

산성 조건에서 부드러운 강철용 부식억제제로 사용되는 플라보노이드계 화합물의 부식억제성질과 흡착성질

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Corrosion Inhibitive and Adsorption Properties of a Flavonoid compound for Mild Steel in Acidic Medium

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요 약. 플라보노이드계 화합물인 HMPC (3-hydroxy-7-methoxy-2-phenylchromen-4-one)의 부식억제성질, HMPC와 TBAB (n-tetrabutylammonium bromide) 간 상승효과, 염산 조건하 부드러운 강철의 흡착성질을 무게 감량, 변전위 편극, 전기화학 임피던스 분광기를 사용하여 연구하였다. 다양한 온도에서 무게 감량 측정 실험한 결과 부식 억제 효율은 억제제 농도가 증가함에 따라 증가하였고, 계의 온도가 증가함에 따라 감소하였다. 전기화학 실험 결과 부식 억제는 여러 혼합된 형태의 억제 방법에 의해 가능하였다. 금속 표면에 흡착된 억제 화합물 분자는 보호막을 형성하였다.

주제어: 상승 효과, 흡착 등온선, 변전위 편극, 전기화학 임피던스 분광기(EIS)

ABSTRACT. The corrosion inhibitive nature of a flavonoid compound, 3-Hydroxy-7-methoxy-2-phenylchromen-4-one (HMPC), the synergistic effect between HMPC and n-Tetrabutylammonium bromide (TBAB) and their adsorption behavior on mild steel in hydrochloric acid solution were studied by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. The results of weight loss study at different temperatures revealed that the inhibition efficiency increases with inhibitor concentration and decreases with increase in the temperature of the system. The electrochemical studies showed that the inhibitor acts through mixed mode of inhibition and the inhibitor molecules adsorb on the metal - solution interface forming a protective layer. The adsorption of the inhibitor molecules over the metal surface was supported by the obeyed Langmuir's adsorption isotherm, Scanning Electron Microscopic analysis (SEM) and Fourier Transform Infrared (FT-IR) spectroscopic studies.

Keywords: 3-Hydroxy-7-methoxy-2-phenylchromen-4-one, n-Tetrabutylammonium bromide, Synergistic effect, Adsorption isotherm, Potentiodynamic polarization, Electrochemical impedance spectroscopy (EIS)

INTRODUCTION

Acids are widely used in many industrial processes. The aggressive solutions used for acid pickling, cleaning and de-scaling are hydrochloric, sulphuric and phosphoric acids, due to their special chemical properties. There is a danger of metal dissolution upon the already cleaned metal surface during these processes after the removal of the oxides, scale, or other coatings. This involves the loss of dissolved metal as well as larger acid consumption. The corrosion inhibitors are added to prevent metal from corrosion in aggressive media. The heterocyclic compounds

which contain N, S and O atoms have been proved as effective corrosion inhibitors¹⁻⁴ for metals in acid media. The polar groups act as the reaction center for the adsorption process.⁵ The protection efficiency depends on adsorption ability of inhibitor molecules, where the resulting adsorption film acts as a barrier that separates the metal from the corroding medium.^{6,7} During corrosion, the inhibitor molecules will constitute a distinct phase between the metal and the aqueous solution, there by interacts with this inter phase.⁸ The efficiency of corrosion inhibitors depends on the mechanical, structural, and chemical properties of the layer formed.⁹

As many synthetic compounds are highly toxic to both human beings and environment, nowadays, attention has been focused on many alternative eco-friendly and harmless green corrosion inhibitors.

In the present work, the corrosion inhibition potential of a flavonoid compound, HMPC for mild steel in 1 M hydrochloric acid medium, was investigated through weight loss, electrochemical, FT-IR and SEM techniques. The study also includes the synergistic effect of TBAB on the performance of the inhibitor.

EXPERIMENTAL

Reagents

The mild steel specimen with chemical composition (wt.%): Si(0.002%), C(0.060%), Mn(0.308%), P(0.001%), S(0.009%) and Fe(99.62%) was used for the study.

