

The Use of Conducting Polyaniline as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid

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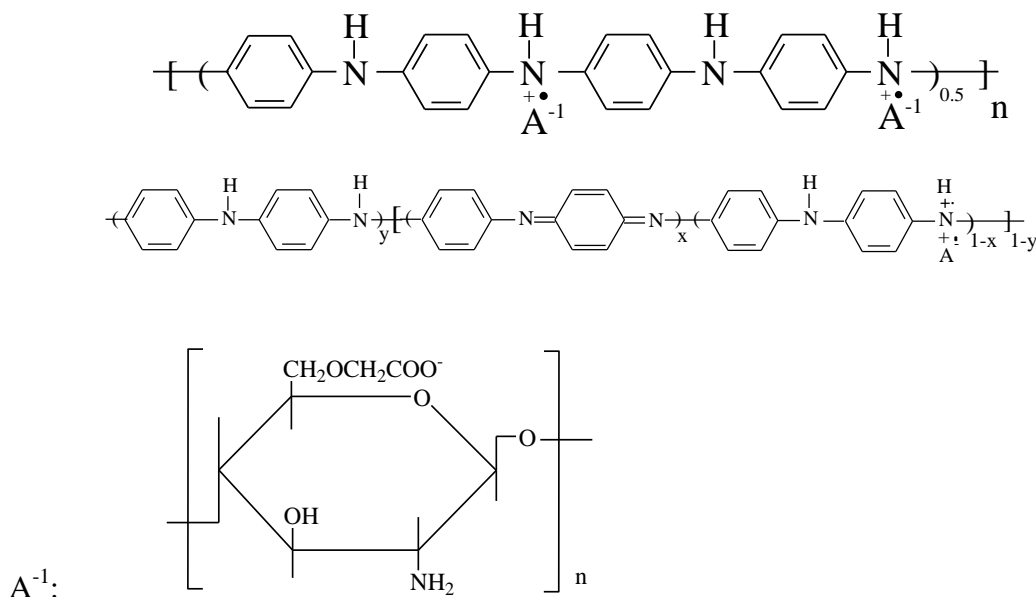
Sulfonated chitosan (S-CTS) doped polyaniline (PANI) was synthesized by “template-free” method successfully, and it is reported as corrosion inhibitor for the first time. The corrosion inhibition property of PANI was demonstrated for mild steel in acidic environment using weight loss test, Tafel polarization, electrochemical impedance spectroscopy (EIS), scanning electronic microscope (SEM) and adsorption isotherm. The results revealed S-CTS doped PANI had excellent corrosion inhibition for mild steel in 0.5 M hydrochloric acid media and its inhibitive efficiency was more than 92.3% even with a low concentration of 40 mg/L.

Keywords: Polyaniline, Mild Steel, electrochemical impedance spectroscopy, scanning electronic microscope, Quantum chemistry

1. INTRODUCTION

Acids are widely used in industries such as pickling, cleaning, descaling etc. Because of their aggressiveness, inhibitors are applied to reduce the rate of unexpected metal dissolution [1, 2]. Organic compounds rich in heteroatoms such as nitrogen and oxygen, the unsaturated bonds, and the plane conjugated systems including all kinds of aromatic cycles have been reported as effective inhibitors [3, 4]. In the past few years, conducting polymers have been recognized as excellent corrosion inhibitors for metals in acid environment [5, 6]. A small quantity of polymer may be effective in inhibiting the corrosion of metals in acidic medium. Polyaniline (PANI) has been hot topic of intensive research due to its high environmental stability [7-10]. However, the highly insoluble nature of PANI in aqueous medium is the major limitation in corrosion inhibition application. Recently, several attempts have been made to use the soluble PANI for corrosion inhibition [11, 12].

