

Effect of Scan Rate on Corrosion Inhibition of Carbon Steel in the Presence of Rice Straw Extract - Potentiodynamic Studies

(Kesan Kadar Imbasan Terhadap Perencatan Kakisan Keluli Karbon
Dalam Kehadiran Ekstrak Jerami Padi - Kajian Potensiodinamik)

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ABSTRACT

The effect of scan rate on the accuracy of corrosion parameter in evaluating the efficiency of rice straw extract as corrosion inhibitor has been studied via potentiodynamic polarization measurement. Scan rate in the range of low ($0.1-0.25 \text{ mV s}^{-1}$), medium ($0.5-1.0 \text{ mV s}^{-1}$) and high ($1.5-2.0 \text{ mV s}^{-1}$) scan were carried out on the carbon steel in 1 M HCl . The corrosion parameters such as corrosion rate, polarization resistance and corrosion current density have been analyzed through Tafel polarization curve. High scan rate gave poor accuracy of corrosion parameter compared to medium and low scan. Medium scan at 1.0 mV s^{-1} has been chosen as the optimum scan rate due to the approached steady-state and small disturbance of charged current. As a result, the addition of rice straw extract in 1 M HCl has reduced the values of corrosion current density in both cathodic and anodic reactions signified the corrosion has been inhibited. The efficiency of rice straw extracts as a corrosion inhibitor offer good result as much as 86%.

Keywords: Corrosion; potentiodynamic polarization; rice straw extract; scan rate

ABSTRAK

Kesan kadar imbasan ke atas ketepatan parameter kakisan dalam menilai kecekapan perencat kakisan ekstrak jerami padi telah dikaji menerusi ukuran pengutuban potensiodinamik. Penggunaan kadar imbasan pada julat imbasan rendah ($0.1-0.25 \text{ mV s}^{-1}$), sederhana ($0.5-1.0 \text{ mV s}^{-1}$) dan tinggi ($1.5-2.0 \text{ mV s}^{-1}$) telah dilakukan ke atas sampel keluli karbon dalam medium 1 M HCl . Parameter kakisan seperti kadar kakisan, rintangan pengutuban dan ketumpatan arus kakisan telah dianalisis menerusi keluk pengutuban Tafel. Penggunaan kadar imbasan yang tinggi memberikan keputusan parameter kakisan yang kurang tepat berbanding kadar imbasan rendah dan sederhana. Kadar imbasan sederhana pada 1.0 mV s^{-1} telah dipilih sebagai kadar imbasan yang optimum berdasarkan keadaan-mantap yang telah tercapai dan gangguan kecil pada arus tercas. Keputusan menunjukkan penambahan ekstrak jerami padi di dalam 1 M HCl telah menurunkan nilai ketumpatan arus kakisan di kedua-dua tindak balas katodik dan anodik menandakan kakisan telah direncatkan. Kecekapan ekstrak jerami padi sebagai perencat kakisan memberikan keputusan yang baik sebanyak 86%.

Kata kunci: Ekstrak jerami padi; kadar imbasan; kakisan; pengutuban potensiodinamik

INTRODUCTION

Corrosion is a degradation or destructive attack of metals due to its environments. Most of the science and engineering aspects in the field of corrosion focusing on knowing how to mitigate the impact of corrosion. Generally, the weight lost method is the easy process to determine the corrosion rate. However this technique is time-consuming and requires several weeks, months or years to accomplish the whole test. Due to the slower process, direct current (DC) techniques such as polarization resistance, Tafel plots and cyclic polarization are preferable to be used strictly for corrosion measurement in corrosion science studies. The uses of those electrochemical techniques are very fast methods since electrochemical instruments polarize the sample to accelerate the corrosion process and make the measurement in minutes or hours. Scan rate is an essential experimental parameter in performing polarization measurements and measuring the corrosion rate. The effect

of scan rate at which the potential is scanned may have a significant effect on the amount of current produced at all values of potential. The selection of optimized scan rate values is very important to ensure the readability and stability of charge transfer within the substrate, electrolyte and other device involved such as reference electrode and counter electrode to achieve the steady state for the corrosion reaction. The system is able to obtain a sufficient time in performing the interaction and transferring the charge movement within the electrochemical process. Several studies have attempted to explore the effect of scan rate in potentiodynamic polarization measurement (Bard & Faulkner 2001; Galal et al. 2005; Khaled & Abdel Rehim 2011; Oguzie et al. 2010; Otieno-Alego et al. 1995, Poursae 2010; Quraishi et al. 2010; Zhang 2009). Many works in corrosion inhibitor studies have performed numerous values of scan rate depends heavily on the metal used, electrolyte, medium and types of inhibitors as well as

