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Research Article

Inhibition of Corrosion of Carbon Steel in 3.5% NaCl Solution by *Myrmecodia Pendans* Extract

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Inhibitor is a substance that is added to the corrosive media to inhibit corrosion rate. Organic inhibitors are preferred to inorganic ones since they are environmentally friendly. One of the organic compounds which is rarely reported as a corrosion inhibitor is *Myrmecodia Pendans*. The organic compounds can be adsorbed on the metal surface and block the active surface to reduce the rate of corrosion. In this study, the used pipe was carbon steel API 5L Grade B with 3.5% NaCl solution as the corrosion medium. The objective of this research was to analyze the inhibition mechanism *Myrmecodia Pendans* towards carbon steel in a corrosion medium. Concentration variations of extract *Myrmecodia Pendans* were 0–500 ppm. Fourier Transform Infrared (FTIR) was used for chemical characterization of *Myrmecodia Pendans*. Polarization and Electrochemical Impedance Spectroscopy (EIS) were used to measure the corrosion rate and behaviour. From the electrochemical measurements, it was found that the addition of 400 mg/L inhibitor gave the highest inhibition efficiency. *Myrmecodia Pendans* acted as a corrosion inhibitor by forming a thin layer on the metal surface.

1. Introduction

Corrosion is a material degradation caused by the chemical reaction with other materials and/or the environment [1]. This process often occurs in the industry of a material oil and gas. In the industrial field, carbon steel is a type of material that is commonly used for various applications. One of those types of carbon steel which is often used in the industrial field is API 5L steel Grade B. The API 5L steel is one of the steels used in the applications of water transport, oil, and natural gas. One of the problems that often occur in the distribution process of crude oil is the existence of sediment called the crust (scale). The crust is the result of mineral precipitation which is derived from the water formation produced along with the oil and gas [2]. This type of steel is easy to be corroded in acidic solution environment. In fact, corrosion cannot be prevented but its speed can be controlled by the addition of an inhibitor. Inhibitor is a substance which is capable of inhibiting or reducing the rate of metal corrosion with the environment [1]. It can also be said that the inhibitor forms a protective layer on the metal surface by the reaction between the solution and the corroded metal surface [3].

In this case, there are many researches done in order to find a new source of the corrosion inhibitor mainly from the natural materials. Natural materials are chosen as the alternative because of their characteristics which are safe, easily available, biodegradable, cheap, and ecoenvironment [4–6].

The organic material used as the inhibitor can prevent the material oxidation reaction of the contained flavonoid element through a certain mechanism [5]. The flavonoid works by donating the electron to the oxidant compounds so that the activity of oxidant compound can be inhibited. One of the organic materials which contains the flavonoid is *Myrmecodia Pendans* plant [7]. The result of *Myrmecodia Pendans* extract has previously been analyzed showing that it contains the flavonoid which can be used in the process of green inhibitor making [8–11].

According to previous research, *Myrmecodia Pendans* can be applied as an organic inhibitor for carbon steel API 5L

Table 1: The corrosion parameters obtained from polarization plots.

Concentration (mg/L)	E_{corr} (mV)	I_{corr} (μA)	$\beta_{katodik}$ (mV/dec)	β_{anodik} (mV/dec)	Corrosion rate (mpy)	Efficiency inhibition (%)
0	−753.745	−323.257	370.595	193.269	95.93	—
100	−612.544	−62.705	77.561	127.57	18.608	74.28
200	−813.921	−56.624	63.864	99.92	16.803	79.85
300	−699.827	−26.359	38.387	47.68	7.822	90.39
400	−620.445	−19.222	36.772	42.58	5.704	91.41
500	−638.899	−28.097	46.097	60.73	8.338	87.75

Grade B in NaCl 3.5% solution with inhibitor concentration 0–500 mg/L by using polarization method [9]. Therefore, this study investigates the mechanism of *Myrmecodia Pendans* as a corrosion inhibitor. It was suggested that the mechanism of *Myrmecodia Pendans* as corrosion inhibitor could be both physical and chemical interaction between flavonoid compound of *Myrmecodia Pendans* and the surface of carbon steel API 5L Grade B as specimen [11]. In order to observe this mechanism, all samples will be analyzed and characterized systematically by polarization method, Electrochemical Impedance Spectroscopy (EIS), and Fourier Transform Infrared (FTIR) spectroscopy.

