STUDY OF CIGARETTE BUTTS EXTRACT AS CORROSIVEINHIBITING AGENT IN J55 STEEL MATERIAL

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Abstract

Cigarette butts are the one of the most common garbage worldwide, as an estimated 4.5 trillion cigarette butts are deposited somewhere into the environment every year. Chemicals such as arsenic, nicotine, polycyclic aromatic hydrocarbons, and heavy metals have been found to leach into water and can be the source of toxicity to life in marine and freshwater environments. The present study is to isolate crude extracts from littered cigarette butts using polar solvents, which is used as corrosion inhibitor for J55 oil well tubular steel used in acidization of oil well and gas production. The chemical compounds present in the crude extracts analyzed using LC-MS and ASS. Weight loss and electrochemical techniques were used to evaluate corrosion inhibitive effects on J55 oil well tubular steel in 15% HCl solution at 30°C and 105°C.Result shows that the highest inhibition efficiencies of 99% and 61% are obtained for 30^{o}C and 105^{o}C respectively at 6% concentration.Hence delivered a potential remedial solution for the littered cigarette butts and provide a clean environment.

Keywords: *cigarette butts, corrosion, inhibitor, environment, acidization*

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1. INTRODUCTION

It is an eminent fact that thousands of chemicals are found in cigarette smoke with dozens of these chemicals being identified as human and animal carcinogens (United States Department of Health and Human Services [USDHHS], 2010). However, it is not known if cigarette butts, which have become a huge litter problem in recent decades, can be a toxic risk and become a health risk to marine as well as freshwater habitats. One of effective ways to reduce pollution is introduced byrecycling the cigarette butts. But, there are few reports onreusing cigarette butts.

Acidization of petroleum oil well is a stimulation technique for enhancing production.Hydrochloric acid (15-20%) solution is commonly used for the purpose. The 15% HCl used for acidizing process leads to severe corrosion of oil well casing,tubing and accessories.The total annual cost of corrosion in the oil &gas productions are estimated to be $1.372 billion, broken down into $589 million in surface pipeline and facility costs, $463 million annually in down hole tubing expenses, and another $320 million in capital expenditures related to corrosion (Matthew, May 2008.) corrosion inhibitors are added along with the acid to reduce the corrosion attack on well equipment.This study focuses on detecting specific chemicals present in the cigarette butts extract and used as a corrosion inhibitor for J55 steel pipe used in acidization process. In this investigation, 15% of hydrochloric acid and cigarette butt waterextracts on corrosion inhibition are taken into account.

2. EXPERIMENTAL SECTION

The tested material is J55 oil well tubular steel with the chemical composition of C 0.33,Mn 1.45, Si 0.25, S 0.06, P0.04and Fe 97.87.Before the corrosion test, the surfaces of the sample are mechanically polished and rinsed with Clark solution and then dried.The apparatuses used in this study are as follows: The chemical compositions of the cigarette buttwater extracts are detected by liquid chromatography (Agilent 2100)/mass spectrometry (Agilent 6410) with the followingdetermination conditions: C18 column (2.1 mm × 50 mm, 3.5μm, Agilent), column temperature -30 °C, mobile phasemethanol + 0.1% formic acid, flow rate 0.4 mL/min, sampling amount 2 μL, ion source model ESI+, atomizing gas pressure15 psi, atomizing gas flow rate 6 L/h, atomizing gas temperature350 °C, capillary voltage 150 V, scanning model full scanningmodel, direct sampling after filter by 0.45 μm micro porous membrane. The electrochemical techniques such as potentiodynamic polarization and impedance are investigated by a potentiostat. The littered cigarette butts were used in this study.

3. RESULTS AND DISCUSSION

3.1 Collection of Sample

Sample (littered cigarettes) was collected from various places in Tiruchirappalli which includes airport, central bus stand, streets, sidewalks, and other open areas. All glassware's (Borosil) was washed and rinsedwith deionized water,and further sterilized at 120°C for 20 minutes prior to use. The collected cigarette butts were used for the preparation of crude extracts by using water as a polar solvent.

