Effect of Halide Concentration on the Effectiveness of Banana Peel Waste Inhibitor at 60^0C

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Abstract—**Organic inhibitors have been widely studying to be an alternative corrosion prevention because of its abundance and non-hazardous effect to the environment. One of organic inhibitors which is obtained from plant extract is banana (*Musa Paradisica*) peel, because it has gallocatechin which is a strong antioxidant. Otherwise, inhibition effectiveness from organic compound decreases during increasing of temperature. However, the addition of other substance like halide ion has provided multiple effect of corrosion inhibitor effectiveness. The addition of the halide ions can enhanced the inhibition efficiency of the organic inhibitors. This research highlights the effect of additional halide concentration to the inhibition effectiveness of *Musa Paradisica* (banana) peel on API 5 L steel in 3,5% NaCl at temperature 60^0C. This inhibition performance is investigated using weight loss measurement and electrochemical measurement. Result shows that the maximum inhibition efficiency was observed with the mixture of 500 ppm banana peel waaste extract and 100 ppm potassium iodide at 60^0C. Also, The blends behaved as mixed type inhibitor. The effectiveness was found to be in order of KI > KBr due to the larger ionic radius in iodide ion.**

Keywords— **Banana Peel Waste, Halide Concentration, Organic Inhibitor, Temperature 60˚C.**

I. INTRODUCTION

Iron and alloys are one of the most consumed metals for constructional and industrial applications [1] especially carbon and low alloy steels which are the most commonly used material for pipeline in oil and gas industry. Corrosion attack can be happened in mild steel which involves the electrochemical reaction and can cause the degradation and damage to the properties of attacked material. Usually, temperature and salt content are high in oil and gas transmission medium ground medium and drilling fluid [2]. One of the methods to prevent corrosion attack is inhibitor, the use of inhibitors is one of the most practical methods for the surface protection against the corrosive media. So, it is great to examine the corrosion inhibitor resistance in high temperature and salt content.

Scientists have focused their research on green corrosion inhibitors from various plant biomass because of their low operating cost and non-hazardous environmental effect [3][4][5], and [6]. One of plant extract that can be utilized as corrosion inhibitor is banana (*Musa Paradisica*) peel waste. However, most of banana peel extract was found more efficient in corrosion inhibition of steel than other studied extracts, because gallocatechin is a stronger antioxidant than catechin [7][8]. But, it is known that the effectiveness of organic inhibitor decreased while the temperature increased [9]. Some types of synergetic chemical matter like halide ion when added to organic inhibitor sometimes can increase the efficiency of corrosion inhibitor in high temperature [10].

The objective of this present study is to investigate the effect of halide ions addition namely potassium iodide and potassium bromide in the effectiveness of inhibition efficiency of banana peel waste (BPW) in concentration of 500 ppm against API 5L grade B corrosion in 3,5% NaCl solution at high temperature especially at temperature 60^0C. Approximately 36 million tonnes of banana peel is generated every year and this is a potential material for further utilization [11]. Hence, the blends from BPW would be cheap, renewable, non-toxic and abundant.

TABLE 1.
EFFICIENCY OF EACH MIXTURE ON WEIGHT LOSS TESTING

Temperature	Testing	Corrosion rate (mmpy)	Efficiency (%)
60^0C	-	0.9618	-
	500 ppm BPW	0.4707	51.060
	500 ppm BPW + 25 ppm KI	0.3553	63.060
	500 ppm BPW + 50 ppm KI	0.3092	67.849
	500 ppm BPW + 75 ppm KI	0.2820	70.680
	500 ppm BPW + 100 ppm KI	0.2539	73.594
	500 ppm BPW + 25 ppm KBr	0.3766	60.846
	500 ppm BPW + 50 ppm KBr	0.3342	65.254
	500 ppm BPW + 75 ppm KBr	0.3111	67.650
	500 ppm BPW + 100 ppm KBr	0.2919	69.644

II. METHOD

A. Material Preparation

Test were performed using steel type API 5L Grade B with dimension 2 cm x 2 cm x 0.3 cm for both of weight loss and potentiodynamic polarization measurement. Material was polished with silicon carbide abrasive paper from grade 400-1200 then cleaning using aceton and dried in warm air. For potentiodynamic polarization, material was covered with epoxy resin.

