

1 **THE POTENCY OF GRASS JELLY EXTRACT AS**
2 **CORROSION INHIBITOR ON STEEL IN**
3 **HYDROCHLORIC ACID SOLUTION**

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5 **Grass Jelly Extract as Corrosion Inhibitor on Steel in HCl Solution**

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18 **Abstract**

19 **The investigation of the effect of Grass Jelly (*Platostoma palustre*) extract to**
20 **the corrosion behavior of carbon steel had been carried out using**
21 **electrochemical methods such potentiodynamic polarization and**
22 **electrochemical impedance spectroscopy (EIS). Those experiments define**
23 **corrosion rate, efficiency of inhibition and adsorptions isotherm values in 0.1**

24 M hydrochloric acid solution. That extract was added gradually in acid
25 solution up to 1000 ppm. It found that the maximum of inhibition efficiency
26 could reach 93 % at 250 ppm concentration of extract. Typically, the
27 efficiency of inhibition increased with increasing concentration of extract
28 which tends to stable in the concentration range between 300 ppm and 1000
29 ppm. The type of the extract is mixed inhibitor where it can inhibit the
30 corrosion process in both anodic and cathodic sides. It presumed that the
31 mechanism of adsorption on surface of metal corresponds to Langmuir
32 adsorption isotherm.

33
34 **Keywords:** Corrosion, Carbon steel, Electrochemical method, Grass Jelly,
35 Corrosion Inhibitor

36 37 Introduction

38 The use hydrochloric acid solution is the economical manner to minimize
39 the problem of scaling in pipeline of oil and gas application (Abd El-Aziz *et al.*,
40 2017). The other usage of that acid solution is also as pickling solution for
41 removing harmful impurities and unexpected oxide film on steel. However, the
42 excessive use of this solution can lead a detrimental effect for the metal which
43 degrades the mechanical and chemical properties of it. The active solution
44 commonly is applied to reduce the aggressiveness of the corrosive solution for
45 metal, which is defined as a corrosion inhibitor (Amitha and Bharathi, 2012).
46 Commercial corrosion inhibitors mostly consist of various synthetic compounds,

47 in which tend to lead severe environmental issues (Savita *et al.*, 2015).
48 Furthermore, in the last decade, there are many **researches** that found new
49 environmental friendly solutions of corrosion inhibitor from natural resource
50 (Namrata *et al.*,2015 ; Mary *et al.*,2018 ; Rahab, 2017 ; Handayani *et al.*,2017 ;
51 Mohd and Tan, 2012 ; Loto *et al.*,2011).

52 One of the proper manners to reduce environmental problem is to find
53 **various** natural plants to be extracted in low cost and easy extraction process. In
54 natural plants, there are many organic compounds such as nitrogen and its
55 derivatives, thioaldehydes, aldehydes, various alkaloids and so on as the main
56 substances of natural **corrosion** inhibitor (Amitha and Bharathi, 2012). The other
57 substance of natural corrosion inhibitor also included polyphenol (Gadang *et*
58 *al.*,2018). Furthermore, there are many **varieties** of grass jelly plant which is
59 selected to be a potential candidate of natural corrosion inhibitor due to abundant
60 number of plants and easy plantation **in Indonesia**. This plant has the high
61 **concentration** of antioxidant substance such polyphenol (Handayani *et al.*, 2017).
62 The other researchers reported that the **presence of** polyphenol could minimize the
63 corrosion rate on metals (Loto *et al.*,2011 ; Gadang *et al.*, 2018 ; Fouda *et*
64 *al.*,2013). In the **preceding** work, Gadang and co-worker had succeeded to
65 elucidate the main role of polyphenol substances in Indonesian dimocarpus
66 longan peel which **minimize** the susceptibility of corrosion attack on mild steel in
67 weak acid solution (Gadang *et al.*,2018). The other **previous** work, Gadang and
68 co-worker had also reported that the extract of belimbing wuluh (Averrhoa
69 bilimbi) leaf could reduce corrosion **process** on steel in diluted acid solution

70 (Gadang *et al.*, 2016). Moreover, the mechanism for reducing corrosion rate of
71 steel is attributed the adsorption mechanism of phenolic derivatives molecules on
72 the surface of metal in passive film layer which have role to inhibit aggressive
73 solution on metal (Fouda *et al.*, 2013). However, there is no or little study for the
74 comprehensive investigation of grass jelly extract as natural corrosion inhibitor.
75 Therefore, the main objective of present work is to elucidate the effectiveness of
76 grass jell extract for minimizing corrosion process of carbon steel in acid solution.
77 The other objective is also to propose the inhibitive mechanism of the extract.

