PERFORMANCE EVALUATION OF CINNAMALDEHYDE AS CORROSION INHIBITOR FOR CARBON STEEL IN DECONTAMINATION PROCESS

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Abstract:

Water cooled nuclear reactors contribute a major share towards power production all over the world. This is true in India also where thirteen pressurized heavy water reactors and two boiling water reactors are currently producing power commercially. Decontamination is performed in nuclear reactors with organic acids for reducing the radiation field on structural surfaces to minimize the personnel dose rate. In the present investigation, the corrosion behavior of carbon steel has been studied in the absence and presence of different concentrations of cinnamaldehyde in formulation containing Ethylenediaminetetraacetic acid (EDTA), Citric acid (CA), and Ascorbic acid (AA) EDTA: CA: AA (400:300:300 ppm*)* for 6 h at 80 ℃ by weight loss, potentiodynamic polarization and impedance techniques. Maximum inhibition efficiency of 77% was obtained at 2000 ppm of cinnamaldehyde for 6 h immersion. Electrochemical results follow the same trend as those observed in weight loss measurements. The formation of the adsorbed inhibitor film on the carbon steel was further confirmed by FTIR and SEM studies.

Key words: Carbon steel, EIS, Polarization, Decontamination, Organic acids, Electrochemical studies.

1. Introduction

Carbon steel finds wide application as a construction material for heat transport system in nuclear, petrochemical and chemical process industries due to its low cost and easy availability and fabricability. It is, however, highly prone to corrosion in aqueous environment and continuous operation results in the formation of surface oxide films. These deposits are oxides and oxy-hydroxides of iron such as magnetite in reducing environment and γ-Fe_2O_3 in oxygen rich solutions. In the reactor coolant systems of nuclear power plants, these corrosion product oxides are transported across the reactor core leading to the formation of neutron activated corrosion product isotopes such as ^{59}Fe, ^{60}Co, [58]Co etc., In addition, fission products escaping from the failed fuel bundles contribute to the surface radioactivity though its contribution is less. Transportation and deposition of these activated corrosion / fission product isotopes causes radiation field build-up which in turn leads to the exposure of operating personnel to radiation. One way of solving this problem is to remove the radioactive deposits by decontamination process [1-4] so that the radiation field is reduced and the exposure of personnel to radiation is minimized.

Out of the several decontamination methods available, chemical decontamination method is very effective in reducing occupational radiation exposure during large-scale tasks in nuclear plants such as overhaul of primary recirculation pumps, shroud replacement, enmass coolant channel replacement and so on. Therefore, many different chemical decontamination methods have been developed [5-10] and successfully employed in several decontamination campaigns. . Most of the chemical decontamination processes being used employs formulations consisting of a reducing agent, for reducing the ferric in the oxide lattice that facilitates the dissolution of oxide by the acidity provided by the other constituents viz. complexing organic acids, The complex forming organic acids helps to keep the dissolved metal ions in solution. In systems containing carbon steel as structural materials, presence of a corrosion inhibitor greatly helps to minimize the corrosion of carbon steel during decontamination [11].

In the last few years, a considerable amount of research on the chemical cleaning of nuclear steam generators has been performed in many laboratories. The

chemical dissolution reactions and the corrosion processes involved in the steam generator chemical cleaning are akin to the chemical decontamination. Among other aspects studied the corrosion mechanisms involved in the use of the cleaning solvent [12-16] and the development of process applications and evaluation of corrosion inhibitors. [17-23]

Most of the well known inhibitors used for prevention of corrosion of steel in acidic media are organic compounds containing nitrogen, sulphur and oxygen atoms. The influence of organic compounds containing nitrogen such as amines and heterocyclic compounds on the corrosion of steel in acidic solutions has been investigated by several workers [24-25] .Considering the possible contribution of pi-bonding features the aromatic aldehydes are more effective as inhibitors than the aliphatic aldehydes