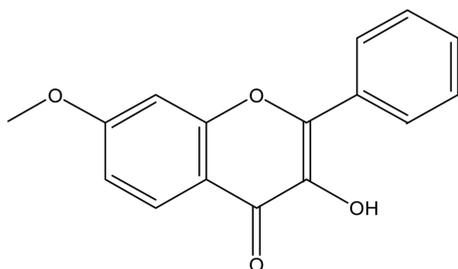
The aggressive medium was made from AnalaR Grade hydrochloric acid and conductivity water. The flavonoid compound HMPC (*Fig. 1*) was purchased from Research Organics, Chennai, India, and re-crystallized from methanol.

Recommended procedure

The mild steel specimens were mechanically polished with different grades of emery papers, degreased with acetone, rinsed with double-distilled water, and finally dried before immersion in the acid solution.

Weight loss method

The weight loss measurements were carried out¹⁰ with the solution volume of 100 ml. The polished and pre-weighed mild steel specimens of size 3 cm × 1 cm × 0.2 cm were immersed for 2 hours in both blank and inhibited solutions. The specimens were carefully washed at the end of these tests with acetone, dried, and then reweighed and the weight loss was calculated. The percentage inhibition efficiency (IE%) was calculated¹¹ using the follow-



3-HYDROXY-7-METHOXY FLAVONE

Fig. 1. 3-Hydroxy-7-methoxy-2-phenylchromen-4-one (HMPC).

ing equation.

$$IE(\%) = (W_0 - W_i) / W_0 \times 100$$

where W_0 and W_i are the weight losses in uninhibited and inhibited corroding solutions respectively. The degree of surface coverage (θ) can be determined by the expression, $\theta = IE(\%) / 100$. The corrosion rate in $g/cm^2/min$ was also calculated.

It has been reported that TBAB is adsorbable on steel.¹⁰ So, the effect of TBAB along with HMPC was tested. The weight loss study was carried out in triplicate to get reproducible results at three different temperatures (303K, 313K and 323K).

Electrochemical studies

The electrochemical experiments, including potentiodynamic polarization measurements and electrochemical impedance spectroscopy measurements were carried out using PRINCETON versaSTAT Potentiostat-Galvanostat. A conventional three-electrode cell configuration was used for the electrochemical studies. The working electrode was prepared from mild steel specimen mounted in epoxy resin in such a way that the area exposed to solution was 1 cm^2 . A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and counter electrodes, respectively and all potentials were reported versus SCE. The polarization measurements were recorded after 60 minutes immersion at room temperature at 300 $mV \pm OCP$ with a scan rate of 10 mVs^{-1} . The percentage inhibition efficiency (IE%) values were calculated from the I_{corr} values using the following equation.

$$IE(\%) = (I_{corr} - I'_{corr}) / I_{corr} \times 100$$

where I_{corr} and I'_{corr} are corrosion current densities without and with the inhibitor, respectively.

The electrochemical impedance spectroscopy measurements were performed over a frequency range between 1 Hz to 200 Hz at an amplitude of 10 mV and the impedance diagrams were given in Nyquist representations. In the represented electrical equivalent circuit (*Fig. 2*), R_s is the solution resistance, R_{ct} is the charge transfer resistance and C_{dl} is the double layer capacitance. The inhibition efficiency was calculated from the charge transfer resistance (R_{ct}) values^{12,13} using the following formula

$$IE(\%) = (R'_{ct} - R_{ct}) / R'_{ct} \times 100$$

where R_{ct} and R'_{ct} are charge transfer resistances without and with inhibitor, respectively.

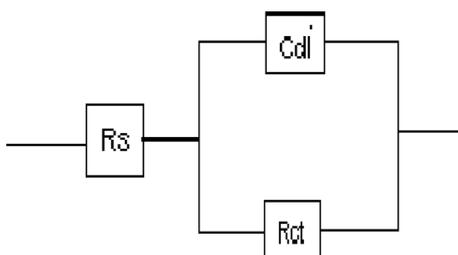


Fig. 2. The electrical equivalent circuit for the ac impedance measurement.

