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Inhibitory Effect of Red Onion Skin Extract on the Corrosion of Mild Steel in Acidic Medium

Choon Chieh Ong, Khairiah Abd Karim*

School of Chemical Engineering, Universiti Sains Malaysia Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia
chkhairiah@usm.my

The inhibition efficiency of methanol extract of red onion peel on the corrosion of mild steel in hydrochloric acid (HCl) solution has been investigated through weight loss measurements. This study was conducted by immersing mild steel coupon into 1.0 M of HCl solution without and with the presence of red onion peel extracts (ROPE) (0.5 – 2.0 g/L) and at various temperatures (303 to 333 K) for 7 d. Fourier Transform Infrared (FT-IR) spectroscopy analysis indicated that the inhibition of mild steel corrosion was mainly contributed by C-O and aromatics compounds. These compounds were adsorbed on the mild steel surface and formed a thin layer of protective barrier. From the weight loss measurement, the inhibition efficiency of 90 % was obtained in the HCl solution containing 2.0 g/L of ROPE at temperature of 303 K. The inhibition efficiency was found to increase with increasing inhibitor concentration but decrease with increasing temperature of acid solution. This is because mild steel is oxidised at a higher rate at high temperature which causes the ROPE to desorb from the surface of mild steel. The adsorption mechanism of ROPE on the mild steel obeys the Langmuir adsorption isotherm within the range of temperature studied.

1. Introduction

Metals such as steel are commonly used as piping system to transport acid or alkali in industrial process. When metal is in contact with acid or alkali, an unavoidable metal corrosion on the metal surface will occur. Metal corrosion can be defined as a gradual deterioration of metal by anodic and cathodic reactions when the metal is exposed to weather, moisture or other corrosive medium (Ching, 2011). Metals are mostly inherently unstable in the environment because metals are produced from its minerals or ores. Metal corrosion is also known as natural electrochemical reaction. It consists of the dissolution of metals into the corrosive medium and oxidants reduction that occurred at anodic and cathodic site of the electrochemical reaction (Sato, 2012). Since metals have been converted into other stable form of products, the original physical and chemical properties of the metals have been degraded. Continuous damage to the metal structure due to corrosion by the environment will cause the plant unit to collapse or pipe leakage. Cost of maintenance, repair and replacement will trigger significant loss of revenue for chemical industry (Patni et al., 2013). Corrosion of metal cannot be prevented but it is controllable. Addition of corrosion inhibitor into the corrosive medium is the most common method used to prevent metal corrosion. Small amount of inhibitor added will improve the lifetime of the metal by physisorption or chemisorption of inhibitor compound on the metal surface (Fuchs-Godec, 2006). Corrosion inhibitor will not induce any significant effect to the process since it is added in a small concentration to the process stream (Raja and Sethuraman, 2008). It possesses strong benefit due to easy application, effective in reducing corrosion rate, and inexpensive. It will inhibit corrosion by formation of enhanced protective oxide film or formation of barrier due to adsorbed inhibitor compound on the metal surface (El Rehim et al., 2001). Due to the toxic effects of synthetic or inorganic inhibitor, the researchers started to study the inhibition efficiency of various types of natural corrosion inhibitor on metal corrosion. Plants are sources of naturally occurring compounds. Corrosion inhibitors by using plant extracts are environmentally friendly, lower cost, and less harmful to human health and the environment (James and Akaranta, 2014). These advantages of using green corrosion inhibitor are more than enough to support that plant extracts are an alternative inhibitor for non-renewable synthetic or inorganic inhibitor.

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Onion peels are commonly disposed as solid waste from almost every kitchen in Malaysia since it is one of the major vegetables consumed every day. From the survey by Hertog et al. (1992), onion (Allium cepa L.) mainly composed of quercetin content as compared with other 28 vegetables and nine fruits. Quercetin is the major flavonoid compound that can be found in red onion peel (James and Akaranta, 2011). The research studied by Patil et al. (1995) showed that the colour of onion is not the main criterion that affects the quercetin content in onion. Red onion is still the most commonly used vegetables in every household compared with white or yellow onion. The objective of this study was to investigate the inhibitory effect of red onion peel extract (ROPE) for mild steel in HCl solution. The inhibition behaviour of ROPE on mild steel was determined using weight lost measurements.