others interest topics (Galal et al. 2005; Khaled & Abdel Rehim 2011; Oguzie et al. 2010; Quraishi et al. 2010). In potentiodynamic analysis, inhibitor reduces the corrosion processes by decreasing the anodic or cathodic polarization behavior indicated in Tafel slopes. The reduction of ion diffusion on the metallic surface and increments of electrical resistance of the metallic interface was also the sign of the inhibited corrosion process. In this present work, a range of scan rate has been optimized to evaluate the potential of rice straw extract as a corrosion inhibitor for carbon steel in 1 M HCl.

METHODS

In potentiodynamic polarization measurements, three electrode systems were used. A carbon steel specimen (chemical compositions in wt. %: Fe 99.3%, C 0.12%, Mn 0.5%, P 0.04% and S 0.045%) was used as a working electrode. Graphite electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The metal specimens were then placed in an electrochemical cell containing 1 M HCl in the present of rice straw extract, as corrosion inhibitors. The potentiodynamic polarization experiments were performed in the applied potential range from ± 250 mV with different scan rate of 0.1, 0.25, 0.5, 1.0, 1.5 and 2.0 mV s^{-1} by using a potentiostat-galvanostat, equipped with Gamry software. In this study, the level of scan rates are defined as 'low scan' for 0.1 to 0.25 mV s^{-1} , 'medium scan' for 0.5 to 1.0 mV s^{-1} and 'high scan' for 1.5 to 2.0 mV s^{-1} .

RESULTS AND DISCUSSION

In this study, potentiodynamic curve (Tafel plot) is determined to describe the polarization characteristics of the corrosion system. The corrosion current density, I_{corr} , is obtained from Tafel plot by extrapolating the linear portion of the curve to E_{corr} , as shown in Figures 1, 2 and 3. The

corrosion rate, CR can be calculated from the corrosion current by using (1),

$$\text{CR} = \frac{0.13 \cdot I_{\text{corr}} \cdot (\text{EW})}{d}, \quad (1)$$

where I_{corr} is the corrosion current density, ($\mu\text{A cm}^{-2}$), EW is the equivalent weight of metal specimen (g) and d is the density of the metal (g cm^{-3}).

Resistance polarization, R_p can be calculated from β_a (anodic Tafel slope) and β_c (cathodic Tafel slope) as following;

$$R_p = \frac{\beta_a \beta_c}{2.3 I_{\text{corr}} (\beta_a + \beta_c)}, \quad (2)$$

where corrosion inhibition efficiency (% IE) can be expressed as;

$$\text{IE} = \frac{\text{CR}_o - \text{CR}_i}{\text{CR}_o} \times 100, \quad (3)$$

where CR_o is the corrosion rate without inhibitor and CR_i is the corrosion rate with inhibitor.

Table 1 shows the potentiodynamic parameters of carbon steel in 1 M HCl in the presence of corrosion inhibitors. As the metal polarized from low (0.1 mV s^{-1}) to high scan rate (2.0 mV s^{-1}), E_{corr} were shifted to more negative values. The highly reducing initial potential will cause the partial removal of the passive film (Zhang et al. 2009). In this present experiment, the average value of open circuit potential, E_{ocp} prior to the polarization was 0.455 mV s⁻¹. From the tabulated data after polarization, the values of $E_{\text{corr}} - E_{\text{ocp}}$ gives significant differences for both low and high scan. The shift of E_{corr} away from E_{ocp} was resulted from the high scan rate due to the enhancement of the disturbance of the charging current (Zhang et al. 2009). The charging current was raised from both positive and negative polarization directions. During the positive scan, the electrons stored in carbon steel were forced out and results in the increase

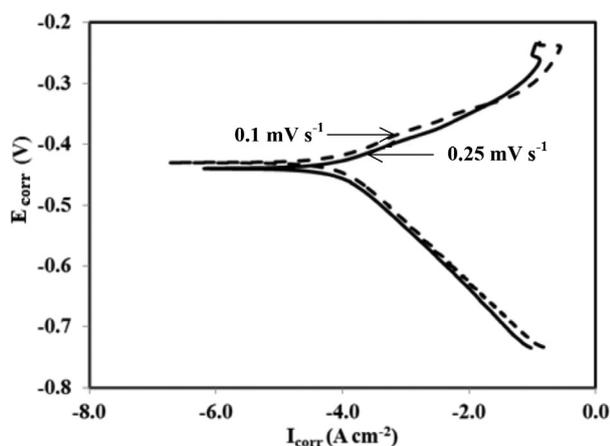


FIGURE 1. Potentiodynamic curve of carbon steel in rice straw extract + 1 M HCl at low range of scan rate