3.2 Preparation of Inhibitor

The methodology for making corrosion inhibitor with cigarette butt -water extracts is as follows: Five grams of littered cigarette butts were soaked in 100 mL of deionizedwater for seven days. Each container was sealed with paraffin strip and placed in a shaker conical flask covered with aluminum foil. The polar solvent sample was prepared. After 7 days the sample was filtered using vacuum pumpfor the removal of solid and suspended particlesand a filter paper made of cellulose fiber.The filter paper was 9.0 cm in diameter, with particle retention of 1-5 micrometer, fine porosity and a slow flow rate of 5 milliliter per minute. There was approximately 75-100 mL of liquid present in the conical flask after the 7 day period soaking. The volume of each sample depended on the sample itself. The amount of sample that was filtered was extracted using rotary evaporator (Make: IKA) and stored in a glass vials at room temperature. The cigarette butts extract was analyzed for corrosion inhibition by weight loss and electrochemical methods. The extract had also been determined by the LC/MS. In the rough, seven chemical compounds with the heteroatom (N, O) and π-bonds in favor of metal corrosion inhibition were detected in the LC/MS results. There may also be others it hasbeen not detected.Among them nicotine contain 1.43% high concentration.

3.3 Presence of Heavy Metals in the Aqueous Extract

The presence of heavy metals in the aqueous solution of cigarette butts extract as analyzed through atomic absorption spectroscopy the results are followed as

Heavy metals	Concentration(mg/L)
Cu	0.72
Fe	1.06
Zn	0.02
Cr	0.12
Ni	0.21

3.4 Mass Loss Measurements

The mass loss parameters of J55 oil well tubular steel in 15% commercial HCl containing various concentrations of Cigarette Butt Water Extractsat 30^{o}C and 105^{o}C are given in Table 3. From the Table 3, it can be observed that the corrosion rate values decrease and the inhibitor efficiency values increase with the increase of the Cigarette Butt Water Extracts concentrations for both the temperatures. But at a particular concentration of the inhibitors, the corrosion rate increases and the inhibitor efficiency decreases with the increase of temperature as can be observed from Table 3. It can also be observed that the corrosion rate values decrease from 165 mmpy to 1 mmpy and from 427 mmpy to 136 mmpy for Cigarette Butt Water Extractsat 30^{o}C and 105^{o}C respectively.The highest inhibition efficiencies of 99% and 61% are observed for Cigarette Butt Water Extracts at 6% concentration and at 30^{o}C and 105^{o}C, respectively. The addition of Cigarette Butt Water Extracts changes the corrosion rate and the inhibition efficiency.At higher temperature, Cigarette Butt Water Extracts is not an effective inhibitor.Figure.1 shows the plot of inhibitor efficiency as a function of inhibitor concentration for both the temperatures.

3.5 Potentiodynamic Polarization Measurements

The polarization behaviors of J55 oil well tubular steel in 15% HCl and without various concentration of Cigarette Butt Water Extractsat 30^{o}C and 105^{o}C is shown in Fig.2. From these polarization curves, the polarization parameters like E_{corr}, ba, bc and I_{corr} are obtained. From the values I_{corr}, the corrosion rates and inhibitor efficiencies are calculated and tabulated in Table 4. In the Cigarette Butt Water Extracts, it can be observed that the I_{corr} values decrease from 771 μA.cm^{-2} to 130 μA.cm^{-2} at 30^{o}C and from 1, 35,000 μA.cm^{-2} to 47,600 μA.cm^{-2} at 105^{o}C. The highest inhibitor efficiency of 83% and 65% are achieved for both the temperatures respectively. From the E_{corr} values, it can be observed that there are tides in the E_{corr} values for the inhibitors. This indicates clearly that Cigarette Butt Water Extractsare mixed type of inhibitors.