B. Inhibitor Preparation

The fine powder of banana peel was mixed with solvent 70% methanol and 30% distilled water for 72

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TABLE 2.
PARAMETER RESULTS ON POLARIZATION TESTING

Testing	E_{corr} (V)	I_{corr} (x 10^{-6} Am/cm^2)	Tafel slope b_a (mV/dec)	Tafel slope b_c (mV/dec)	Corrosion Rate (mmpy)	Efficiency (%)
Blank	-0.78757	79.41	149.02	119.8	0.9269	-
500 ppm BPW	-0.78261	44.099	104.08	90.137	0.51179	44.4667
500 ppm BPW + 100 ppm KBr	-0.76088	28.454	111.08	65.194	0.33212	64.1682
500 ppm BPW + 100 ppm KI	-0.75122	11.132	103.86	113.31	0.12993	85.9816

TABLE 3.
PARAMETER RESULTS ON EIS TESTING

Testing	Rs(Ωcm^2)	Rp(Ωcm^2)	Cdl(μF/cm^2)	%EI
None	1.834	50.08	110.92	-
500 ppm BPW	3.949	23.63	44.13	53.5579
500 ppm BPW + 100 ppm KBr	4.006	44.76	46.9	54.2187
500 ppm BPW + 100 ppm KI	4.071	30.19	53.7	54.9496

hours with ratio between powder and solvent is 1:10. The extraction method using maceration process.

C. Weight Loss Measurement

In weight loss measurement, the prepared material were suspended in 3.5% NaCl test solution at 60ºC for 24 hours with absence and presence inhibitor. Three types of inhibitor that will be used. First only using inhibitor with concentration 500 part per million (ppm). Second, mixture of inhibitor and potassium iodide (KI) with concentration of inhibitor 500 ppm and KI 25 ppm, 50 ppm, 75 ppm and 100 ppm. Third, mixture of inhibitor and potassium bromide (KBr) with concentration of inhibitor 500 ppm and KI 25 ppm, 50 ppm, 75 ppm and 100 ppm. The corrosion rate (mmpy) was calculated using formula (1) :

$$CR = \frac{K\,W}{D\,A\,T} \quad (1)$$

where K is constant, W is different of weight before and after immersion (gr), D is density (gr / cm3), A is surface area of immersion material (mm) and T is time (hour). The inhibition efficiency (IE) of inhibitor was calculated using formula (2) :

$$\text{IE (\%)} = \frac{CR_1 - CR_2}{CR_1}\ x\ 100 \quad (2)$$

where CR_1 is corrosion rate in the absence of inhibitor and CR_2 is corrosion rate in the presence inhibitor [12].

D. Electrochemical Measurement

Electrochemical measurement method is used to know the electrical properties of the inhibitor were conducted with conventional three electrode arrangement. Material specimen with 2x2x0,3 cm steel specimen size were used as working electrode, graphite rod as counter electrode and saturated calomel electrode (SCE) as reference electrode. The experiment was held in solution for 30 minutes to obtain stable state without stirring in temperature 60^{0}C.

The Polarization Testing is based on standard (ASTM G5: Potentiostatic and Potentiodynamic Polarization Measurements), and some parameters such as potential (Ecorr), corrosion current density (i_{corr}), tafel slope and corrosion rate in open circuit potential (OCP) with scan rate 1mV•s^{-1} using Corrtest Studio 5 version 5.2 software. The inhibition efficiency (IE) were calculated using formula (3)

$$\text{IE (\%)} = \frac{i_{corr} - i^{(1)}{}_{corr}}{I_{corr}}\ x\ 100 \quad (3)$$

where i_{corr} and $i^{(1)}{}_{corr}$ is corrosion current density without and with inhibitor, respectively [13].