In present work, PANI was prepared by “template-free” method, and sulfonated chitosan (S-CTS) was chosen as doping acid in order to enhance the solubility of PANI. The inhibiting performance of PANI was evaluated by weight loss test, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electronic microscope (SEM). The molecular structure of doped PANI shown as follows:



2. EXPERIMENTAL

2.1. Synthesis of S-CTS doped PANI

S-CTS doped PANI was prepared by “template-free” method [13] using ammonium peroxydisulphate (APS) as an oxidant. Typical preparation process is as follows: 0.2ml aniline and a quantity of S-CTS were dissolved in 10 ml deionized water to form uniform solution under magnetic stirring in the ice-bath (0~5°C) for 30 minutes. APS aqueous (0.50g/5ml) solution was added slowly in the above solution with constant stirring. After complete addition, the solution was kept stirring for 1 h and then was on standing for 16 h to produce dark-green powder. The resulted PANI precipitate was washed with water, ethanol and ether for several times respectively. Three different molar ratios of S-CTS to aniline represented by [S-CTS]/[An] ratios of 0.01:1, 0.1:1, and 1:1 were used to searching for the optimal formation conditions to prepare the water soluble PANI. PANI showed a solubility of 80 mg/l in 0.5 M HCl and kept soluble for days was selected for corrosion studies.

Infrared spectra (see Fig. 1) in the range 400-4000 cm^{-1} on the PANI sample made with KBr were measured by means of an infrared spectrophotometer (Bruker Tensor 27). In the Infrared spectra, all characteristic bands of the emeraldine salt of PANI, for example, the C=C stretching vibration of quinoid and benzenoid rings at 1580 and 1501 cm^{-1} , the C-N stretching mode at 1246 cm^{-1} , the N=Q=N absorption peaks (Q representing the quinoid ring) at 1148 cm^{-1} and the N-H stretching

vibration at 3440 cm^{-1} [13,14], are observed for S-CTS doped PANI, indicating that the PANI is identical to the emeraldine salt form.

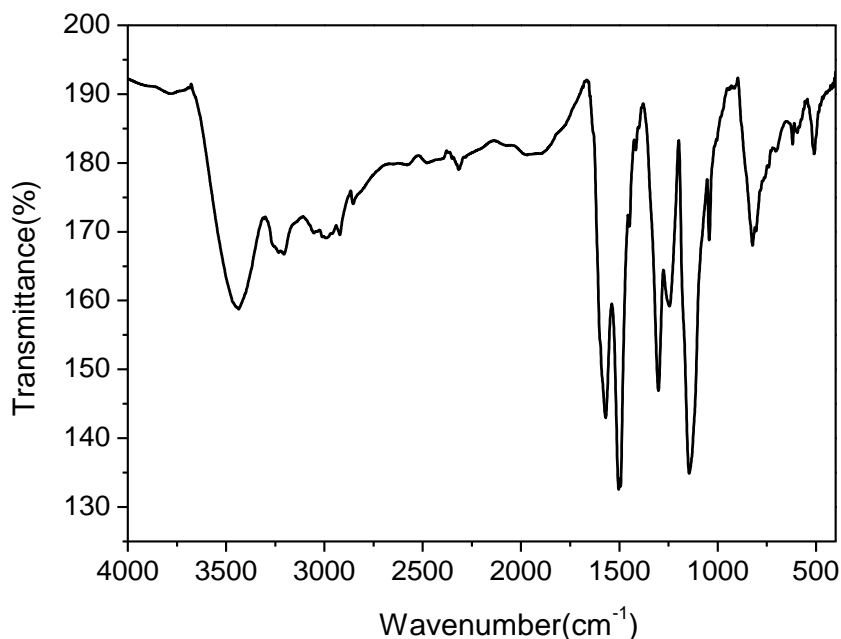


Figure 1. Infrared spectra of the S-CTS doped PANI. APS/An = 1:1; adding time = 1h

2.2 Experiment materials

PANI was dissolved in 0.5 M HCl solution at various concentrations (from 5.4 to 40mg/L). The inhibitive efficiency of S-CTS with different concentrations (from 50 to 1000mg/L) was tested for comparison.

The composition (wt.%) of mild steel was: C, 0.17; P, 0.0047; S, 0.017; Mn, 0.46; Si, 0.26; Cu, 0.019. Specimens were cut into $5\text{ cm} \times 2.5\text{ cm} \times 0.5\text{ cm}$ (weight loss test) and $1.0\text{ cm} \times 1.0\text{ cm} \times 1.0\text{ cm}$ (electrochemical experiment) dimensions, polished with SiC abrasive papers to 1200 grade, rinsed with deionized water, degreased ultrasonically in ethanol and acetone, and then dried at room temperature.

