Corrosion Kinetics of Mild Steel in Water Based Neutral and Acidic Mediums Accounting Corrosive-inhibitive Natures

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ABSTRACT

Gravimetrically the corrosion of mild steel was studied in water and different water based acid solutions like 0.1 M HCl, 0.01 M citric acid, 1:1 volume ratio of 0.1 M HCl & 0.01 M citric acid. The corrosion studies were analysed in terms of first order kinetics of the steel where water was found very mild corrosive medium as the corrosion rate constant was found 8.0661×10^{-4} g/day. 0.1 M HCl was recognized to possess highest corrosion rate constant of 3.3866 g/day among the four mediums. The unexpectedly high corrosion of mild steel in 0.01 M citric acid-water medium was explained in terms of possible solubilisation of iron hydroxide. The presence of [citrate]/[Fe(III)] <1/3 in HCl-citric acid medium inhibited the corrosion by possible polymerization of polyneuclear citrate-iron complexes and their sedimentation.

Keywords: Mild steel, Corrosion kinetics, Gravimetric method, Organic inhibitors, Citric acid

INTRODUCTION

Mild steel one of the widely used forms of iron alloy and very often it is observed in our day to day lives. The corrosion of mild steel is not only concerned of the objects made of it but also its soluble products for their unwanted impact on environments [1-4]. Though there are several methods of cathodic and anodic coatings and protections to steel or iron, they are sometimes expensive and detrimental to the environment by their corrosions for protection of the steel. Sometimes, the uses of the corrosion inhibitors have been found beneficial due to their practical and applicable operation in many systems. Though various inorganic and organic inhibitors were listed for their specific purposes, the present trends in green inhibitors have been found beneficial in terms of environmental costs. It has been found that the alkaloids and flavonoids and other natural products derived from natural sources are categorized as organic green inhibitors for their negligible toxicities [5]. Apart from only inhibitions, there are several natural carboxylic acids are available responsible for the corrosion of steel [6]. Though corrosive and inhibitive effects of citric acid ($CitH_4$) on iron based alloys were studied for various aspects [6-8], the study on the corrosion kinetics in different corrosive medium is essential to monitor the corrosion based effects on environment and their controls.

In this present study, the corrosions of mild steel were studied in a neutral medium (water), in an inorganic acid medium (HCl), in an organic acid medium ($CitH_4$) and in a mixture of organic and inorganic acid ($CitH_4$ and HCl). The corrosion in an alkaline medium was excluded from the present study as the extensive iron hydroxide formation subject to corrosion inhibition by its insoluble nature in water.

MATERIALS AND METHODS

Freshly bought mild steel nails of 2.54 cm length made of mild steel were cross checked by density measurement employing Archimedes principle of water volume occupation and weighing the mass of nails. The rust free mild steel were cleaned and immersed in 60 ml of water, 0.1 M of HCl, 0.01 M of $CitH_4$–water solution and 1:1 volume of 0.1 M HCl and 0.01 M $CitH_4$ solution. All analytical grade chemicals were employed for the preparation of corrosive medium and all the measurements and calculations were rounded off to three decimal. The mediums were kept in the tightly closed stoppered bottles to avoid atmospheric interference mostly in terms of dissolved oxygen and even the mild steel were kept lying horizontally at the bottom of glass bottles. The measurements of mass were done by digital weighing balance before keeping them in their respective solution medium. Each 2 days interval the steel samples were brought out using magnetic retriever and kept them out of the solution in the closed bottles to minimize the adhered solution to the steel. After bringing the samples out, they were kept on tissue papers for the soaking of the remaining adhered solution on the sample surfaces before weighing their masses. The wiping out of the sample surfaces were avoided as the activity might have exposed the fresh steel surface to corrode. The measurements were continued for 13 days and the separate sets of experiment were kept undisturbed to measure on 13th day to compare the effect of measurement on the intervals of 2 days. The first set of experiments has been shown in Figure 1.