The EIS test uses standard (ASTM G 59: Polarization Resistance Measurements), using frequency intervals of 10000 to 0.1 Hz with 1mV amplitude observed in Zview Corrtest Software with some parameters such as Resistance solution (Rs), Resistance polarization (Rp), Coefficient double layer (Cdl) By Nyquist plot. With the efficiency using formula (4) and (5),

$$Cdl = \frac{1}{2\pi f R_p} \quad (4)$$

$$\%EI = \frac{Rp_1 - Rp_2}{Rp_1} \times 100 \quad (5)$$

where f is the frequency (Hz), Rp_1 is the polarization resistant without the inhibitor and Rp_2 is polarization resistant with the inhibitor [13].

III. RESULTS AND DISCUSSION

A. Wieght Loss Measurement

The corrosion of API 5L grade B steel in 3,5% NaCl solution in the absence and presence of banana peel waste (BPW) as inhibitor and the mixture of halides including Potassium Iodide (KI) and Potassium Bromide (KBr) was studied using weight loss measurement at temperature 60^{0}C. Table 1 gives the values of the corrosion rate and the inhibition efficiency as a function of the presence of 500 ppm inhibitor and halide concentration.

From Table 1, it is known that banana peel waste (BPW) can reduces the corrosion rate and the inhibition efficiency of BPW is increased with the increasing concentration of halide. The reason that banana peel can reduces the corrosion rate can be explained as adsorption of organic matters of the extract on metal surfaces which increased the surface coverage area as well as declining corrosion rate [8]. From the Table 1 it is also known that the addition of halide reduces the corrosion rate of API 5L grade B steel at temperature 60^{0}C. The maximum inhibition efficiency was found in the addition of 100 ppm halide in Potassium Iodide and Potassium Bromide addition. The results reveal that there is a synergistic effect between inhibitor molecules and halide ions. The addition of KI reduces the corrosion rate larger than the addition of KBr. The order of inhibition efficiency of halide ions were KI > KBr with percentage of inhibition efficiency given by the highest concentration of each halide ions (100 ppm) where KI (73,594 %) followed by KBr (69,645 %).

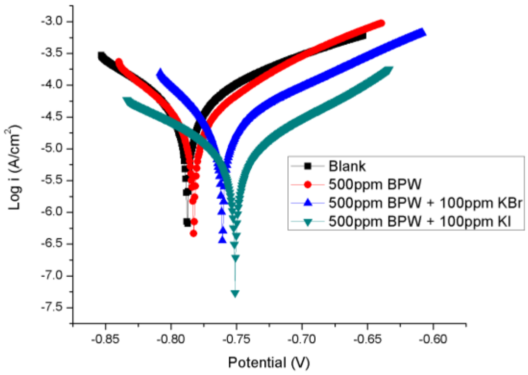

Figure 1. Tafel Polarization Curve in Different Conditions at 60⁰C.

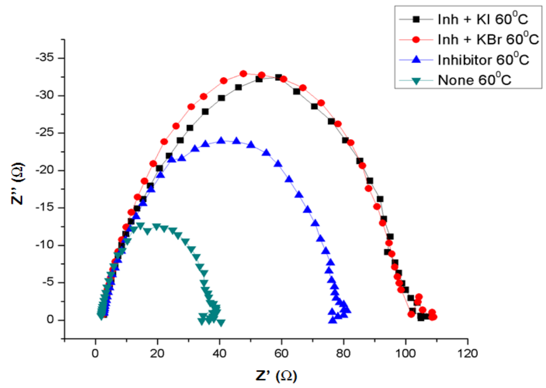

Figure 2. Nyquist Curve EIS Testing in Different Conditions at 60⁰C.