2.3 Weight loss test

Mild steel specimens in triplicate for each inhibitor concentration were immersed in 1M HCl solutions for 3 h at 25°C . The inhibitive efficiency (IE) was obtained by:

$$IE = \frac{(W_0 - W)}{W_0} \times 100\% \quad (1)$$

where W_0 and W are the weight loss values in the absence and presence of the inhibitor.

2.4. Electrochemical measurements

Electrochemical tests were performed in a conventional three-electrode cell assembled with mild steel working electrode with a $2.0\text{cm} \times 1.0\text{ cm}$ platinum foil as counter electrode and a saturated calomel electrode (SCE) with a Luggin capillary as reference electrode. The measurements were performed with PARSTAT2273 Potentiostat/Galvanostat (Princeton Applied Research).

EIS measurements were carried out in the 100 kHz-10 mHz frequency range at steady open circuit potential (OCP) disturbed with amplitude of 10 mV ac sine wave. The polarization curves were obtained from -200 to $+200\text{mV}$ versus OCP with scan rate of 0.5 mV/s . The inhibitive efficiency was calculated by Eqs. (2) and (3) [15, 16].

$$IE_{(i)} = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100\% \quad (2)$$

$$IE_{(R)} = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100\% \quad (3)$$

I_{corr}^0 and I_{corr} signify the corrosion current density in the absence and presence of inhibitors; R_{ct} and R_{ct}^0 are charge transfer resistance in the presence and absence of the inhibitors.

2.5 SEM analysis

After immersing in 0.5 M HCl in the absence and presence of 40mg/L PANI , the surface morphology of specimens was performed on a KYKY2800B scanning electronic microscope

3. RESULTS AND DISCUSSION

3.1. Inhibition by S-CTS

The inhibitive efficiency of S-CTS obtained from weight loss test and electrochemical experiment was summarized in Tab.1. In the weight loss test even at the highest concentration of 1000mg/L , S-CTS can only provide 65.0% inhibitive efficiency.

The Tafel polarization behaviour of mild steel in 0.5 M HCl with the addition of various concentrations of S-CTS was shown in Fig.2. I_{corr} was calculated from the intersection of the anodic and cathodic Tafel lines of the polarization curves at E_{corr} [17]. In Tab.1 it was clear that I_{corr} values decreased with increasing S-CTS concentration. At the highest concentration of 1000mg/L , the inhibitive efficiency of S-CTS was 77.1% .

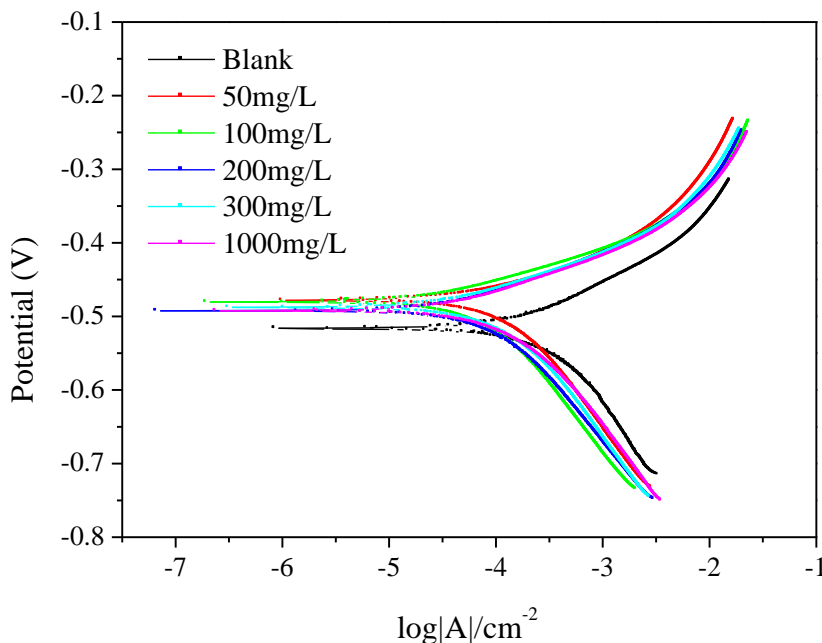


Figure 2. Potentiodynamic polarization behaviour of mild steel in 0.5 M HCl with the absence and presence of various concentrations of S-CTS

