r_c = kC^n{}_{HCl} \qquad (2)$$

The Plot between ln(rc)0, & ln (CHCl)0 enabled finding the reaction order & specific reaction constants. The initial corrosion rate is determined by analyzing the corrosion rate-time data and extrapolating to zero time. However, improper extrapolation by adopting improper trend equation for the corrosion rate-time data will lead to under- or overestimation of the initial corrosion rate. The rate of corrosion is not constant with respect to time, due to complex reaction chemistry, reduction in reactivity of the corrosive medium and effect of other phenomena like adsorption or coating on metal surface.

Following given equation, is that the analysis of Levenspiel [14], in analyzing catalytic reaction under deactivation condition, the experimental corrosion rate-time data were modeled by defining a time dependent variable a(t) , called activity. The activity is defined as:

$$a(t) = \frac{r_c(t)}{r_c(t=0)} \qquad (3)$$

Based on the above Activity definition, the rate of change can be written as:

$$r_c(t) = (r_c)_0 \; a(t) \qquad (4)$$

The rate of Change in the activity is consider to be second order Kinetics, that is given by,

$$-\frac{da}{dt} = k_2 a^2 \qquad (5)$$

At t=0, a(t) equal 1, therefore the integral form of Equation % is given as :

$$a(t) = \frac{1}{1+k_2 t} \qquad (6)$$

Substituting Equation (6) in Equation (4) yield:

$$r_c(t) = \frac{(r_c)_0}{1+k_2 t} \qquad (7)$$

The linearized form of equation (7) is given as

$$\frac{1}{r_c(t)} = \frac{1}{(r_c)_0} + \frac{k_2}{(r_c)_0} t \qquad (8)$$

To check the validity of the proposed model in describing the kinetics of corrosion, a plot between

$\frac{1}{r_c(t)}$ versus (t) must result in a straight line with a slope equal to $\frac{k_2}{(r_c)_0}$ & an intercept equal to $\frac{1}{(r_c)_0}$

The Arrhenius equation can be used to calculate the intrinsic activation energy for the corrosion process (E) (kJ/mol) as it follows.

$$ln \frac{k(T_2)}{k(T_1)} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (9)$$

Where k(T1) & k(T2) are the specific corrosion rate constant at(T1) &(T2), respectively & (R) is the universal gas constant (8.314 J/mol. K)

INHIBITION EFFICIENCY

It is a common practice to evaluate the promotion effect of the inhibitor by defining the inhibition efficiency (IE) based on the following equation:

$$IE = \frac{r_c - r_{c,i}}{r_c} \times 100 \qquad (10)$$

Where, (rc) is the rate of corrosion without inhibition & (rc,i)is the rate of corrosion with inhibition. The rate of corrosion is changing with time; hence, the inhibition efficiency will change with time.

The inhibition efficiency profile can be obtained by substituting Equation (7) in Equation (10), to get:

$$IE = \frac{r_c(t) - r_{c,i}(t)}{r_c(t)} \times 100 = \frac{\left(\frac{(r_c)_0}{1+k_2 t}\right) - \left(\frac{(r_c)_0}{1+k_2 t}\right)}{\left(\frac{(r_c)_0}{1+k_2 t}\right)} \times 100 \qquad (11)$$

RESULTS AND DISCUSSION:-

The kinetics of the corrosion of mild steel in an HCl solution.

The rate of corrosion of mild steel for a different concentrations of HCL solution is, studied at a temperature of 296 K. The rate of the corrosion profile can be calculated by using the Equation (1) under different initial HCl concentrations, namely: 0.25, 0.50 and 0.75M. The rate of corrosion profiles is modeled in terms of an activity energy function that takes into account the corrosively of the system and its decay with time. A second order kinetic model is proposed for the rate of activity decay with time. The profile of the rate of corrosion is plotted in a linearized form based on the proposed model given in the (Equation 8). The results are shown in the following (Fig. 2.)

