A STUDY OF CORROSION INHIBITOR OF MILD STEEL BY CARBOXYMETHYLCHITOSAN IN 1 M HCl

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Abstract

The inhibition effect of commercial carboxymethyl chitosan (CMC) on the corrosion of mild steel in 1 M HCl was studied by various techniques such as weight loss measurement, polarization and electrochemical impedance spectroscopy (EIS). It was found as the inhibition efficiency increase directly with the concentration of CMC. The highest inhibition efficiency for all tests was obtained at the concentration of 7×10^{-4} M. Polarization studies show that CMC behaves as mixed-type inhibitor and predominantly inhibit at the cathodic site. EIS technique revealed that the corrosion inhibition of mild steel was mainly controlled by charge transfer process. The values of activation energy (E_a) for mild steel corrosion inhibition and various thermodynamic parameters were also calculated. The adsorption nature of mild steel corrosion inhibition follows the Langmuir adsorption isotherm.

Keywords: CMC; chitosan; mild steel; corrosion inhibition.

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1.0 Introduction

Corrosion is known as deterioration of metals caused by reaction between its environments. Corrosion has become serious problem to the life system such as sudden failure which can cause explosion and fire and pollutes water because of corroded plumbing. Thus, there are many methods to reduce the corrosion rate. Recently, researches are more focusing on green corrosion inhibitor, compounds that acts as low cost environmentally and show good efficiency [1-5]. Organic inhibitor is one of the good corrosion inhibitor and its efficiency is related to reactive compound such as nitrogen, oxygen or sulphur [6-7]. To prevent the reaction of the metal with the acid medium, only small amount of organic inhibitor needed.

Chitosan, [α-(1➤ 4)2-amino-2-deoxy-β-D-glucan], a polysaccharides that obtained from N-deacytelated of chitin which is the second most abundant natural biopolymer [8-9]. Research on chitosan has been actively carried out for multiple applications due to its multifunction such as biodegradability, low toxicity and acceleration of fibroblast formation in animal body, antimicrobial activity and others [10-13]. However these applications are restricted because the solubility of chitosan is limited in water at various pH. Thus, chemical modification of chitosan has been done to improve the water solubility of chitosan. Carboxymethyl chitosan (CMC) is a water soluble derivative of chitosan and have many reactive functional groups such as amino group, hydroxyl group and carboxyl group which are indicated to be a good inhibitor of corrosion.

This study is to investigate organic inhibitor which is CMC as eco-friendly corrosion inhibitor on the mild steel surfaces in 1 M HCl solution. Weight loss measurement, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) are used for this propose.

2.0 Experimental

2.1   Materials and chemicals

Water soluble of CMC was prepared according to experimental procedure [14]. All the reagents and solvents used such as hydrochloric acid and isopropanol were analytical grade and used without any further purification.
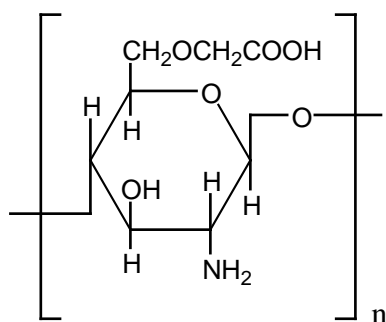

Figure 1: Molecular structure of Carboxymethyl chitosan (CMC)

2.2   Weight loss measurement

The weight loss measurements of mild steels (3 cm x 4 cm x 0.1 cm) were polished by using 400, 600 and 800 grade of SiC paper. After polished, mild steel was washed with distilled water and isopropanol, degreased ultrasonically in isopropanol and dried in air at room temperature. The mild steels were then immersed into 1 M HCl

solution and different concentration of CMC inhibitor at 24 hours in open air and different temperature which is 303, 313, 323 and 333 K.