SEM analysis

The specimens used for surface morphological examination were immersed in the acid containing various concentrations of HMPC and blank for 2 hours. They were then removed, rinsed quickly with acetone, and dried. The analysis was performed on ZEISS model-Supra 40 SEM.

FT-IR analysis

The pure flavonoid compound and the scrapped corrosion products formed on the mild steel surface were analyzed separately with the help of FT-IR (Perkin-Elmer FT-IR spectrometer) spectra using the potassium bromide pellet method.

RESULTS AND DISCUSSION

Weight loss method

The corrosion rate and percentage inhibition efficiency values determined by weight loss method at three different temperatures were summarized in Table 1. It was noted from the results that the IE(%) increases with increase in concentration of the inhibitor. This may be due to the increased number of molecules adsorbed over the mild steel surface by blocking the active sites where direct acid attack proceeds. The inhibition efficiency was also found

Table 1. Effect of temperature on the inhibition efficiency of HMPC alone and in presence of TBAB on mild steel corrosion in 1 M HCl by weight loss method

Concentration of inhibitor × 10 ⁻⁵ M	IE(%)		
	303K	313K	323K
Blank	-	-	-
1	35.73	35.52	34.78
2	73.78	68.03	47.54
3	82.18	76.92	58.42
4	88.09	82.84	63.79
HMPC+TBAB	90.49	83.37	66.48

Table 2. Thermodynamic parameters for the inhibition of corrosion of mild steel in 1M HCl by HMPC alone and in presence of TBAB

Concentration of inhibitor × 10 ⁻⁵ M	E _a kJ mol ⁻¹	Q _{ads} kJ mol ⁻¹
Blank	-	-
1	0.20	-0.71
2	14.97	-22.04
3	19.44	-25.62
4	27.50	-33.65
HMPC+TBAB	42.21	-50.54

to decrease with rise in temperature. This gives a clue that the mechanism of adsorption of the inhibitor may be due to physisorption, because physisorption is due to weak Van der Waal’s forces which disappear at elevated temperatures. Thus the maximum inhibition efficiency is attained at higher concentration of the inhibitor and at lower temperature.

The values of activation energy (E_a) and heat of adsorption (Q_{ads}) are listed in Table 2. It is found that the value of E_a increases with increase in concentration of the inhibitor which indicates the low inhibition efficiency at elevated temperatures. From the Q_{ads} values it is observed that the inhibitor molecules on the mild steel surface are physically adsorbed.

Adsorption isotherm

The degree of surface coverage (θ) for different concentrations of the inhibitor was evaluated by assuming the corrosion inhibition due to the adsorption of the inhibitor (Table 3). The surface coverage increases with increase in concentration of the inhibitor thereby increasing the percentage of inhibition efficiency. The establishment of adsorption isotherms describes the adsorptive behavior of inhibitor molecules which can provide important clues to the nature of the metal inhibitor interaction.

The adsorption of the organic molecule occurs as the

Table 3. Effect of HMPC alone and along with TBAB on rate of corrosion and surface coverage for mild steel in 1 M HCl at 303 K

Concentration of inhibitor × 10 ⁻⁵ M	Rate of corrosion g/cm ² /min	IE(%)	Surface coverage (θ)
Blank	11.67	-	-
1	7.50	35.73	0.3573
2	3.06	73.78	0.7378
3	2.08	82.18	0.8218
4	1.39	88.09	0.8809
HMPC+TBAB	1.11	90.49	0.9049

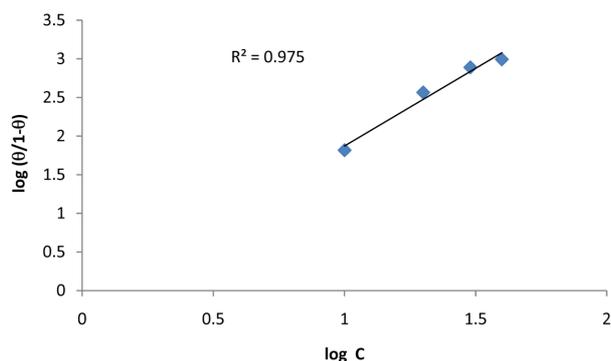


Fig. 3. Langmuir adsorption isotherm for HMPC.

interaction energy between molecule and the metal surface is higher than that between the water molecules and the metal surface.¹⁴ In order to find out the nature of the adsorption isotherm, attempts were made to fit various isotherms like Frumkin, Langmuir and Temkin. However, the best fit was obtained only with the Langmuir adsorption isotherm (Fig. 3), supporting the monolayer adsorption of the inhibitor on the mild steel surface.

