CURCUMINOID COMPOUNDS ISOLATED FROM *Curcuma domestica* Val. AS CORROSION INHIBITOR TOWARDS CARBON STEEL IN 1% NaCl SOLUTION

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ABSTRACT

The corrosion inhibitor of carbon steel in 1% NaCl solution by curcuminoids has been studied at 27°C using weight loss and electrochemical method. The determination of corrosion inhibition efficiency (%eff) utilizing weight loss method at the concentration of 80 ppm showed the result 78.70% for third isolated fraction. Further determination utilizing Tafel method showed the following results: raw pure extract of curcuminoid gave 89.88% at 50 ppm; the first isolated fraction gave 46.50% at 80 ppm; the second isolated fraction gave 44.83% at 30 ppm; and the third isolated fraction gave 92.44% at 70 ppm. Based on the analysis of Tafel extrapolation curve, it is showed that the raw pure extract and the third fraction of curcuminoid acted as anodic inhibitor, whereas the first and the second fraction performed as cathodic inhibitors. The evaluations of synergism parameter (S_θ) indicate that the enhanced in inhibition efficiency towards raw pure extract was caused by the present of second and third fraction as cathodic and anodic inhibitor. The contribution of steric hindrance of methoxy groups in curcuminoid structure causes the decrease in curcuminoids activity to be adsorbed on the electrode (carbon steel) surface.

Keywords: *corrosion inhibitor, Tafel, anodic inhibitor, cathodic inhibitor, synergism parameter*.

INTRODUCTION

Highly available natural resources, which still assumed in having low value, should be explored and manufactured to become higher values materials. One way to enhance the value of materials is the use of organic compounds as corrosion inhibitors. Up to now, organic corrosion inhibitor containing heteroatom O, N, S, as well as aromatics and double bonds functional groups is the most effective organic inhibitor ever used. Curcuminoids are dyes stuff derived from curcuma (*Curcuma domestica* Val.) having various functional groups, which are methoxy ($-OCH_3$), carbonyl (C=O), hydroxyl (-OH), double bonds, and benzene. Those functional groups fulfill the requirements as a potent organic corrosion inhibitor (Jones, 1992; Kelly et.al, 2003, Bundjali, 2005). The aim of this study is to investigate the effectiveness of curcuminoids derived from curcuma (*Curcuma domestica* Val.) as organic corrosion inhibitor and which one of curcuminoids in curcuma having dominant role towards the efficiency of inhibitors.

MATERIALS AND METHODS

Curcuma used in this study obtained from traditional market at Lembang, Bandung, West Jawa, Indonesia. The main material studied is curcuma dyes stuff that is known as curcuminoids, which consist of three main fractions (components). The metal used in this study is carbon steel produced by Krakatau Steel.

PREPARATION OF CURCUMINOIDS

Dried powdered rhizome of curcuma (60 g) was Soxhlet extracted using 200 mL dichloromethane. The dichloromethane extract was washed using 60 mL hexane and crystallized to give 6.5 g of orange crystal. The crystal was subjected to a silica gel column vacuum chromatography and was eluted with various combinations acetone-dichloromethane-methanol. Three main curcuminoids were separated in three fractions. For the identification of all fractions, their FTIR and NMR analysis were compared with those previously reported.

ANALYSIS

The analysis was performed on curcuminoid compounds of the three fractions isolated from curcuma. The purity tests of curcuminoids were carried out by TLC and the functional groups analysis were performed by FTIR and NMR. The physical properties analysis was performed by the measurements of melting points, solubility tests and crystal imaging by photographic capture. The corrosion inhibition efficiency of curcuminoids derived from curcuma toward carbon steel in 1% NaCl solution was determined utilizing weight loss method and potentiodynamic polarization Tafel method. Both methods were carried out toward raw pure extract of curcuminoid and the three fractions isolated and purified from the extract after purification process.

WEIGHT LOSS MEASUREMENTS

Carbon steel coupons size; length 2 cm, width 1 cm, and thickness 0.75 cm with composition (wt%): 0.23% Mn, 0.06% C, 0.05% Al, and 99.56% Fe were immersed in 50 mL in inhibited (80 ppm) and uninhibited 1% NaCl solutions and allowed to stand for 10 days at 27^{o}C. Inhibition efficiencies were calculated from the differences of weight-loss values in the presence and absence of inhibitors.

POTENTIODYNAMIC POLARIZATION STUDY

Potentiodynamic polarization studies-cathodic and anodic polarization curves were recorded using Potentiostate/Galvanostate PGZ 301 Volta Lab. 30 model . The concentration range of inhibitor employed 10 ppm to 90 ppm in 1% NaCl solutions. Carbon steel was used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and platinum as the counter electrode. The specimens were aerated using CO_2 gas for 20 minutes before polarization tests.