2.3   Electrochemical measurement

The cell that were used in electrochemical experimental was conventional three-electrode cell which is consisting saturated calomel as reference electrode, platinum auxiliary platinum and mild steel as working electrode. Curves of potentiodynamic polarization were plotted from -250 mV to +250 mV versus open circuit potential (OCP) with scan rate 1.0 mV s^{-1} by using Volta Master 4. The electrochemical impedance spectroscopy (EIS) experiments were carried out by using Gamry Reference 600 Potentiostat/Galvanostat/ZRA.

2.4   Surface analysis

By using Scanning Electron Microscopy (SEM) method, surface of mild steel specimen which is untreated and mild steels which were immersed in 1 M HCl solution in the absence and presence of inhibitor were observed.

3.0 Results and discussion

3.1 Weight loss measurement

Table 1 shows the corrosion rate and the value of the inhibition efficiency (%IE) for CMC from the weight loss measurement. From the weight loss data, the IE percentage can be calculated by using following equation:

$$\% \ IE = \frac{W_o - W_{corr}}{W_o} \ x \ 100 \ \%$$

(1)

Where W_o and W_{corr} are corrosion rate of steel with and without inhibitor respectively.

Table 1: Weight loss measurement of mild steel in 1 M HCl with and without CMC at 298 K

Concentration (mM)	W ($\mu g/cm^2 h$)	IE%
1 M HCl	532.1522	…..
0.01	85.1378	84.00
0.1	74.3110	86.04
0.3	72.8346	86.32
0.5	69.0617	87.02
0.7	67.0932	87.39

From the data collected, it shows that as the concentration of inhibitor (CMC) increase, the inhibition efficiency also increase and has highest IE at 0.7 mM which is 87.39 %. This can be reported that as the concentration of inhibitor increase, the surface area that covered by the inhibitor also increase and protects mild steel from corrosion.

3.2   Polarization measurement

By using potentiodynamic polarization, the inhibition effect of CMC on mild steel in 1 M HCl at room temperature was investigated. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}) and Tafel slopes (β_a and β_c) which is obtained from polarization curves (Figure 1) were presented in Table 2. The inhibition efficiency was calculated by using equation:

$$\% \ IE = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \ \%$$

(2)

Where I_{corr} and $I_{corr(inh)}$ are the values of corrosion current density of uninhibited and inhibited specimen respectively.

Table 2: Electrochemical parameter of mild steel in 1 M HCl in the absence and presence of different concentration of CMC.

Concentration (mM)	E_{corr} (mV)	I_{corr} (mA/cm^2)	R_p ($\Omega.cm^2$)	β_a (mV)	β_c (mV)	IE%
1M HCl	-493.2	0.6571	103.96	134.9	-171.3	....
0.01	-472.7	0.2126	136.96	92.4	-103.4	67.65
0.1	-483.4	0.1896	209.73	100.4	-159.8	71.15
0.3	-489.9	0.1572	262.59	105.2	-152.9	76.08
0.5	-491.4	0.0928	312.29	92.0	-131.6	85.88
0.7	-515.9	0.0918	335.40	104.6	-115.7	86.03

From the data shown in Table 2, it can be clearly seen that the inhibitor efficiency of CMC increase as the concentration of CMC increase. This behavior shows that CMC acts as good corrosion inhibitor for mild steel in acidic. Figure 2 showed that CMC is