Synergistic effect

When equal volumes of TBAB and HMPC of same concentration were taken together, there has been an enhancement in the inhibition efficiency of HMPC. It may be due to the synergistic effect of TBAB. The hydrocarbon part of TBAB may form a closed network structure, which prevents the approach of the aggressive ions to the metal surface.

Electrochemical studies

The polarization behaviour of steel in 1 M hydrochloric acid in presence and absence of inhibitor is shown in

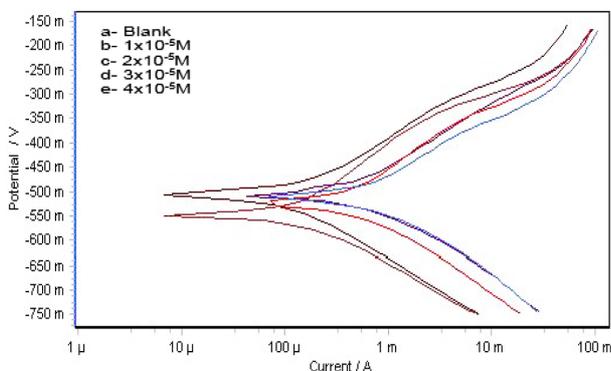


Fig. 4. Potentiodynamic polarization curves for the corrosion of mild steel in 1 M HCl in the absence and presence of HMPC at various concentrations at 303 K.

Table 4. Potentiodynamic polarization parameters for the corrosion of mild steel in the absence and presence of HMPC alone and along with TBAB in 1 M HCl

Concentration of inhibitor $\times 10^{-5}$ M	E_{corr} mV	I_{corr} $\mu\text{A}/\text{cm}^2$	IE(%)
Blank	-512	4718	-
1	-488	2850	39.60
2	-492	1009	78.61
3	-510	538	88.58
4	-508	434	90.79
HMPC+TBAB	-481	316	93.30

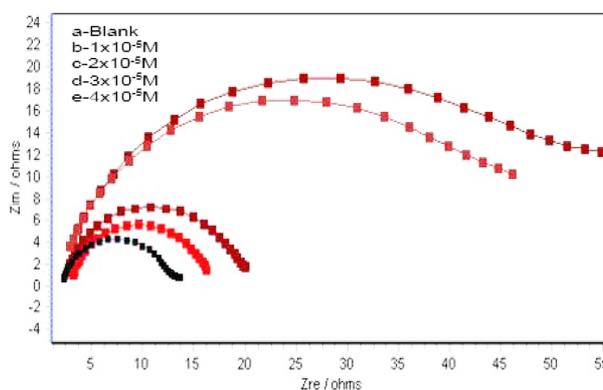


Fig. 5. Nyquist plots for mild steel in 1 M HCl in the absence and presence of HMPC at various concentrations at 303 K.

Fig. 4. The values of corrosion current (I_{corr}), corrosion potential (E_{corr}) and the percentage inhibition efficiency are depicted in Table 4. The decrease in I_{corr} values is more pronounced with the increase in the inhibitor concentration. The addition of inhibitor shifts the E_{corr} values and thus alters both anodic and cathodic Tafel slope values indicating the mixed mode of action of inhibitor.¹⁵

The corrosion behavior of steel at 303K in the acidic solution in the absence and presence of green inhibitor is also investigated by the EIS method after 60 minutes of immersion. The R_{ct} values were calculated from the difference in impedance at lower and higher frequencies from Nyquist plot (Fig. 5) and from R_{ct} values, C_{dl} values were computed by using the following equation.