2. Materials and Methods

2.1 Materials preparation

Mild steel coupons were obtained locally and were mechanically press-cut into dimensions of 5 cm x 3 cm with thickness of 0.1 cm. The coupons were first degreased with absolute ethanol (James and Akaranta, 2014), immersed in acetone and air dried overnight. The initial mass of metal coupons was recorded and stored in a desiccator before use. The red onion peel (6.25 g) was extracted using ultrasound-assisted extraction unit with 80 vol% methanol (250 mL) as a solvent. The extraction process took 5 min and the mixture was taken out from the ultrasonicator and stirred at 200 rpm for 10 min at room temperature. These two steps were repeated for six times to optimise the extraction process. The mixture was filtered and the methanol was evaporated using a rotary evaporator at 373 K. The residues were collected and weighted. The ROPE was characterised by Fourier Transform Infrared (FT-IR) analysis. The wavelength in the range from 4,000 – 400 cm^{-1} was used. The spectrum was expressed in terms of % transmission against the wavelength.

2.2 Experimentation

To study the effect of inhibitor concentration, five beakers which contained concentrations of 0 (control), 0.5, 1.0, 1.5 and 2.0 g/L of ROPE in 1 M HCl solution at temperature of 303 K were used to determine the corrosion rate of mild steel coupons. The cleaned and weighed mild steel coupons were each fully immersed into the HCl solution. The duplicate sets of experiments were conducted for 7 d. The experiment was repeated for temperature of 313, 323 and 333 K. The temperature of solution was maintained at specified temperature by using a water bath. Each beaker was covered with parafilm to minimise the amount of solution vaporised at elevating temperature. The coupons were retrieved from the HCl solution after 7 d of immersion time. The surface of metal coupon was cleaned using tissue paper and then immersed in absolute ethanol. The surface was cleaned again using tissue paper and then dried in acetone. The weight of the metal coupon was measured using analytical balance. The weight loss for each metal coupon was recorded and tabulated.

2.3 Weight loss determination

Weight loss of mild steel in HCl solution at specified time (W_t) was calculated as in Eq(1) (Iroha et al., 2015):

$$\Delta W_t = W_{initial} - W_t \tag{1}$$

where, $W_{initial}$ is initial weight of mild steel before immersed in HCl solution and W_t is the weight of mild steel retrieved after t days of immersion in HCl solution.

2.4 Corrosion rate and inhibition efficiency

Corrosion rate, CR of the mild steel in hydrochloric acid solution was calculated using Eq(2);

$$\text{Corrosion Rate, CR (mm/y)} = 87.6\left(\frac{\Delta W_t}{\rho . A_s . t}\right) \tag{2}$$

where, W_t is the weight loss, ρ is metal density, A_s is area of metal surface, t is time of exposure. The corrosion rate of mild steel is expressed on the basis of the apparent surface area. The approximated density of mild steel is 7.85 g/cm^3.

Inhibition efficiency (IE) and surface coverage, θ were determined by using Eq(3) and Eq(4):

$$\%\ IE = \frac{CR_{without} - CR_{with\ I}}{CR_{without}} \times 100\ \% \tag{3}$$

$$\theta = \frac{CR_{without} - CR_{with\ I}}{CR_{without}} \tag{4}$$

where $CR_{without}$ and $CR_{with\ I}$ are the corrosion rates in the absence and presence of the extract.

The high corrosion rate of mild steel indicates that the inhibition efficiency of corrosion inhibitor is low, and vice versa.

2.5 Langmuir adsorption isotherm

The linearised Langmuir isotherm equation as in Eq(5) that has been modified is given by (El-Aila et al., 2011):

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \quad (5)$$

where, K_{ads} is equilibrium constant of adsorption, C concentration of inhibitor and n is corrective factor for the linearised Langmuir equation with slope not equal to unity. By plotting a graph of C/θ against C, the value of K_{ads} can be determined from the y-intercept value of the plot.