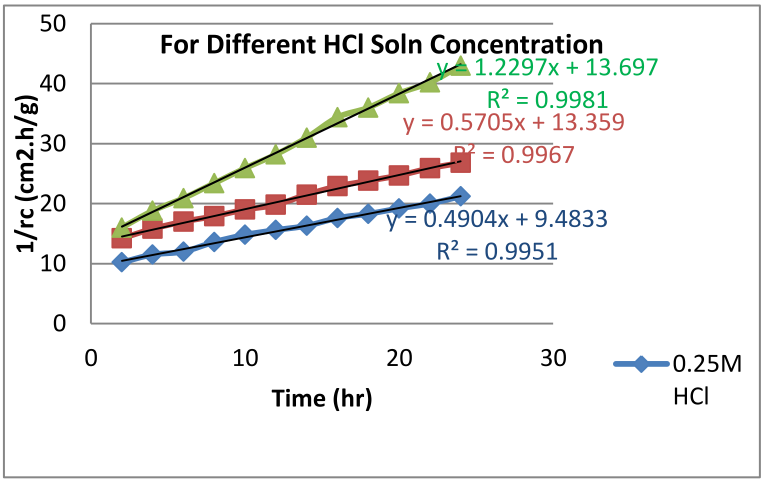

Figure2 Corrosion profile of mild steel in different concentrations of HCl at T=296K.

The results clearly show that the, proposed model is satisfactorily fitting that the behavior of the corrosion rate profile with a high coefficient of determination (R2value) for the three set of data. The R2 values are found to be 0.995, 0.996 and 0.998 for the 0.25, 0.50, and 0.75 M HCl solution fitted experimental data, respectively. The initial rates of corrosion, as obtained from the reciprocal of intercept of trend lines, are found to be 0.105, 0.074 and 0.073 g/cm2.h for 0.25, 0.50 and 0.075 M initial acid concentration, respectively. Based on the above results, it is evident that increasing the initial acid concentration increased the initial metal corrosion rate.

To obtain the order of corrosion rate and specific rate constant, a linearized plot between ln(rc)0 & ln(CHCl)0 is constructed on the following graph, and the result are shown in following (Fig. 03)

A linear fitted line is obtained with R2 value, which equals to 0.916. The slope value of the line used to calculate the order of reaction is found to be 0.374, while the intercept is used to calculate the specific reaction rate constant, and is found to be 2.19 g.L0.374/cm2.h.mol0.374, at a temperature of 296 K.

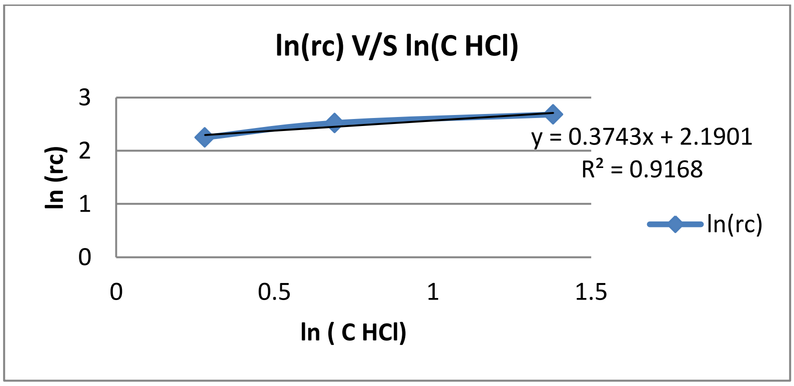

Figure:-3. Initial rate-concentration plot for the corrosion of mild steel in HCl at 298K.

To obtain the activation energy of the corrosion process, the corrosion rate profiles at various temperatures and initial acid concentration of 0.25 M are experimentally determined and linearly fitted, as shown in Fig. 4.

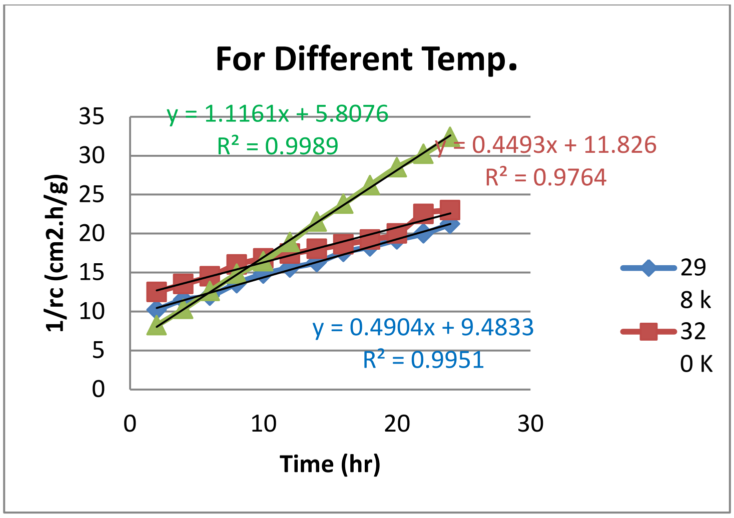

Figure: - 4. Kinetics of the corrosion of mild steel in 0.25M HCl at different temperatures.