78

79 **Materials and Methods**

80 **Preparation of specimen and test solution**

81 In this current work, a plate of as-received carbon steel was cut into 1 cm x
82 1 cm x 0.2 cm for test specimen. The specimen was abraded up to 1000 of grit
83 with silicon carbide paper. Then that washed with distilled water and acetone
84 solution. After this process, it is ready to conduct the electrochemical test as soon
85 as possible due to the rapid oxidation of surface on steel. The compositions of
86 carbon steel are given in Table 1.

87 The fresh grass jelly leaves were dried under sunlight and ground into fine
88 powder. 50 grams of the powder was added in 500 mL of ethanol solution. This
89 solution was stored in ambient temperature at least 24 hours. Then the solutions
90 were filtered and dried in vacuum oven for obtaining fine pure extract.
91 Furthermore, the main solution of 0.1 M HCl was prepared by the dilution of
92 solution stock of concentrated HCl with ultrapure water, where the concentration

93 range of the extract was 100 -1000 ppm. For the comparison, there was blank
94 solution without addition of the extract.

95 **Electrochemical test**

96 This test was conducted in a three electrode glass cell assembly using a
97 potentiostat (Reference 600, Gamry Instrument), connected to a **desktop** computer.
98 The assembly consisted of cell glass with three opening one each for a working
99 electrode, counter electrode of platinum, and saturated calomel electrode (**SCE**) as
100 reference electrode. The surface of the working electrode was covered in one side
101 with hardened resin at the surface area 1 cm². In addition, the electrochemical
102 tests consist of potentiodynamic polarization and electrochemical impedance
103 spectroscopy (EIS) in the same preparation of specimen. Prior to both tests, the
104 preliminary process was carried out to stabilize open circuit potential (OCP) at
105 least 1 hour under open air condition. The temperature solution was maintained at
106 303 K. In polarization test, the potential range was between -250 mV and +500
107 mV in a controlled low scan rate of 0.167 mV/s. From **the results of** this test, the
108 parameters consist of corrosion potential (E_{corr}), corrosion current **density** (I_{corr}),
109 Tafel slopes anodic (β_a) and cathodic (β_c) were calculated with Tafel equation
110 (Mary and Suruthi, 2018). An electrochemical reaction obeys the Tafel equation
111 which showed by following equation:

112

$$113 \quad I = I_0 e^{2.308(E-E_0)/\beta} \quad (1)$$

114

115 where, I and I_o are the resulted current density from the reaction and the exchange
 116 current density, respectively. E and E_o are the electrode potential and the
 117 equilibrium potential, respectively. The last parameter is β which defined as
 118 reaction's Tafel constant. In above equation, it only defines one reaction.
 119 Commonly, corrosion system should describe two opposing reaction such as
 120 anodic and cathodic reactions. Thus, the Butler-Volmer equation generates Tafel
 121 equation in both reactions, which later is applied to be a Tafel plot. In addition,
 122 Tafel plot is defined as a plot log I versus E.
 123 Furthermore, from I_{corr} acquired, the surface coverage of inhibitor layer on metal
 124 (θ) and efficiency of inhibition (η) was calculated by common following
 125 equation :

126

$$127 \quad \eta\% = \frac{C_o - C_i}{C_o} \times 100 \quad (2)$$

128

$$129 \quad \theta = \frac{C_o - C_i}{C_o} \quad (3)$$

130

131 where, C_o and C_i are the corrosion rate values in the with or without of inhibitor,
 132 respectively.