The synergistic effect of each halide concentration in all measurement was found to increase in order Br^- < I^-, which seems to indicate that the radii of halide ions may influence this effect. The iodide ion has the radius of 1.35 Å is more influence to adsorption than bromide ion which has the radius of 1.14 Å. Because of the larger ionic radius, the iodide ion has higher hydrophobicity as compared to the bromide ion [14]. The adsorption of I^- ions onto the metal surfaces will decrease the hydrophilicity of the metal surfaces, which is likely to promote the adsorption of organic molecule in replace of the water molecules. Thus, the inhibition efficiency of BPW is enhanced to a considerable extent in the presence of KI.

B. Polarization Measurement

In order to study further about the inhibitor mechanism and the type of inhibitor of BPW at temperature 60⁰C, polarization curve experiment was conducted. Figure 1 shows the potentiodynamic polarization behaviour of API 5L grade B in 3,5% NaCl solution in the absence and presence of banana peel waste (BPW) as inhibitor and the mixture of 100 ppm halides.

The corrosion electrochemical parameters, such as corrosion potential (E), cathodic and anodic Tafel slopes (b_c and b_a) and corrosion current density (i) obtained by extrapolation of Tafel lines and the inhibition efficiency are shown in the Table 2.

It is clear from the figure that the E_{corr} values were shifted positively in the addition of inhibitor and the combination with KBr and KI. The result in the Table shows that i_{corr} decreased when BPW was added with the halide ions. This fact indicating that the addition of halide ions in BPW inhibitor retard corrosion rate of API 5L Grade B sample in 3.5% NaCl solution. If the value (Ecorr = Ecorr uninhibited -Ecorr inhibited) is more than 85mV including anodic or cathodic inhibitor whereas if the value is less than 85mV including mixing inhibitor [15]. As can be seen from the electrochemical parameters, the largest displacement of corrosion potential of API 5L grade B steel shifted less than 85 mV after BPW and halide ion addition. So, this mixture between BPW and halide ion was classified as mixing inhibitor.

C. Electrochemical Impedance Spectroscopy Measurement

The corrosion of API 5L grade B steel in 3,5% NaCl solution in the absence and presence of banana peel waste (BPW) as inhibitor and the mixture of halides including Potassium Iodide (KI) and Potassium Bromide (KBr) was studied using electrochemical impedance spectroscopy measurement at temperature 60⁰C as shown in Figure 2. Table 4 gives the values of some impedance parameters such as Resistance solution (Rs), Resistance polarization (Rp), and Coefficient double layer (Cdl).

The depressed form of semicircles is often referred to as frequency dispersion which has been attributed to surface heterogeneity of structural or interfacial origin such as those found in adsorption processes. The surface heterogeneity usually results from surface roughness, impurities or dislocations, fractalstructures, distribution of activity centers, adsorption of inhibitors, and formation of porous layers [16].

As can be seen in Figure 2 the capacitive reactance arc radius increases gradually after adding the BPW inhibitor, potassium bromide + BPW and potassium iodide + BPW. From Table 3 it is known that the maximum inhibition efficiency occurs in the addition of 100 ppm halide in Potassium Iodide and Potassium Bromide addition where the inhibition efficiency of potassium iodide adding is greater than potassium bromide adding.

The EIS measurement reveals that the mixture of 500 ppm BPW and 100 ppm potassium iodide, the percentage of inhibition efficiency is highest (54,95 %). The result strongly support the observation that the mixture of 500 ppm BPW and 100 ppm potassium iodide could work best as an inhibitor at 60⁰C.

IV. Conclusion

From the result of this study, it is concluded that BPW inhibits the corrosion of API 5 L grade B in 3,5% NaCl solution at temperature 60⁰C. Synergistic effect between BPW and halide ions (KI and KBr) have been studied. The maximum concentration of adding halide was 100 ppm. The addition of both halide ions synergistically improve the inhibition efficiency of BPW. The synergism was found to be in order of KI > KBr due to the larger ionic radius in iodide ion. From Tafel Polarization study, it is revealed that the mechanism of blend was mixing inhibitor.