The profiles of the rate of corrosion (rc) at all the studied temperatures are satisfactorily linearly fitted with high with the (R2) values. The initial rates of corrosion (rc), as obtained from the reciprocal of intercept of the trend lines, are found to be 0.105,0.084 and 0.172 g/cm2.h, at temperatures of 296, 320 and 350 K, respectively. Increasing the temperature (T) resulted in an increase in the initial rate of corrosion (rc). Based on the initial rate values and the reaction rate (rc) form proposed given in the Equation (2), an estimate of the specific reaction constant (K) can be obtained. The calculated values of the specific reaction rate constants are found to be 0.177, 0.141, 0.289 g.L0.374/cm2.h.mol0.387, at temperatures of 296, 320 and 350 K, respectively. To determine the activation energy, Arrhenius plot is constructed and shown in Fig.5.

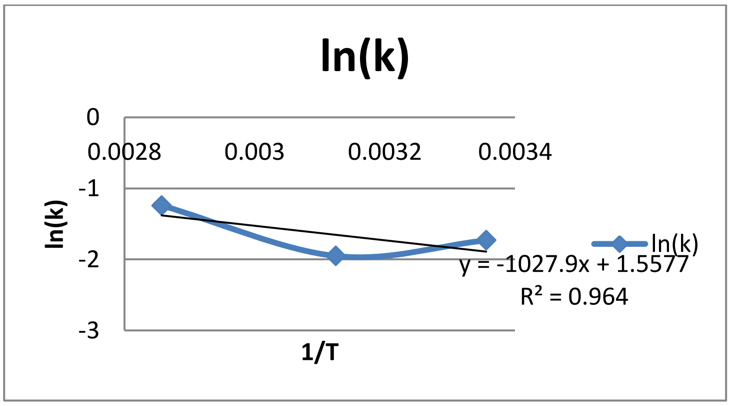

Figure 5. The Arrhenius plot for the corrosion of mild steel in 0.5 M HCl.

From the slope of the fitted line of the Arrhenius equation plot, the activation energy of the reaction is found to be 10.27 kJ/mol. As reported in literature, several values have been determined for the value of the activation energy for the corrosion of mild steel in hydrochloric solutions. 41.7 kJ/mol by Mr. Salah H. Aljbour [1], while Oguzie [15] was reported the value of 49.3 kJ/mol; while Behpouretal. [16] was reported a value of 53.6 kJ/mol; & Benabdellahetal. [17] was reported a value of 59.39 kJ/mol; while Naqvi et al. [18] was reported a value of 36.8 kJ/mol; while Abdel Hameed [19] was reported a value of 40.37 kJ/mol; & Singh [20]was reported a value of 42 kJ/mol; while Youse fietal. [21] reported value 60.94 kJ/mol. These variations in the reported activation energy values could be attributed to the assumptions of zero order kinetics of the corrosion process, as well as to variations in the metallurgical properties of the used mild steel.

INHIBITION EFFICIENCY

The drug inhibitor "Nyctanthes arbor-tristis (Naf)" was utilized to inhibit the corrosion of mild steel in a 0.25 M HCl solution at 296 K. Several inhibitor doses were employed, namely: 50, 100, 200 and 300 ppm. The corrosion rate (rc) profiles are shown in the following (Fig. 6), based on the proposed kinetic model.