RESULTS AND DISCUSSION

FTIR AND NMR SPECTRA ANALYSIS

The comparison analysis between infrared spectrums obtained from FTIR measurements of the first, second and third fraction of curcuminoids showed the decrease in the absorption intensity at wave numbers regions of 2854.65 – 2970.38 cm^{-1} that significantly present in the spectra of the second and third fraction showed the most decrease intensity. This phenomenon was assumed to be originated from the decrease in the amount of fatty acid. The decrease amount of methoxy (-OCH_3) groups in the structure of the third fraction that showed in the decrease of absorption intensity at 1512.19 cm^{-1} and 1431.18 cm^{-1}. Further analysis used ^{1}H-NMR and ^{13}C-NMR spectroscopy showed that the first fraction consists of therpenoid compounds, the second fraction is curcumin, and the third fraction consist of bisdemethoxycurcumin, demethoxycurcumin, and curcumin. The analysis of H-NMR for first fraction showed the present of curcumin in a few and the other are therpenoid or fatty acid. This fact appropriate with the other analysis that showed the non-polar fractions in curcuma except curcuminoids are fatty acid and terpenoids compounds (Rosmawani et.al, 2006; Triyani, 2008).

WEIGHT LOSS MEASUREMENTS

Weight loss data of carbon steel in 1% NaCl solutions in the absence and presence of inhibitors were obtained and are given in Table 1. The weight loss data in a year were calculated according to:

$$W_{corr(g/Y)} = \left(W_0 - W_f\right) x \frac{\Sigma days\ in\ a\ year}{\Sigma days\ used\ in\ experiment} \qquad (1)$$

where W_o and W_f are the weight of carbon steel (in gram) before and after immersed in the 1% NaCl solutions. The losses of volume were calculated by using the following equation:

$$V_{corr\ (mm^3/Y)} = \frac{W_{corr}}{\rho_{steel}} \qquad (2)$$

Where ρ_{steel} is the density of carbon steel (7.8 g/cm^3), and the corrosion inhibition efficiency (%eff) were calculated by:

$$\%eff = \frac{(W_{corr} - W_{corr(inh)})}{W_{corr}} x100\% \quad (3)$$

Where W_{corr} and $W_{corr(inh)}$ are the weight loss of carbon steel in the absence and presence of inhibitors.

Table 1. Corrosion parameter for carbon steel in 1% NaCl solutions in the presence and absence of different fraction of curcuminoids inhibitor obtained from weight loss measurement at 27^{o}C

Inhibitor	**Coupon weight before immersed (g)**	**Coupon weight after immersed (g)**	**Weight loss (g/Y)**	**Volume loss (mm^3/Y)**	**%eff**
Blank	0.9298	0.9214	0.3024	38.77	-
KurK	0.8662	0.8600	0.2232	28.62	26.63
KurF1	0.9212	0.9143	0.2484	31.85	18.34
KurF2	0.8593	0.8530	0.2268	29.08	25.44
KurF3	0.9170	0.9152	0.0648	8.31	78.70

Note: raw pure extract = KurK; first fraction = KurF1; second fraction = KurF2; third fraction = KurF3

The determination of corrosion inhibition efficiency utilizing weight loss method showed the result 78.70% for the third fraction, which means that the third fraction can effectively be used as corrosion inhibitor. The influence of the third fraction cause the decreased rate of corrosion, hence the loss of volume and loss of weight are insignificant.

POTENTIODYNAMIC MEASUREMENTS

The corrosion inhibition efficiency (%eff) at different concentrations of the curcuminoids in 1% NaCl solutions was calculated from the corresponding electrochemical polarization measurements according to:

$$\%\,eff = \frac{(i_{corr} - i_{corr(inh)})}{i_{corr}} x100\% \quad (4)$$

Where i_{corr} and $i_{corr(inh)}$ (in mA/cm^2) are the corrosion current density in the absence and presence of inhibitors. The values of %eff are also included in Table 2. The result showed that the ability as high potent corrosion inhibitor of the pure extract and the third fraction is comparable to the increase in inhibitor concentration. The increase in corrosion inhibition activity of the raw pure extract was caused by the presence of the third fraction in the raw pure extract, which has the capability to adsorb onto metal surface and assisted by the combination act of the first and second fraction.