Among the aldehydes, Cinnamaldehyde has been chosen considering the fact that it does not contain sulphur and nitrogen. Sulphur containing compounds are not preferred in chemical decontamination processes because of their incompatibility with copper and nickel containing materials. Most of the nitrogen containing inhibitors are amino compounds that form cationic species which causes problem in the regenerative type of dilute chemical decontamination processes. In the regenerative decontamination processes cation exchange resin is used for regeneration of the formulation chemicals by the cation exchange resin. The cationic inhibitors are absorbed by the cation exchange resin and gets removed from the solution. Hence, efforts are being made to look for corrosion inhibitor that does not contain sulphur or amino compounds and at the same time effective in inhibiting the corrosion of carbon steel. The interest for cinnamaldehyde is also emphasized due to its non-toxic character. [26-27]. It has been postulated [28-29] that substances having conjugated double bonds, poor solubility, a large number of unpaired electrons in anchoring atom, large dipole moments and large molecular areas will be effective as corrosion inhibitors. Work carried out with cinnamaldehyde in citric acid medium has been already reported [30]

In the present work, the corrosion behavior of carbon steel in organic acids such as Ethylenediaminetetraacetic acid (EDTA), Citric acid (CA), and Ascorbic acid (AA) with different concentrations of cinnamaldehyde has been studied using

3

potentiodynamic polarization and impedance measurements. FTIR studies were made to characterize the film, and SEM studies for the morphology of the surface in the presence of inhibitor.

2. Experimental details

2.1. Weight loss measurements

Weight loss measurements were carried out on the carbon steel specimens of size 5 × 1 × 0.1 *cm* in solution containing EDTA,CA,AA in concentrations of 400,300,and 300 ppm respectively (herein after called as EDTA:CA:AA (400:300:300 ppm), along with different concentrations of cinnamaldehyde. The duration of experiment was 6 h and the temperature was maintained at 80 ℃. The initial *pH* and final *pH* values were noted during the experiment. The initial weight of the triplicate carbon steel specimens were measured and immersed in a 500 ml solution with the help of glass hooks. At the end of the experiment, the carbon steel specimens were taken out dried and final weights were measured. The solutions were not closed and deaerated.

The corrosion rate *CR* (mmpy) and inhibition efficiencies were calculated using the formula,

$$CR(mmpy) = \frac{87.6 \times W}{ATD}$$

where W = weight loss in *mg*, A = area in square.*cm*, T = time of exposure in hours and D = density in *g/cm³*

$$Inhibition\ efficiency(\%) = \frac{W_B - W_1}{W_B}$$

Where W_B and W_1 are weight loss per unit time in the absence and presence of inhibitors.

2.2. Electrochemical impedance spectroscopy (EIS)

Impedance measurements were carried out on carbon steel (working electrode) immersed in mixture of acids EDTA: CA: AA (400:300:300 ppm) containing different concentrations of cinnamaldehyde using the Electrochemical Measurement Unit (Solartron Model 1280B). A saturated calomel electrode and platinum electrode were used as reference and counter electrode respectively. The working electrode was immersed in test solutions for approximately 10-15 min for the attainment of steady state equilibrium. The studies were carried out over a frequency range of 10 KHZ to 10 mHZ Measurements were done initially and after 6 h of immersion in the test solutions at 80 ℃ The impedance parameters such as charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were evaluated from Nyquist plots.

The percentage of inhibition efficiency was calculated using the following equation

$$IE(\%) = \frac{R_{t*} - R_t}{R_{t*}}$$

Where R_t and R_{t*} are charge transfer resistance values in the absence and

 presence of inhibitors.

2.3. Potentiodynamic polarization measurements

Potentiodynamic polarization measurements were carried out using the same instrument as mentioned in impedance spectroscopic studies at 80 ℃ for carbon steel immersed in mixture of acids EDTA: CA: AA (400:300:300 ppm) containing different concentrations of cinnamaldehyde. Measurement was done after 6 *h* of immersion in the test solution at 80 ℃ . The area of the working electrode exposed was 1 cm^2 and the remaining portion was covered with red lacquer. The polarization parameters such as corrosion potential (E_{corr}), corrosion current (i_{corr}) and Tafel slopes (b_a and b_c) were evaluated from potentiodynamic polarization measurements. The corrosion rate (mmpy) was calculated using the formula.

$$CR(mmpy) = 3.2 \times I_{corr}\,(mAcm^{-2}) \times \frac{Equivalent\ Weight}{Density}$$

The inhibitor efficiency was calculated using the following formula:

$$IE(\%) = \frac{I_{corr} - I_{corr*}}{I_{corr*}}$$

where I_{corr} and I_{corr*} are corrosion current values in the absence and presence of inhibitors.