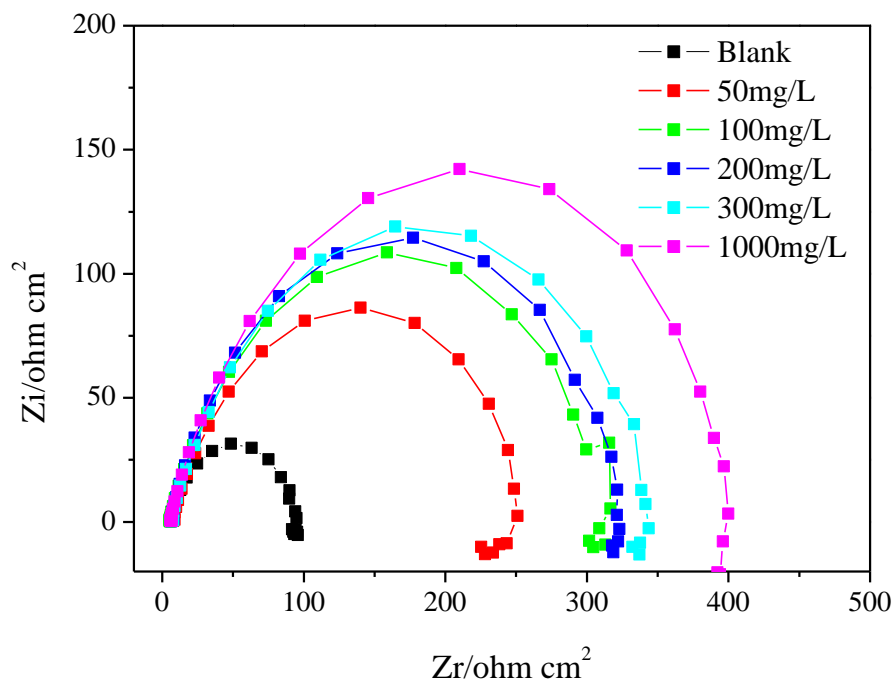


Figure 3. Nyquist plots of mild steel in 0.5 M HCl with different concentrations of S-CTS

Nyquist plots of mild steel in 0.5 M HCl with different concentrations of S-CTS were given in Fig.3. Double layer capacitance (C_{dl}) and R_{ct} in the Nyquist plots were obtained from impedance as described elsewhere [18, 19]. Optimal inhibitive efficiency obtained from this method was 71.9% at the highest concentration of S-CTS.

The results revealed that inhibitive efficiency of S-CTS was about 70% and it had no obvious change when its concentration differs from 50 to 1000mg/L.

3.2 Inhibition by S-CTS doped PANI

The results of weight loss test of S-CTS doped PANI in 0.5 M HCl were shown in Tab.2. It was observed that inhibitive efficiency increased with increasing the PANI concentration. At the highest concentration of 40mg/L, PANI had the highest inhibitive efficiency (85.6%). As mentioned above, even a small quality of PANI can greatly inhibit mild steel corrosion in HCl solution.