2. Experimental

2.1. Inhibitor Preparation. *Myrmecodia Pendans* can be found in many local markets in Indonesia from the original form to powder. The extraction method used was maceration process. 100 grams of *Myrmecodia Pendans* powder was dissolved in 1 liter of ethanol 80% for 24 hours. Then, it was filtered by filter paper to get the *Myrmecodia Pendans* extract. The dissolving process was done for three times [9]. Finally, the *Myrmecodia Pendans* extract was evaporated by rotary evaporator at ±50°C for 4 hours so that the *Myrmecodia Pendans* extract could be used for bioinhibitor.

2.2. Solution Preparation. Corrosion solution was attained by mixing 35.24 grams of NaCl and 1000 mL distilled water to get NaCl 3.5%.

2.3. Electrochemical Measurements. The electrochemical measurements were carried out using three-electrode setup comprised of electrode (graphite rod), a working electrode (carbon steel surface area 1 cm^2 which was covered by resin in the back side), and a reference electrode (saturated calomel electrode). The sample surface was polished using abrasive paper grades 500–1000. Then, it was cleaned by the acetone and distilled water and dried at room temperature before dipping to corrosion solution.

Scan rate was applied at 0.1 mV/s for testing polarization. The time limit for reaching equilibrium potential before doing electrochemical measurement was 30 minutes. Frequency range from 10000 to 0.1 Hz was used for measuring impendence by using signal amplitude of 1 mV. Next, the data of impendence was analyzed by using Zview software to determine parameters from circuit equivalent used; meanwhile, value constant phase element (CPE) and charge transfer resistance (R_{ct}) were counted by using Nyquist plot.

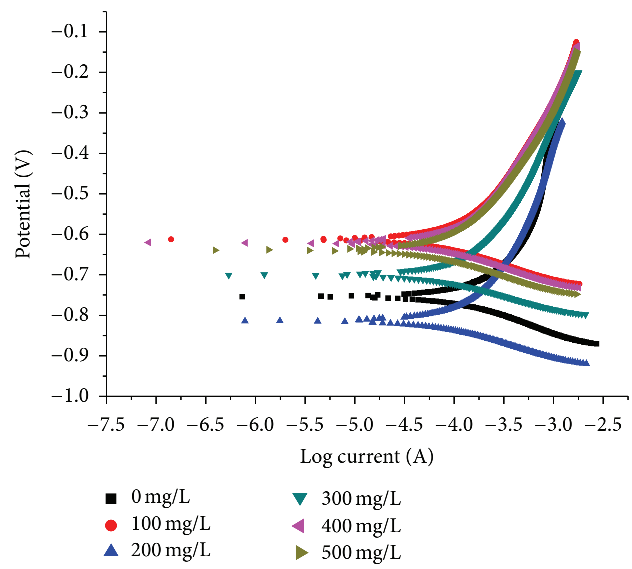

Figure 1: The representative Tafel polarization plots in the absence and presence of different concentration of *Myrmecodia Pendans* inhibitor.

3. Result and Discussions

3.1. Electrochemical Measurements. Polarization Tafel method was applied to analyze the inhibitor efficiency of *Myrmecodia Pendans*. Figure 1 showed Tafel plots for potentiodynamic behaviour in 3.5% NaCl solution containing the different concentration of *Myrmecodia Pendans* extracts. The electrochemical parameters such as corrosion potential (E_{corr}), current density (I_{corr}), Tafel slope cathodic and anodic (β_c and β_a), and inhibitor efficiency inhibition (% EI) can be seen from Table 1.

Inhibitor efficiency (EI) formula is

$$\mathrm{EI} = \frac{I_0 - I_i}{I_0} \times 100\%. \quad (1)$$

I_0 is current density without inhibitor and I_i is current density with inhibitor.

It can be seen from Table 1 that the polarization result showed that *Myrmecodia Pendans* extract had an influence on corrosion process in 3.5% NaCl solution. In general, the result indicated that inhibitor efficiency increases the adding of *Myrmecodia Pendans* extract concentration. This result was in line with El-Etre and Abdallah [12]. The highest inhibitor was obtained from the addition of concentration *Myrmecodia Pendans* extract 400 mg/L in amount of 91.41%.