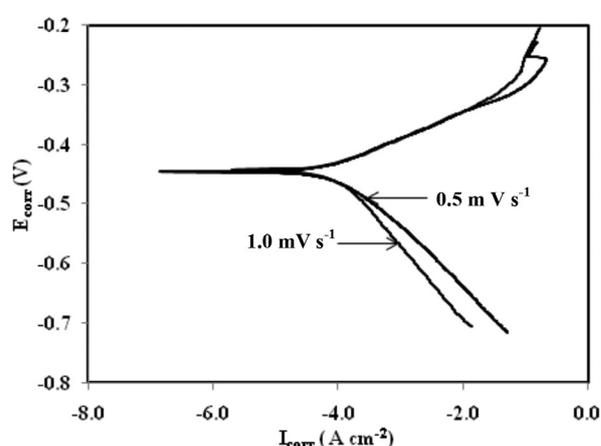


FIGURE 2. Potentiodynamic curve of carbon steel in rice straw extract + 1 M HCl at medium range of scan rate

of positive charge density. Therefore, the charging current flows in direction of anodic faradaic current which make the electrode become cathodic polarization and thus, the E_{corr} is negative to E_{ocp} at high scan rate. Furthermore, at negative scan, the charging current flows in the direction of cathodic faradaic current due to the continuously driven electrons into the carbon steel specimen. Therefore the E_{corr} is positive to E_{ocp} at low and medium scan rate.

The corrosion current density, I_{corr} obtained at 1.0 mV s^{-1} almost equals to that obtained at 0.1 mV s^{-1} . Compared to the results scanned at high rate, the I_{corr} were showed relatively large different values. This indicates that the corrosion reaction does not approach the steady state during the potentiodynamic scan conducted at high scan. Once the scan rate drops to 1.0 mV s^{-1} , the steady state of the corrosion reaction in this experiment were approached. The electrodes in the electrochemical system have been getting sufficient time to deliver and transfer the electrons and charges involves in the corrosion reaction. Generally, as the scan rate falls to the lower scan, the steady state of the corrosion reaction is approached, as reported by others (Scully et al. 2003; Zhang et al. 2009).

In polarization resistance measurements, detected errors are due to the incomplete charge transfer within

the interface of the working electrode. This will happen once a rapid scan rate is used and consequences to the overestimated of corrosion rate values. In spite of, there are several works reported in evaluating corrosion inhibitors using high scan rate in potentiodynamic polarization scan (Abd El Rehim et al. 2001; Chou et al. 2003; El-Etre 2003). In optimizing the scan rate, a result from this study shows that the low and medium scan rate seems to be performed consistently and relatively small difference in corrosion rate and polarization resistance values (Table 1). The Tafel slopes were also slightly close to each other (Figures 1 and 2). Tafel slope values for both β_a and β_c were almost equal for 0.1, 0.25, 0.5 and 1.0 mV s^{-1} represented that the disturbance of the charging current is very small and almost negligible. The small charging effect is due to the presence of the electrical double layer and it is always present in all potentiodynamic polarization measurements (Bard & Faulkner 2001; Zhang et al. 2009).

In this present work, the electrical double layer is defined as a structure of electrical charges that appears on the metal surface when it is placed into an electrolyte (corrosion inhibitor). The double layer refers to the two parallel layers of charge surrounding the metal. The first layer might be the surface charge (either positive or

TABLE 1. Potentiodynamic parameter of carbon steel in 500 ppm rice straw extract + 1 M HCl

Range of scan rate	Scan rate (mV s^{-1})	I_{corr} (A cm^{-2})	E_{corr} (V)	$(E_{\text{corr}} - E_{\text{ocp}})$	β_a	β_c	R_p ($\Omega \text{ cm}^2$)	CR (mpy) $\times 10^{-11}$
Low	0.10	-7.08×10^{-5}	-0.43	0.025	0.05	0.10	204.70	3.25
	0.25	-7.94×10^{-5}	-0.44	0.015	0.05	0.09	176.00	3.64
Medium	0.50	-8.13×10^{-5}	-0.45	0.005	0.05	0.09	175.37	3.73
	1.00	-8.32×10^{-5}	-0.45	0.005	0.05	0.11	179.64	3.81
High	1.50	-1.00×10^{-4}	-0.48	-0.025	0.06	0.06	130.43	4.59
	2.00	-1.29×10^{-4}	-0.46	-0.005	0.06	0.07	107.61	5.90

