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Corrosion Protection Studies of Modified Mild Steel Surface in Hydrochloric Acid Medium

S. K. Rajappa[1]* and T.V. Venkatesh[2]

1. Department of Chemistry, Karnatak University's, Karnatak Science College, Dharwad-580 001, **INDIA**
2. Department of PG studies and Research in Chemistry, Kuvempu University, Shankarghatta-577 451, **INDIA**

Email: drrajappask@gmail.com, drtvvenkatesha@yahoo.co.uk

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ABSTRACT

The modification of mild steel surface was achieved by immersion method using a condensation product formed between furfural and amino benzoic acid (FFBA). The product molecule possesses heterocyclic ring, imine group and -COOH group. The corrosion protection of modified mild steel surface was investigated using electrochemical method. The studies pertain to the effect of surface treatment time, concentration of the surface treatment solution, acid concentration and temperature. The results showed that the treated mild steel surface possessed good corrosion resistant compare to untreated mild steel. The corrosion protection was interpreted on the basis of formation of protective film on the modified metal surface, which isolates metal surface from the corrosive medium. Scanning electron microscopic analysis, FTIR spectra and UV-Visible spectral studies were carried out to confirm the formation of protective organic layer formed on the modified mild steel surface.

Keywords: Corrosion protection, mild steel, polarization measurements, Tafel lines and SEM analysis.

INTRODUCTION

Iron and its alloys have been extensively used under different conditions in chemical and allied industries for handling alkalies, acids and salt solutions. But its susceptibility to rusting in humid air and high dissolution rate in acidic medium are the major obstacles in its use on a large scale. Hydrochloric acid is an important pickling acid, which is widely used in steel and ferrous alloy industries. Also it is used for removal of undesirable scales and rust present on the steel [1-3]. The formation of rust on the mild steel surface is prevented by the application of chromate treatment. The effluent obtained during chromate treatment induces the environmental pollution. But recent environmental regulations restrict the use of chromate solution and recommended its replacement with other non-toxic and non-polluting agents. Therefore, there is a need for change in the formulation of corrosion inhibition by an increasing demand for reduced environmental impact [4-8].

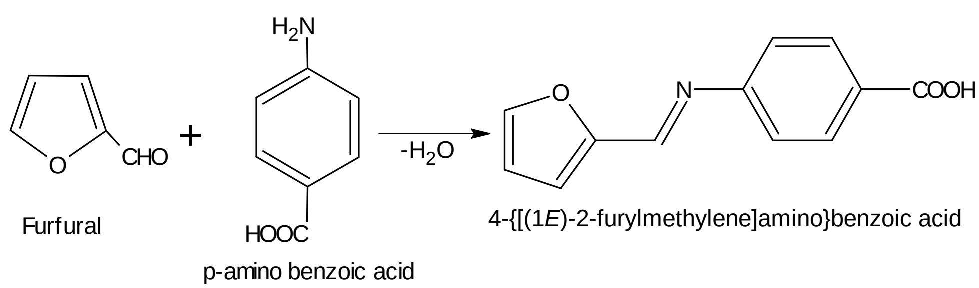
The mild steel materials treated with a solution of organic compounds provided effective corrosion protection. These compounds contain hetero atoms like N, S, P and O in their functional group and are capable of forming thin film or molecular layers on the metal surface. The role of this film is to isolate the corroding metal from the corrosive medium and reduce the formation of rust on the metal surface [9-12]. Several condensation products showed corrosion protection of mild steel in acid, neutral and alkaline media. These compounds form stable, almost insoluble film on mild steel surface through their electroactive groups and acts as protective coatings. The Condensation products of aldehydes and amines are good surface modifiers for metals than single aldehydes and amines [13-14].

In the present investigation, a condensation product of furfural and p-aminobenzoic acid [FFAB] was synthesized and used for the modification of mild steel surface. The modified mild steel surface is subjected to corrosion protection studies in hydrochloric acid medium using galvanostatic polarization technique.

MATERIALS AND METHODS

Sample preparation: Mild steel samples having the composition C= 0.05, Mn = 0.35, P = 0.032, S = 0.033% and the remainder being Fe was selected. Coupons of rectangular specimens of the size 5 x 1 x 0.1 cm were used. Prior to surface treatment, the samples were subjected to surface polishing sequences. The samples were degreased with the vapours of trichloro ethylene followed by mechanical polishing with different grits sizes (200-1200) SiC papers. The samples were rinsed with ethanol, followed by distilled water and dried with a clean tissue paper. Finally, the dried samples were kept in desiccators until use.

