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Synergistic Corrosion Inhibition Effect of Rice Husk Extract and KI² For Mild Steel In H₂SO₄ Solution

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Abstract

Corrosion inhibition effect of rice husk extract as bio corrosion for mild steel in 1M H₂SO₄ solution and the impact of the addition of potassium iodide were investigated by using weight loss method with the variable of solution temperature and bio inhibitor concentration. It was found that the addition of potassium iodide can significantly increase the efficiency value of rice husk extract. The highest efficiency is 95.89% at 1250 ppm inhibitor concentration and 313K temperature. The inhibition efficiency of rice husk extract synergistically increased addition of potassium iodide. The characteristic of adsorption inhibitors was approached by Langmuir isotherm adsorption at all concentrations and temperatures studied. The synergistic of rice husk extract and potassium iodide were examined by thermodynamic and kinetic parameters.

Keywords: corrosion inhibitor; rice husk extract; synergistic; plant extract; mild steel

1. Introduction

The use of mild steel as a corrosion material that occurs in metals is a natural event because it has an impact on maintenance and repair costs in the industry [1]. Factors that cause corrosion include temperature, solution concentration, pH flow rate and so on. Therefore it is necessary to protect the metal so that corrosion can be minimized. Corrosion is a metal deterioration event due to interaction with the environment. The use of acidic solutions is quite large and extensive in the industry, for example acid cleaning, acid descaling, acid pickling and oil well acidizing, so that it requires corrosion inhibitors which aim to be able to withstand corrosion attacks on metal materials [2]. The use of bio corrosion inhibitors continues to be developed because it has the advantages of being biodegradable and does not contain heavy metals or other toxic compounds. Rice husk extract (RHE)

has the potential to be developed into a bio-corrosion inhibitor[3]. RHE contains amorphous silica which is safe, environmentally –friendly. Based on the results of the study, the addition of halide compounds is able to synergistic which affects the increase in the efficiency value of corrosion inhibitors[4-8]. In acid solutions, halides are known to be able to stimulate and inhibit corrosion. The objective of the study is to investigate the synergistic corrosion inhibition effect of RHE and KI for mild steel in H₂SO₄ solution, the authors undertake kinetic and thermodynamic studies of corrosion inhibition.

2. Materials and Methods

2.1. Materials preparation

Mild steel used has a composition (wt%): 0.54Mn, 0.05Si, 0.01S, 0.01P, 0.16C and remaining Fe were used. Coupons are cleaned using 250 - 1000 abrasion paper, then washed with distilled water and cleaned again with acetone and ethanol finally dried in a hot air blower. Weight loss experiments were conducted on mild steel coupons with dimensions of 3 x 2 x 0,5 cm.

2.2. RHE Preparation

The rice husk used is the Ciherang rice husk from Cilegon, Banten Indonesia. The cleaned rice husk is dried in the sun for three days, then burned at 700⁰C for two hours to isolate silica and eliminate other substances. The burning results in the form of white ash, then sieved with a size of 60 mesh. Rice husk ash was weighed 10 grams and extracted by reflux at a temperature of 85⁰C using 1M NaOH solvent for one hour. The extract is filtered to separate the residue and the filtrate. Furthermore, the filtrate was neutralized with 1M HCl by maintaining pH 6.5 - 7. Then the filtrate was deposited for 18 hours until the gel form was precipitated. Then filtered and dried at a temperature of 105⁰C until the weight is constant.

2.3. Weight loss measurements

The samples of mild steel which have been cleaned and weighed initially were soaked in corrosive media, ie 1M H₂SO₄ and bio inhibitors of rice husk extract with a concentration of 0.250,500,750,1000,1250 ppm and KI concentration was 50 ppm for 6 hours at 313K, 333K and 353K. After measurement, the sample is cleaned with running water and dried then weighed as the final mass.

3. Results and discussion

3.1. Weight loss measurements

The corrosion of mild steel in 1M H₂SO₄ in the RHE – KI mixtures was investigated at temperature range of 313 – 353K using weight loss measurements. The calculated values of corrosion rate

(mppy), inhibition efficiency (I.E%) and surface coverage (θ) for mild steel corrosion in 1M H₂SO₄ (blank) and the presence of RHE-KI in combination with different concentration of RHE (250,500,750,1000 and 1250 ppm) and 50 ppm KI at 313 – 353K from the weight loss measurement are shown in table 1. The corrosion rate, inhibition efficiency and surface coverage were evaluated using the following ASTM G31 standard equations :

$$CR \text{ (mppy)} = \frac{87500 \times \Delta W}{A \rho t} \quad (1)$$

where CR is the corrosion rate, ΔW is the weight loss (gram), A is the coupon area (cm²), ρ is the density of mild steel (gram/cm³), t is the immersion time (hours).

$$I.E \% = \left(1 - \frac{CR_{inh}}{CR_{blank}}\right) \times 100 \quad (2)$$

$$\theta = \left(1 - \frac{CR_{inh}}{CR_{blank}}\right) \quad (3)$$

Where CR_{inh} and CR_{blank} are the corrosion rate presence and without inhibitor.