3. Surface examination studies

3.1 FT-IR Spectral studies

The FT-IR spectra were recorded using Nicolet–380 FT-IR spectrophotometer for the carbon steel surface immersed in EDTA: CA: AA (400:300:300 ppm) for 6 h at

80 ℃ in the absence and presence of the inhibitor.

3.2 Scanning Electron Microscopic Studies

Surface examination of carbon steel specimens were made using JEOL-scanning electron microscope (SEM) with the magnification of 1000× for the carbon steel specimens immersed in EDTA: CA: AA (400:300:300 ppm) for 6 h at 80 ℃ in the absence and presence of the inhibitor.

4. Results and Discussion

4.1 Weight loss measurements

The corrosion rate values obtained for carbon steel immersed in EDTA: CA: AA (400:300:300 ppm) with different concentrations of cinnamaldehyde for an immersion period of 6 h at 80 ℃ are given in Table 1. From the table it can be seen that the corrosion rates of carbon steel, are low in the presence of cinnamaldehyde. An inhibition efficiency of 87 % was obtained when the experiment was carried out with 500 mg/l of cinnamaldehyde. The inhibition efficiency did not change much at concentrations more than 500 mg/l. Thus, it is found that cinnamaldehyde inhibits corrosion of carbon steel in EDTA: CA: AA (400:300:300 ppm) medium, considerably even at 500 mg/l concentration. Hence, the corrosion inhibition behavior of cinnmaldehyde was investigated electrochemically to understand the mechanism by which it inhibited corrosion of carbon steel in this medium.

4.2 Electro chemical methods

4.2.1 Electrochemical impedance spectroscopy (EIS)

Fig1 shows the Nyquist plot for carbon steel immersed in EDTA: CA: AA (400:300:300 ppm) medium containing different concentrations of cinnamaldehyde obtained immediately after immersion (initially) and after 6 h of immersion in the solution at $80℃$ The impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}) and inhibition efficiency are given in Table 2. From the Table 2, it can be seen that the inhibition efficiency is increased from initial to 6 h duration The increase in the charge transfer resistance with time indicates that dissolution rate of carbon steel decreases with time. This is due to increasing surface coverage with time by inhibitor which leads to an increase in inhibition efficiency with time. From the charge transfer resistance values obtained after 6 hour of immersion in the medium and at different concentrations of cinnamaldehyde, it was observed that inhibition efficiency increased from 23 % at 500 mg/l to about 70% at 1500 mg/l concentration. . Thus, the impedance technique confirms the effectiveness of cinnamaldehyde in inhibiting the corrosion of carbon steel in EDTA: CA: AA (400:300:300 ppm) medium. However, the values of inhibition efficiency obtained by impedance measurement technique is lower

7

as compared to the weight loss method. This difference is attributed to the method of measurement. The weight loss method gives an inhibition efficiency values that is an average of six hour, whereas the value obtained with the impedance and the polarization technique are instantaneous values.

4.2.2 Potentiodynamic polarization studies:

Fig 2 shows the polarization curves for carbon steel immersed in EDTA: CA: AA (400:300:300 ppm) with different concentrations of cinnamaldehyde obtained initially and after 6 h of immersion in the solution at 80 ℃. The extrapolation of Tafel straight lines allows the calculation of the current (I_{corr}). The values of $I_{corr,}$ the corrosion potential (E_{corr}) the corrosion rate and percentage inhibition efficiency are given in Table 3. From the table, it can be seen that corrosion current decreases with increase of immersion time and the inhibition efficiency increases from initial to 6 h duration.

4.2.3 SEM Studies

Surfaces of polished carbon steel specimens that were immersed for 6 h at

80 ℃ in EDTA: CA: AA (400:300:300 ppm) medium in the absence and presence of 2000 ppm of cinnamaldehyde, were examined by scanning electron microscope (SEM). In the case of specimen exposed to solution which did not contain cinnamaldehyde, the metal surface was etched and the grain boundaries could be seen. In addition, some corrosion products are also clearly seen. [Fig-3 (a)]. But for the specimen exposed to the solution containing the inhibitor, was should be smooth without any corrosion products as seen in Fig.3 (b). Some original surface defects of the specimen are also seen in the figure. The above studies have shown that cinnamaldehyde is found to be effective in controlling corrosion of iron in decontaminating acid mixture.