2.6 Arrhenius equation

Arrhenius equation was used to explain the corrosion phenomenon at higher temperature, as given in Eq(6):

$$CR = A \exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

where, E_a is activation energy, A is pre-exponential factor, R is molar gas constant and T is operating temperature (in K). By taking natural log on both sides of the equation, the plot of linearised Arrhenius equation can be used to determine E_a and A using the slope and *y*-intercept of the graph.

3. Results and Discussions

3.1 FT-IR analysis

Red onion peel extract (ROPE) was characterised using FT-IR spectroscopy. The FT-IR spectrum of ROPE is shown in Figure 1. A peak with broad and intense band at the region of 3,500 - 3,200 cm^{-1} is the O-H stretch of alcohols since antioxidant compound of ROPE is extracted by using methanol. The peaks at wavenumber of 1,622.20 cm^{-1} and 1,438.96 cm^{-1} are due to the C-C stretch of aromatic rings. This showed the presence of polyphenolic component. The peak at wavenumber of 1,622.20 cm^{-1} is also corresponded to the C=O bond (Nnaji et al., 2013). The peaks at 1,276.93, 1,188.20 and 1,065.72 cm^{-1} signalled the presence of C-O-C and C-OH stretch bonds. Bonding of C-H in aromatic ring is corresponded to the peak at wavenumber of 812.07 cm^{-1}. At wavenumber of 614.35 cm^{-1}, the band showed the C-H bend bonding. The analysis above showed the same agreement with that from other studies. The bond that present in the ROPE sample analysed using FT-IR is consistent with quercetin compound (Figure 2) that is mainly found in red onion peel (Lee et al., 2015).

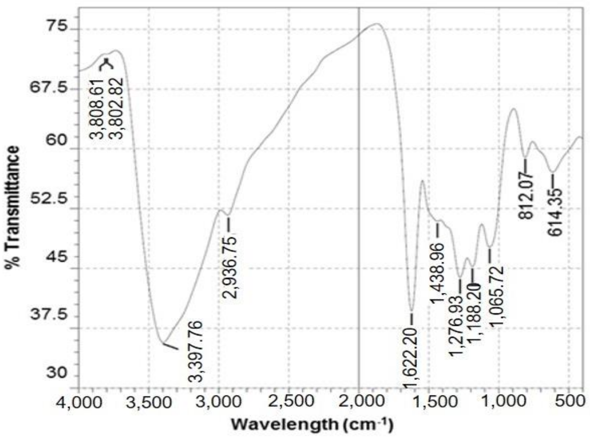

Figure 1: FT-IR spectrum of ROPE

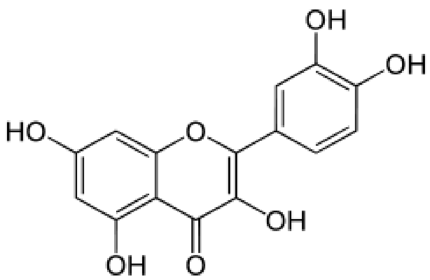

Figure 2: Chemical structure of quercetin that present in red onion peel

3.2 Effect of ROPE inhibitor concentration on its inhibition efficiency

The inhibition efficiency was increased with increasing inhibitor concentration from 0.5 to 2.0 g/L at specified temperature with constant HCl concentration (Figure 3). This is due to the decrease of corrosion rate of mild steel. Since more active molecules are able to be adsorbed on the metal surface at higher concentration of ROPE, thus, prevent the contact between corrosive medium and metal surface (Ibrahim et al., 2011). ROPE with concentration of 2.0 g/L in HCl solution reached its highest inhibition efficiency of 89.97, 89.49, 80.49 and 69.43 % at temperature of 303, 313, 323 and 333 K. The inhibition efficiency of ROPE at each specified temperature showed no significant changes from concentration of 1.5 to 2.0 g/L. This behaviour indicated that ROPE achieved its optimum inhibition ability at concentration of 1.5 g/L. Further increase in the inhibitor concentration did not show any significant increase in inhibition efficiency on mild steel under this operating condition.