3.6 Electrochemical Impedance Measurements

The impedance behavior of J55 oil well tubular steel in 15% commercial HCl with and without various concentrations of inhibitor at 30^{o}C and 105^{o}C is shown in Figure.3. From these impedance curves, the impedance parameters like charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values are obtained. From the values of R_{ct}, the inhibitor efficiency is calculated and tabulated in Table 5. From this table, it can be observed that the R_{ct} values of inhibitor increased from 32Ω cm^2 to 272 Ω cm^2 respectively and C_{dl} values decreased from 265 μF.cm^{-2} to 32 μF.cm^{-2} respectively with the increase of the inhibitor concentrations. The decrease in C_{dl} values indicates that the adsorption of inhibitor molecules on the J55 oil well tubular steel surface and the corrosion process involved is activation-controlled reaction. The plots Φ vs. log C are drawn for Cigarette Butt Water Extractsinhibitors at 30^{o}C and 105^{o}C and they are shown in Figure.4. From these plots, it can be seen that the Φ vs. log C curve is linear. This linear trend confirms that Cigarette Butt Water Extractsinhibitors obey Tem kin’s adsorption isotherm at both the temperatures.From the above weight loss and electrochemical studies,cigarette butt water extracts may establish its inhibition actionvia the adsorption onto the metal surface. The adsorption of the inhibitor could be occurred due to the formation of oxidation film or the electrostatic interactions. The oxidants in inhibitor may oxidize the iron atoms forming the insoluble salt (oxidation film) covered on the iron surface. The lonely electron pairs present on the N and O atoms of the heterocyclic compounds in the inhibitor may also adsorb through the electrostatic interactions between the acid solution and the metal surface.Thus, the metal surface can be protected and the iron atom'sfurther dissolution can be prevented(Behpour, M *etal.,Corros.Sci.***2009**).

3.7 Effect of Temperature on Thermodynamic Properties

The values of activation energy (E_a), heat of adsorption (Q_{ads}), free energy of adsorption ($\Delta G^o a$), Enthalpy ($\Delta H^o a$) and the Entropy ($\Delta S^o a$) are calculated for the studied system and given in Table 6. From the table, it can be found that the E_a value of uninhibited system is 11380 kJ mol^{-1} and the values of inhibited systems of inhibitor are 60679 kJ mol^{-1}. The E_a value of the inhibited system is higher than the value of uninhibited system. The higher values indicate the physical adsorption of the inhibitor on the J55 steel surface (I.N.Putilova *et al.*1960).The Q_{ads} values of inhibitor is -46337 kJ mol^{-1}. As they are more negative, the temperature effect is there. As the temperature increases, the $\Delta G^o a$ values for 30^{o}C and 105^{o}C decreases to more negative of -37333 and -34953 kJ mol^{-1}. It shows that the inhibitors are more efficient which suggests that the inhibitor is strongly adsorbed on the metal surface (J.D.Talati *et al.*1988*)*. The $\Delta H^o a$ values are positive of 58160 and 57495 kJ mol^{-1} at 30^{o}C and 105^{o}C respectively, which indicate the endothermic nature of the reaction suggesting that higher temperature favors the corrosion process (D.Agarwal, *et al.* 2003). The $\Delta S^o a$ values are also positive of 58283 and 57586 kJ mol^{-1} at 30^{o}C and 105^{o}C respectively, which confirm that the corrosion process is entropically favorable (R.M.Issa*et al.2002*).

3.8 Scanning Electron Microscopic Studies

Figure.5 shows the surface morphology of the specimens immersed in 15% HCl with and without 6% of inhibitor for 6 hours at 30^{o}C and 105^{o}C. The microphotograph of Fig.5a represents the polished J55 oil and gas well tubular steel, which has smooth and homogenous. Figure.5b and 5c represent the specimens immersed in HCl at 30^{o}C and 105^{o}C. The entire surface is corroded with uniform attack, which corresponds to the maximum corrosion rate. Figure.5d and 5e represents the sample immersed in 6% inhibitor at 30^{o}C and 105^{o}C. From the figures, we can see that the surface of J55 steel is attacked negligibly. In the presence of inhibitors, the surface condition is better at 30^{o}C than at 105^{o}C. This shows the temperature effect of the inhibitor film stability on the metal surface.