4.2.4 FT-IR Spectral Studies

The FTIR spectrum obtained on the carbon steel specimen immersed in mixture of acids EDTA: CA: AA (400:300:300 ppm) for 6 h at 80 ℃ is shown in Fig.4 (a). Spectrum of the film formed on the surface of the carbon steel immersed in mixture of

acids containing 2000 ppm of cinnamaldehyde is shown in Fig.4 (b).It is clear from the Fig 4 (b) that peak corresponding to >C=O stretching frequency of aldehyde are present . A peak at 1740 cm^{-1} has been attributed to carbonyl groups. Weiss et al [31] discovered that α ,β- unsaturated carbonyl compounds can complex iron through the >C=C< moiety. The peak at 1645 cm^{-1} is assigned to the complexed >C=C< group. Growcock etal [32] have reported that cinnamaldehyde undergoes irreversible reduction at the steel surface, which initiates polymerization reactions that lead to formation of low molecular weight aromatic hydrocarbons, including polyene species. The polymeric products that are ultimately formed do not adhere directly to the steel surface, but appear to be held via a strongly sorbed species, perhaps cinnamaldehyde itself.

Inhibitors decrease the corrosion rate by adsorption onto active surface sites, thereby decreasing the available surface area for corrosion. Aldehydes and unsaturated hydrocarbons in general are thought to chemisorb on ferrous materials [33].α,β Unsaturated carbonyl compounds, such as cinnamaldehyde, are known to form stable complexes (through >C=C<) with iron compounds such as Fe (CO)$_4$. Consequently, it is expected that the cinnamaldehyde is adsorbed onto steel and inhibited corrosion. .Cinnamaldehyde polymerizes as well as adsorbs, forming a barrier film that enhances the inhibition; the surface complex may serve in the secondary capacity as an anchor for the film so formed. Other unsaturated compounds have also been found to form protective polymeric films on steel in nonoxidising acids [34]. Loss of double- and triple-bond character in the dissolved inhibitors and discrepancies between rates of H$_2$ evolution and mass loss are cited as evidence that the polymers are formed via reduction. In the case of cinnamaldehyde, large decrease in the rate of H$_2$ evolution vs. rate of mass loss and spectroscopic analysis of organic products formed on the steel surface indicate that it, too, undergoes reduction to initiate polymerization.

Reduction of cinnamaldehyde may involve either the double bond or the carbonyl group, depending on the reducing agent and the reaction conditions, one such mechanism, for which there is a precedent, is reductive coupling through the formation of free radicals. Other studies indicate that there are feasible alternative reduction

mechanisms, including reduction of $-C(OH$ to $-CH_2OH$ to form cinnamyl alcohol and reduction of $>C=C<$ to $>CH-CH<$ to form 3-phenylpropionaldehyde.

5. Conclusion

Cinnamaldehyde is found to inhibit the corrosion of carbon steel in chemical formulation viz. EDTA: CA: AA (400:300:300 ppm) used for decontamination of nuclear coolant system/components. The increase of charge transfer resistance with time indicates that dissolution rate of carbon steel decreases with time. The formation of the adsorbed protective inhibitor film on the carbon steel was also confirmed by FTIR and SEM studies.

6. Acknowledgement

7. References

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11

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Table 1

Corrosion rate and pH of carbon steel immersed   in mixture of acids
(EDTA: CA: AA – 400:300:300 ppm) containing different concentrations of
Cinnamaldehyde for an immersion period of 6 h at 80 $°C$ based on weight loss
measurement.

Concentration of inhibitor (mg/l)	pH		Cinnamaldehyde	
	Initial	After 6 h	Corrosion rate (mmpy)	Inhibition efficiency (%)
Blank	3.10	4.17	4.63	--
100	3.10	4.01	4.33	6.4
500	3.10	3.13	0.61	86.8
1000	3.07	3.08	0.48	89.6
2000	3.06	3.06	0.53	88.4

Table-2

Impedance parameters for carbon steel immersed in mixture of acids
(EDTA: CA: AA -400:300:300 ppm) with different concentrations of cinnamaldehyde at
80 $^oC.$ for an immersion period of 6 h.