Figure 1: The corrosion of mild steel in different corrosive mediums, (1) water, (2) 0.1 M HCl, (3) 0.01 M CitH₄–water, (4) 1:1 volume ratio of 0.1 M HCl and 0.01 M CitH₄, (5) water for 13 days and (6) 0.01 M CitH₄-water for 13 days

RESULTS AND DISCUSION

Maximum corrosion of mild steel

To account maximum corrosion in the chosen mediums, the relevant possible reactions were tabulated (Table 1) comparing experimental and estimated mass losses. The chosen reactions were expressed limiting the oxidation state +2 as expected to be the minimum oxidation state leading to maximum corrosion in those mediums, where the formation of most probable oxidation +3 is subject to less corrosive. Some of the earlier reported complexes of iron and citrate [9-12] were considered for the suitable formations that could lead to the maximum corrosion of mild steel by CitH₄.

Table 1: Comparison between expected and observed mass loss of mild steel in different medium kept at room temperature for 13 days

Medium	Expected complete reactions	Expected mass loss (in g)	Observed mass loss (in g)	Remarks
Distilled water	$Fe + 2H_2O = Fe(OH)_2 + H_2 \uparrow$	All	0.004	Corrosion not maximized
0.1 M HCl	$Fe + 2HCl = FeCl_2 + H_2 \uparrow$	0.1675	0.113	Corrosion not maximized
0.01 M CitH₄	$5\,Fe + 2CitH_4 \rightarrow 2[Fe(HCit)]^0 + 3Fe^{2+} + 3H_2 \uparrow$	0.084	0.125	Unexpected mass loss
0.1 M HCl + 0.01 M CitH₄ (1:1 volume ratio)	Both the reactions expected from HCl & CitH₄	0.12575	0.073	Corrosion not maximized

From the tabulated data it was noticed that the mass losses could not reach the maximum value irrespective of mediums like water, HCl and HCl-CitH₄ and it could be the indication of the formation of higher oxidation sate of Fe resulting lesser amount of mass loss in mild steel. On the contrary CitH₄-water medium the observed mass loss was unexpectedly higher than the estimation and the observation is subject to further research activity as the Fe-citrate complexes were mostly synthesized from Fe(III) not being frequently studied as the reactions between metallic Fe and CitH₄ in water medium. According to the earlier report on the flocculation of iron hydroxides in presence of CitH₄ and iron citrate complexes [5], the enhanced corrosion of iron in the particular medium was accounted as the result of water induced iron hydroxide formation which gets stabilized in the near neutral or alkaline solutions instead the rapid precipitation. As the precipitation of iron-citrate complexes inhibits the corrosion by covering the reactive Fe surface, it was expected that the prolonged corrosion continued in such medium. By means of the mass losses the corrosion kinetics of Fe in the water, HCl, CitH₄-water and CitH₄-HCl solution were also studied and analysed for the better insight of its corrosion.

Corrosion rate kinetics in water

The observation of mass loss of mild steel in water medium was compared to its decay or corrosion with respect to time. The corrosion kinetics in the medium was expressed as $\frac{dW}{dt} = -kW$ where W = mass of Fe, k=rate constant and t=time and the derived equation $W = W_0 e^{-kt}$ was employed to the corrosion analysis where W_0 = initial corroding mass of Fe. The time dependent loss of mass in mild steel was fitted with the derived equation mentioned above and it showed that the half of the mass loss with respect to initial mass in the water medium requires 882.664 or almost 883 days. Hence the half-life ($t_{1/2}$) of mild steel in water medium was concluded as 883 days (Figure 2).
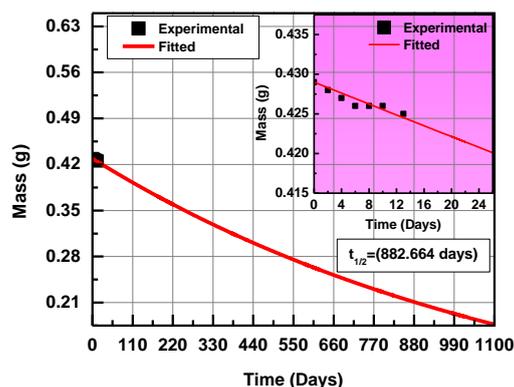
Figure 2: Corrosion of mild steel as change in mass with respect to time in water medium as experimental observation along with the fitted curve of first order corrosion kinetics. Inset: magnified presentation of observed data with corrosion curve fitting

As the remained mass of mild steel under study was not noticed to stabilized, it was assumed that the corrosion inhibition due to iron hydroxide formation could be neglected within the short period of study.