References

[1] N. Singh, B. Singh, and B. Gaur, "The Role of Metal Cations in Improving the Inhibitive Performance Of Hexamine On The Corrosion Of Steel In Hydrochloric Acid Solution," *Corros. Sci*, vol. 37, pp. 1005–1019, 1995.

[2] J. Zhang, X. Sun, Y. Ren, and M. Du, "The Synergistic Effect Between Imidazoline-Based Dissymmetric bis-Quaternary Ammonium Salts and Thiourea Against CO2 Corrosion at High Temperature," *J Surfact Deterg*, vol. 18, pp. 981–987, 2015.

[3] M. Krishnegoweda, V. T. Venkatesha, P. K. M. Krishnegoweda, and S. B. Sivayogiraju, "Acalypha Torta Leaf Extract as Green Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution," *Ind. Eng. Chem. Res.*, vol. 52, pp. 722–728, 2013.

[4] S. Deng and X. Li, "Inhibition By Ginkgo Leaves Extract of The Corrosion of Steel in HCl and H2SO4 Solutions," *Corros. Sci*, vol. 55, pp. 407–415, 2012.

[5] K. Abiola and A.O. James, "The effect of Aloe Veraextract on Corrosion and Kinetics of Corrosion Process of Zinc in HCl Solution," *Corros. Sci*, vol. 52, pp. 661–664, 2010.

[6] Y. El-Etre, "Inhibition of Aluminium Corrosion Using Opuntia Extract," *Corros. Sci*, vol. 45, pp. 2485–2495, 2003.

[7] S. Someya, Y. Yoshiki, and Kazuyoshi Okubo, "Antioxidant Compounds From Bananas (Musa Cavendish)," *Food Chem*, vol. 79, pp. 351–354, 2002.

[8] S. Ji, S. Anjum, Sundaram, and R. Prakash, "Musa Paradisica Peel Extract As Green Corrosion Inhibitor for Mild Steel in HCl Solution," *Corros. Sci.*, vol. 90, pp. 107–117, 2015.

[9] M. Sangeetha, S. Rajendran, S. Muthumegala, and A. Krishnaveni, "Green Corrosion Inhibitor : An Overview," *Zast. Mater.*, vol. 52, pp. 3–19, 2011.

[10] M. Finsgar and J. Jackson, "Application of Corrosion Inhibitors for Steels in Acidic Media for The Oil And Gas Industry: A Review," *Corros. Sci.*, vol. 86, pp. 17–41, 2014.

[11] T. Vu, C. J. Scarlett, and Q.V. Vuong, "Phenolic Compounds Within Banana Peel And Their Potential Uses: A Review," *J. Funct. Foods*, vol. 40, pp. 238–248, 2018.

[12] M. Shyamala and P. K. Kasthuri, "The Inhibitory Action of the Extracts of Adathoda vasica, Eclipta alba, and Centella asiatica on the Corrosion of Mild Steel in Hydrochloric Acid Medium: A Comparative Study," *Hindawi Publ. Corp.*, pp. 852–827, 2012.

[13] R. Aslam, M. Mobin, J. Aslam, and H. Lgaz, *Sugar Based N,N'-Didodecyl-N,N' Digluconamideethylenediamine Gemini Surfactant As Corrosion Inhibitor for Mild Steel in 3.5% NaCl Solution-Effect of Synergistic KI Additive*. Springer Nature Publisher, 2018.

[14] R. Solmaz, M. E. Mert, G. Kardaş, B. Yazici, and M. Erbil, "Adsorption and Corrosion Inhibition Effect of 1,1′-Thiocarbonyldiimidazole on Mild Steel in H2SO4 Solution and Synergistic Effect of Iodide Ion," *Acta Physico-Chimica Sin.*, vol. 24, no. 7, pp. 1185–1191, Jul. 2008.

[15] M. Ridhwan, A. Rahim, and A.M. Shah, "Synergistic Effect of Halide Ions on the Corrosion Inhibition of Mild Steel in Hydrochloric Acid using Mangrove Tannin," *Int. J. Electrochem. Sci*, pp. 8091–8104, 2012.