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Abstract

Stingless bee is the species that produce honey in the Northern and North-eastern regions of Brazil which is known as indigenous bees and stingless bees. Stingless bees also produce honey as well. Honey offers interesting possibilities for corrosion inhibition due to several factors such as it is safe, inexpensive, readily available and highly soluble in water (Gerengi, Goksu, & Slepski, 2014). Then, the corrosion inhibition properties of honey have been investigated in various environment and different types of materials (Berkovic, Kovac, & Vorkapic-Furac, 2008) (El-Etre & Abdallah, Natural honey as corrosion inhibitor for metals and alloys. II. C-steel in high saline water, 2000) (El-etre, 1998). The great interest in honey which it is might be the responsible of characterization of the components in honey itself. About 200 substances including sugars, phenolic acids, flavonoids, amino acids, proteins, vitamins and enzymes (Spilioti, et al., 2014). The main constituents that contributing to the beneficial properties of honey (Stephens, Schlothauer, Morris, Yang, & Fearnley, 2010), (Beretta, Orioli, & Facino, 2007), (Al-Mamarya, Al-Meerib, & Al-Haborib, 2002), (Aljadi & Kamaruddin, 2004) and the antioxidant are phenolic compounds that has in the honey itself. In the present study, the focus is more to the one of the phenolic acid which is p-coumaric acid. P-coumaric acid is one of the phenolic acid which is normally present in honey and has higher antioxidant properties. The effect of stingless bee honey and natural honey as corrosion inhibition for aluminium in 1 M phosphoric acid was done using weight loss measurement at various temperatures. Free energy of adsorption ΔG_{ads} indicates that it was spontaneous and physically adsorbed onto aluminium surface. Stingless bee honey showed the best performance of inhibition efficiency rather than natural honey.

Keywords: Stingless bee honey, natural honey, inhibition efficiency, adsorption

Introduction

There are several native stingless bee species that produce honey in the Northern and North-eastern regions of Brazil which is known as indigenous bees and stingless bees. It is known as the 'Kelulut' which is stingless bee species that found in Malaysia. Generally, the stingless bees will make their hives in tree trunks and even underground. Like natural honey, stingless bees also collect pollen however they used trunks to prepare the honey and its sour taste. According to the Malaysian Agricultural Research and Development Institute (MARDI), stingless bee honey is twice as nutritious as ordinary honey. Honey that is produced by stingless bee honey is a small type of bees. Phenolic materials that commonly found in plants and human food are such as phenolic acids and hydroxy-cinnamic. Phenolic acid accounted one-third of the overall phenolic materials in food.

Natural honey which is in contrast with stingless bee honey, is from the member of the single genus Apis from the tribe of Apini where the most popular subspecies, Apis mellifera. Generally, the bees will eat nectar and pollen from the flowers. Pollen which is the substance that transferred from one flower to another and make more flowers whilst nectar is the solution or liquid in a flower. Then, from the nectar that they collecting from all the trees and plants, the bees make honey. Honey offers interesting possibilities for corrosion inhibition (Gerengi, Goksu, & Slepski, 2014). Previously, the corrosion inhibition properties of honey have been investigated in various environment and different types of materials (Berkovic, Kovac, & Vorkapic-Furac, 2008) (El-Etre & Abdallah, Natural honey as corrosion inhibitor for metals and alloys. II. C-steel in high saline water, 2000) (El-etre, 1998).

P-coumaric acid is one of the phenolic acid which is normally present in honey. It is one of the most common hydroxycinnamic acid. Hydroxycinnamic acid is an organic compound that is a hydroxyl derivative of cinnamic acid. It is also a group of compounds that have highly abundant in food that have for about one third of the phenolic compounds in our diet. Hydroxycinnamic acids known to be as potent antioxidant (Teixeira, Gaspar, Garrido, Garrido, & Borges, 2013) and it is contributed to the interest of researchers. P-coumaric is one of the major phenolic acids that have in honey. As mentioned before, it is the highest antioxidant among the other main phenolic acid in honey. P-coumaric is a major components of pollen grains which is present in the natural diet of honey and also have a function as a nutraceutical regulating immune and detoxification processes.

Corrosion is the process of chemical attack or reaction with its environment toward the metals. This process is developing fast after the disruption of the protective barrier. They are responsible for all the bad effect in the industrial scope. The best way to cope the effect is with prevention. Prevention is the more practical way and achievable than complete elimination to prevent from major accident due to the corrosion problem. Corrosion inhibitors will decrease the rate of either anodic oxidation or either cathodic reduction or mixed-type of inhibitors. Hence, this study is to determine the performance of anticorrosive of stingless honey and natural honey using various methods.

Experimental

2.1 Material

Honey samples which is representing the stingless bee honey (Trigona spp. honey) was selected. The stingless bee honey was collected in Sungai Petani, Kedah whilst the natural honey is from Terengganu. The kelulut honey was supplied by a local bee honey collector from the forest in Kedah where the nectar source is mainly from flowers. The natural honey which was harvested by the Apis spp. was also supplied by a collector from the forest in Terengganu.

