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Curcuminoid Compounds Isolated from *Curcuma domestica* Val. as Corrosion Inhibitor Towards Carbon Steel in 1% NaCl Solution

(Pengasingan Sebatian Kurkuminoid daripada *Curcuma domestica* Val. sebagai Perencat Pengaratan Aloi Karbon dalam 1% Larutan NaCl)

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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) utilising weight loss method at the concentration of 80 ppm showed the best result of 78.70% for third isolated fraction. Further determination utilising 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, 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 enhancement in inhibition efficiency towards raw pure extract was caused by the presence of second and third fractions as cathodic and anodic inhibitors. The contribution of steric hindrance of methoxy groups in curcuminoid structure causes the decrease in curcuminoid activity to be adsorbed on the electrode (carbon steel) surface.

Keywords: Anodic inhibitor; cathodic inhibitor; corrosion inhibitor; Tafel

ABSTRAK

Perencat kakisan daripada kumpulan kurkuminoid terhadap aloi karbon dalam larutan NaCl 1% telah dikaji pada suhu 27°C menggunakan kaedah hilang-berat dan elektrokimia. Penentuan kecekapan perencat kakisan (%eff) menggunakan kaedah kehilangan berat pada kepekatan 80 ppm menunjukkan hasil terbaik 78.70% untuk fraksi ketiga hasil pemencilan. Penentuan lebih lanjut menggunakan kaedah Tafel menunjukkan hasil seperti berikut: ekstrak kasar kurkuminoid tulen memiliki kecekapan perencat kakisan 89.88% pada 50 ppm; peringkat pemisahan pertama 46.50% pada 80 ppm; peringkat pemisahan kedua 44.83% pada 30 ppm; dan peringkat pemisahan ketiga 92.44% pada 70 ppm. Analisis terhadap lengkung ekstrapolasi Tafel menunjukkan bahwa ekstrak kasar tulen dan peringkat pemisahan ketiga kurkuminoud bertindak sebagai inhibitor anodik, sedangkan peringkat pemisahan pertama dan kedua berfungsi sebagai inhibitor katodik. Parameter sinergisme (S_θ) menunjukkan bahawa peningkatan kecekapan perencat pemangkinan dalam ekstrak kasar tulen disebabkan oleh adanya peringkat pemisahan kedua dan ketiga sebagai inhibitor katodik dan anodik. Sumbangan halangan sterik daripada kumpulan metoksi dalam struktur kurkuminoid menyebabkan penurunan keaktifan kemampuan kurkuminoid untuk terjerap pada permukaan elektrod (aloi karbon).

Kata kunci: Perencat anodik; perencat katodik; perencat pengaratan; Tafel

INTRODUCTION

Highly available natural resources with low value should be explored and manufactured to become higher value 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 bond functional groups is the most effective organic inhibitor ever used. Curcuminoids are dyes 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 (Bundjali 2005; Jones 1992; Kelly et al. 2003). The aim of this study was to investigate the effectiveness of curcuminoids derived from curcuma (*Curcuma domestica*) as organic corrosion inhibitor and which is one of curcuminoids in curcuma having dominant role towards the efficiency of inhibitors.

MATERIALS AND METHODS

Curcuma used in this study was obtained from traditional market at Lembang, Bandung, West Jawa, Indonesia. The main material studied was curcuma dyes and material that is known as curcuminoids, which consist of three main fractions (components). The metal used in this study was 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 crystallised 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 group analysis were performed by FTIR and NMR. The physical property 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 utilising weight loss method and potentiodynamic polarisation 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. The concentration of NaCl solution (as corrosive environment in the measurement system) used is 1% (*w/v*), because it is the common concentration used in general corrosion measurements of carbon steel, which corresponds to the seawater brine salinity that found to be a corrosive medium in the offshore oilfield mining (Jones 1992).

WEIGHT LOSS MEASUREMENTS

Carbon steel coupons of size; length 2 cm, width 1 cm, and thickness 0.075 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°C. Inhibition efficiencies were calculated from the differences of weight-loss values in the presence and absence of inhibitors.

POTENTIODYNAMIC POLARISATION STUDY

Potentiodynamic polarisation studies-cathodic and anodic polarisation 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 min before polarization tests.

RESULTS AND DISCUSSION

FTIR AND NMR SPECTRA ANALYSIS

The comparison analysis between infrared spectra obtained from FTIR measurements of the first, second and third fractions of curcuminoids showed the decrease in the absorption intensity at wave number regions of 2854.65 – 2970.38 cm^{-1} that significantly present in the spectra of the second and third fractions 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 presence 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 are given in Table 1. The weight loss data in a year were calculated according to:

$$W_{corr}(\text{g/Y}) = (W_o - W_f)x \frac{\sum_{days\ in\ a\ year}}{\sum_{days\ used\ in\ experiment}} \quad (1)$$

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:

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

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

$$\%eff = \frac{(W_{corr} - W_{corr(inh)})}{W_{corr}} x1000\% \quad (3)$$

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°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 utilising 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 caused the decrease of the rate of corrosion, hence the loss of volume and loss of weight of carbon steel in the inhibited system (with the presence of the third fraction of curcuminoid as corrosion inhibitor) are insignificant compared to the loss of volume and loss of weight of carbon steel in the uninhibited system. However, the loss weight method is usually only used as a preliminary study because of its uncertainity of measurements up to 10% (Ferreira et al. 2004), therefore it is necessary to take a electhochemical method, such as potentiodynamic measurements, to have better understanding concerning the corrosion inhibition mechanism (Kelly et al. 2003).