From the polarization curves, it can be seen that the polarization with increased inhibitors shifts to the positive side (anodic). But the addition of the *Myrmecodia Pendans* extract concentration of 200 mg/L shifts it to the negative side (cathodic). According to the literatures [13, 14], it is said that if the difference in the value E_{corr} ($\Delta E_{corr} = E_{corr} - E_{corr}$ with inhibitor) is higher than 85 mV, the inhibitor can be classified as cathodic or anodic inhibitor. Then, if the difference in value E_{corr} is lower than 85 mV, the inhibitor can be classified as an inhibitor mixture. This study observed that the 3.5% NaCl solution has some variants of the differences of the results E_{corr}. The difference in value E_{corr} higher than 85 mV occurs in concentrations 100, 400, and 500 mg/L, while the difference in value E_{corr} lower than 85 mV occurs at concentration of 200 and 300 mg/L.

Each additional concentration determines the type of inhibitor. As we can see the difference occurs in value E_{corr} at concentrations of 400 and 100. The addition of 500 mg/L indicates that the *Myrmecodia Pendans* extract acts as an anodic inhibitor. This is supported by the curve shifted to the positive side (anodic). Meanwhile, the addition of 200 and 300 mg/L indicates that extracts of *Myrmecodia Pendans* acted as a mixed inhibitor. In addition, extract concentration of 200 mg/L extract *Myrmecodia Pendans* acted as mixed inhibitor dominant cathodic effectiveness, while the addition of 300 mg/L extract *Myrmecodia Pendans* acts as a mixed inhibitor dominant anodic effectiveness. This is supported by polarization curve shifted to the negative side (cathodic) to a concentration of 200 mg/L and shifted to the positive side (anodic) to a concentration of 300 mg/L.

When the *Myrmecodia Pendans* extract acts as an anodic inhibitor, inhibition process occurs in the presence of *Myrmecodia Pendans* extract adsorption on the steel surface. This occurred with the addition of 100, 300, 400, and 500 mg/L. Hussin and Kassim [14] say that when *Uncaria gambir* extract acts as an anodic inhibitor, adsorption of inhibitors may occur on the steel surface so that a thin layer of a barrier is formed. Then, when the addition of concentration of 200 mg/L *Myrmecodia Pendans* extract acts as a cathodic inhibitor, *Myrmecodia Pendans* extract the role of being the anode, it is easily oxidized compared to steel. This is in line with research from Kurniawan and Madurani [15], who proposed that capsicol covered steel by using a cathodic protection where capsicol first acts as the anodic compared to steel.

The β_a and β_c values decrease when the addition of *Myrmecodia Pendans* extract concentration increased from 100 to 400 mg/L. However, the addition of concentration of 500 mg/L increases the values of β_a and β_c. This happens because the layer formed was broken so fast in moving cathodic reaction [15, 16]. Potential corrosion occurs randomly moving into anodic and cathodic not followed by changes in the current density. The current density is to be lower when the addition of *Myrmecodia Pendans* extract

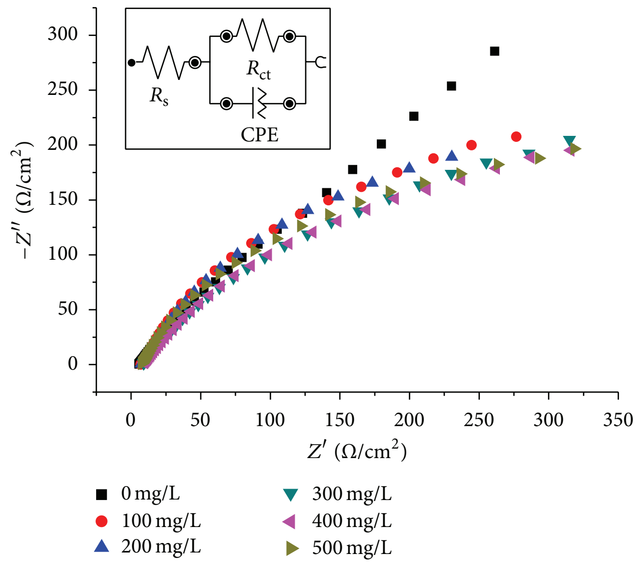

Figure 2: The representative Nyquist plots in the absence and presence of different concentration of *Myrmecodia Pendans* inhibitor (insert: equivalent circuit).