The results shown in table 1 show that the corrosion rate increased with increasing temperature for all concentrations, the highest corrosion rate (813.89 mppy) was obtained at 353K. Based on the corrosion rate and the efficiency of inhibition, RHE and KI have the ability to significantly inhibit the corrosion rate in the acidic environment. The efficiency increases with increasing inhibitor concentration and decreases with increasing temperature. Decreasing the efficiency of inhibition with increasing temperature shows an increase in the solubility of the film and from any corrosion product deposited on the metal surface. Previous researchers also got results like those in this study with various plant extracts[6, 7, 9, 10]. One of the possible mechanisms of corrosion inhibition occurs is the adsorption inhibitor to the metal surface that blocks the corrosion process. Heteroatoms such as oxygen, nitrogen, phosphorus and sulfur enable the adsorption process, because they are considered as the adsorption center[11, 12]. In the RHE structure there are oxygen and sulfur atoms which have free electron pairs and phi electrons. The compound could be adsorbed because of the interaction between the free electron pair of oxygen and sulfur at the mild steel surface. This process occurs because of the presence of d-vacant orbital of iron, because iron is a transition metal. Protonated species formation due to the electrostatic interaction between organic molecules and metal surface[13].

3.2. Adsorption consideration

The trend in inhibition efficiency with temperature for RHE + KI on surface of mild steel is decrease

with increase in temperature, langmuir isotherm adsorption is comfort to describe it. For studying the natural interaction between molecule inhibitor and metal surface then isotherm adsorption is used. The weight loss method is used to obtain the degree of surface coverage (θ). The preferred adsorption method is isotherm adsorption Langmuir. Equivalent Langmuir adsorption isotherm equations[10] :

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + C \quad (4)$$

where C is the concentration of the inhibitor, θ is the surface coverage, and K_{ads} is the adsorption equilibrium constant. Langmuir isotherm assumes that a solid surface has a fixed number of adsorption sites and each site has one adsorbed species[14]. For Determining of K_{ads} value by plotting a $\log (C / \theta)$ vs. C, is shown in Figure 1.

The value of K_{ads} is obtained from the linear results of the plot (C / θ) vs. (C). The K_{ads} value shows the strength between asorbate and adsorbent. The greater the K_{ads} value, the adsorption will be efficient and effective.

the value of k_{ads} from the calculation results shows (Table 3.) that the higher the temperature of the K_{ads} value decreases. It means that the strength between adsorbate and adsorbent decreases with increasing temperature.

3.3. Kinetics and Thermodynamic studies

In acidic solution the corrosion rate is related to temperature by Arrhenius equation, according to Arrhenius equation of the logarithm of corrosion rate (Log CR) is a linear function with $1/T$ [10, 15, 16] :

$$\text{Log CR} = \log A - \frac{E_a}{2.303 RT} \quad (5)$$

Where CR is corrosion rate, E_a is activation energy, A the Arrhenius constant, R the molar gas constant and T is the absolute temperature. The activation energy was determined by slopes of $\log CR$ versus $1/T$ graph depicted in figure.2.

Kinetic parameter of activation energy is important to study the inhibitive mechanism. If the E_a value increases, it can be interpreted as physical adsorption. Conversely, if the E_a value decreases, it is possible to chemisorption[9, 17]. the results in table 2 show that the tendency is chemisorption.

Free energy of adsorption, ΔG_{ads}° values were obtained from intercept of fig.1. The equation is using :

$$\Delta G_{ads}^{\circ} = -R \times T \ln(55,5 \times K_{ads}) \quad (6)$$

Where R is the gas constant, T is absolute temperature, $\Delta G^{\circ}_{\text{ads}}$ is standard free energy of adsorption and C_{water} is the concentration of water.

the calculated value of $\Delta G^{\circ}_{\text{ads}}$ can be seen in Table 4 shows that the process takes place spontaneously, meaning the formation of the film layer by RHE + KI on the surface of mild steel takes place immediately. The value of $-\Delta G^{\circ}_{\text{ads}}$ is at. 10.66 kJ/mol - 11.243 kJ/mol.

3.4. Synergistic Effect

Synergism is the effect of the combined action of a compound that has a better ability than the effect of individual abilities. Synergistic inhibition is the most effective way to increase the ability of inhibitors to inhibit corrosion rate and also to reduce the use of inhibitors in acidic media. Synergism inhibitors are able to work because of interactions between inhibitor components or due to interactions between inhibitors and one of the ions in aqueous solutions. The use of iodide ions is often attributed to the radius of a large atom, high electronegativity and hydrophobicity compared to other halide ions [18].