CONCLUSIONS

The results of this research were promising and suggest that littered cigarette butts are point sources for prolonged heavy metal contamination. Furthermore, the apparent rapid release of multiple metals from littered cigarette butts increases the potential for acute harm to living biota. So recycling of cigarette butts will prevent the environmental pollutions and also reducing the corrosive problem occurring in the steel industryThe following conclusions can be drawn from the above investigations inhibitor extracted from discarded cigarette butts extract are very good inhibitor for J55 steel corrosion in 15% HCl at 30° C. They are not effective inhibitors for the similar system at 105° C. The highest inhibition efficiencies of 99% and 61% are obtained for 30°C and 105°C respectively at 6% concentration. It is mixed type of inhibitors, which obey Temkin's adsorption isotherm at both the temperatures.The SEM studies confirm the results obtained through weight loss, polarization and impedance techniques while seeing the morphology of the J55 steel surface.

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Table 1: LC/MS Results of the Cigarette Butt Water Extracts

Rt(mint)	Mol.Wt	Name	Peak Area Percent
1.06	177.2	N-nitroso-nornicotine	0.32%
1.15	162.2	Nicotine	1.43%
1.29	176.2	Cotinine	0.11%
1.71	164.2	2,2dimethyl-2,3-dihydrobenzofuran-7-ol	0.07%
2.13	270.1	5-(4,6-dichloropyridin-3 yl)pyridine-1(2H)-carboxiamide	0.02%
3.23	271.1	6-(2,6-dicholorophenoxy)pyrimidine-2,4-diamine	0.04%
4.043	610.5	Rutin	0.01%

Table 2: Chemical composition of J55 tubular steel

Material	c	Mn	si	p	s	Fe
J55steel	0.33	1.45	0.25	0.04	0.06	97.8

Table3: Mass loss parameters of J55steel in 15% commercial HCl with and without various concentrations of Inhibitors at 30^{o}C and 105^{o}C

S.No	I.C (%)	Weight loss(mg)		Corrosion rate(mmpy)		Inhibitor efficiency	
		30°C	105°C	30°C	105°C	30°C	105°C
1	BLANK	1434	3672	165	427	-	-
2	2%	195	1762	22	204	86	52
3	4%	127	-	15	-	91	-
4	6%	13	1432	1.5	166	99	61
5	8%	10	-	1.2	-	99	-
6	10%	8	1173	1	136	99	68

Table4: Polarization parameters of J55 steel in 15% commercial HCl with and without various concentrations of Inhibitors at 30^{o}C and 105^{o}C

S.No	I.C (%)	E_{corr} (mV vs.SCE)		b_a (mV/decade)		b_c (mV / decade)		I_{corr} (μA / cm^2)		Inhibitor efficiencies (%)	
		30°C	105°C	30°C	105°C	30°C	105°C	30°C	105°C	30°C	105°C
1	Blank	-466	-456	97	205	111	221	771	135000	-	-
2	2%	-444	-483	87	110	165	248	382	60900	50	55
3	4%	-456	-	122	-	160	-	250	-	68	-
4	6%	-461	-437	115	146	148	257	200	56300	74	58
5	8%	-459	-	111	-	172	-	164	-	79	-
6	10%	-467	-468	101	176	154	178	130	47600	83	`65

Table5: Impedance parameters of J55 steel in 15% commercial HCl with and without various concentrations of Inhibitors at 30^{o}C

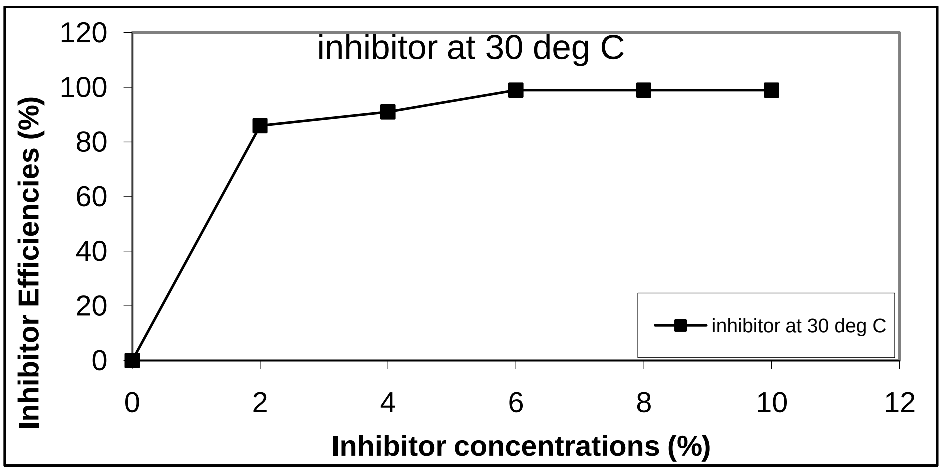
S.No	I.C (%)	R_{ct} (Ω cm^2)	C_{dl}(μFcm^{-2})	I.E (%)
1	Blank	32	265	-
2	2%	76	111	58
3	4%	79	109	59
4	6%	115	74	72
5	8%	173	49	81
6	10%	274	31	88