Table 2. The electrochemical polarization parameters for the carbon steel in 1% NaCl solutions containing different concentration of curcuminoids fractions

Inhibitor	C (ppm)	E_{corr} (mV)	Rp (ohm.cm^2)	Ba (mV)	Bc (mV)	I_{corr} (μA.cm^{-2})	V_{corr} (mm/Y)	%eff
Blank	-	-637.10	241.80	64.60	-174.70	184.07	2.17	-
KurK	10	-661.80	317.94	41.40	-96.30	99.18	1.17	46.12
	30	-649.00	384.70	34.40	-85.30	65.07	0.77	64.65
	50	-630.00	1040.00	33.10	-128.10	18.63	0.22	89.88
	70	-646.80	574.82	35.50	-162.40	34.32	0.40	81.36
	80	-615.30	885.66	41.00	-117.60	30.86	0.36	83.23
KurF1	10	-655.50	230.83	43.60	-110.30	135.63	1.60	26.32
	30	-701.10	210.04	50.00	-157.60	151.40	1.78	17.75
	50	-697.20	259.07	47.60	-120.90	131.59	1.55	28.51
	70	-698.30	219.53	49.60	-139.80	152.05	1.79	17.39
	80	-680.60	318.07	49.80	-128.40	111.06	1.31	39.67
KurF2	10	-688.00	307.98	46.70	-124.40	105.41	1.24	42.73
	30	-687.70	358.35	49.60	-121.50	101.56	1.19	44.83
	50	-629.50	291.34	48.10	-122.20	118.22	1.39	35.77
	70	-642.50	294.50	44.20	-98.50	118.22	1.39	35.78
	80	-673.10	271.19	41.40	-71.10	158.69	1.87	13.79
KurF3	10	-674.40	244.05	48.60	-152.50	126.92	1.49	31.05
	30	-637.20	1010.00	45.50	-111.00	33.15	0.39	81.99
	50	-673.30	640.74	43.40	-113.10	47.72	0.56	74.07
	70	-652.80	2030.00	38.50	-94.30	13.92	0.16	92.44
	80	-626.20	4600.00	48.30	-67.00	16.34	0.19	91.13

Note: raw pure extract = KurK; first fraction = KurF1; second fraction = KurF2; third fraction = KurF3

LINEAR POLARIZATION

Anodic and cathodic polarization curves for carbon steel in 1% NaCl solutions with various fractions of curcuminoids are shown in Figure 1. Based on the analysis of the Tafel extrapolation curve, it is showed that the raw pure extract and the third fraction of curcuminoid acted as anodic inhibitor, whereas the first and the second fraction performed as cathodic inhibitors. The increase in inhibitors concentration was cause the increasing of cathodic and anodic characteristic (Table 2). This phenomenon influents towards the increase in corrosion inhibition activity of the raw pure extract, which has assisted by the combination act of the cathodic and anodic inhibitors.

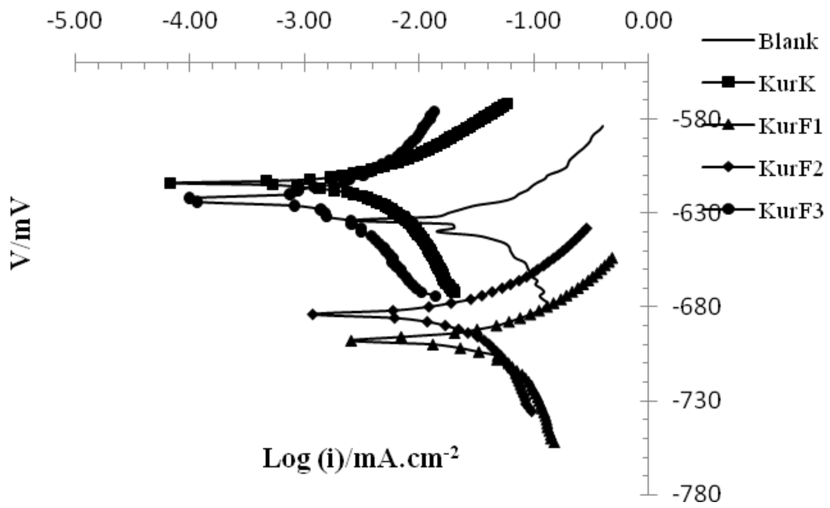

Figure 1. Polarization curves for carbon steel in 1% NaCl solutions with various fractions of curcuminoids

SYNERGISM PARAMETERS

The synergistic effect while Schmitt and Bedhur (Fauda et.al, 2004, Burstein, 2005) have proposed two types of joint adsorption namely competitive and cooperative. In competitive adsorption, the anion and cation are adsorbed at different sites on the metal surface. In cooperative adsorption, the anion is chemisorbed on the surface and the cation is adsorbed on a layer of the anion.

The synergism parameter, S_{θ}, was calculated using the relationship given by Aramaki and Hackerman:

$$S_{\theta} = 1 - \frac{\theta_{1+2}}{\theta'_{1+2}}$$

(5)

Where $\theta_{1+2} = \theta_1 + \theta_2 - \theta_1\theta_2$; θ_1 is the measured surface coverage by first inhibitor; θ_2 is the measured surface coverage by second inhibitor; and θ'_{1+2} is the measured surface coverage by both first and second inhibitor.