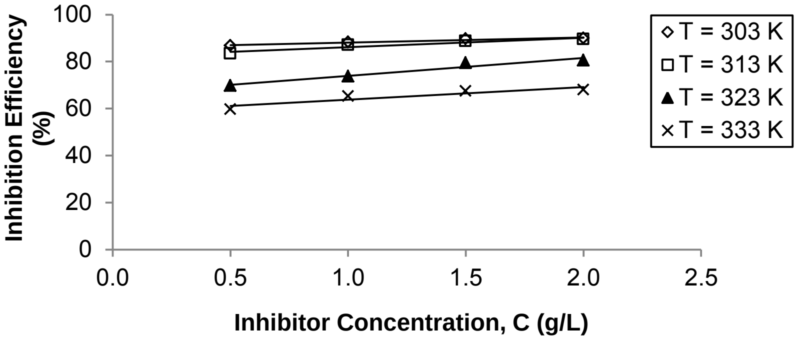

Figure 3: Effect of various concentrations of ROPE on its inhibition efficiency on mild steel in 1.0 M HCl solution at different temperatures

3.3 Effect of temperature on inhibition efficiency of ROPE

From Figure 4, the inhibition efficiency decreased with increasing temperature of corrosive medium. This is due to the increase in corrosion rate of mild steel and decrease in the ability of adsorption process at high temperature. When temperature increased from 303 to 333 K, disintegration of mild steel in HCl solution outweighs the adsorption of ROPE active molecules on the mild steel surface. This can also prove that the adsorption of inhibitor molecule on the metal surface is a physisorption interaction (Kairi and Kassim, 2013).

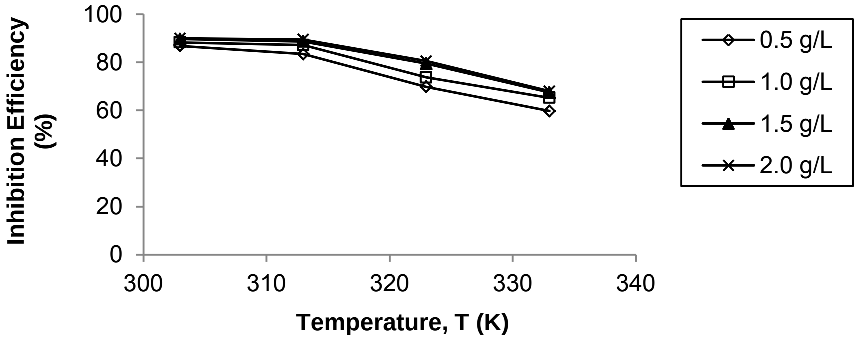

Figure 4: Effect of various temperatures on inhibition efficiency of different concentration of ROPE on mild steel in 1.0 M HCl solution

3.4 Langmuir adsorption isotherm

Figure 5 shows the plots of Langmuir isotherm. The experimental data fit the isotherm with a linear best fit line. The R2 of Langmuir isotherm is closed to unity for temperature range between 303 and 333 K. This demonstrated that ROPE inhibitor obeyed Langmuir adsorption isotherm on mild steel surface. According to Langmuir isotherm model, the adsorption of inhibitor molecules on metal surface is monolayer of adsorbed molecules and even distribution of the molecules at all sites (Masel, 1996). One inhibitor molecule will only be adsorbed on an active site of metal surface. There is no interaction between the adsorbed molecules.