Preparation of Condensation product: The condensation product of Furfural and p-amino benzoic acid (FFBA) was synthesized and recrystalized compound was used as surface modifier. The purity of the compound was monitored by TLC and FTIR techniques. The scheme of condensation reaction is given below.



Surface treatment of mild steel: The different concentration of bath solutions containing 0.5 % to 2% w/v of FFAB was prepared. A known amount of FFAB dissolved in minimum amount of ethanol and then diluted to the required volume using distilled water. The polished mild steel samples of 1cm^2 exposed areas was immersed in a 100mL beaker containing 50 ml of treatment solution. The treatment time for mild steel was performed at 2 to 6 h. After treatment the specimen were removed from the bath and washed with distilled water followed by air-drying. The specimens treated were subjected to corrosion protection studies.

Polarization measurements: A conventional three- electrode cell consisting of mild steel as working electrode with exposed surface area of 1 cm^2 was employed for polarization studies. Saturated calomel and platinum were used as reference and counter electrodes respectively. The anodic and cathodic polarized potentials were recorded under galvanostatic condition using Equiptronic digital potentiometer (Model EQ 600). Tafel lines were constructed by ploting a graph of polarized potentials against log (current densities). Using tafel lines, the corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}) and anodic tafel slope (β_a) and cathodic tafel slope (β_c) were calculated. The percentage of corrosion protection efficiency (η) was calculated using the following relation 13:

$$\eta = \frac{I_{corr} - I^{1}_{corr}}{I_{corr}} \times 100$$

Where I_{corr} and I^{1}_{corr} are the corrosion current densities for treated and untreated mild steel respectively.

Surface analysis

FTIR studies: The modification of mild steel surface was characterized by FTIR spectra. The mild steel specimens was immersed in test solution for a period of 3 h, the specimens were taken out and dried. The surface film was scratched carefully and its FTIR spectra were recorded using Nicolet Avtar FT-IR instrument.

Scanning electron microscopic studies (SEM): The change in surface morphology of modified mild steel was assessed using scanning electron microscopic technique using a JSM-5800 electron microscope with the working voltage of 20 kV.

RESULTS AND DISCUSSION

Electrochemical Investigation

Effect of concentration of FFAB: The different concentrations of treatment bath solutions containing 0.5 % to 2% w/v of FFAB were prepared. The mild steel surface treatment time was taken 2 hours for all the specimens at different concentration of the bath solutions. The result showed that increase the concentration of FFAB solution, the corrosion protection efficiency of the mild steel also increased. The specimens which were surface modified from treatment solution containing 2% w/v of FFAB showed maximum corrosion resistance. Further increasing the concentration of FFAB, there was no change in the corrosion protection efficiency of surface treated specimens. The concentration 2% w/v of FFAB was taken as optimum concentration.

Effect of treatment time: The treatment baths solution containing optimum concentration of FFAB was taken and then polished samples were immersed in these treatment baths at different time duration of 2 to 6 h. The surface treated samples were subjected to polarization studies. The polarization curves for the treated and untreated samples are shown in the figure 1.

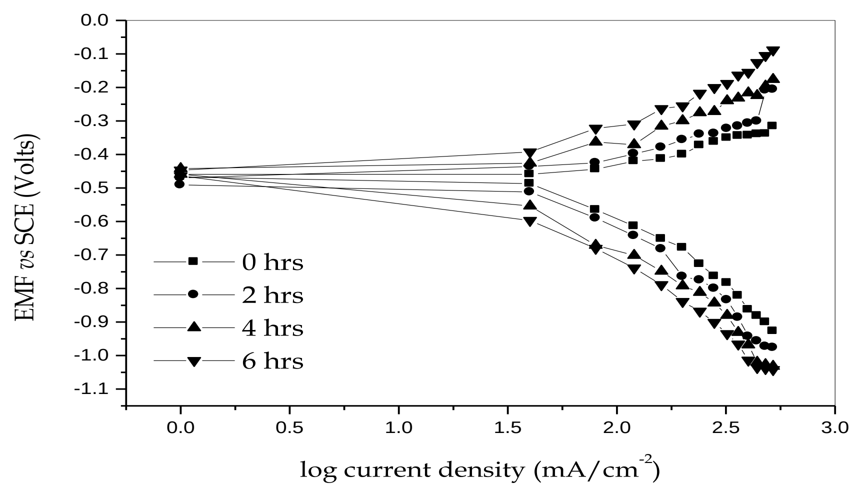


Figure 1: Polarization curves for untreated & treated mild steel in 0.5M HCl at different treatment time.