Table 6: Effect of temperatures on various thermodynamic parameters

S.No.	Inhibitor name	E_a (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})	ΔG_a^o (kJ mol^{-1})		ΔH_a^o (kJ mol^{-1})		ΔS_a^o (kJ mol^{-1})	
				30°C	105°C	30°C	105°C	30°C	105°C
1	Blank	11380	-	-	-	8863	8195	-	-
2	Inhibitor	60677	-46334	-37331	-34951	58160	57494	58283	57584

Captions for Figures

Figure – 1: Variation of inhibitor efficiencies as a function of InhibitorConcentrations at 30°C and 105°C
Figure – 2a: Polarization curves of J55 steel in 15% commercial HCl Without various concentrations of Inhibitors at 30°C and 105°C.
Figure – 2b: Polarization curves of J55 steel in 15% commercial HCl with Various concentrations of Inhibitors at 30°C and 105°C.
Figure – 3:Impedance curves of J55 steel in 15% commercial HCl with and Without various concentrations of Inhibitors at 30°C.
Figure – 4: Tem kin's adsorption isotherm plot for inhibitors at 30°C and 105°C.
Figure – 5:SEM photographs of J55 steel in 15% commercial HCl with and without 10% inhibitors at 30°C and 105°C.



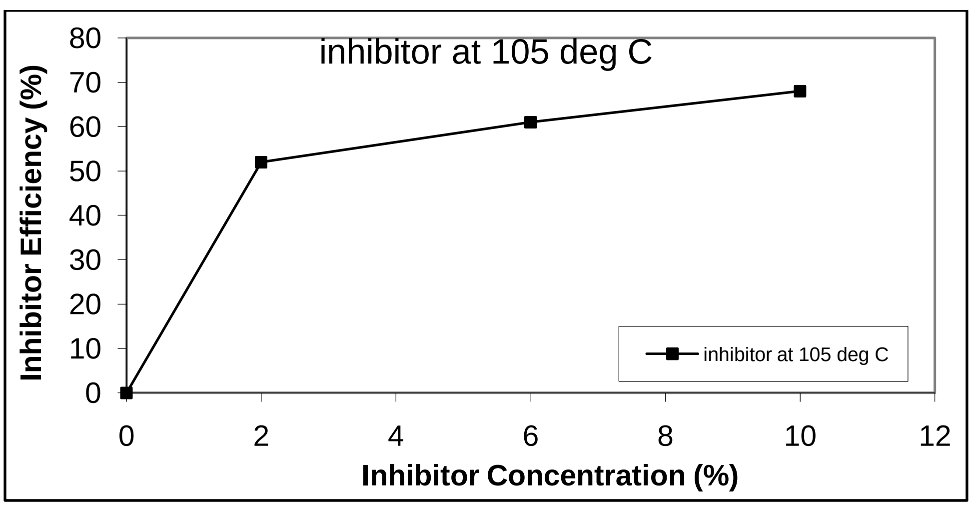


Fig. 1: Variation of inhibitor efficiencies as function of inhibitor concentrations at 30°C and 105°C