mixed type inhibitor because there was no distinct on reduction of current density in
anodic and cathodic current area. Value of both anodic and cathodic current densities are
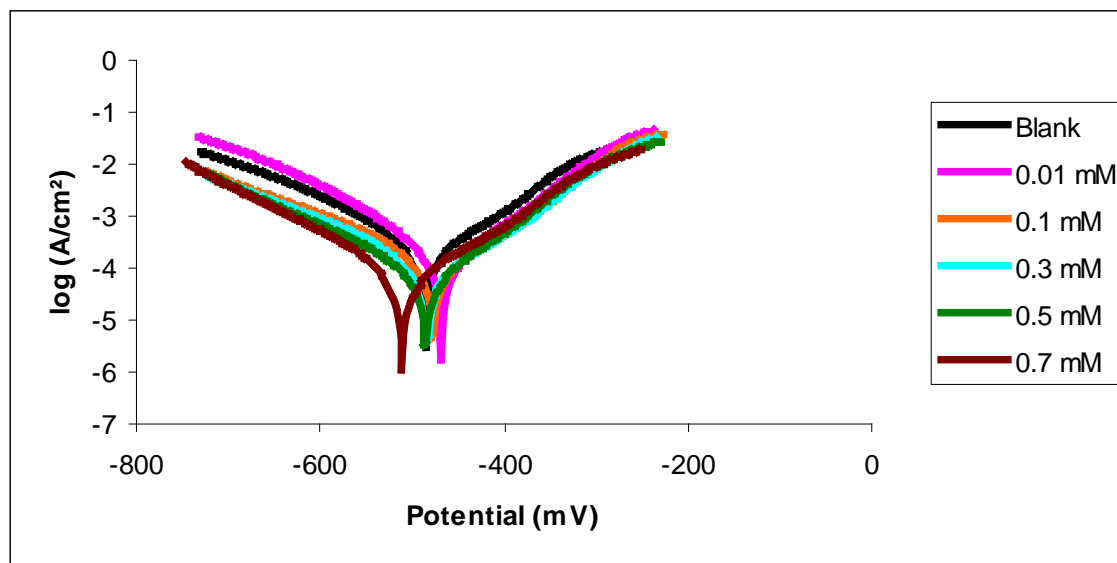change in the presence of inhibitor supported that CMC is mixed type inhibitor [15].

Figure 2: Tafel plots of mild steel in 1 M HCl and different concentration of CMC.

3.3   Electrochemical impedance spectroscopy (EIS)

The Nyquist plots for mild steel in 1 M HCl in the absence and presence of
different concentration of CMC are shown in Figure 3 and impedance parameters are
summarized in Table 3. A semicircular appearance of Nyquist shows process that mainly
control corrosion on mild steel is a charge transfer process. The semicircular diameter is
significantly increase with increasing CMC concentration indicate the increase in
corrosion inhibitor that is related to decrease double layer capacitance, C_{dl}. Percentage of
inhibition efficiency (%IE) is calculated by using the relation :

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$$\% \ IE = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \ x \ 100 \ \%$$

(3)

Where R_{ct} and $R_{ct(inh)}$ are the charge transfer resistance values in the absence and presence

of inhibitor respectively.

Table 3: Data from electrochemical impedance measurements of mild steel in 1 M HCl for various concentration of CMC.

Concentration (mM)	Resistance, Rs ($\Omega.cm^2$)	CPE ($\mu F/cm^2$)	Resistance, Rct ($\Omega.cm2$)	IE %
1M HCl	1.103	177.1	61.98	….
0.01	1.210	161.1	100.80	38.51
0.1	1.327	132.9	177.80	65.14
0.3	1.496	131.7	227.60	72.77
0.5	2.268	121.5	260.80	76.23
0.7	1.843	113 .0	318.00	80.51

The Nyquist impedance plots were analyzed by using simple equivalent circuit

model which is Randle's model (Figure 4). The values of element fitted the model

includes the solution resistance (R_s) and the constant phase element (CPE) which is