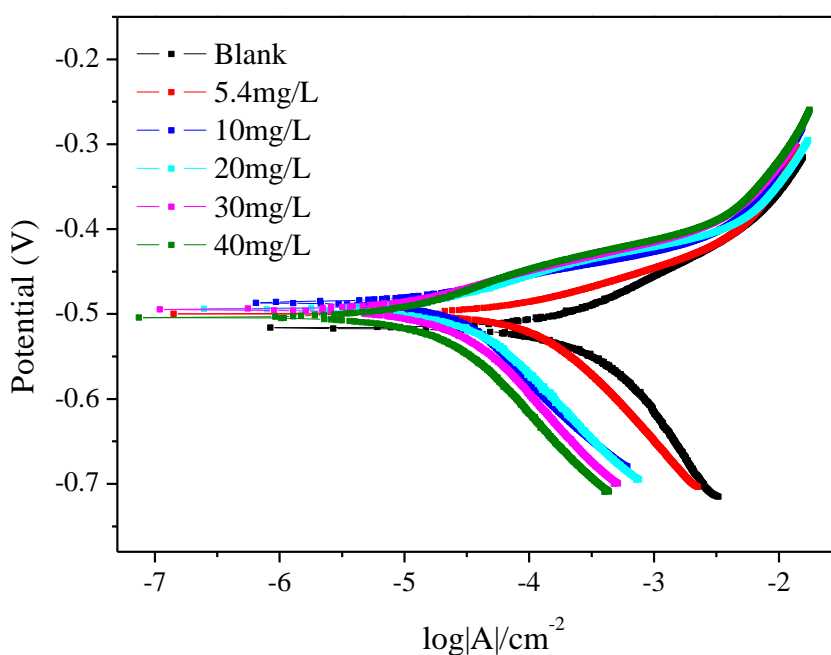


Figure 4. Potentiodynamic polarization behaviour of mild steel in 0.5 M HCl with the absence and presence of PANI

The parallel anodic and cathodic Tafel curves in Fig.4 suggested that the corrosion mechanism had not changed and the inhibitor acted by simple blocking the steel surface. There was no definite trend in the shift of E_{corr} values which can be recognized as a classification evidence of the compounds whether it is mixed-type inhibitors [20]. PANI acted as an excellent acid inhibitor with 91.6% inhibitive efficiency at the highest concentration of 40 mg/L, which is far good than S-CTS monomer even at the concentration of 1000 mg/L with inhibitive efficiency of 77.1% as shown in Tab.1.

Nyquist plots of mild steel in 0.5 M HCl solution in various concentrations of PANI were given in Fig.5. The R_{ct} values increased while C_{dl} values decreased with the increase in PANI concentration suggesting an in local dielectric constant between the metal and electrolyte induced by the adsorption.

Table 1. Weight loss data, polarization parameters and impedance parameters for mild steel in 0.5 M HCl with different concentrations of S-CTS

		C (mg/L)					
		0	50	100	200	300	1000
Weight loss data	Weight loss/(mg cmh ⁻¹)	0.987	0.455	0.388	0.390	0.383	0.345
	IE (%)	--	53.9	60.7	60.5	61.2	65.0
Polarization parameters	E _{corr} (mV)	-514.1	-447.3	-489.3	-	-489.3	474.6
	I _{corr} (μA cm ⁻²)	222.8	74.8	65.7	65.9	59.7	51.1
	β _c (mV dec ⁻¹)	122.8	115.0	103.7	128.7	106.4	138.1
	β _a (mV dec ⁻¹)	91.6	52.4	64.8	69.4	60.5	51.0
	IE(%)	--	66.4	70.5	70.4	73.2	77.1
Impedance parameters	R _{ct} (Ω cm ²)	89.2	256.4	315.1	318	346.9	405
	C _{dl} (10 ⁻⁵ F cm ⁻²)	22.57	20.07	18.42	18.56	14.41	14.22
	IE(%)	--	65.2	71.7	71.9	74.3	77.9

Table 2. Weight loss data, polarization parameters and impedance parameters for mild steel in 0.5 M HCl with different concentrations of S-CTS doped PANI

		C (mg/L)					
		0	5.4	10	20	30	40
Weight loss data	Weight loss/(mg cmh ⁻¹)	0.987	0.456	0.247	0.210	0.156	0.142
	IE (%)	--	53.7	75.0	78.7	84.2	85.6
	θ		0.537	0.750	0.787	0.842	0.856
Polarization parameters	E _{corr} (mV)	-514.1	-499.7	-483.2	-485.4	-490.9	-490.4
	I _{corr} (μA cm ⁻²)	222.8	99.8	26.9	23.3	19.5	18.5
	β _c (mV dec ⁻¹)	122.8	114.8	151.8	144.7	139.9	158.5
	β _a (mV dec ⁻¹)	91.6	54.3	45.2	44.3	58.2	51.5
	IE(%)	--	55.2	87.9	89.6	91.3	91.6
Impedance parameters	R _{ct} (Ω cm ²)	89.2	176	550.9	764.2	926.8	1102
	C _{dl} (10 ⁻⁵ F cm ⁻²)	22.57	16.1	10.44	13.94	15.27	11.96
	IE(%)	--	51.6	84.5	88.8	90.8	92.3