Figure 1 showed that, both anodic and cathodic curves were well separated from the untreated mild steel in hydrochloric acid medium. The well separated curves for 2 h, 4 h and 6 h treated mild steel surface indicated the progressive formation of protective film on the mild steel surface. The corrosion parameters like corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic (β_a) and cathodic tafel (β_c) slopes and percentage of protection efficiency (η) were presented in the table 1. The results showed that increase in the treatment time, the η values were also increases this was evident from the progressive formation of a protective film on the electrode surface [16-18]. For an immersion time of 6 hours, η was stabilized and reached a maximum value of 78%. Further increasing in treatment time produced no effect on η values and therefore 6 hours treatment time was considered as an optimum treatment time.
The experimental data inferred that the formation of surface film on mild steel surface blocking the active sites on the metal surface and control both anodic and cathodic reactions.

Table 1. Corrosion Parameters for steel in 0.5 M HCl with the variation of treatment time.

Time (hours)	**E_{corr} (mV)**	**I_{corr} (μA/cm^2)**	**β_a (mV/dec)**	**β_c (mV/dec)**	η
0	-0.495	89.12	110	-280	--
2	-0.483	50.11	103	-276	43
4	-0.466	35.48	97	-298	60
6	-0.423	22.38	88	-326	77

Effect of acid concentration: The protection efficiency for the modified mild steel surface was decreased with increase in the acid concentration. The protection efficiency 78% was almost constant up to the acid concentration of 0.5M. At higher concentrations of acid (>0.5M) the protection efficiency was decreased. The higher concentration of acid liberates more of H_2 gas and this accelerates the anode dissolution of metal. Further the film ruptured due to hydrogen evolution and protection rendered by the film decreased. In addition the other added factor is that the Schiff base enhances the H_2 evolution by following mechanism.

$$(\text{Schiff's base} + H)^+_{ads} + e^- = (\text{Schiff's base} + H)_{ads}$$

$$(\text{Schiff's base} + H)_{ads} = (\text{Schiff's base})_{ads} + (H)_{ads}$$

$$2\,(H)_{ads} = H_2$$

The increase in the rate of hydrogen evolution enhanced the corrosion rate and there by decreases the protection efficiency.

Effect of temperature: The mild steel specimens were treated in optimum concentration (2% w/v) of FFAB solution for 6 h and subjected to polarization study at different temperature ranging from 303-333K. The polarization studies showed that the protection efficiency against corrosion of steel offered by FFAB was found to decrease with increase in the temperature of the corrosive medium and finally it reduced to 50% at 333K and the corrosion parameters are shown in table 2.

Table 2. Corrosion current density & corrosion protection efficiency of mild steel in 0.5M HCl at different temperatures.

Temperature [K]	**I_{corr}/μA cm^{-2}**	η
303	22.38	77
313	63.0	64
323	75.85	57
333	89.13	49

The variation of corrosion current density (I_{corr}) and η with temperature as shown in the figure 2. The higher temperature causes increase the transport action of hydrogen and enhances the hydrogen evolution, which makes the rupture of organometallic film from the surface of mild steel. As a consequence the metal surface is exposed to corrosive medium and the corrosion rate was increased.