For the surface covered were calculated using:

$$\theta = \frac{(i_{corr} - i_{corr(inh)})}{i_{corr}}$$

(6)

Because the first and second fractions of curcuminoids act as cathodic inhibitor and the third fraction act as anodic inhibitor, the types of joint adsorption is competitive adsorption.

Figure 2 represents the plot of synergism parameter versus concentration where θ_1 used for the measured surface coverage by the first and second fraction ; θ_2 for third fraction; and θ'_{1+2} for raw pure extract curcuminoids. In this plot was given suggesting that the enhanced inhibition efficiency towards raw pure extract curcuminoid was caused by the present of the second fraction as cathodic inhibitor and the third fractiont as anodic inhibitor.

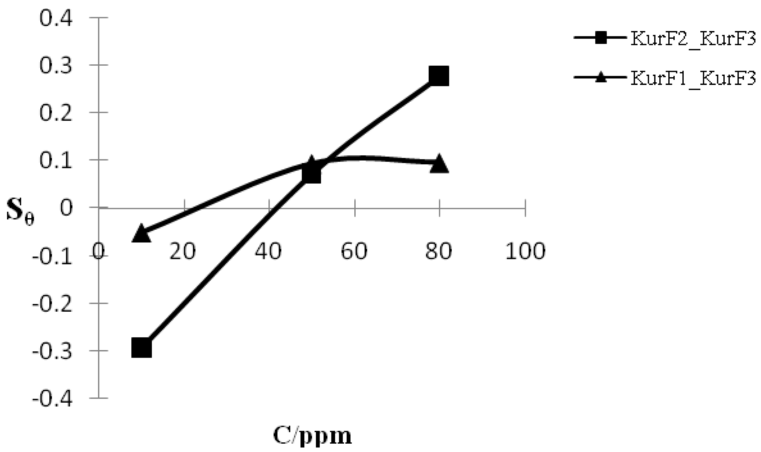

Figure 2. The plot of synergism parameter versus concentration of curcuminoids

EFFECT OF METHOXY GROUPS

Based on the analysis of Tafel data, it is showed that the ability as high potent corrosion inhibitor of the raw pure extract and the third fraction is comparable. The increase in corrosion inhibition activity of the raw pure extract suggested caused by the presence of bisdemethoxycurcumin compound (the third fraction) in the raw pure extract, which has the capability to adsorb onto metal surface and assisted by the combination act of the first and second fraction as cathodic inhibitors. The presence of methoxy groups in curcuminoids structure endorsing the decrease of adsorption on the cathode surface. This phenomenon was caused by the contribution of steric hindrance of methoxy groups in curcuminoid structure, which decrease the activity of curcuminoids to adsorb on the electrode surface (Figure 3). The analysis data of the second fraction gave small efficiency. This result showed that this compounds are difficult to adsorb on metal surface which also caused by the presence of methoxy groups in this structure. The third fraction, which its structure did not contain methoxy groups, showed high value of efficiency because of the ability of this compounds to adsorb on electrode surface.

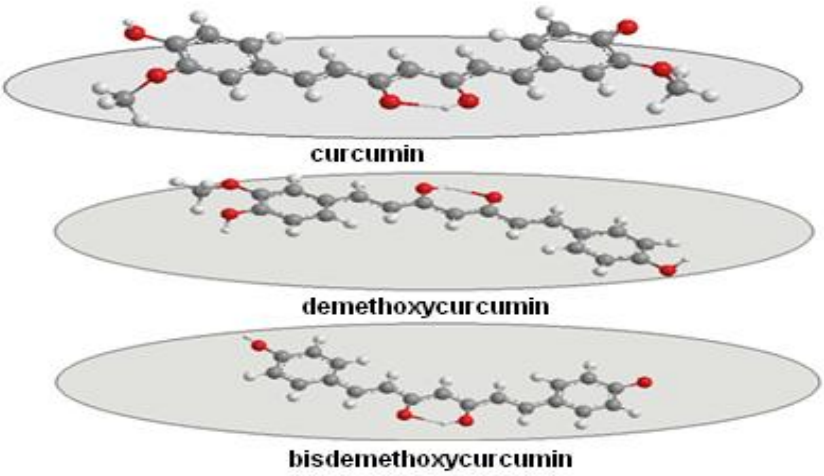

Figure 3. The effect of steric hindrance towards methoxy groups in curcuminoids structure when adsorbed on the carbon steel surface

Based on the previous analysis, curcuminoids isolated from *Curcuma domestica* Val. have been successfully examined as corrosion inhibitors toward carbon steel in 1% NaCl solution and the third fraction having dominant role towards the efficiency of inhibitors.

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