acts as an inhibitor. In the absence of inhibitor, the value of the current density is 323.257 μA/cm^2. When adding inhibitor, the current density becomes lower. This occurs when *Myrmecodia Pendans* extract 200 mg/L is added where the current density is 56.624 μA/cm^2. The current density becomes lower when added to a concentration of 400 mg/L reaching 19.222 μA/cm^2. The phenomenon occurs because of the process of adsorption on metal surfaces [14]. The value of the current density affects the value of the rate of corrosion. The corrosion rate without inhibitor is 95.93 mpy while the corrosion rate with the addition of inhibitor *Myrmecodia Pendans* extract 400 mg/L decreased to 5.704 mpy.

Figure 2 shows Nyquist plots of API 5L Grade B in 3.5% NaCl solution in the absence and presence of different concentration Myrmecodia Pendans extracts. When the API 5L Grade B immersed into a solution of 3.5% NaCl, EIS will detect NaCl solution and form a resistance solution (R_s). Once past that, the metal will form a passive layer which tends to be protective for their bond between Fe and functional groups extract *Myrmecodia Pendans*. The thicker the passive layer than the value, the higher the R_{ct}. Results of testing the electrochemical resistance at 3.5% NaCl solution can be seen in Table 2.

Table 2 shows that the increased concentration of the inhibitor to a solution of the value of the charge transfer resistance (R_{ct}) will increase and the value of the capacity will decrease. R_{ct} value without inhibitor is 27.27 Ω whereas, with the addition of inhibitors 500 mg/L, the R_{ct} value is 120.5 Ω. Maximum value R_{ct} occurs when adding the extract concentration of 400 mg/L, which is 134.3 Ω. With the addition of inhibitor concentration in the solution, the resulting value R_{ct} increases.

Table 2 shows that the addition of the value of the extract concentration decreased capacity double layer. This

Table 2: The parameters obtained from EIS measurements.

Concentration (mg/L)	R_s (Ω)	R_{ct} (Ω)	C_{dl} (μF/cm^2)	Efficiency inhibition (%)
0	5.34	27.27	0.01921	—
100	6.15	101	0.00573	73
200	6.83	112.9	0.00326	75.85
300	6.90	129.7	0.00224	78.96
400	6.43	134.3	0.00211	79.70
500	6.65	120.5	0.00279	77.37

shows that the relationship between R_{ct} and C_{dl} is inversely proportional. This is a phenomenon that occurs due to a decrease in local dielectric constantan or increasing the density of electric double layer. The presence of *Myrmecodia Pendans* extract modifies the structure of the electric double layer by adsorption inhibitor molecules at the interface of a metal with a solution. Adsorption inhibitor on the metal surface forms a barrier layer to prevent mass transfer. With the addition of the value of the extract concentration, the R_{ct} values increased, but the C_{dl} values tended to decrease. This is mainly due to the adsorption of inhibitor on the metal surface. C_{dl} maximum value occurs when the addition of the extract concentration of 400 mg/L is 0.00211 μF/cm^2.

R_{ct} value reached a maximum level at 400 mg/L, for next R_{ct} value has decreased. This is caused by a thin layer formed on the metal surface that may be abraded by corrosion solution. The existence of a functional group of compounds intended to bind ions which cause corrosion reaction with metals. Extra resistance value decreased at a concentration of 500 mg/L. Addition at a concentration of 400 mg/L is an effective concentration to *Myrmecodia Pendans* extract adsorbed on the surface of the steel API 5L Grade B 3.5% in 3.5% NaCl solution. This is in accordance with the potentiodynamic polarization test which states that the addition of the 400 mg/L of the ant nest extract resulted in the highest inhibition efficiency.

Table 3: Estimated functional group on *Myrmecodia Pendans* extract.