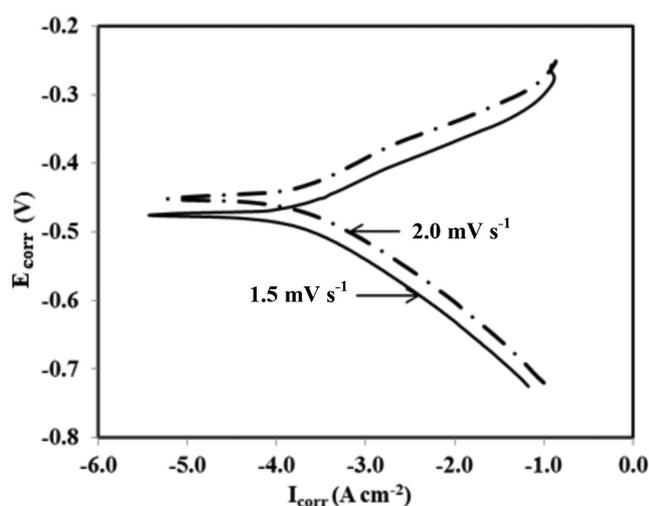


FIGURE 3. Potentiodynamic curve of carbon steel in rice straw extract + 1 M HCl at high range of scan rate

negative), comprises ions adsorbed directly onto the metal due to chemical interactions. The second layer is composed of ions attracted to the surface charge via the Coulomb force or electrostatic interaction within first layer. The small charging effect of both charges is suggested due to the lack of simultaneous attraction and repulsion force. In comparison with high scan rate at 1.5 and 2.0 mV s^{-1} , a significant large difference values in corrosion rate and polarization resistance were achieved (Table 1) whilst Tafel slope also was definitely far away from each other (Figure 3). This phenomenon leads to the high current disturbance. It is expected that some of the current generated would reflect charging of the double layer surface in addition to the corrosion process. The measured current would then tend to be larger than the current actually generated by the corrosion reactions (Poursae 2010).

In evaluating the potential of rice straw extract as corrosion inhibitors for carbon steel, even though the lowest corrosion rate and the highest polarization resistance was demonstrated at 0.1 mV s^{-1} as summarized in Figure 4, the medium scan rate at 1.0 mV s^{-1} was selected as optimized parameter in this studies. The purpose for the polarization scan rate chosen at 1.0 mV s^{-1} is to allow the electrochemical interface in the corrosion measurement system remains fully charged. This is to ensure the current/voltage relationship measure the interfacial corrosion process at every potential of the scan with less current disturbance. The lowest scan rate is time-consuming and it may affect the interface corrosion system, moreover the electrolyte used is very corrosive medium (1 M HCl) which carried a bulky of anion and cation species of H^+ and Cl^- ions. Extending the polarization time will cause some irreversible changes to the interface structure of corroding system. For the corrosion system with an extremely low corrosion rate, the scan rate must be controlled in a very low level to make the disturbance of the charging current negligible (Zhang et al. 2009). Lowest scan rate such at 0.1 mV s^{-1} is very applicable for concrete materials and less-corrosive electrolyte system (Atashin et al. 2011; Poursae 2010; Poursae & Hansson 2009). In fact ASTM G5-94 (2004) which is standard reference test method for making potentiostatic and potentiodynamic anodic polarization measurement recommended that 0.1667 mV s^{-1} as an applicable scan value. However, numerous studies have performed their work in evaluating corrosion inhibitors

at 1.0 mV s^{-1} as appropriate scan rate values dependent on many aspects (Galal et al. 2005; Khaled & Abdel Rehim 2011; Quraishi et al. 2010).