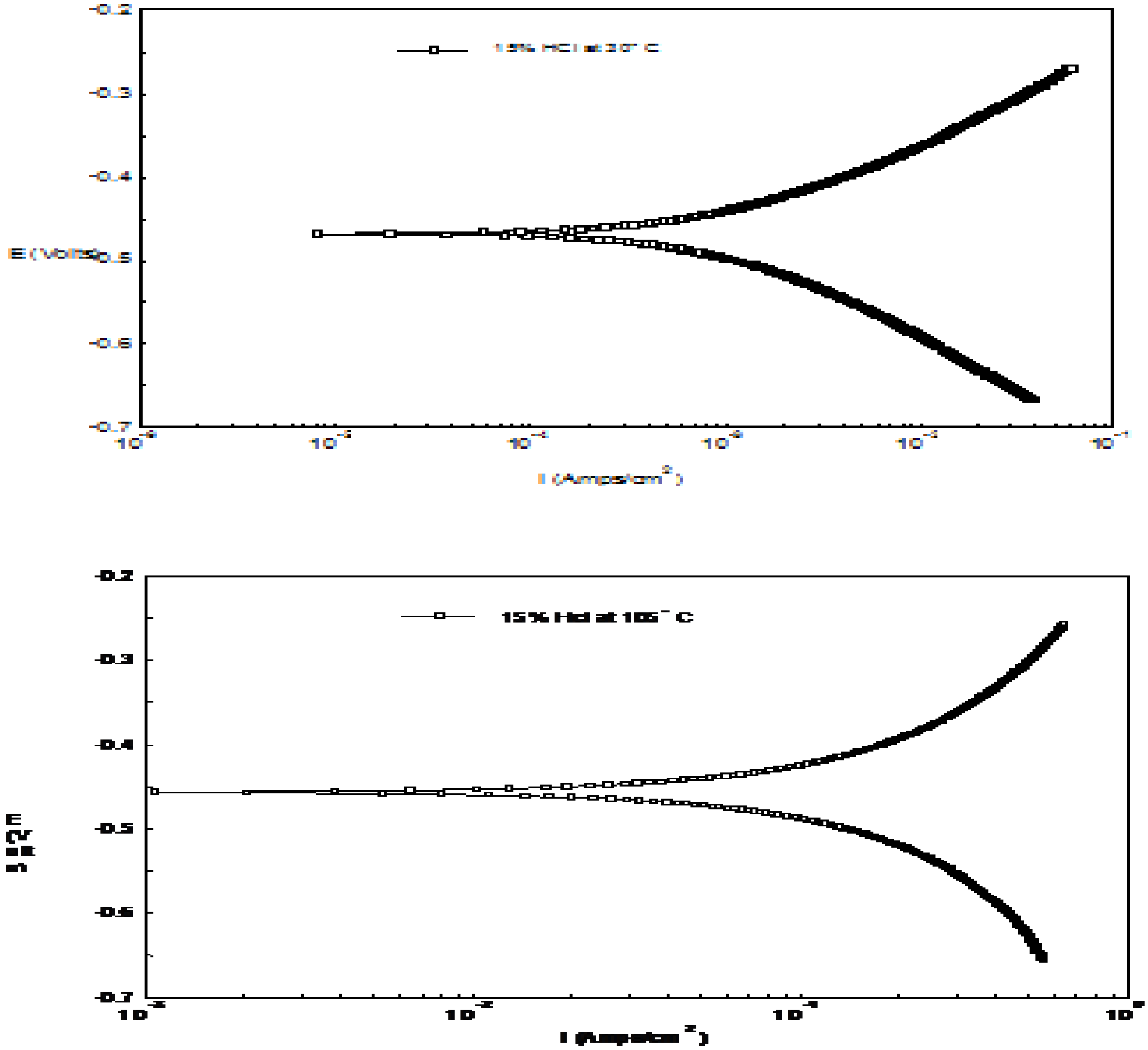
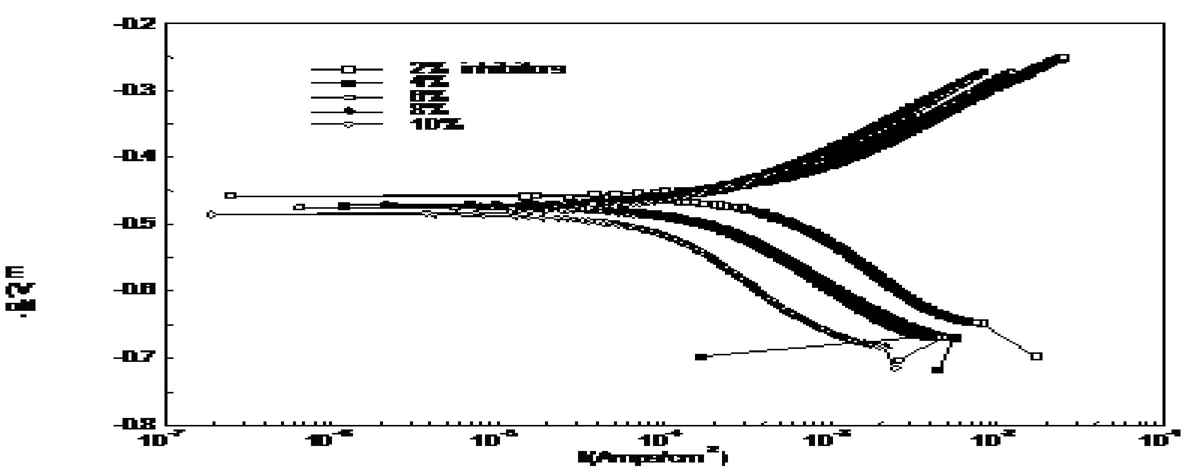