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_{corrr} 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

TABLE 2. The electrochemical polarisation 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} ($\mu A\ cm^{-2}$)	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 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 fractions.

LINEAR POLARISATION

Anodic and cathodic polarisation 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 fractions performed as cathodic inhibitors. The increase in inhibitors concentration caused the increasing of cathodic and anodic characteristics (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.

SYNERGISM PARAMETERS

The synergistic effect while Schmitt and Bedhur (Fouda et al. 2005; 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, $S_{\theta,}$ was calculated using the relationship given by Aramaki and Hackerman (Aramaki and Hackerman 1969; Fouda et al. 2005):

$$S_\theta = 1 - \frac{\theta_{1+2}}{\theta'_{1+2}} \quad (5)$$

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.

The surface coverage, θ, is calculated using:

$$\theta = \frac{(i_{corr} - u_{corr(inh)})}{i_{corr}} \quad (6)$$

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 fractions; 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 presence of the second fraction as cathodic inhibitor and the third fraction as anodic inhibitor.

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 fractions 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

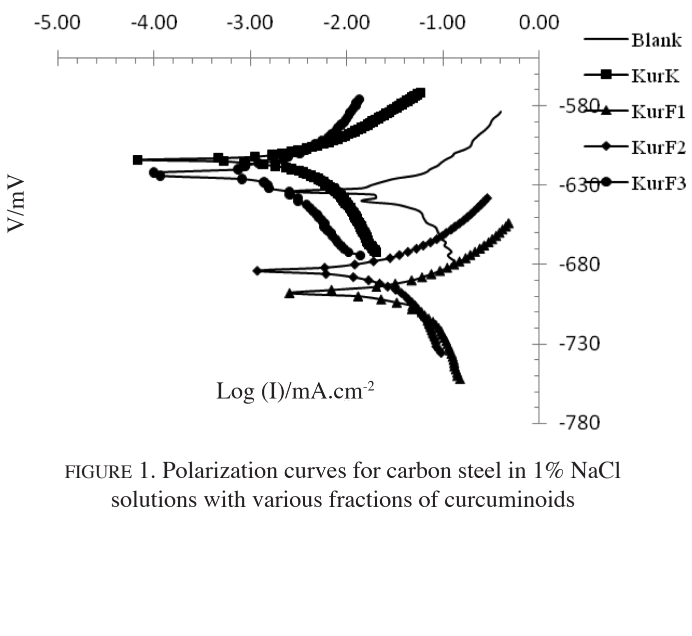

FIGURE 1. Polarization curves for carbon steel in 1% NaCl solutions with various fractions of curcuminoids

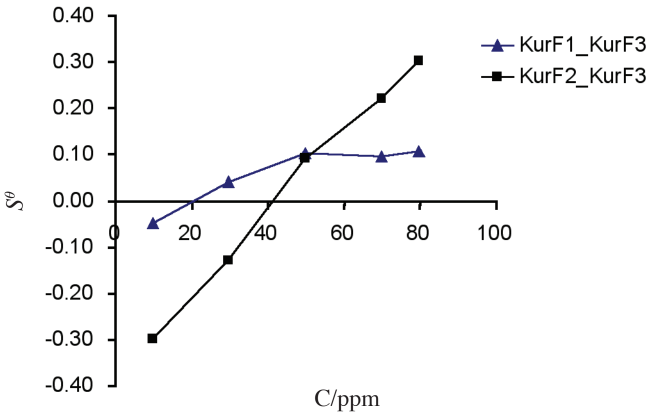

FIGURE 2. The plot of synergism parameter versus concentration of curcuminoids

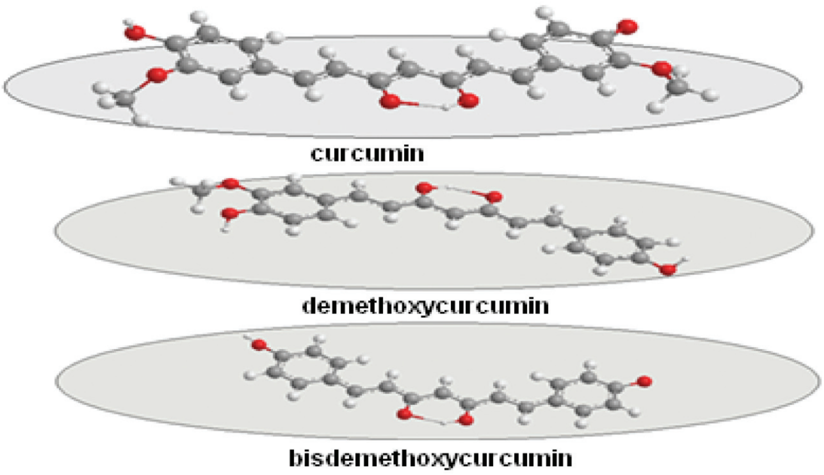

FIGURE 3. The effect of steric hindrance towards methoxy groups in curcuminoids structure when adsorbed on the carbon steel surface

data of the second fraction showed small efficiency. The results showed that these compounds were difficult to adsorb on metal surface caused by the presence of methoxy groups in this structure. The third fraction, with structure not contain methoxy groups, showed high value of efficiency because of the ability of these compounds to adsorb on electrode surface.

Based on the previous analysis, curcuminoids isolated from *Curcuma domestica*. 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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