133 On the other hand, the other electrochemical test is electrochemical
 134 impedance spectroscopy (EIS), in which were conducted in the frequency range
 135 between 1 Hz and 300 MHz using alternative current (AC) signal at OCP.
 136 Basically, EIS test yields Nyquist plot, which consist of the real part (Z') and
 137 imaginary part (Z'') of the cell impedance for main parameters. Those parameters

138 were determined in ohm unit at various applied frequencies. From Nyquist curve,
139 the main data is essential to determine the behavior of metal surface before and
140 after test, consisting of charge transfer resistance (R_p), double layer capacitance
141 (C_f) and solution resistance (R_u) (Quraishi *et al.*, 2009). In addition, the tests were
142 repeated in three times to make ensure the reliability of the results.

143

144 **Results and Discussion**

145 **Electrochemical Measurement**

146 Figure 1 shows polarization curves of carbon steel with or without
147 addition of extract in 0.1 M HCl solutions. From those curves, generally, the
148 addition of grass jelly extract in all various concentrations reduce the magnitude
149 of both anodic and cathodic reactions compared to blank solution with no addition
150 of extract. In addition, the reduction of anodic side means the low dissolution of
151 metal ions from metal bulk where that of cathodic side describes the low cathodic
152 hydrogen discharge reaction. Furthermore, the corrosion rate is measured from the
153 estimated corrosion current (i_{corr}), gained from the intercept of the two linear
154 segment of the tafel slope in polarization curve. Corrosion potential (E_{corr}) shows
155 corrosion tendency but not corrosion rate (I_{corr}). The magnitude of current density
156 rate both anodic and cathodic sides and corrosion current density (I_{corr}) of carbon
157 steel decrease significantly in all concentration of extracts compared to those in
158 blank solution as shown in Table 2. However, there is no the significant shift of
159 E_{corr} values after addition of the extract. It is implies that this extract is
160 categorized as mixed corrosion inhibitors where the shift of E_{corr} is less than

161 $\pm 85\text{mV}$ vs SCE as well as the extract of *dimorcarpus longan* peel (Gadang *et*
162 *al.*, 2018). In addition, the mixed corrosion inhibitor has ability to retard both
163 anodic and cathodic reaction involved in electrochemical process (Gadang
164 *et.al.*, 2018)

165 Electrochemical Impedance Spectroscopy (EIS) is common quantitative
166 technique for evaluating the performances of a coating or protective layer on
167 metal substrate, where the ability of a system to resist the electrical current is easy
168 to be observed. An integrated system of coating includes electrolyte, coating and
169 substrates as well as the system of corrosion inhibitor. Figure 2 shows Nyquist
170 curves where various single semicircle curves shifted with or without the addition
171 of extract. The presence of each semicircle curve represents the anodic dissolution
172 with the process of charge transfer. The rise of extract concentration could
173 increase gradually the diameter of each semicircle curve due to the large number
174 of inhibitive molecules on substrate (Shanmuga and Vasudha, 2015). In addition,
175 on the basis of results, the diameter of that curve with adding the extract is larger
176 than that without the extract. A simple fitting model of Randle's equivalent circuit
177 diagram is applied to gain the values of R_p , C_f and R_u as shown in Figure 3. Each
178 Nyquist curve was analyzed by fitting through this model (Vrsalović *et al.*, 2009).

179 On the basis of present work, the addition of the extract increase R_u and
180 decrease C_f values, respectively as shown in Table 3. The increase of R_u value
181 denotes that the inhibitor molecules tends to more adsorbs and forms a protective
182 layer on the interface between solution and metal surface (Bentiss *et al.*, 2000).
183 On the other hand, the decrease of C_{dl} value is attributed a reduction in local

184 dielectric constant by increase in thickness of the electrical double layer
 185 (Shanmuga and Vasudha, 2015 ; Belkhaouda *et al.*, 2013). The inhibitor
 186 molecules on the metal surface influence the electric double layer by inducing a
 187 shift in the dielectric properties of water molecules in the electric double layer
 188 (Wang *et.al.*, 2001). The high R_u is commonly related to slower corroding system
 189 (Fouda *et al.*, 2013), where barrier sites formed on the surface of metal.