Corrosion rate kinetics in HCl

The mass loss with respect to time was presented in Figure 3 and it was noticed that there was no significant corrosion due to HCl after 4th day of study. The mass loss of 0.113 g by 4 days was correlated with the formation of +3 oxidation state of Fe and it was close to calculated value of 0.112 g as expected in 60 ml of 0.1 M HCl where the initial mass of Fe was 0.437 g.
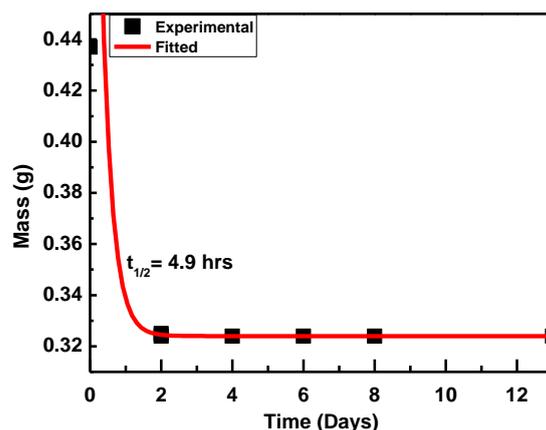
Figure 3: Corrosion of mild steel in terms of reduction in mass with respect to time in 0.1 M HCl medium

As the corroded mass in the medium was maximized by 4 days, to find out the reaction kinetics the corrosion equation was modified including a parameter W_{res} = residual mass. Using the modified equation $W = W_{res} + W_0 e^{-kt}$ the observed data were fitted to it and the found rate constant k=3.3866 g/day whereas the corrosion half-life was recorded 5 h.

Corrosion rate kinetics in citric acid

The rate kinetics of iron corrosion was found different in 0.01 M CitH$_4$-water medium than above mentioned two mediums. In CitH$_4$ solution, two different corrosion rate constants were found from the first order curve fitting of mass loss with respect to time (Figure 4). Such different types of corrosion were possible in CitH$_4$ being tetrabasic ligand for iron having different dissociation constants pKa$_1$=3.13, pKa$_2$=4.76, pKa$_3$=6.40 and pKa$_4$=14.4 including hydroxyl proton [9]. The different dissociations have the probability of different mode of protonation to corrode Fe with different kinetics. The expression of corrosion kinetics was modified to $W = W_1 e^{-k_1 t} + W_2 e^{-k_2 t}$ where, W$_1$ and W$_2$ are initial active masses to response the different ways of corrosion, k$_1$ and k$_2$ are their respective rate constants and their obtained values are 1.295 g/day and 0.005 g/day, respectively. The difference between the rate constants indicates though the four rate constants were expected relating four dissociation constants, only two dissociation constants dominated for the detectable corrosion kinetics of Fe and rest two dissociation constants might be effective in complex formation reconstructing molecular structures of between Fe and citrate. As the reconstruction to Fe citrate complex could lead effective corrosion through the release of proton to the medium, the corrosion process should be considered as a collective corrosion process that followed two different and effective first order kinetics. There are some schemes of possible corrosion reactions involving different dissociation constants shown below:

Corrosion Scheme with respect to pKa$_1$ or pKa$_1$ & pKa$_2$
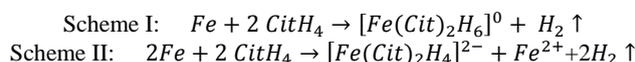
$$\text{Scheme I:} \quad Fe + 2\ CitH_4 \rightarrow [Fe(Cit)_2 H_6]^0 + H_2 \uparrow$$
$$\text{Scheme II:} \quad 2Fe + 2\ CitH_4 \rightarrow [Fe(Cit)_2 H_4]^{2-} + Fe^{2+} + 2H_2 \uparrow$$