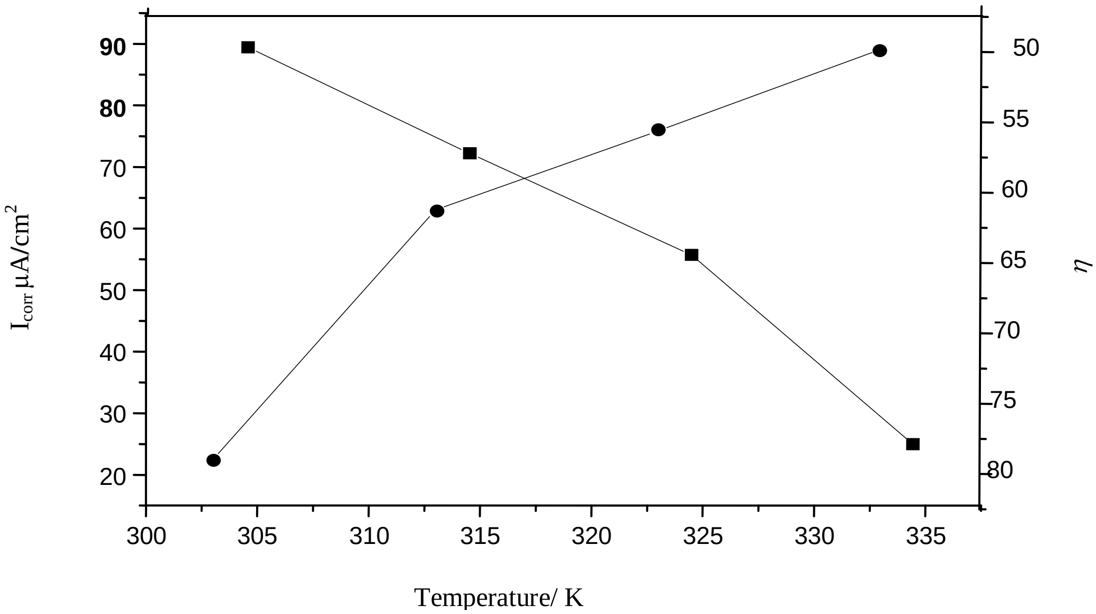


Figure 2: Variation of I_{corr} and η mild steel with different temperature.

Surface analysis techniques: Surface analysis techniques were carried out to confirm the formation of a protective film on the mild steel surface and also to investigate the establishment of chemical interaction between the electro active groups with metal surface.

SEM studies: The SEM images of treated and untreated steel surfaces after anodic polarization were taken. Figure 3a showed the photomicrograph of the corroded steel surface in 0.5M HCl solution. The surface contained large number pits distributed over the entire surface and covered with grooves of corrosion product which indicates the high dissolution rate of mild steel. Figure 3b shows the photomicrograph of treated mild steel sample taken after 10 min of anodic polarization. The surface shows only a few pits covered with less amount of corrosion product, it suggests that treated samples were exhibited higher resistance to corrosion. This revealed that the compound FFAB interacting effectively with anodic sites of steel and forms surface films [18]. Figure 3c showed a passive film, which was not subjected to the corrosion process.

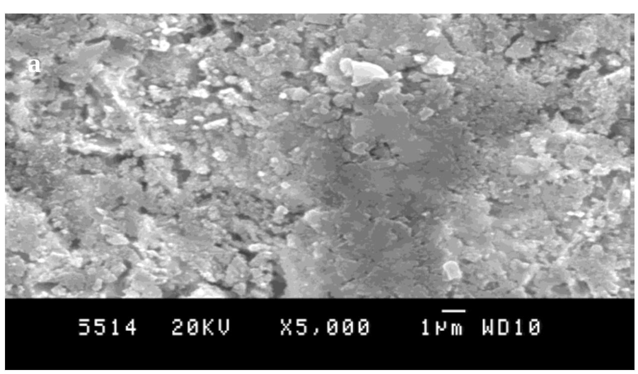


Figure 3a: SEM photoimage of anodic polarized untreated mild steel surface in 0.5M HCl.

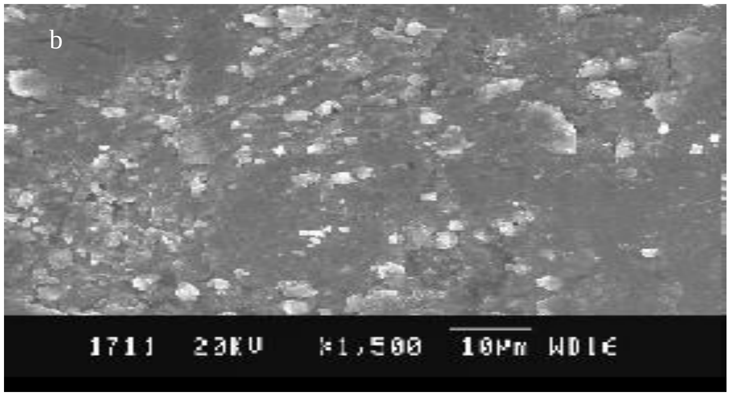


Figure 3b: SEM photoimage of 2 hrs treated anodic polarized mild steel surface in 0.5M HCl.