The Langmuir's equilibrium constant of adsorption, K_{ads} can be calculated based on the slope and y-intercept of the linearised Langmuir isotherm equation (5). The K_{ads} values decreased with increasing temperature; i.e K_{ads}, 303 K = 35.83 L g^{-1}; K_{ads}, 313 K = 19.46 L g^{-1}; K_{ads}, 323 K = 7.65 L g^{-1}. This indicates that the interaction between inhibitor molecule and metal surface is weak due to the physical adsorption of the molecules on metal surface (El Rehim et al., 2001). At higher temperature, the inhibitor molecules were desorbed easily from the metal surface due to the weak attraction force with metal surface. This eventually lowered the inhibition efficiency and induced higher rate of corrosion of mild steel at higher temperature.

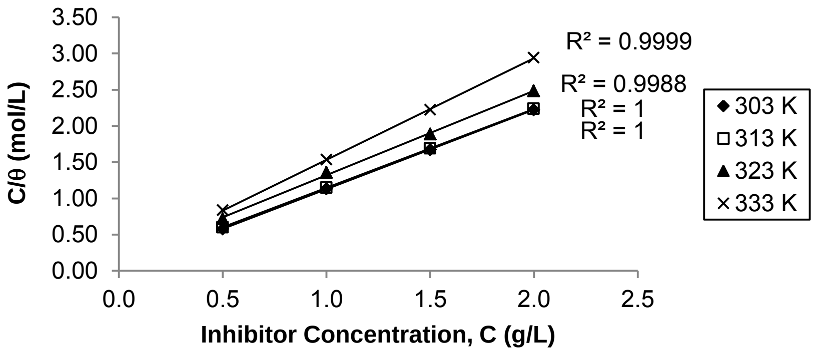

Figure 5: Langmuir isotherm for the adsorption of ROPE on mild steel in 1.0 M HCl solution at different temperatures

3.5 Arrhenius equation

The values of R^2, activation energy and pre-exponential factor for different concentration of ROPE inhibitor are calculated and tabulated in Table 1. The activation energy for acid solution without addition of inhibitor (74.92 kJ/mol) is lower than that with corrosion inhibitor. With the presence of ROPE, the activation energy increased which induced the reduction of corrosion rate. Active molecules of inhibitor are able to be adsorbed on the metal surface easily at high inhibitor concentration (Essa, 2012). More energy is needed to overcome this high activation energy for corrosion of metal surface to proceed. Reducing of available reaction area and changing the activation energy of the anodic and/or cathodic reactions can affect the adsorption of an inhibitor molecule on metal surface. The inhibition of mild steel corrosion is due to the physical adsorption of organic inhibitor on the metal surface with the formation of protective layer.

Table 1: Activation energy and pre-exponential factor of corrosion of mild steel in HCl solution with different concentration of inhibitor.

Concentration of Inhibitor (g/L)	R^2	Activation Energy, E_a (kJ/mol)	Pre-exponential Factor, A
Blank	0.9652	74.92	1.79×10^{13}
0.5	0.9675	108.01	1.13×10^{18}
1.0	0.9566	108.17	1.01×10^{18}
1.5	0.9662	108.68	1.07×10^{18}
2.0	0.9635	109.05	1.18×10^{18}

4. Conclusions

The present study shows that red onion peel extract (ROPE) has successfully retarded the mild steel corrosion in hydrochloric acid solution. Protective film is formed on the metal surface through the interaction between the active site of metal surface and the lone pair of electrons of oxygen atom and/or aromatic ring. These chemical bonds are found in the extract of red onion peel analysed using FT-IR and also consistent with the chemical structure of quercetin. Inhibition efficiency of 90 % by the ROPE inhibitor on the corrosion of mild steel in 1 M HCl solution containing 2.0 g/L of inhibitor at 303 K was achieved through weight loss measurement. Increasing concentration of inhibitor has increased the inhibition efficiency but it decreased with rising temperature. The adsorption of ROPE on the metal surface obeys Langmuir adsorption isotherm. The K_{ads} values decreased with increasing temperature which indicated the physisorption of inhibitor molecules on metal surface. The activation energy observed experimentally has also proposed that the corrosion inhibition was due to the adsorption of inhibitor molecules on the mild steel surface. It is clear from the study that ROPE can be used as an effective solution to the mild steel corrosion in acidic medium.

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