Corrosion Scheme with respect to pKa$_1$, pKa$_2$ & pKa$_3$

$$\text{Scheme I:} \quad 4\,Fe + 2\,CitH_4 \rightarrow 2[Fe(Cit)_2H_3]^{2-} + 2Fe^{2+} + H_2 \uparrow$$
$$\text{Scheme II:} \quad 2Fe + 4\,CitH_4 \rightarrow 2[Fe(Cit)_2H_5]^{0} + 3H_2 \uparrow$$
$$\text{Scheme III:} \quad 3Fe + 4\,CitH_4 \rightarrow 2[Fe(Cit)_2H_4]^{1-} + Fe^{2+} + 3H_2 \uparrow$$

Corrosion Scheme with respect to pKa$_1$, pKa$_2$, pKa$_3$ & pKa$_4$

$$\text{Scheme I:} \quad 3\,Fe + 2\,CitH_4 \rightarrow [Fe_2(Cit)_2]^{2-} + Fe^{2+} + 4H_2 \uparrow$$
$$\text{Scheme II:} \quad 9\,Fe + 6CitH_4 \rightarrow 2[Fe_3(Cit)_3]^{3-} + 3Fe^{2+} + 12H_2 \uparrow$$
$$\text{Scheme III:} \quad 7\,Fe + 6CitH_4 \rightarrow 2[Fe(Cit)_3]^{5-} + 5Fe^{2+} + 12H_2 \uparrow$$
$$\text{Scheme IV:} \quad 5\,Fe + 2CitH_4 \rightarrow 2[Fe(HCit)]^{0} + 3Fe^{2+} + 3H_2 \uparrow$$
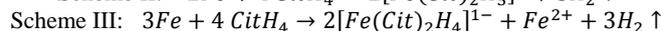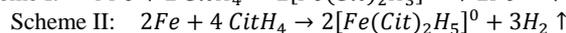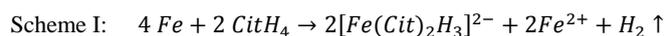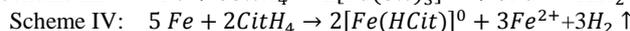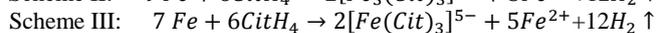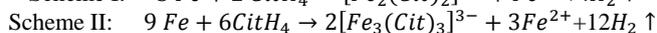
Among the two rate constants in corrosion kinetics relatively smaller rate constant could be the reason for the higher order dissociation constants being responsible for poor protonation. It was noticed that k$_2$ is just around one order higher than the rate constant recorded in water medium which is 0.0008 g/day. Though corrosion rate due to the presence of water is very less in comparison to CitH$_4$, the corrosion due to water cannot be avoided. As already mentioned above near neutral pH the formed colloids of iron hydroxides are stabilized in solution phase due the presence of iron-citrate complexes [13]. The enhanced corrosion of iron in the CitH$_4$-water medium was accounted as the additive effect of water induced iron hydroxide formation and solubilisation in presence iron-citrate complexes near neutral pH.
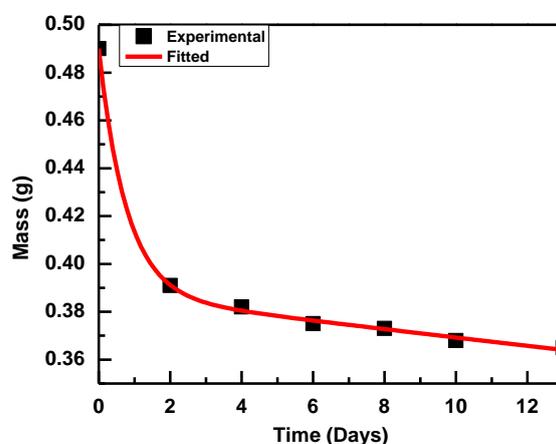
Figure 4: Corrosion of mild steel in terms of mass loss in 0.01 M citric acid solution with respect to time, fitted with two different type 1st order corrosion kinetics