Concentration of inhibitor (mg/l)	Initial R_t (Ω)	Initial C_{dl} (F/cm^2)	After 6 h R_t (Ω)	After 6h C_{dl} (F/cm^2)	Inhibition efficiency (%)
Blank	300	5.02×10^{-6}	630	9.81×10^{-6}	-
500	550	1.62×10^{-6}	822	1.58×10^{-4}	23
1000	733	8.06×10^{-5}	1017	1.26×10^{-5}	38
1500	750	4.48×10^{-5}	2002	3.49×10^{-5}	68
2000	769	1.68×10^{-6}	2123	1.24×10^{-5}	70

Table-3

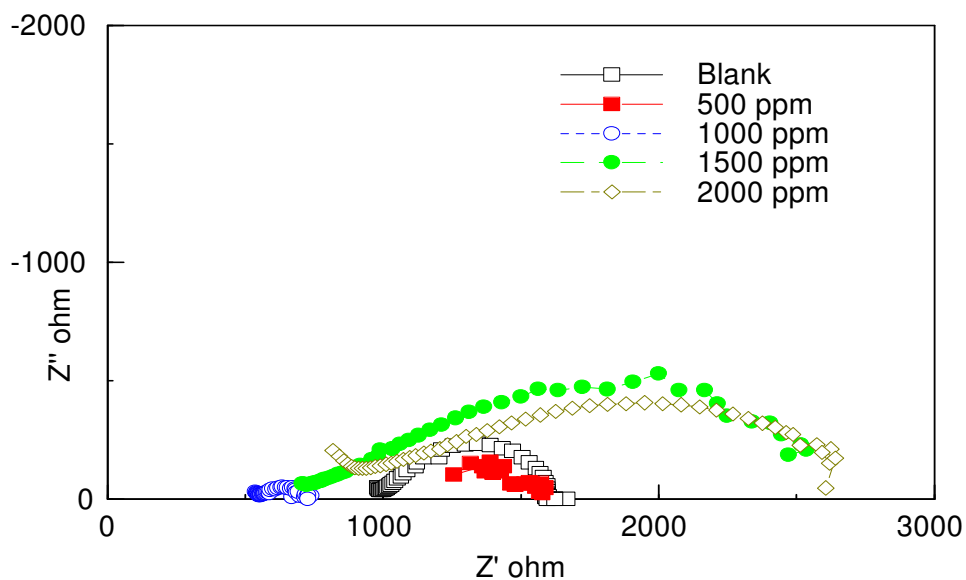Potentiodynamic polarization parameters for carbon steel immersed in mixture of acids (EDTA: CA: AA- 400:300:300 ppm) with different concentrations of cinnamaldehyde at 80 ^oC for an immersion period of 6 h

Concentration of inhibitor (mg/l)	Initial E_{corr} (Volts)	Initial I_{corr} (A/cm^2)	Final E_{corr} (Volts)	Final I_{corr} (A/cm^2)	Corrosion rate (mmpy)	Inhibition efficiency (%)
Blank	-0.557	3.1493 x10^{-5}	-0.479	3.2068 x10^{-5}	0.37	-
500	-0.581	2.2709 x10^{-5}	-0.552	2.6187 x 10^{-5}	0.30	18
1000	-0.638	2.3981 x10^{-5}	-0.554	2.6637 x 10^{-5}	0.30	18
1500	-0.766	1.9371 x 10^{-5}	-0.546	1.0824 x 10^{-5}	0.12	66
2000	-0.546	2.6637 x10^{-5}	-0.494	6.5313 x10^{-6}	0.07	77