The rate of corrosion (rc) profiles for all inhibitor concentrations is satisfactory fitted by the linearized form given by equation with high R2 values. The initial rates of corrosion (rc) that are obtained from the reciprocal of the trend line intercepts are found to be 0.070, 0.065, 0.061 and 0.057 g/cm2.h for 50, 100, 200, and 300 ppm inhibitor concentrations, respectively

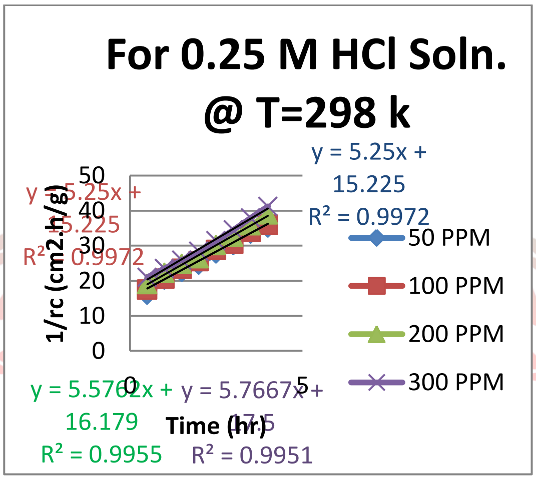

Figure 6:-. Corrosion profile of mild steel in 0.75 M HCl at T = 296 K under different inhibitor Concentration

As reported earlier in this paper, the initial rate of corrosion without inhibitor was 0.074 g/cm2.h. The results clearly show that increasing the inhibitor concentration is decreasing the initial rate of corrosion, which confirms the inhibition effect and the feasibility of "Nyctanthes arbor-tristis (Naf)" as a possible inhibitor for mild steel corrosion.

Another insight can be made based on the 2nd order activity rate constant (k2), which is considered as a measure for the speed of decay in the system activity toward corrosion. The (k2) values are obtained from the slopes of the trend lines shown in Fig. 6. The (k2) values were found to be 5.39,5.25,5.58,5.77h-1 for 50, 100, 200, and 300 ppm inhibitor concentrations, respectively, and 2.46 h-1 for a blank solution. These research results clearly show that the use of inhibitor reduced the activity of the system towards metal corrosion by, at least, two orders-of-magnitude compared to conditions without inhibition. Maximum reduction in activity was obtained with 300 ppm inhibitor concentration. The inhibition efficiency of "Nyctanthes arbor-tristis (Naf)" was calculated under different inhibitor concentrations by using Equation 11, and the results are plotted in Fig.7.

The inhibition efficiency of the inhibitor under different concentrations increased by increasing the immersion time up to 10h, and thereafter it is barely increased. Long immersion time will ensure high loading of the adsorbed inhibitor on the surface of metal, which results in a persistent film that inhibits further corrosion. Similar trend was observed by other researchers. Mr. Salah H. Aljbour noticed that the inhibition efficiency of "cefixime " bases on the corrosion of mild steel in an HCl solution was found to increase with time up to 06h, and thereafter remained almost constant.

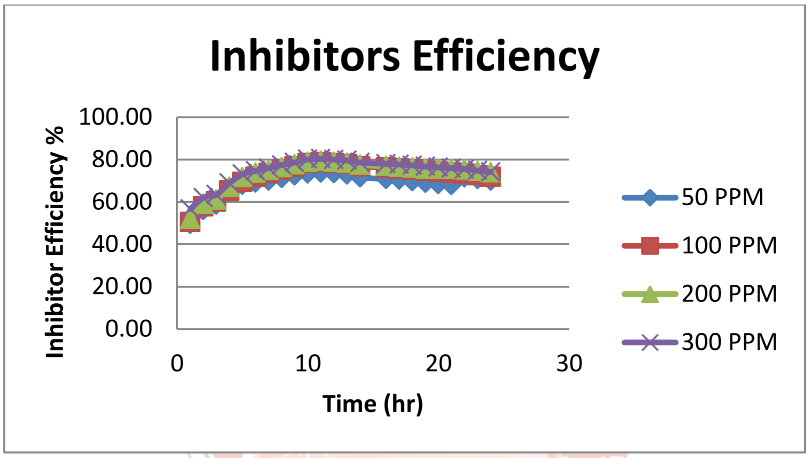

Figure 7. Corrosion inhibition efficiency of mild steel in 0.75 M HCl at T = 296 K under different inhibitor concentrations

CONCLUSIONS

The corrosion rate of mild steel in a hydrochloric solution is dependent on the acid concentration. The activation energy for mild steel corrosion in a hydrochloric solution is found to be 10.27kJ/mol. Nyctanthes arbor-tristis (Naf) trihydrate is found to be efficient in increasing the inhibition efficiency for all inhibition concentrations. The corrosion rate profile follows second-order kinetics with respect to corrosion activity.

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