2.2 Preparation of specimens

The aluminium alloy with dimensions 3cm x 4 cm x 0.1 cm was polished with 400, 600, 800 and 1000 grits of emery paper. 1 M H_3PO_4 was prepared and it is used to get a blank for the corrosion inhibition process. The specimen was rinsed with distilled water and then followed by isopropanol. It is to remove the residue on the alloy.

2.3 Electrolyte

The electrolyte used in this study was from phosphoric acid 85 %. The concentrations of acids were prepared by using distilled water and the concentration range of both inhibitors (stingless bee honey and natural honey) was prepared from 100 ppm to 2500 ppm.

2.4 Weight loss technique

The aluminium alloy with dimensions 3cm x 4 cm x 0.1 cm was polished with 400, 600, 800 and 1000 grits of emery paper. 1 M H_3PO_4 was prepared and it is used to get a blank for the corrosion inhibition process. The specimen was rinsed with distilled water and then followed by isopropanol. Aluminium specimen were immersed in the 100 mL electrolyte absence and presence the addition of different concentrations of both honey at different temperature (303, 313, 323, 333 K). The weight loss was determined after the immersion for 24 hours. The formula to calculate the percentage of inhibition efficiency (IE %) is :

$$IE\ \% = \frac{W_O - W'}{W_O} \times 100 \qquad (1)$$

Where W_O and W' are the weight losses of aluminium without and with the inhibitors respectively.

Result and Discussions

3.1 Effect of temperature

The effect of the temperature in this studied was to understand more about the behaviour of the inhibitors in the processes such as adsorption and activation process. In this factor, the method that being run to get the results of the both inhibitor's performances is by weight loss measurement. The weight loss measurements were studied with the range of the temperature 303, 313, 323 and 333 K in 24 hours of immersion. The degree of surface coverage (θ) was calculated from following equation:

$$\theta = \frac{W_O - W'}{W_O} \qquad (2)$$

where W_O and W' are the weight losses of aluminium without and with the inhibitors respectively.

The results in Table 1 and 2 shows that the corrosion rate (CR) and inhibition efficiency (IE %) were obtained from the weight loss method at various temperatures. From this study, it can be seen that the weight decreased with the increasing of the concentration of both inhibitors. It was also observed that the corrosion rate decreased when the inhibitor concentration increased. This phenomenon is attributed to active inhibitor's molecule which adsorbed at higher level of adsorption on the aluminium surface (Loto, Loto, & Popoola, 2015). Other than that, it also can be seen that at high temperature, both inhibitors showed poor performances. It might be due by the process desorption of inhibitors from the aluminium surface (Fakrudeen, C., & V., 2012). The activation thermodynamic parameters such as activation energy E_a, activated entropy ΔS and enthalpy ΔH are calculated by using the Arrhenius equation:

$$CR = K \exp\left(\frac{-Ea}{RT}\right) \tag{3}$$

Where CR is the corrosion rate of aluminium (mg cm^{-2} h^{-1}), Ea is apparent activation corrosion energy, K is Arrhenius pre-exponential constant, R is the universal gas constant (8.3142 J K^{-1} mol^{-1}), and T is the absolute temperature.

Arrhenius plots for the corrosion density of the aluminium in both inhibitors which are stingless bee honey and natural honey in 1 M H_3PO_4 solution are given in Figure 2 and 3. Values of activation energy of corrosion (E_a) for aluminium without and with various concentrations of stingless bee honey and natural honey can be determined from the linear slope of ln CR versus 1/T plots. The following equation is the alternative formulation of Arrhenius equation:

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \tag{4}$$

where h is Planck's constant (6.626 x 10^{-34} J s), N is Avogadro's number (6.023 x 10^{23} mol^{-1}), ΔS is the entropy of activation and ΔH is the enthalpy of activation. The value of ΔH and ΔS can be calculated from this relation.

The activation energy in the presence of stingless bee honey was showed higher value than natural honey. Physisorption is the process of adsorptive film of electrostatic character is formed on the aluminium surface. The negative value of the enthalpy of activation ($\Delta H < 0$) shows the process was an exothermic adsorption process which may involve either physisorption, chemisorption or mixture of both processes. This process had difficult process of dissolution of aluminium and it needs more energy to achieve the equilibrium state. Then, the magnitude and sign for the ΔS shows the indication which adsorption reaction is an associative or dissociative mechanism (El-Naggar, Zakaria, Ali, Khalil, & El-Shahat, 2012). The positive values of activated entropy ΔS, indicate that increase in disordering takes place on going from reactants to the activated complex. Thermodynamic parameters (ΔH and ΔS) of the dissolution reaction of aluminium in the presence of stingless bee honey is higher rather than natural honey.

3.2 Adsorption Isotherm

In order to understand the mechanism of corrosion inhibition in this study, the adsorption of inhibitors molecules at the metal-solution interface must be known. The information on this interaction can be provided by adsorption isotherm. The adsorption of the inhibitors molecule is often a displacement reaction which is involving removal the adsorbed water molecules from the metal surface (Ahamad, Prasad, Ebenso, & Quraishi, 2012).