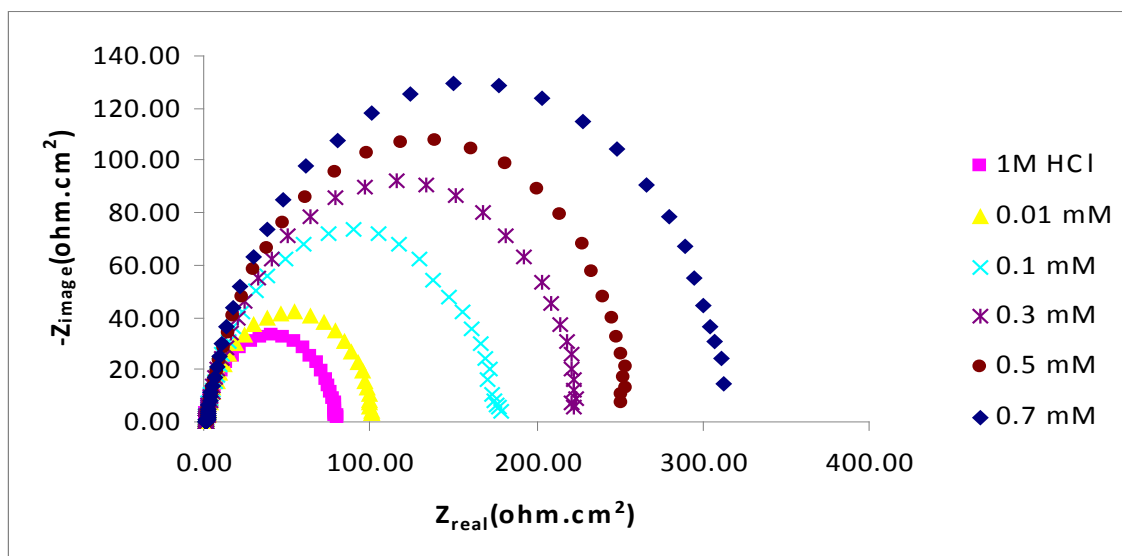placed in parallel to charge transfer resistance (R_{ct}).

Figure 3: Nyquist plots for mild steel in 1 M HCl for various concentration of CMC.
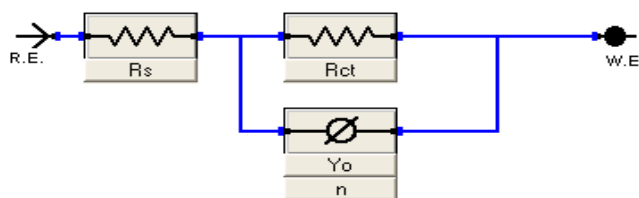

Figure 4: Randle's CPE circuit model.

As seen the %IE values that obtained from impedance studied showed the same trend as in the weight loss and polarization measurement which is CMC has the highest inhibition property at 0.7 mM.

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3.4 *Effect of temperature*

Temperature is an important parameter that gave a great effect to corrosion rate of mild steel in acidic medium. As the temperature increases, the corrosion rate also increases. This is due to decrease hydrogen evolution overpotential. The effect of temperature on the performance of CMC as corrosion inhibitor was studied using weight loss measurement in the temperature range 303-333 K in absence and presence of CMC.

Table 4: Effects of temperature for mild steel I 1 M HCl for various concentration of CMC.

Temperature (K)	Concentration, C (mM)	IE %	θ
303	1 M HCl	……	….
	0.01	82.86	0.8286
	0.1	85.60	0.8560
	0.3	86.08	0.8608
	0.5	86.37	0.8637
	0.7	86.60	0.8660
313	1 M HCl	…..	…..
	0.01	80.60	0.8060
	0.1	82.75	0.8275
	0.3	83.32	0.8332
	0.5	83.37	0.8337
	0.7	84.06	0.8406
323	1 M HCl	…..	…..
	0.01	76.49	0.7649
	0.1	80.58	0.8058

	0.3	81.02	0.8102
	0.5	81.33	0.8133
	0.7	81.84	0.8184
333	1 M HCl	…..	…..
	0.01	51.22	0.5122
	0.1	55.47	0.5547
	0.3	56.08	0.5608
	0.5	56.83	0.5683
	0.7	57.03	0.5703

Table 4 shows values of inhibition efficiency (%IE), corrosion rate (W) and degree of surface coverage (θ). From the results in Table 4, it is clear seen that inhibition efficiency slightly decrease as the temperature increase which is due to adsorption of inhibitor onto the mild steel surfaces. The slightly decrease of IE support the idea that the adsorption of CMC on the mild steel may be in physical in nature [16].