$$C_{\text{dl}} = 1 / 2\pi f_{\text{max}} R_{\text{ct}}$$

where f_{max} is the frequency at which the imaginary component of the impedance ($-Z_{\text{max}}$) is maximal. The impedance parameters derived from these investigations are given in Table 5. It is worth noting that the presence of the inhibitor does not alter the profile of impedance diagrams which are almost semi-circular in shape indicating that the

Table 5. Electrochemical Impedance measurements for the corrosion of mild steel in the absence and presence of HMPC alone and along with TBAB in 1 M HCl

Concentration of inhibitor $\times 10^{-5}$ M	R_{ct} Ωcm^2	$C_{dl} \times 10^{-4}$ F/cm ²	IE(%)
Blank	10.62	3.766	-
1	17.14	0.074	38.04
2	37.34	0.021	71.56
3	52.33	0.019	79.71
4	75.42	0.017	85.92
HMPC+TBAB	89.70	0.014	88.16

corrosion of steel is mainly controlled by the charge transfer process.

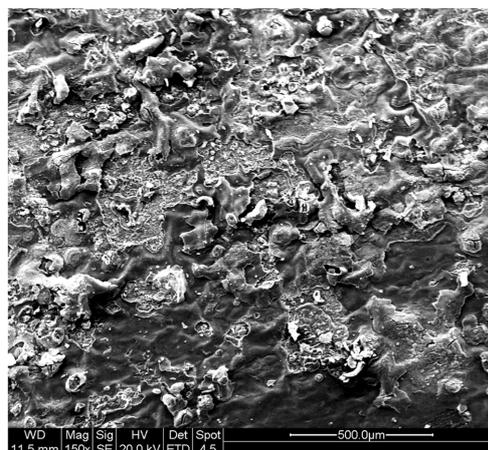
The deviations from the perfect semicircular shape are often referred to as the frequency dispersion of interfacial impedance. This anomalous phenomenon is interpreted by the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena.¹⁶ In fact, the presence of HMPC enhances the values of R_{ct} in the acidic solution. The values of the double layer capacitance have been decreased to the maximum extent in the presence of inhibitor revealing the adsorption of the inhibitor on the metal surface in the acidic solution.

SEM analysis

The SEM images of the surface of mild steel before and after immersion in 1M hydrochloric acid solution, for 2 hours in the absence and presence of inhibitor are shown in Figs. 6(a) and 6(b), respectively. The Fig. 6(a) reveals that the surface is highly damaged in the absence of inhibitor. The surface morphological features of the mild steel specimen in the presence of inhibitor under identical condition are shown in Fig. 6(b). It can be seen from this micrograph that the inhibitor exhibits substantially higher protective effect on mild steel surface in 1 M hydrochloric acid medium.

FT-IR analysis

The FT-IR spectra taken for the characterization of both pure HMPC and the corrosion product have been displayed in Fig. 7(a) and 7(b) respectively. The spectrum 7(a) shows all the characteristic bands corresponding to the functional groups present in the inhibitor and spectrum 7(b) shows the characteristic bands of scrapped sample deposited over the mild steel surface in 1 M hydrochloric acid. The spectrum 7(b) is almost identical with the spectrum 7(a) which proves the absence of coordination bond



(a)



(b)

Fig. 6. (a) SEM image of mild steel sample kept in 1 M HCl for 2 h at 303 K, (b) SEM image of mild steel sample kept in 1 M HCl along with HMPC for 2 h at 303 K.

with the metal surface through the above said heterocyclic centers of the inhibitor.

CONCLUSION

The flavonoid compound 3-Hydroxy-7-methoxy-2-phenylchromen-4-one acts as a good inhibitor for the corrosion of mild steel in 1 M hydrochloric acid at room temperature and found to follow the Langmuir adsorption isotherm. It is evident from the polarization studies that HMPC acts as a mixed type inhibitor. The electrochemical impedance measurements also clearly revealed the inhibitive action of HMPC. The SEM analysis provided supporting evidence for the adsorption of this flavonoid compound over the mild steel surface. The FT-IR analysis of the corrosion product also revealed the same.