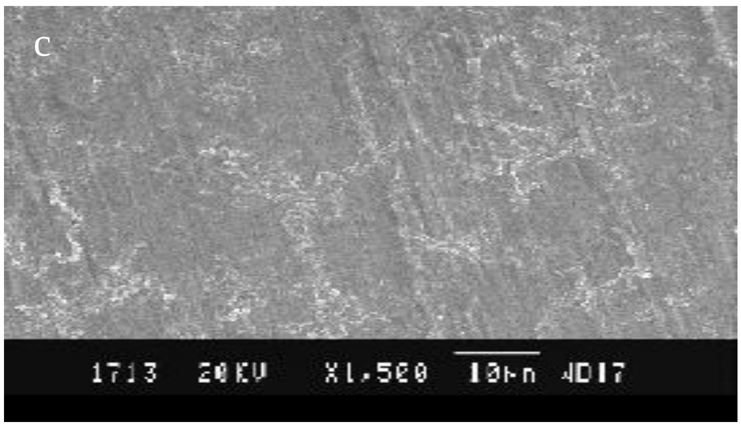


Figure 3c: SEM photoimage of 2 hrs treated mild steel surface.

FTIR study: Figure 4a shows the IR spectrum of FFBA molecule. The spectrum showed that the characteristic absorption band at 1591.7 cm^{-1} indicates the presence of > C=N- group. Figure 4b shows the spectrum of corrosion products formed on the treated mild steel samples during anodic polarization was scrapped from the mild steel surface. The spectrum showed the modification in the absorption peaks at the region 3472- 2853 cm^{-1} and 1723- 1482 cm^{-1}. These modifications of peaks suggested the interaction of organic molecule with surface atoms and leads to the formation of surface complex [19]. These types of interaction favors the formation of surface film and this film get adsorbed on the surface. Thus the active sites of metal surface were blocked by the film and reduce the rate of corrosion.