The activation energy of CMC can be calculated by using Arrhenius equation:

$$K = A \exp\left(\frac{-E_a}{RT}\right)$$

(4)

Where K is reaction rate, A is the Arrhenius pre-exponential constant, E_a the activation energy of the corrosion reaction, T is the absolute temperature and R is the universal gas constant. The apparent activation energy for corrosion process in absence and presence of CMC are determined by linear regression between ln W versus 1000/T as revealed by Figure 4. The values of activation energy calculated from the linear regression in Figure 4

are 45.61 kJ mol^{-1} and 75.77 kJ mol^{-1} for absence and presence of CMC respectively. The obtained results show that E_a value of presence of CMC is higher than in its absence indicates physisorption of corrosion inhibitor [17].

3.5   *Adsorption isotherm*

The nature of interaction between inhibitor and the corroding surface can be studied by applying adsorption isotherms. The degree of surface coverage, θ for different concentration of the inhibitor in 1 M HCl has been evaluated from weight loss measurement (%IE/100). The three isotherms which is Langmuir, Temkin and Frumkin adsorption isotherm were made to fit the θ at various concentrations according to the following equation and shown in Figure 4.

Langmuir : $C/\theta = 1/K + C$ (5)

Temkin : $\log(\theta/C) = \log K - g\theta$ (6)

Frumkin : $\log(\theta/(1-\theta)C) = \log K + g\theta$ (7)

Where θ is degree of surface coverage, K the adsorption-desorption equilibrium constant, C the inhibitor concentration and g the adsorbate interaction parameter.
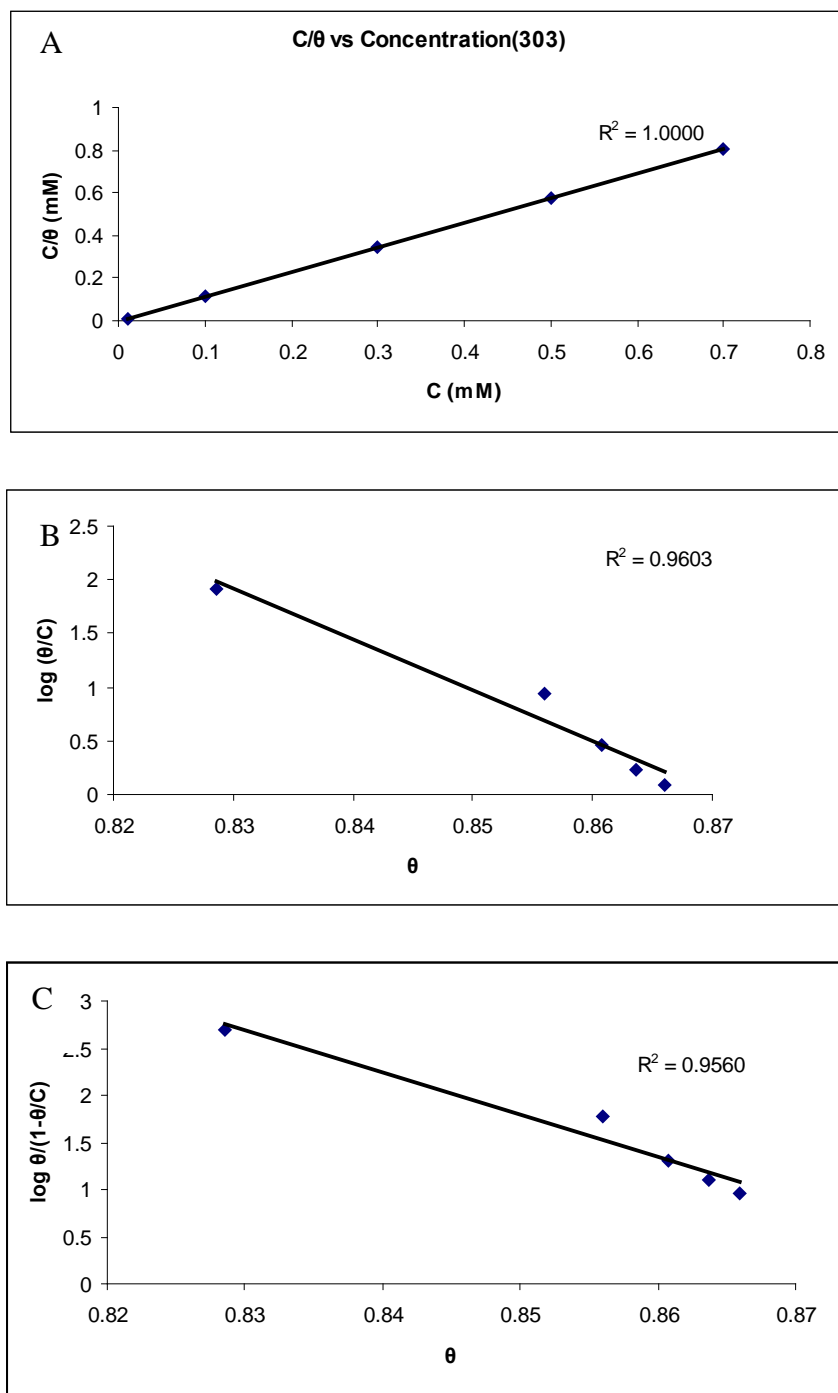
Figure 4: A) Langmuir, B) Temkin, C) Frumkin isotherm for the adsorption of CMC in 1