Fig-1 Impedance curves for carbon steel immersed in mixture
of acids (EDTA: CA: AA-400:300:300 ppm) with different concentrations of
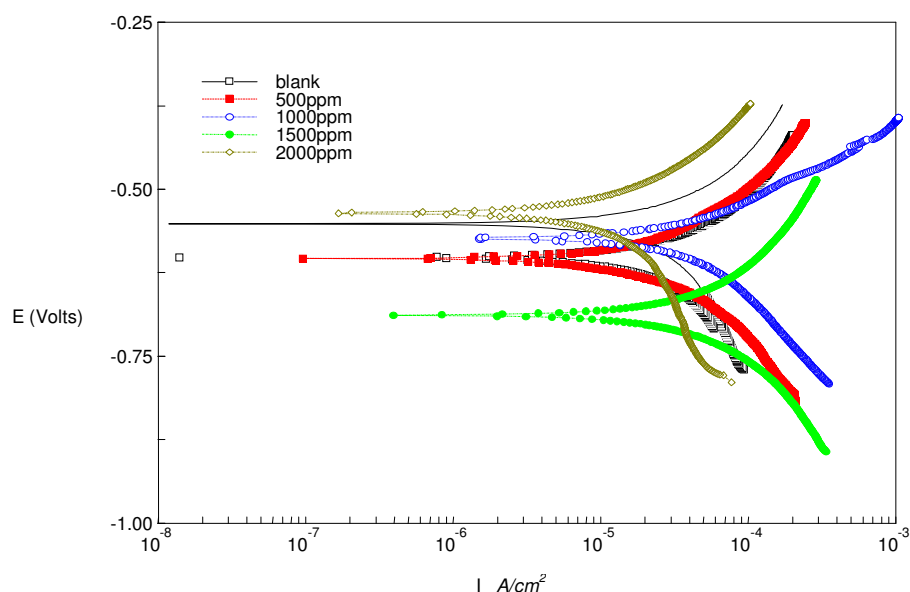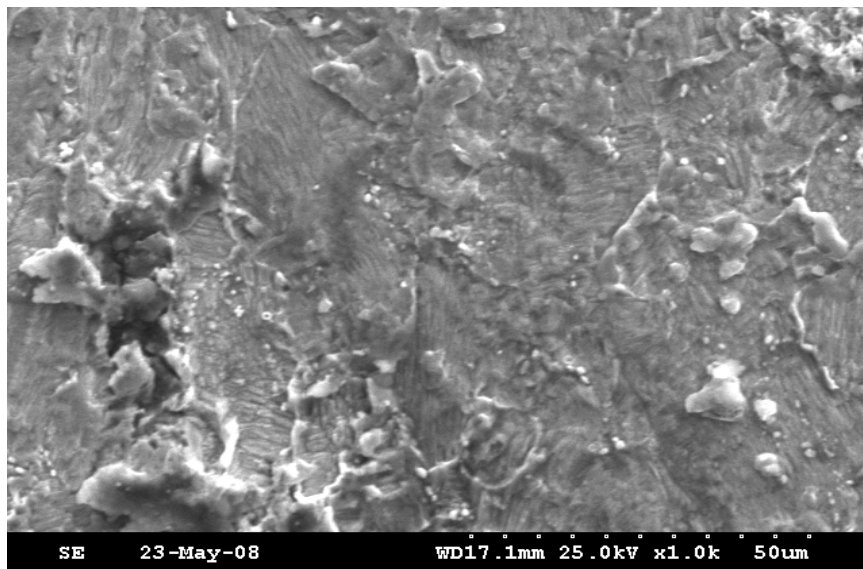cinnamaldehyde at 80 ^{o}C for an   immersion period of 6 h

Fig-2 Potentiodynamic polarization curves for carbon steel immersed in mixture of acids (EDTA: CA: AA- 400:300:300 ppm) with different concentrations of cinnamaldehyde at 80 ^{o}C for an immersion period of 6 h.

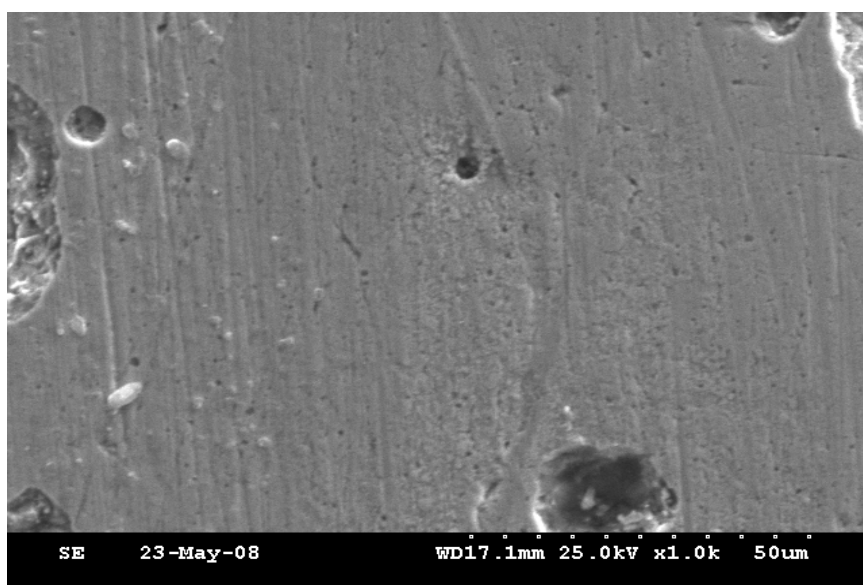Fig-3 (a) SEM photograph of carbon steel immersed in mixture of acids (EDTA: CA: AA) at 80 ^{o}C for 6 h