Fig.2a: Polarization curves of j55 steel in 15% commercial HCl without inhibitors at 30^{0}C and 105^{0}C



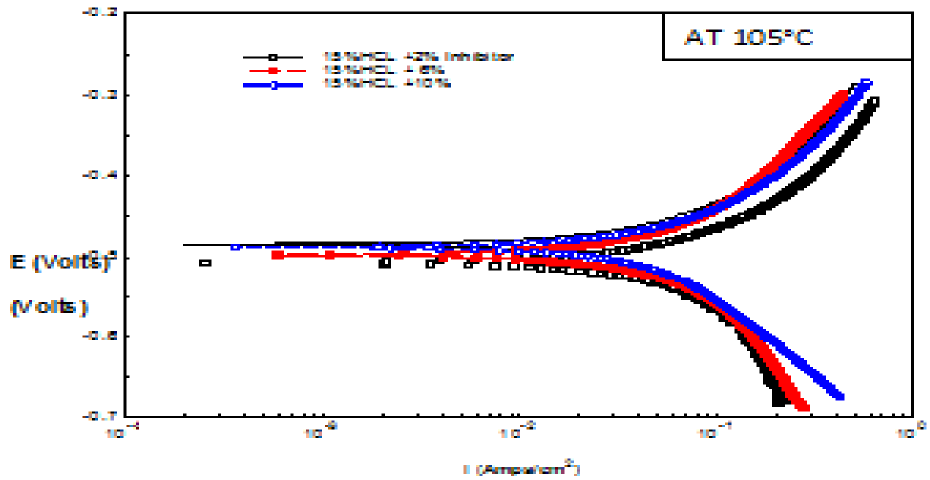


Fig. 2b: Polarization curves of J55 steel in 15% commercial HCl with various concentrations of inhibitors at 30^{0}C and 105^{0}C.

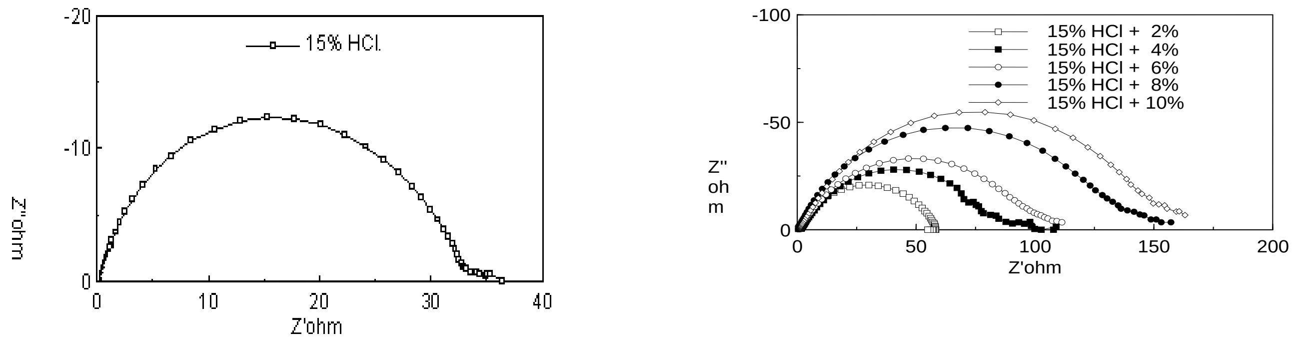


Fig.3: Impedance Curves of J55 steel in 15% commercial HCl with and without various concentrations of Inhibitors at 30^O C.