M HCl on the mild steel.

The value of the correlation coefficient, R^2 for Langmuir isotherm is 1.0000 while for Temkin and Frumkin isotherm is 0.9603 and 0.9560 respectively. From the correlation coefficient value, the best results have been obtained for Langmuir adsorption isotherm. Free energy of adsorption ΔG_{ads} can be determined with equation 8 by using the value of K obtained from Langmuir adsorption isotherm.

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \tag{8}$$

Where 55.5 is the water concentration of solution in ml/l and K adsorption constant. The calculated value of K and ΔG_{ads} were found to be 1000 and -27.52 kJ ml^{-1}. The negative sign of ΔG_{ads} indicates that the adsorption of CMC on the mild steel surface is a spontaneous process [18]. From previous study, the free energy of adsorption (ΔG_{ads}) can be explained by two cases which is the value of ΔG_{ads} around -20 kJ mol^{-1} are consistent with electrostatic forces between inhibiting organic and electrically charged surface of metal, physisorption while the value of ΔG_{ads} -40 kJ mol^{-1} or more negative involve charge sharing or charge transfer from inhibitor to the mild steel surface to form a coordinate-type bond [19]. In this study, the value of ΔG_{ads} that obtained is -27.52 kJ mol^{-1} which is more than -20 kJ mol^{-1} but less than -40 kJ mol^{-1}. This indicates that the adsorption of inhibitor on the mild steel surfaces involves both physisorption and chemisorption.

The thermodynamic parameter which is enthalpy, ΔH_{ads} and entropy, ΔS_{ads} for the adsorption of CMC on mild steel can be calculated by linear regression between ΔG /T

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versus 1/T and values of ΔH_{ads} and ΔS_{ads} that obtained was -78.0 kJ mol^{-1} and -146.3 kJ mol^{-1} respectively. Negative value of ΔH_{ads} shows that the adsorption of inhibitor on mild steel surface is an exothermic process which suggests either physisorption or chemisorption [16]. While the negative sign of ΔS_{ads} indicates decrease in the disorder from reactants to the activated complex and accompanied with exothermic process.