Corrosion rate kinetics in CitH$_4$–HCl medium

From the Table 1, expected maximum mass loss in CitH$_4$-HCl medium was 0.12575 g but the observed mass loss was recorded 0.073 g by 13 days. Such lesser amount of mass loss than the calculation was analysed by the formation carboxylic corrosion inhibition of CitH$_4$ or citrate (Cit) ions. As the strengths of the acids were reduced by 2 folds, the total loss was expected to be half of the total observed corrosion in their respective acid solutions and it was estimated to be 0.1190 g accounting corrosion from both acids. On the contrary the observed corrosion of 0.073 g was the indication of the carboxylic corrosion inhibition as at lower pH the iron-citrate polymerization is relatively faster than at the neutral and higher pH resulting sedimentation [13]. According to the earlier report [13] polymerization of citrate and Fe(III) to polyneuclear complexes is a faster process in acidic pH where [citrate]/[F(III)] ≤ 1/3. As the present corrosion consists of the molar ratio of 0.01/0.1, the sedimentation of the polymerized citrate-iron complexes was expected.
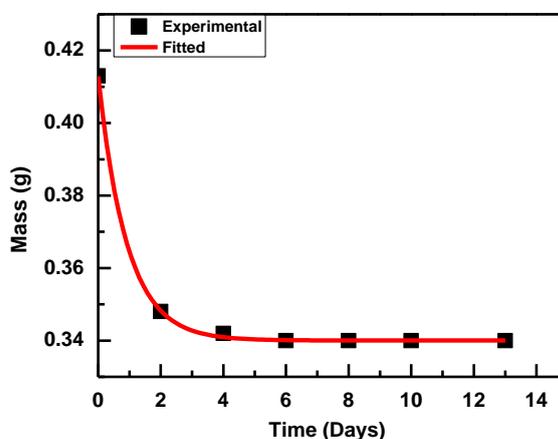
Figure 5: Corrosion of Fe in terms of mass loss in the mixed environment of citric acid and HCl solution with respect to time fitted with the combined expression of 1st order corrosion & growth kinetics

The expression for the corrosion along with the growth of corrosion inhibitor was formulated as $W = W_{corr}e^{-k_{corr}t} + W_{inhib}e^{k_{inhib}t}$ where W_{corr} & W_{inhib} are initial masses for corrosion and inhibition and k_{corr} & k_{inhib} are their respective rate constants. As the corrosion inhibition by carboxylic group could be possible by the, (i) Chemisorption of the molecules containing the functional group, (ii) Adsorption of hydrolysed iron surface to citrate-iron complexes and (iii) Precipitation of polyneuclear citrate-iron complexes. They were assumed as the integral part of Fe that were deposited or grown on the surface of it. On the basis of such assumption the growth of inhibitors were expressed as 1st order kinetics that countered the corrosion process on Fe surface. The stabilization of mass loss with respect to time was the result of sufficient growth of inhibitors to cover the corrosion surface and the process was mathematically expressed in the above equation. From the fitting of data (Figure 5), the obtained rate constant of corrosion was 1.091 g/day where the rate constant of inhibitor growth was noted as 0.118 g/day.