R_{ct} values increased from 89.2 to 1102 Ω cm² while PANI concentration varied from 0 to 40mg/L and at the highest concentration the inhibitive efficiency reached 92.3%

3.3 Adsorption isotherm

To determine the adsorption mode of S-CTS doped PANI, various isotherms were tested and the Langmuir mode ($\theta/(1-\theta) = k_{ads} \cdot C$) should be the best (Fig.6) for the slope of the plot of C/θ versus C is very close to 1 and the linear regression coefficients (R²) is almost equal to 1 (0.998). Here

surface coverage values (θ) for the inhibitor were obtained from the weight loss test for various concentrations at 298 K respectively.

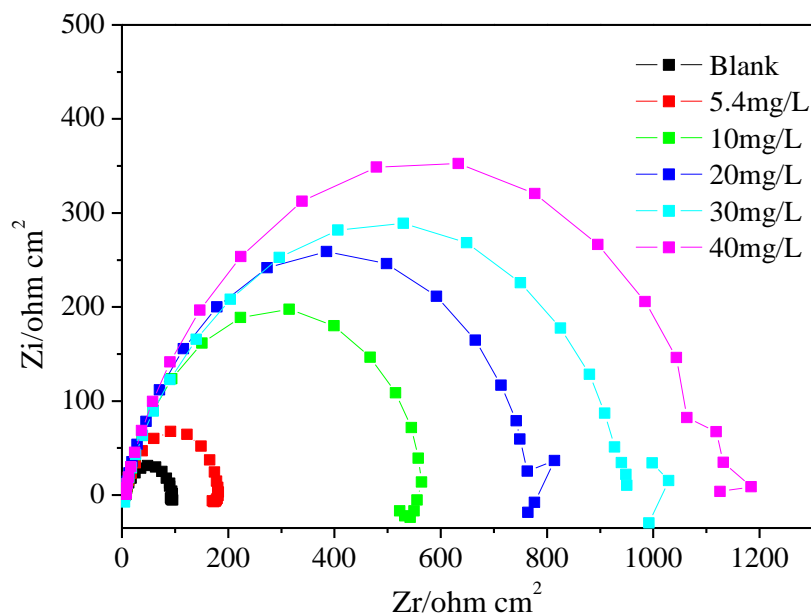


Figure 5. Nyquist plots of mild steel in 0.5 M HCl with the absence and presence of PANI

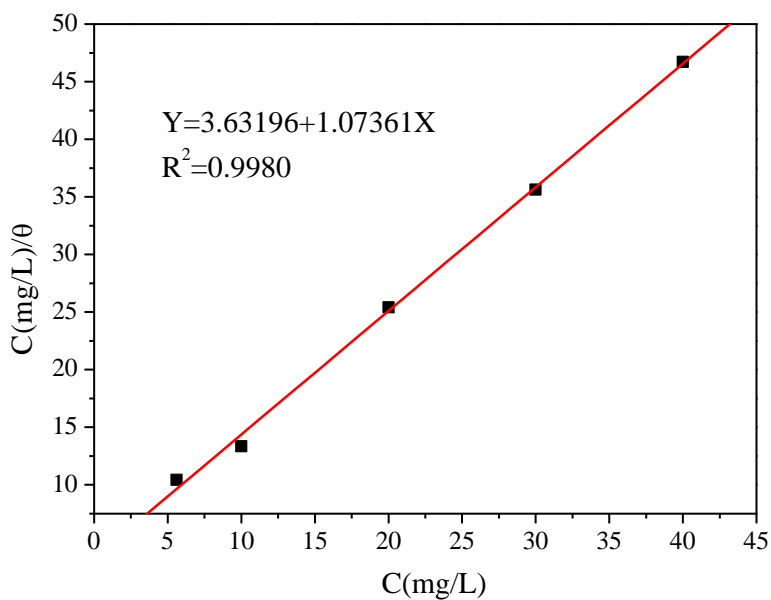


Figure 6. Langmuir isotherm adsorption model of PANI on the mild steel surface at 298K

$$\theta = \frac{W_0 - W}{W_0} \tag{4}$$

K_{ads} , which can be calculated from the intercept of the straight lines on the C/θ axis, is related to the standard free energy of adsorption (ΔG_{ads}) with the following equation [21]:

$$k_{ads} = (1/55.5)\exp(-\Delta G_{ads}^0 / RT) \quad (5)$$

Generally speaking, the adsorption type is regarded as physisorption if the absolute value of ΔG_{ads} is lower than 20 kJ/mol; but it is seen as chemisorption if the value is higher than 40 kJ/mol [22]. In this process, ΔG_{ads} of S-CTS doped PANI is -35.94 kJ/mol calculated by Eq.(5) meaning the adsorption would involve two types of interaction, chemisorption and physisorption. And the negative values of ΔG_{ads} revealed that the adsorption of PANI is a spontaneous process [23].

In acidic solutions, PANI exists as cations [24]. These protonated ions adsorb on the surface of the mild steel and decrease the process of corrosion. The higher inhibitive property of PANI is attributed to the presence of long p-electrons conjugation, quaternary nitrogen atom and the larger molecular size which insures greater coverage of the metallic surface.

3.4 Surface morphology: SEM studies

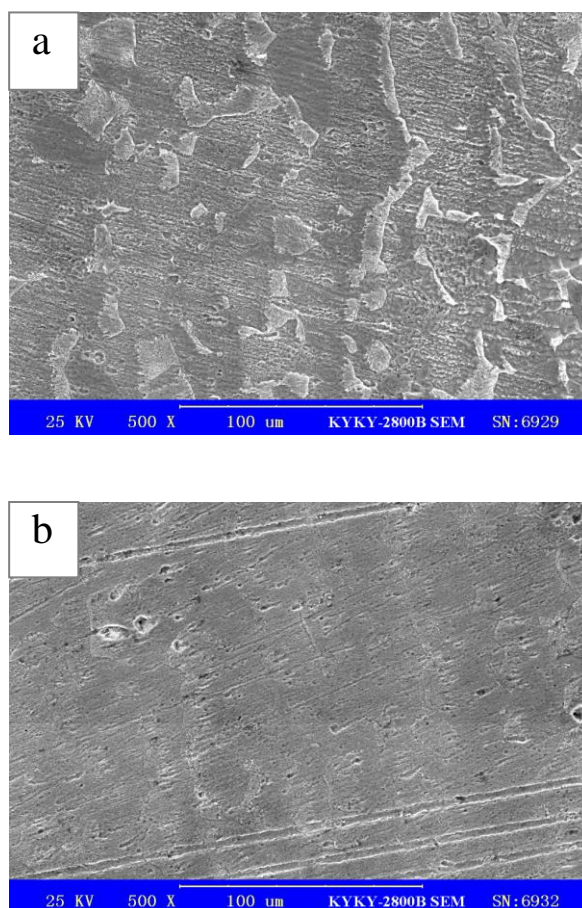


Figure 7. SEM images of mild steel specimens after immersion in 0.5 M HCl (a) with no inhibitor, (b) with 40mg/L PANI

Surface morphology was studied after mild steel specimens immersion in 0.5 M HCl solution for 3 h in the absence and presence of PANI (40mg/L), respectively. As Fig.7 shows, specimen surface was strongly damaged and produced flock of granules in the absence of the inhibitor. However, Fig.7 (b) shows an appreciable inhibiting ability to corrosion on mild steel surface. It is revealed that there is a good protective film adsorbed on specimen surface, which is responsible for the inhibition of corrosion.

4. CONCLUSIONS

1. S-CTS doped conducting polymer PANI was synthesized by “template-free” method. An optimum condition was established for synthesizing water soluble PANI for the corrosion inhibition studies as S-CTS/ aniline monomer was 2:1, adding APS oxidizing agent in 1hour with constant stirring.

2. The corrosion inhibition for mild steel was studied in 0.5 M HCl using weight loss test and electrochemical techniques. It was obtained that the inhibitive efficiency of PANI increased with increasing compound concentration. PANI showed 92.3% inhibitive efficiency at 40 mg/l which is much higher than S-CTS monomer with inhibitive efficiency of about 70% even at 1000mg/l concentration. The result revealed PANI was an efficient mix-type polymeric inhibitor which acted through adsorption mechanism.

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