The inhibitory efficiency with the addition of KI is higher in value than using RHE only. This result has been done by previous researchers[8, 9, 19]. The relationship between efficiency and concentration of each inhibitor added by KI can be shown in Figure 1.

4. Conclusion

1. RHE + KI is effective as synergistic bio-corrosion Inhibitor for the corrosion of mild steel in H_2SO_4 solution.
2. The inhibition efficiency increases with increasing concentrations of RHE + KI.
3. Synergistic effects between RHE and KI have been observed. The addition of KI enhances the inhibition efficiency significantly.
4. The adsorption of RHE + KI onto mild steel surface was a spontaneous process.

Aknowledgement

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TABLE CAPTIONS

Table 1. Calculated values of corrosion rate (mppy), Inhibition efficiency (%) and degree of surface coverage (θ) for mild steel corrosion in 1M H₂SO₄ for different concentration at 313 – 353K from weight loss measurements.

Table 2. K_{ads} Values

Table 3. Activation energy for mild steel in 1M H₂SO₄

Table 4. ΔG_{ads}° values

FIGURE CAPTIONS

Figure.1. Langmuir isotherm for the adsorption of RHE+KI on mild steel in 1M H₂SO₄ at 313 K, 333K and 353 K

Figure.2. Arrhenius plot for mild steel corrosion in 1M H₂SO₄ in the absence and present RHE and KI

Table 1.

Concentration ppm	Corrosion rate (mmpy) , Inhibition efficiency (%) and degree of surface coverage (θ)								
	313 K			333K			353K		
	CR	%E.I	θ	CR	%E.I	θ	CR	%E.I	θ
Blank	575,7	0	0	706,69	0	0	813,89	0	0
250 RHE + 50 KI	191,6	66,72	0,67	313,86	55,59	0,56	527,01	35,25	0,35
500 RHE + 50 KI	178,13	69,06	0,69	243,24	65,58	0,66	461,98	43,24	0,43
750 RHE + 50 KI	162,04	71,85	0,72	190,21	73,08	0,73	401,07	50,72	0,51
1000 RHE + 50 KI	148,66	74,18	0,74	173,18	75,49	0,75	331,6	59,26	0,59
1250 RHE + 50 KI	121,6	78,88	0,79	161,29	77,18	0,77	280,98	65,48	0,65

Table 2.

Temperature K	K _{ads}	R-square
313	1,08354	0,99
333	0,91810	0,99
353	0,83072	0,99

Table 3.

Systems/Concentration	Activation energy Ea (kJ/mol)
Blank	0,959
250 ppm RHE +50 ppm KI	2,7906
500 ppm RHE + 50 ppm KI	2,6115
750 ppm RHE + 50 ppm KI	2,4685
1000 ppm RHE + 50 ppm KI	2,1863
1250 ppm RHE + 50 ppm KI	2,2961

Table 4.

Temperature K	ΔG ads, J/mol
313	-10660,55
333	-10883,02
353	-11243,13

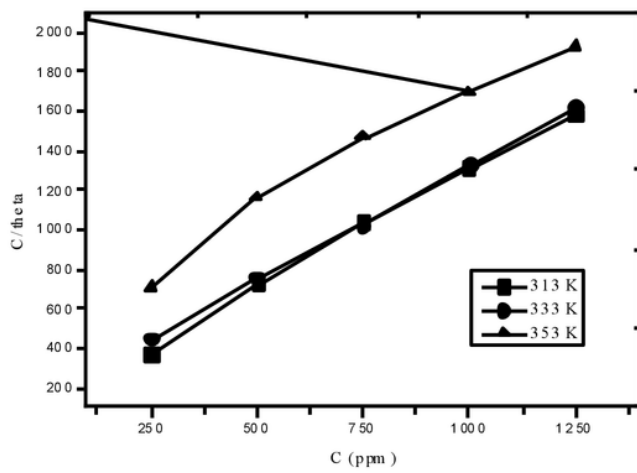


Figure.1.

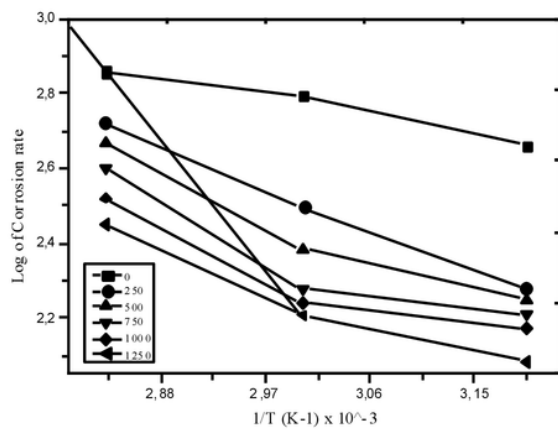


Figure 2.

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