Fig-3(b) SEM photograph of carbon steel immersed in mixture of acids (EDTA: CA:AA) containing 2000 ppm of cinnamaldehyde at 80 ^{o}C for 6 h
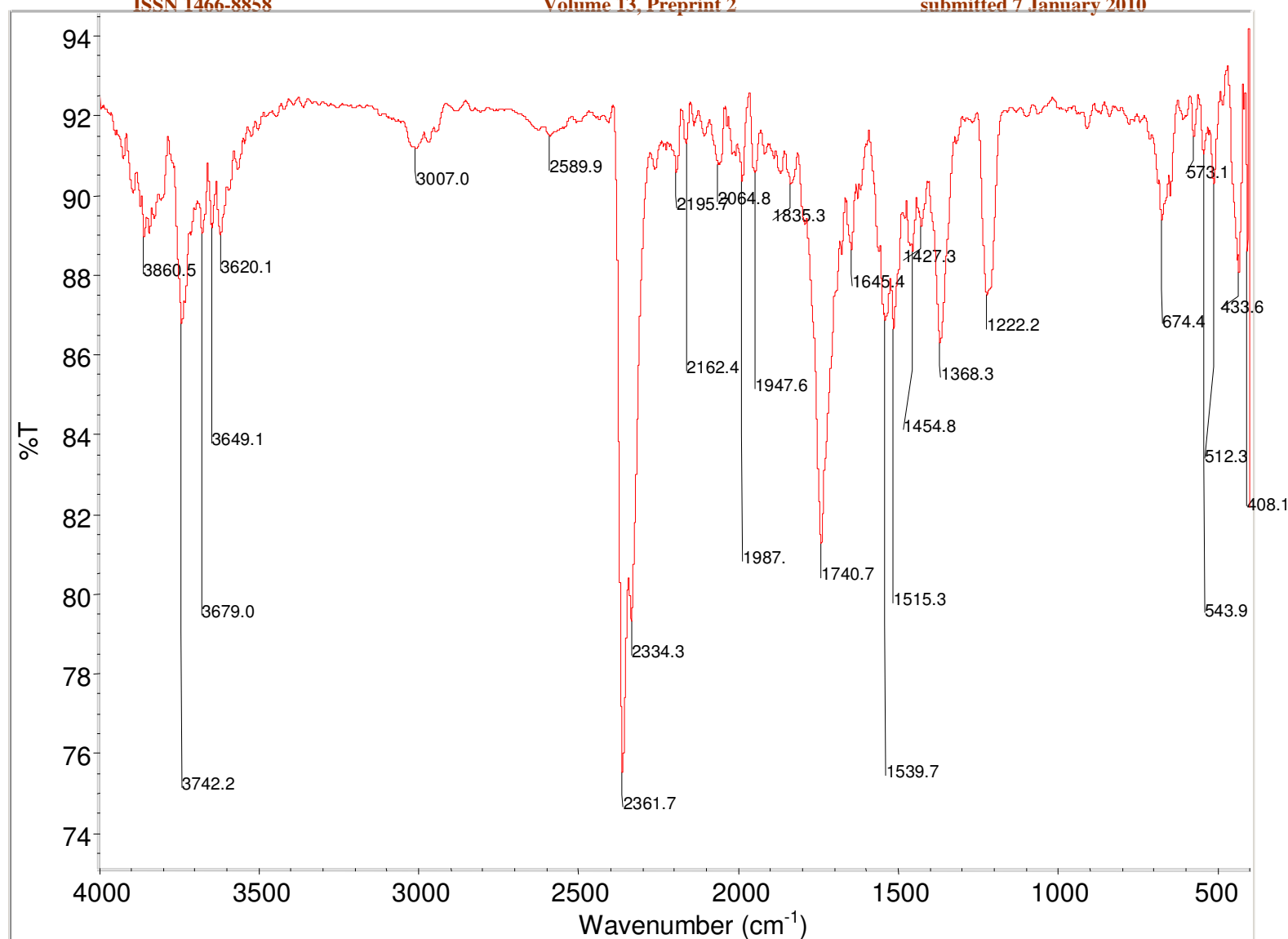
Fig-4 (a) FTIR spectrum of carbon steel immersed in mixture of acids