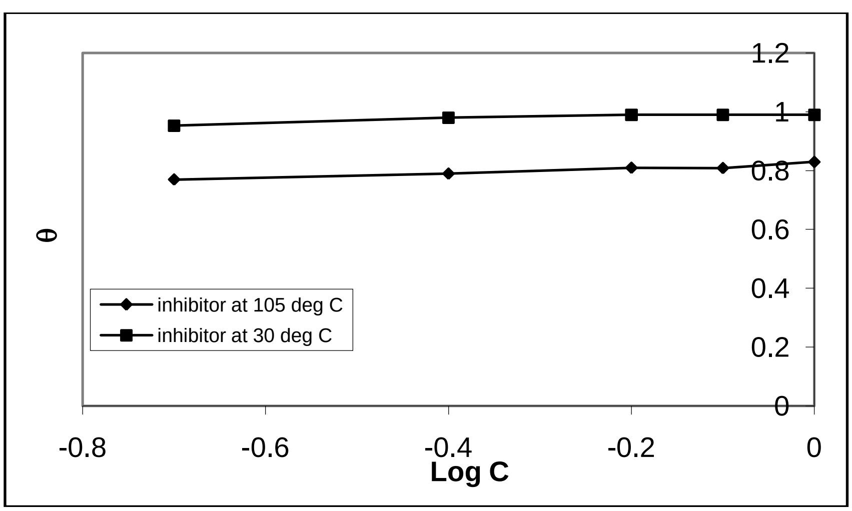
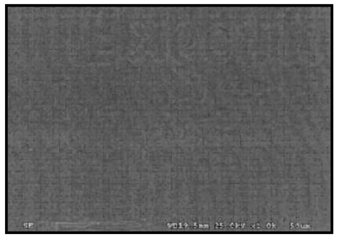
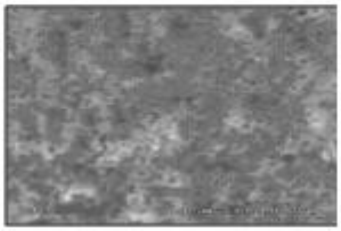
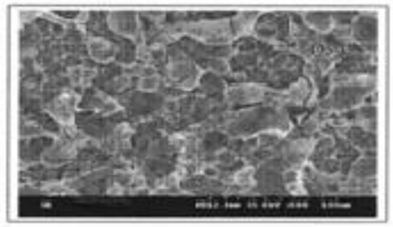


Fig. 4 – Tem kin's adsorption isotherm plot for inhibitor on J55 Oil well tubular steel



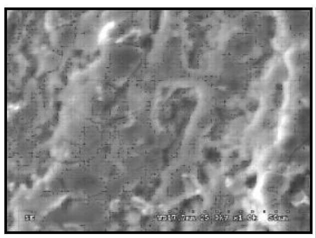
(a) Polished J55 steel (PJS)

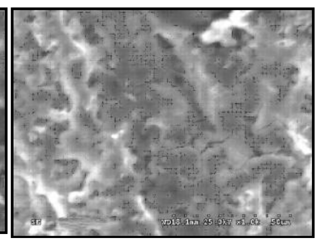




(b) PJS in 15% HCl at 30°C

(c) PJS in 15% HCl at 105°C





(d) PJS in 15% HCl with 6% Inhibitor at 30°C

e) PJS in 15% HCl with 6% Inhibitor at 105°c

Fig. 5(a to e): SEM Photographs of J55 Steel in 15% commercial HCl with and without 6% Inhibitors at 30°C and 105°C