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191 Adsorption behavior of inhibitor

192 The effectiveness of organic corrosion inhibitor is commonly is
 193 corresponded to the behavior of molecular adsorption (Bozorg *et al.*, 2014).
 194 Generally, good adsorption behavior of inhibitor molecules on the metal subtract
 195 has proper fitting to Langmuir isotherm which elucidate the interaction between
 196 inhibitor molecules and active sites on metal surface (Gadang and Lutviasari,
 197 2016 ; Belkhaouda *et al.*, 2013 ; Bozorg *et al.*, 2014). In present work, Figure 4
 198 shows Langmuir isotherm plot which fitted by Langmuir adsorption isotherms
 199 equation in following equation 3

200

$$201 \quad \frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (3)$$

202

203 where, K_{ads} is the equilibrium constant of the process of adsorption, C_{inh} the
 204 inhibitor concentration, and the θ is the degree of surface coverage of inhibitor
 205 molecules. Moreover, the value of surface coverage degree (θ) in different
 206 concentrations of the inhibitors have been analyzed from polarization data as

207 shown in Table 2, where the addition of the extract tend to cover the inhibitor
208 molecules up to 90% in whole metal surface.

209 In Figure 4, the best fit was obtained with the Langmuir isotherm, which
210 yield a straight line with strong correlation of regression coefficient ($R^2 > 0.99$).
211 The high regression coefficient means that the inhibitor of grass jelly extract
212 obeys Langmuir adsorption isotherm. Furthermore, the present work reported that
213 the value of K_{ads} of grass jelly extract is higher compared to those of ginger and
214 turmeric extracts (El-Etre and Abdallah, 2000), dimorcarpus longan peel extract
215 (Gadang *et al.*, 2018) and capsicum annuum extract (Savita *et al.*, 2015). The high
216 magnitude of K_{ads} indicates the capability of adsorption of inhibitor molecules on
217 the metal surface. On the other hand, the higher K_{ads} of this extract also
218 corresponded to the higher inhibitor efficiency at ambient temperature. It implies
219 that the addition of grass jelly extract has the higher inhibitive effect.

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221 Conclusions

222 The addition of jelly grass extract can minimize the corrosion process of carbon
223 steel in acid solution which has potency as natural corrosion inhibitor. The
224 corrosion rate and inhibition efficiency decrease and increase in addition of its
225 extract, respectively. This extract behaves as a mixed corrosion inhibitor which
226 inhibits both anodic and cathodic sides. The inhibition of corrosion process may
227 be attributed by adsorption mechanism of the inhibitor molecules on carbon steel
228 surface which obeys the Langmuir adsorption isotherm.

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Table 1 Chemical composition (wt%) of carbon steel used.

Elements	Percentage
C	0.13
Cu	0.013
Mn	0.304
Si	0.118
P	0.029
S	0.008
Ni	0.013
Cr	0.316
Mo	0.001
V	0.003
Ti	0.016
Al	0.003
Nb	0.001
B	0.001
F	0.719
Fe	Remainder

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326 **Table 2 The parameters of carbon steel in 0.1 M HCl solution with or without the**
327 **addition of the extract at 303K.**

Concentration of Inhibitor (ppm)	E_{corr} (mV) vs SCE	I_{corr} (A/cm ²)	Corrosion rate (mpy)	Inhibition efficiency (%)	Surface Coverage (θ)
0	-512.6	0.000574	262.7	0	0
100	-506.4	0.000147	67.16	74	0.744
200	-495.8	0.0000898	41.05	84	0.843
250	-488.6	0.0000411	18.8	93	0.928
300	-508.0	0.0000732	33.46	87	0.872
350	-485.2	0.0000745	34.05	87	0.870
400	-501.9	0.0000883	40.37	85	0.846
500	-493.0	0.000053	24.63	91	0.906
600	-489.9	0.0000660	30.17	89	0.885
700	-485.1	0.0000628	28.71	89	0.890
800	-484.8	0.0000660	30.2	89	0.885
900	-475.3	0.0000640	29.25	89	0.888
1000	-478.8	0.0000521	23.83	91	0.909