3.6   Surface analysis

Figure 5 showed the surface of mild steel specimen before and after immersion in 1 M HCl for 24 hours in the absence and presence of inhibitor which has done SEM analysis with magnification 100 X. From the images obtained, it shows that the surfaces of mild steel specimen is seriously corroded in the absence of inhibitor. While the steel specimen that immersed in the presence of inhibitor in 1 M HCl showed a smooth surface. From the images of SEM analysis, it shows that CMC inhibit corrosion of mild steel in 1 M HCl.
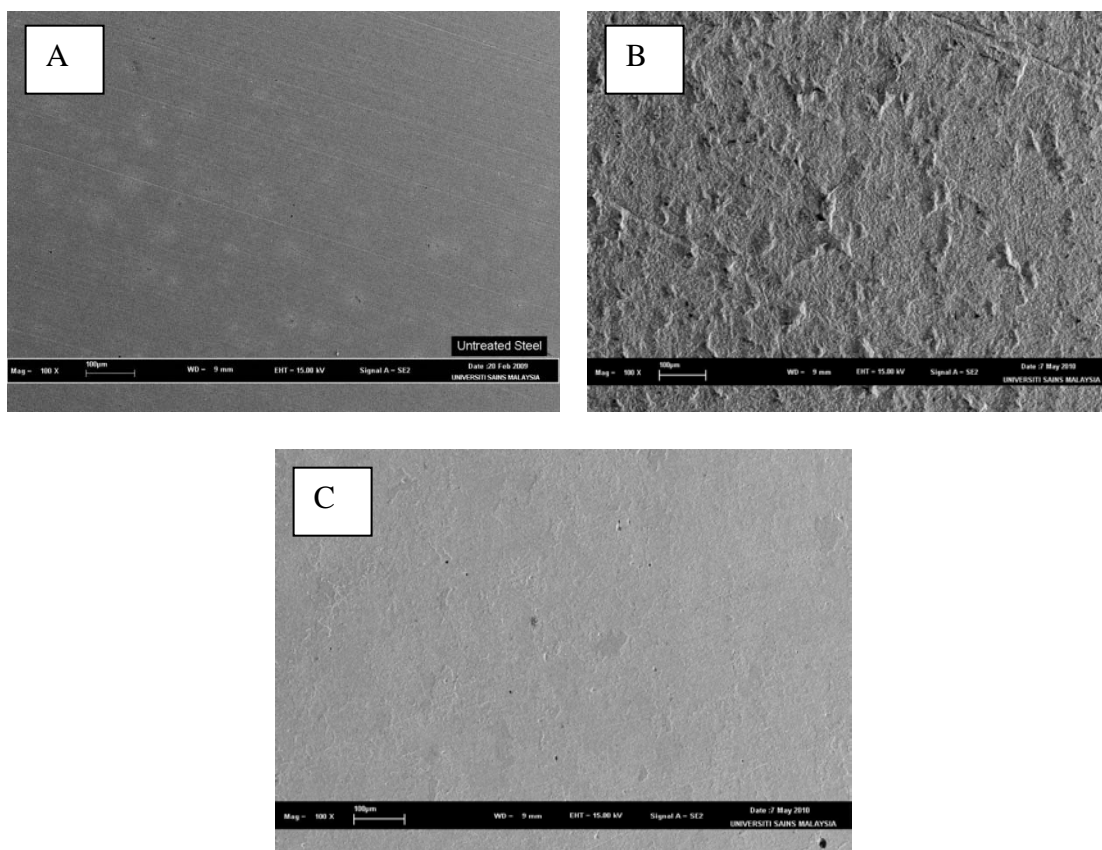
Figure 5: SEM analysis of mild steel (A) polished surface (B) immersed in 1 M HCl
(C) immersed in 1 M HCl in the presence of CMC.

4.0 Conclusions

In conclusion, the results obtained shows that CMC is a good corrosion inhibitor for mild steel in 1 M HCl. The inhibition efficiency of mild steel in 1 M HCl increases with increasing the concentration of CMC and reaches 87.39% at 0.7 mM. Polarization measurement shows that CMC acts as mixed-type inhibitor with dominant inhibition at cathodic site. On the basis of temperature effect study, it was revealed that the inhibition

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efficiency decreases with the rise of temperature and activation energy was higher in the presence of inhibitor proposed physisorption mechanism. Finally, the adsorption process of CMC on the mild steel surface followed the Langmuir adsorption isotherm.

5.0 Acknowledgement

6.0 References

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