Corrosion rate comparison

It was found that the corrosion rate was very high in HCl and least in water among the mediums under investigation. The rate constants were presented in Figure 5 where, the corrosion rate in HCl, CitH$_4$-water, CitH$_4$-HCl and water medium were kept in decreasing order with their respective values of 3.3866, 1.295, 1.091 and 8.0661×10^{-4} g/day. Though the mild steel samples were studied gravimetrically by the interval of 2 days and the last data were taken on 13th day of experiment, similar mild steel samples were kept in water and CitH$_4$-water medium undisturbed and corrosion was studied gravimetrically on 13th day. The corrosions were compared with the samples studied at intervals and the samples kept for 13 days long and it was noticed that in water medium the corrosion was 0.932% by mass loss studied at 2 days of intervals whereas it was found 0.233% measured on 13th day kept undisturbed. Similar comparison in CitH$_4$-water medium showed that the mass was 25.85% when studied at 2 days of interval and was 7.143% when measured on 13th day kept undisturbed. Such difference indicates that the gravimetric study is prone to surface exposure to corrosive medium where in reality if mild steel is kept in the above mentioned medium for longer period, the corrosion rate would be lesser or inhibited (Figure 6).
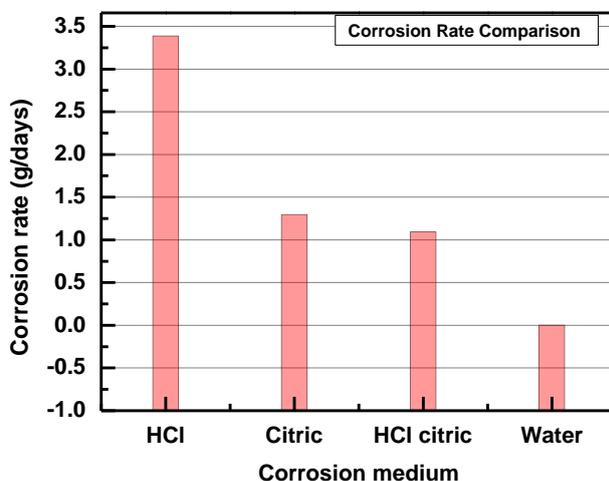
Figure 6: The highest corrosion rate constants in different corrosive medium

Inhibition efficiency

The inhibition efficiency was estimated for mild steel in the respective mediums. According to the earlier reports [14,15], the inhibition efficiency is defined in terms of the formula $\theta(\%) = \left(1 - \frac{w_i}{w_0}\right) \times 100$ Where, w_0 & w_i are the values of corrosion weight losses in uninhibited and inhibited solutions, respectively. The inhibition efficiency in terms percentage with respect to time was presented in Figure 7 and it was found with time the efficiencies in the mediums were increased near 100% where CitH$_4$-HCl medium reached the 100% and the phenomenon was found in the Figure 4. The inhibition efficiency was not calculated in HCl medium as it reached maximum mass loss indicating completion of reaction between HCl and Fe.
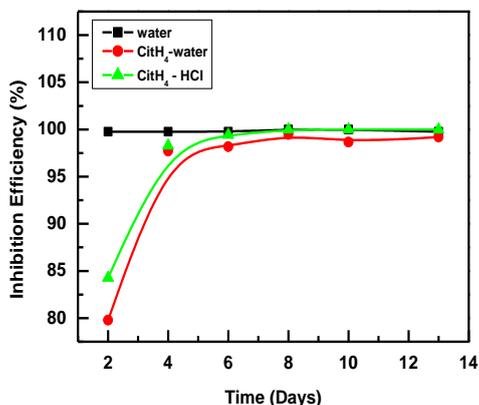
Figure 7: Development of corrosion inhibition efficiency with respect time at different corrosive mediums. (Solid lines are guide to the eyes)

CONCLUSION

The corrosion of mild steel in four different mediums like water, HCl, CitH$_4$-water and CitH$_4$-HCl were studied and it was found that the corrosion kinetics were different for the different mediums. The highest corrosion kinetic rates in HCl, CitH$_4$-water, CitH$_4$-HCl and water were found 3.3866, 1.295, 1.091 and 8.0661 × 10^{-4} g/day, respectively. Though citric acid in general accepted as corrosion inhibitors, it was found as corrosive in water medium and even enhancement of corrosion is possible by solubilizing iron hydroxide. Thus loss of mass was found unexpectedly higher than it could be estimated from tetrabasic citric acid. The corrosion inhibition property of citric acid was found in HCl medium where the ratio of citrate and Fe(III) concentration being 1/10 i.e., lesser than 1/3. Such molar ratio is prone to polymerize to polyneuclear iron-citrate complexes and rapidly precipitated on iron surface and inhibits the corrosion.

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