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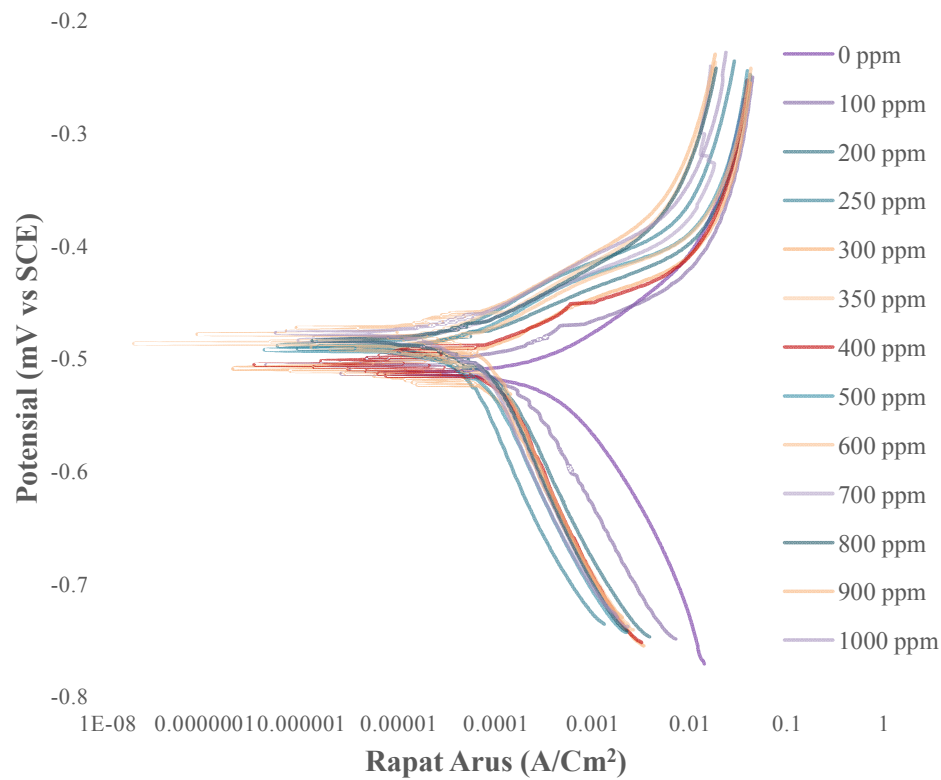
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338 **Table 3 EIS data of steel in the presence and absence of different concentrations of**
339 **grass jelly extract at 303K**

Extract concentration (ppm)	Solution resistance/<i>R_u</i> (ohm)	<i>Charge transfer resistance/R_p</i> (ohm)	Double layer capacitance (Farad)
0	3.35	45.87	0.8675
100	2.70	181.5	0.7849
200	3.12	202.5	0.7682
250	1.88	204.7	0.6894
300	1.89	202	0.8472
350	1.77	207.8	0.7094
400	2.14	209.9	0.7851
500	1.96	257.2	0.7371
600	2.41	230.7	0.7276
700	2.40	223.2	0.8045
800	1.86	254.9	0.7073
900	1.10	290.6	0.6954
1000	1.08	270.7	0.6792

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355 **Figure 1 Polarization curves of carbon steel in 0.1 M HCl solutions with or without**
356 **various concentrations of the extract at 303K.**