Figure 5 represents the potentiodynamic curve of carbon steel at 1.0 mV s^{-1} in 1 M HCl in different concentration of rice straw extract. The curves were extrapolated to provide the parameters, as presented in Table 2. The result showed that the corrosion rate decreased with addition of corrosion inhibitors. The corrosion current density also reduced in both cathodic and anodic reactions relative to the addition of all concentrations of rice straw extract. Due to that, rice straw extract behaves as mixed corrosion inhibitors in 1 M HCl in carbon steel. Nevertheless, the reductions in current density were more noticeable at cathodic site of electrochemical reactions which involved reduction process. It is distinctly can be viewed through the curve of 500 and 1000 ppm inhibitors (Figure 5). The values of β_c slope also exhibit large difference from the system without inhibitors. Rice straw extract was suggested to inhibit corrosion of the metal specimen predominantly on reduction process which is hydrogen evolution. The significant changes in all the parameters tabulated within the data were contributed to the corrosion inhibition effect. In fact, the higher the concentration of rice straw extract used will promote better corrosion resistance.

CONCLUSION

The effect of scan rate on the investigation of rice straw extract as corrosion inhibitor has been identified. It was found that the scan rate optimization is necessary to provide corrosion reaction remains fully charged within the electrode and electrolyte. If the scan rate is too rapid, the alteration of potentiodynamic curves may lead to misinterpretation of the polarized electrode process due to charges disturbance and insufficient time during achieving the steady state. On the other hand, if it is too slow, the interfacial structure of polarized electrode may change during the measurement. In fact, in corrosion inhibitor studies, the appropriate scan rate is very important to determine in the first place, because it would be different dependent on the type of metal used, environment (acidic, basic or neutral) and the types of corrosion inhibitors applied. The used of optimized scan rate at 1.0 mV s^{-1} in the investigation of rice straw extract as corrosion

TABLE 2. Potentiodynamic parameter of carbon steel at 1 mV s^{-1} in 1 M HCl in different concentration of rice straw extract

Corrosion inhibitors	I_{corr} (A cm^{-2})	E_{corr} (V)	β_a	β_c	R_p ($\Omega \text{ cm}^2$)	CR (mpy)	% IE
0 ppm	3.98×10^{-4}	-0.44	0.07	0.07	38.23	1.82×10^{-10}	0
250 ppm	2.00×10^{-4}	-0.43	0.05	0.08	66.89	9.17×10^{-11}	50
500 ppm	8.32×10^{-5}	-0.45	0.05	0.11	179.64	3.81×10^{-11}	80
1000 ppm	5.75×10^{-5}	-0.43	0.04	0.10	216.04	2.64×10^{-11}	86

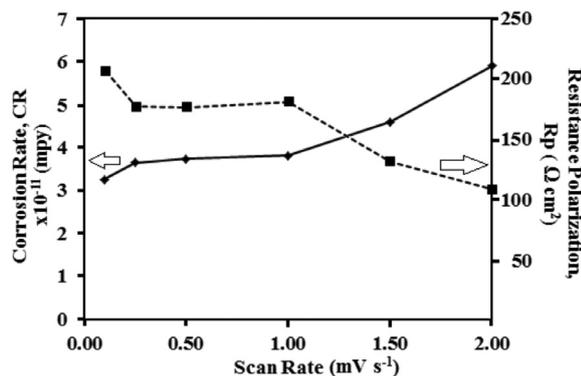


FIGURE 4. Corrosion rate and resistance polarization of carbon steel in rice straw extract + 1 M HCl at different scan rate

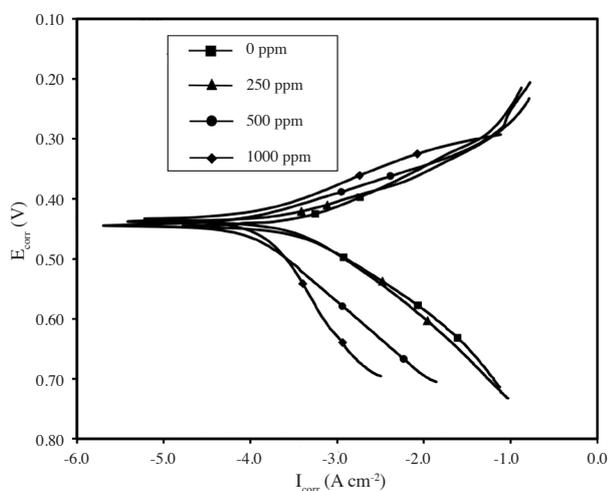


FIGURE 5. Potentiodynamic curve of carbon steel at 1.0 mV s⁻¹ in 1 M HCl in different concentration of rice straw extract

inhibitors exhibits a steady state condition and reliable data of corrosion parameters. The addition of the high concentration of rice straw extract reduce the corrosion attack by inhibiting the hydrogen evolution reaction due to the predominantly reduction in current density at the cathodic site of electrochemical reactions.

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