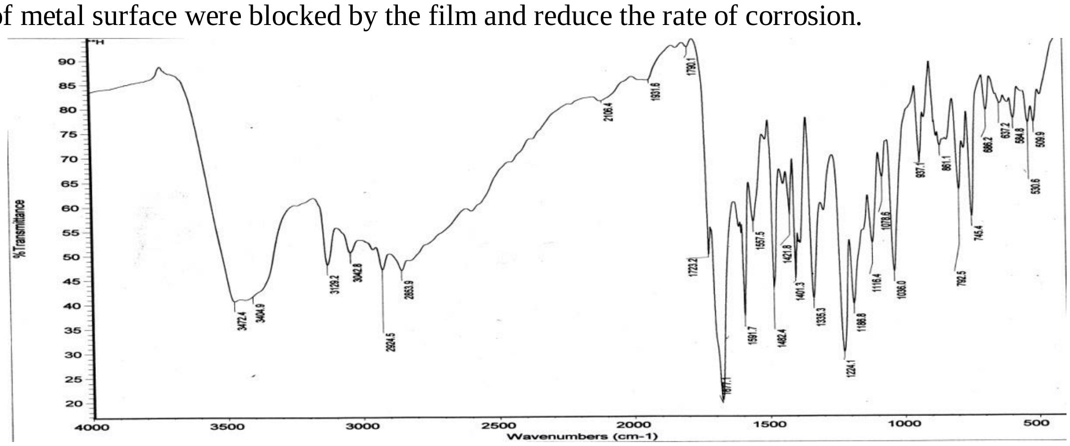


Figure 4a: FTIR Spectrum of FFAB compound

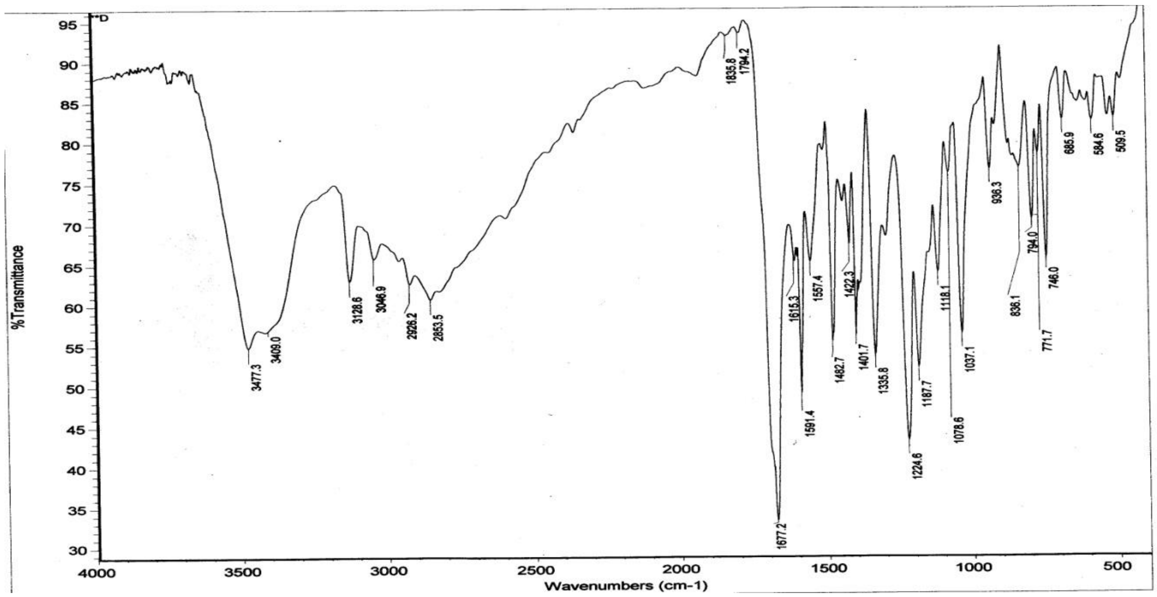


Figure 4b: FTIR spectrum of corroded product scrapped from anodic polarized treated mild steel surface.

UV-Visible Spectra: Figure 5 shows the UV spectra of the solutions obtained from 2 h immersion of treated and untreated mild steel in 0.5M HCl.

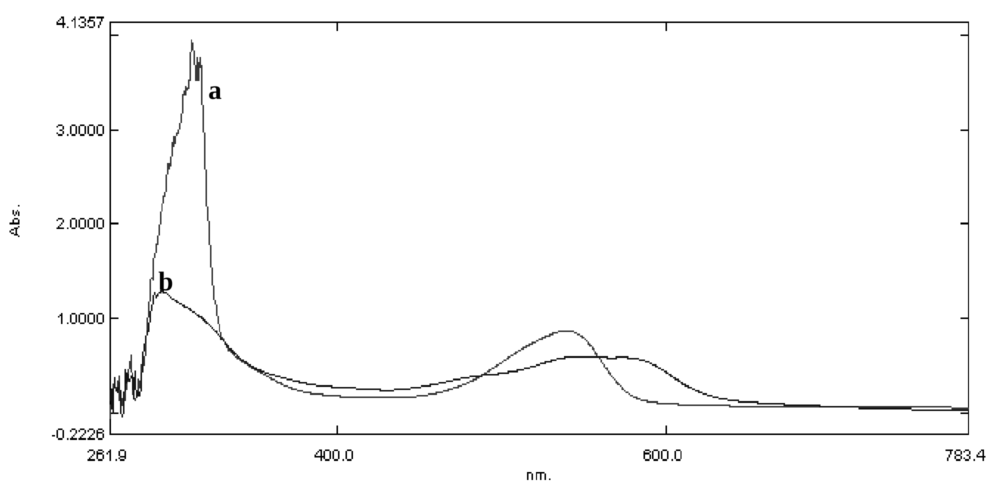


Figure 5: UV-Visible spectra of:
(a) solution resulted from the immersion of modified mild steel in 0.5M HCl
(b) solution resulted from the immersion of unmodified mild steel in 0.5M HCl.

The curve (a) represents the spectrum of solution resulted from the immersion of treated mild steel in 0.5M HCl. The corrosive medium develops colour with time after the immersion mild steel. Curve (b) represents the UV-Visible spectra of 0.5M HCl solution resulted from the immersion of untreated steel. The high intensity peak of curve (a) supports the existence of compound on the treated surface of mild steel and confirms the interaction of FFAB with metal.

APPLICATIONS

The synthesized compound exhibit good corrosion resistance to the mild steel in acid medium. The compound is less toxic compare to chromate based compounds and some extent good corrosion resistance with temperature. Therefore this compound can be used for the replacement of chromate based compounds for the corrosion protection of mild steel in acid medium.

CONCLUSIONS

Electrochemical corrosion studies showed that mild steel surface treated with FFAB exhibited a good corrosion resistance in hydrochloric acid corrosive medium. The observed protection against corrosion due to the formation and adsorption of organic film and was particularly affected by the concentration of FFAB, treatment time, concentration of corrosive medium and temperature. The surface treatment with solution of FFAB induced a modification of the mild steel surface and decreased the corrosion rate to a greater extent. The formation of a stable organometallic film due to the interaction of >C=N- group with the metal surface was confirmed by the spectral studies. The synthesized organic compound can be used as an effective surface modifier for mild steel against corrosion.

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