Wave number (cm^{-1})	Estimated functional group
3261	N-H; C=C-H; ≡C-H; -OH
2913	H-C-H
2289	C≡N
1695	C=O; N-H
1500	C-C=C; N=O; H-C-H
1457	N-H; H-C-H; C-C=C
1349	N=O
1052	C-O

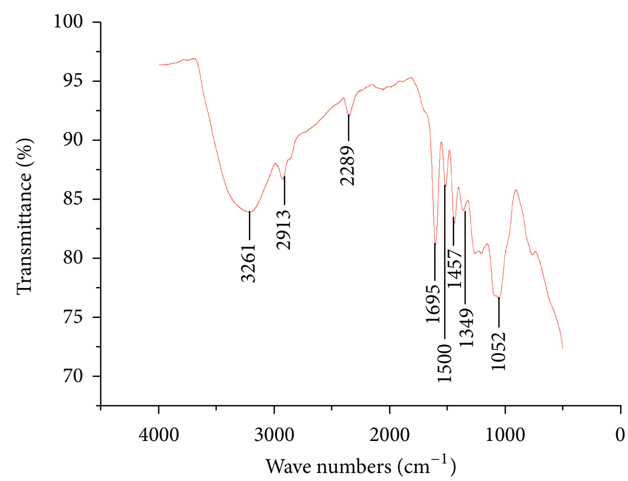

Figure 3: FTIR spectra of *Myrmecodia Pendans* extract.

3.2. FTIR Measurement. The results of polarization and EIS showed that adding *Myrmecodia Pendans* extracts to the steel API 5L Grade B in 3.5% NaCl solution can reduce the current density. Protection process was conducted by forming a thin layer of the adsorption process of *Myrmecodia Pendans* extracts on the steel surface. This layer is formed from a complex compound. FTIR testing aims to identify whether a new bonding exists when corrosion occurs.

The FTIR result from *Myrmecodia Pendans* extract can be seen in Figure 3. From wave number 3261 cm^{-1}, it showed that there were bonds of N-H (amines group); C=C-H (alkenes group); ≡C-H (alkynes group), and -OH (phenols group). N-H bond occurred on phase of 1695 and 1457 cm^{-1}. Alkanes group H-C-H bond occurred on wave numbers 2913, 1500, and 1457 cm^{-1}, while aromatic group C-C=C occurred on 1500 and 1457 cm^{-1}. Wave numbers of 1500 and 1349 occurred on bond N=O classified as nitro group. For more details, the data was presented in Table 3.

FTIR results from the metal surface after an inhibitor of *Myrmecodia Pendans* extract was given in 3.5% NaCl solution and estimation of functional groups can be seen in Figure 4 and Table 4.

From the result of immersion, the metal in the solution and the corrosion inhibitor showed a stretch occurring in some organic functional groups such as OH changed from 3261 cm^{-1} to 3574 cm^{-1}. These changes occurred to the formation of new compounds from bonding the active compound with Fe^{2+} as well as adsorption on metal surfaces [17–19]. From FTIR testing, it also indicates the Fe-O bond at 675 cm^{-1}. This means that the adsorption process flows forming a thin protective layer. Not only that, but another group of Fe-N-H results at 882 cm^{-1} also occurs. This is in line with the research conducted by Li et al. [20]. With the content of functional groups in the *Myrmecodia Pendans* extract, it

Table 4: Estimated functional groups occurring.

Wave numbers (cm^{-1})	Estimated functional group
3574	O-H
1668	C=O
882	Fe-N-H
675	Fe-O

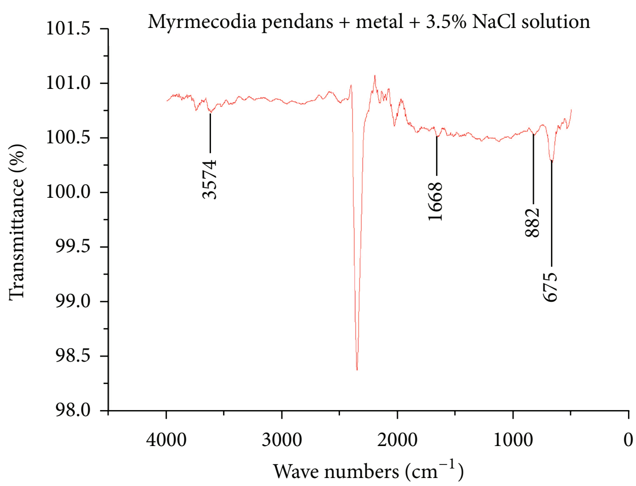

Figure 4: FTIR spectra of adsorption layer formed on the surface metal.

can be concluded that the extract has the ability to form a protective layer in the form of the formation of complex compounds.