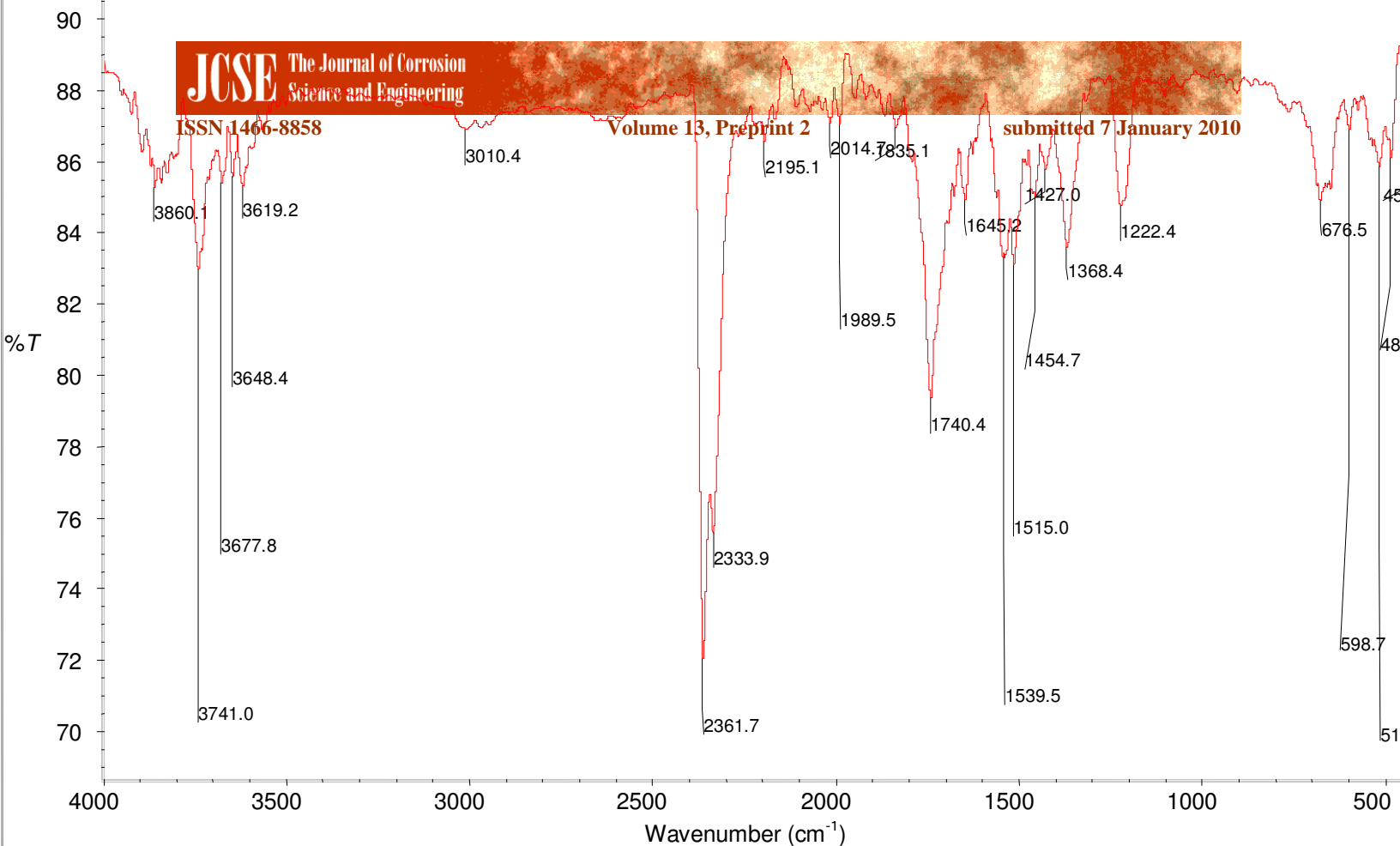
(EDTA: CA: AA) at 80 ^{o}C for 6 h

Fig-4 (b) FTIR spectrum of carbon steel immersed in mixture of acids (EDTA: CA: AA)

containing 2000 ppm of cinnamaldehyde at 80 ^{o}C for 6 h