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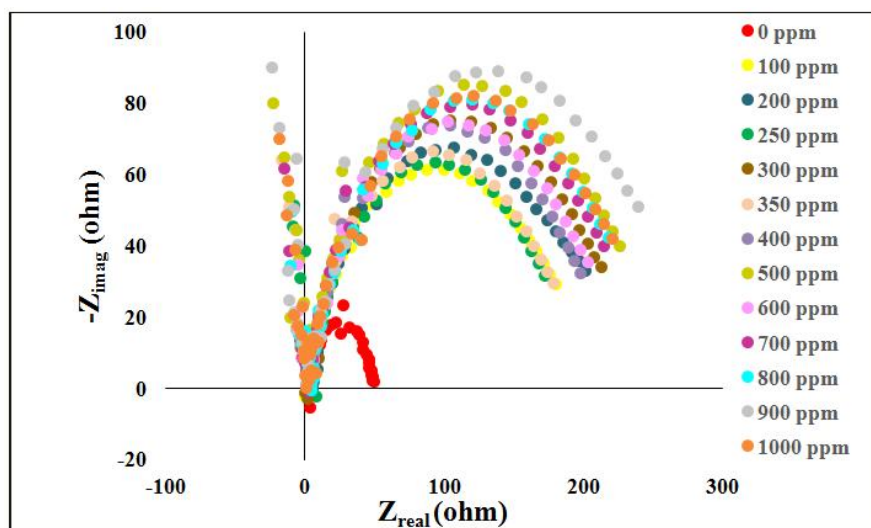


Figure 2 The Nyquist plot for corrosion of mild steel in 0.1 M HCl in the absence and presence of different concentrations of extracts at 303K.

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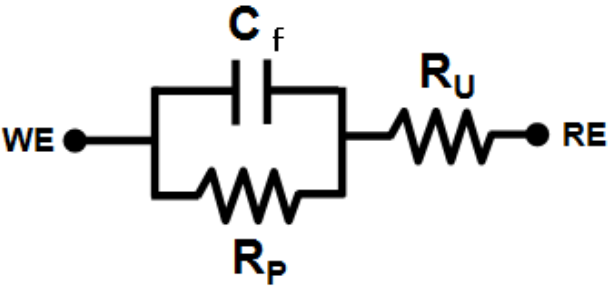
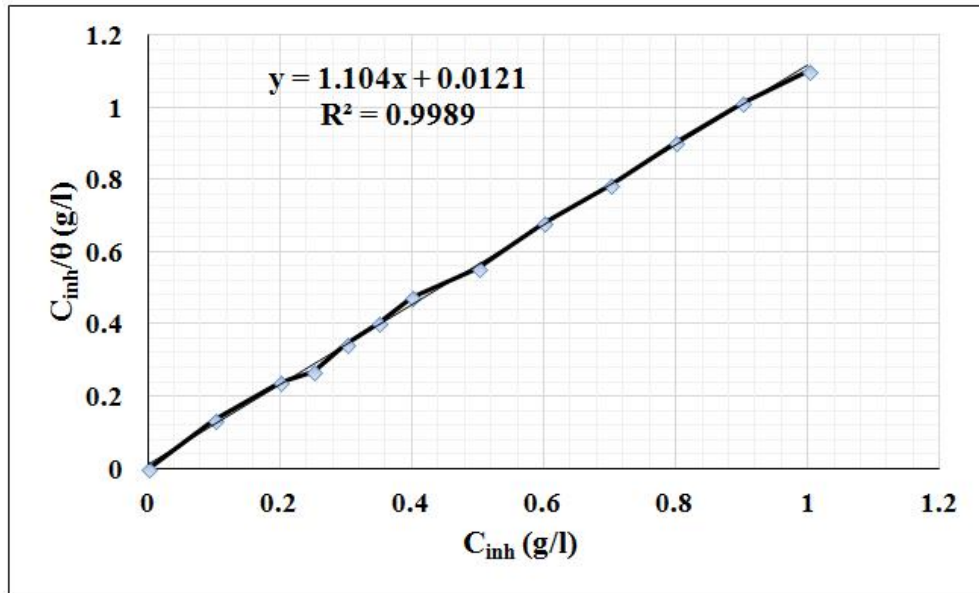


Figure 3. The Equivalent circuit diagram of Randle

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404 **Figure 4 Langmuir isotherm adsorption of grass jelly extracts on the carbon steel in**
405 **0.1 M HCl solutions.**

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