3.3. Isotherm Adsorption. Isotherms adsorption provides basic information about the interaction between the inhibitor and carbon steel surface [21]. On shielded metal surfaces, a thin protective layer is formed. This layer can be expressed as the surface coverage (θ). It has a correlation with inhibition efficiency as follows:

$$\%\ \mathrm{EI} = \theta \times 100\%. \tag{2}$$

Existing data in accordance with the Langmuir adsorption can be seen in Figure 5. This connects the inhibitor concentration (C) with a surface coverage (θ) which is the result of a nearly linear correlation coefficient ($R^2 > 0.9$) that is 0.994.

Langmuir model equation is

$$\frac{C}{\theta} = \frac{1}{K_{\mathrm{ads}}} + C, \tag{3}$$

where θ is surface coverage. K_{ads} is the adsorption-desorption equilibrium constant. C is the concentration of inhibitor. The free energy of adsorption (ΔG_{ads}) can be calculated from Langmuir interception chart according to the equation

$$K_{\mathrm{ads}} = \frac{1}{C_{\mathrm{solvent}}} \exp\left(\frac{\Delta G_{\mathrm{ads}}}{RT}\right). \tag{4}$$

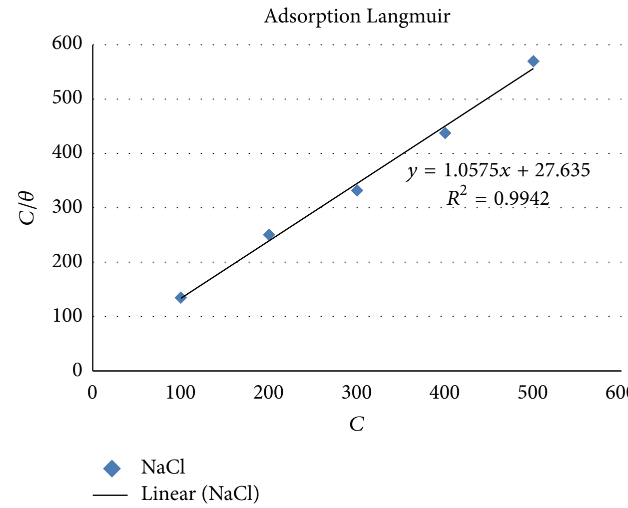

Figure 5: Isotherm Langmuir.

Based on the literature [22] as the inhibitor in the form of extracts, C_{solvent} has a value of 1000 mg/L. R is the ideal gas constant supply of 8.314 J/mol·K and T 298°K. This is in line with the Langmuir equation of the line on the graph in Figure 5 in order to obtain K_{ads} and ΔG_{ads} values. The values are shown in Table 5.

In general, the free energy of adsorption is above −20 kJ/mol, indicating that this is physisorption process. If the interaction of free energy value reaches up to −40 kJ/mol or less, the interaction of adsorption is chemisorption. Table 5 shows that the adsorption occurs because the type of physisorption adsorption free energy value is above −20 kJ/mol. This is due to the interaction between functional groups inhibitor (possibly as electronegative O or N atom electron pairs) and metal. Their thin protective layer on the metal surface thereby blocks the interaction between the metal and corrosive media. The nature of the nonpolar *Myrmecodia Pendans* extract can form a layer of nonpolar molecules that can block the polar of corrosion solution to attack the surface.

4. Conclusion

Results of electrochemical measurements and FTIR showed that the *Myrmecodia Pendans* extract has the inhibition ability in 3.5% NaCl solution. Characteristics of *Myrmecodia Pendans* extracts are nontoxic, inexpensive, readily available, and easily extracted. The highest efficiency occurs during additional inhibitor concentration of 400 mg/L. The mechanism of inhibition that occurs through adsorption processes extracts *Myrmecodia Pendans* on the metal surface to form a thin protective layer. This layer is formed from complex compounds, supported by the new bond such as Fe-O and Fe-N-H.

Table 5: Values of K_{ads} and ΔG_{ads} when adding each concentration in *Myrmecodia Pendans* extracts.

Concentration (C)	NaCl				
	Efficiency inhibition (%)	Surface coverage (θ)	C/θ	K_{ads} Langmuir	$-\Delta G$ (kJ/mol)
100	74.28	0.7428	134.63		
200	79.85	0.7985	250.47		
300	90.39	0.9039	331.90	0.597	14.217
400	91.41	0.9141	437.59		
500	87.75	0.8775	569.80		

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this article.

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