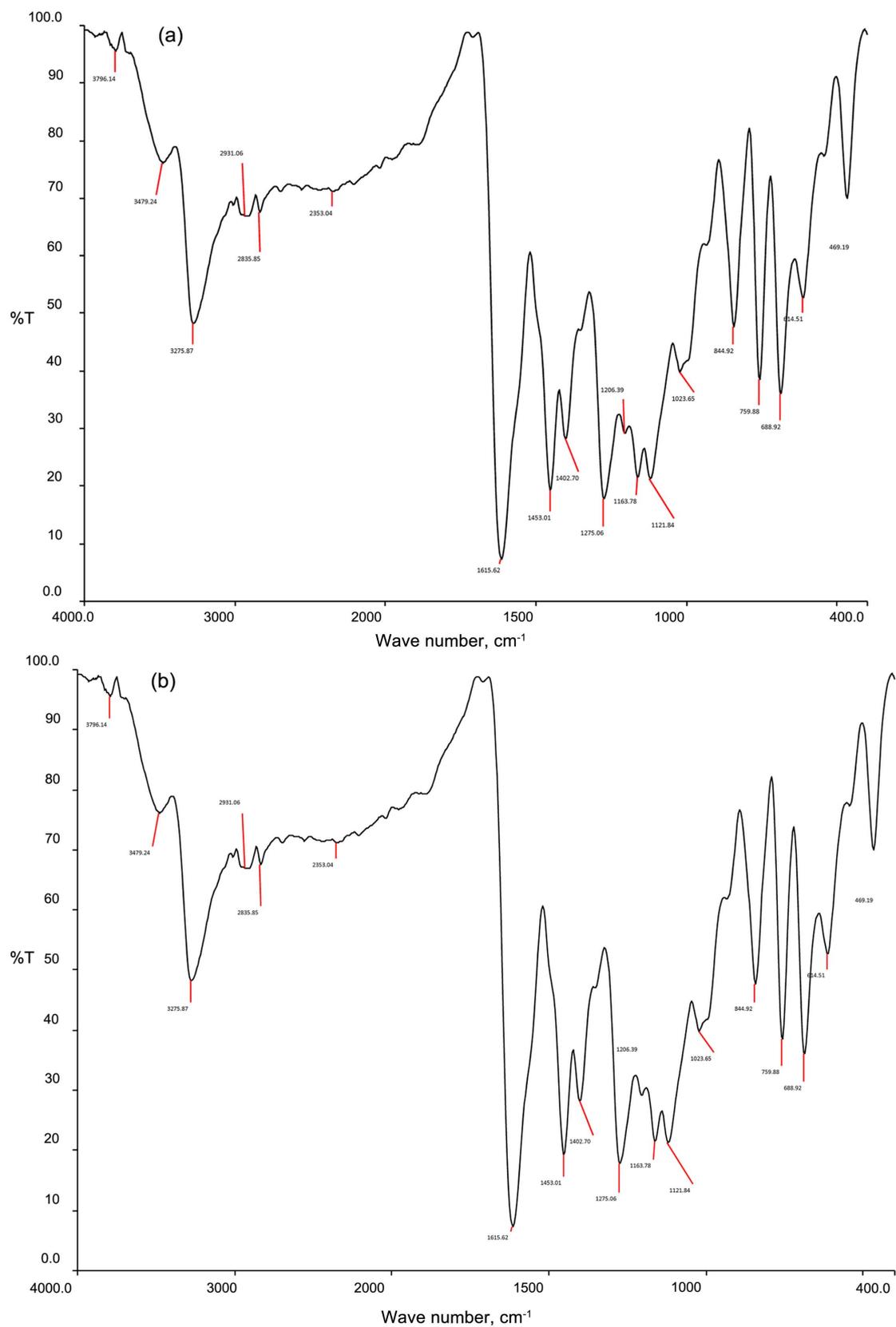


Fig. 7. (a) FT-IR spectrum of pure HMPC, (b) FT-IR spectrum of scrapped sample.

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