From the observation in the temperature range studies, the best correlation between the experimental results and the isotherm function was obtained from Langmuir adsorption isotherm. From the regression coefficient (R^2) values was used to choose the best fit experimental data of isotherms. The value of R^2 confirmed the validity of this approach. From the observation that fitted all three adsorption isotherm, the best fitted was the straight line which is obtained from the plot $\frac{C}{\theta}$ versus C with regression coefficient up to 1.000. Therefore, it was explained that with Langmuir type, monolayer chemisorption of both honeys was formed and there is no interaction between the adsorbed molecules (Al-Anber, 2011). Langmuir adsorption isotherm were applied and given by following equations:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (5)$$

Where θ is surface coverage, C is the concentration of the inhibitors which are stingless bee honey and natural honey, K is the adsorption-desorption equilibrium constant and g is the adsorbate parameter.

The equilibrium constant for the adsorption process was related to the standard free energy of adsorption, ΔG_{ads} with the relationship (Zarrouk, Hammouti, Zarrok, Al-Deyab, & Messali, 2011).

$$\Delta G_{ads} = -2.303RT \log(55.5\, K_{ads}) \quad (6)$$

Where ΔG_{ads} is Gibbs free energy of adsorption, T is the temperature in Kelvin, R is the universal gas constant (8.3142 J K^{-1} mol^{-1}) and 55.5 is the molar concentration of water in solution.

The values of standard free energy of adsorption were calculated and ΔG_{ads} for stingless bee honey was found to be -31.31 kJ mol^{-1} and for natural honey was -24.95 kJ mol^{-1}. The values were calculated at 303K. According to the (Zarrouk, Hammouti, Zarrok, Al-Deyab, & Messali, 2011), the negative values of Gibbs free energy of adsorption are means to the spontaneity of adsorption process. Besides, it is also ensure about the stability of the adsorbed layer on the metal surface and shows the strong interaction of the inhibitor molecule onto the aluminium surface (Shukla, Quraishi, & Ebenso, 2011) (Zarrouk, Hammouti, Zarrok, Al-Deyab, & Messali, 2011).

Normally, the values of ΔG_{ads} up to -20 kJ mol^{-1} are associated with the electrostatic interactions between the charged molecules and the charged of metal surface (physisorption) while those around -40 kJ mol^{-1} or higher (more negative) are chemisorption which is electrons sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) (Khaled & El-Maghraby, Experimental, Monte Carlo and Molecular Dynamics Simulations to Investigate Corrosion Inhibition of Mild Steel in Hydrochloric Acid Solution, 2014). The values of ΔG_{ads} for stingless bee honey and natural honey were found to be -31.31 kJ mol^{-1} and -24.95 kJ mol^{-1} respectively. From the result, the calculated value of G_{ads} form the results obtained are greater than -20 kJ mol^{-1} but less than -40 kJ mol^{-1}. Therefore, it is indicating that mechanism for both honeys are comprehensive adsorption which are physisorption and chemisorption adsorption. However, the major contributor was to be the physisorption while chemisorption only slightly contributed to the adsorption mechanism which is based on the higher value of activation energy earlier which predominant on the physically adsorption.

In this study, as the temperature increases, the number of adsorbed molecules decreases and leading to a decrease in the inhibition efficiency. The inhibition may be attributed by the presence of the electron rich O and also the aromatic ring. There will be the inhibition reaction from the π-electron in aromatic rings and also from the heteroatoms. The protonation of p-coumaric acid which is the main compound in both inhibitors was postulated to be predominantly at the hydroxyl groups of the aromatic ring. In general, the inhibitors can be adsorbed on the aluminium alloy surface in neutral or in the protonated forms (cationic form) (Farag, Migahed, & Al-Sabagh, 2015).

Conclusion

- The optimum concentration of both inhibitors (stingless bee honey and natural honey are at 1500 ppm which is the highest inhibition efficiency
- As the temperature increases, the inhibition efficiency of both inhibitors will decrease
- The inhibitors fitted with the Langmuir adsorption isotherm. Free energy of adsorption ΔG_{ads} showed negative value which indicate the process was spontaneous and physisorption onto the aluminium surface
- Stingless bee honey showed better performance rather than natural honey

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Figures and Tables

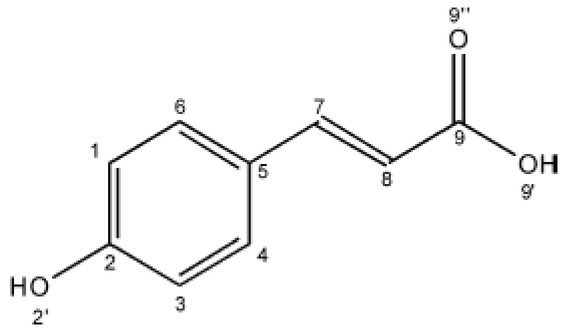


Figure 1: The chemical structure of p-coumaric acid

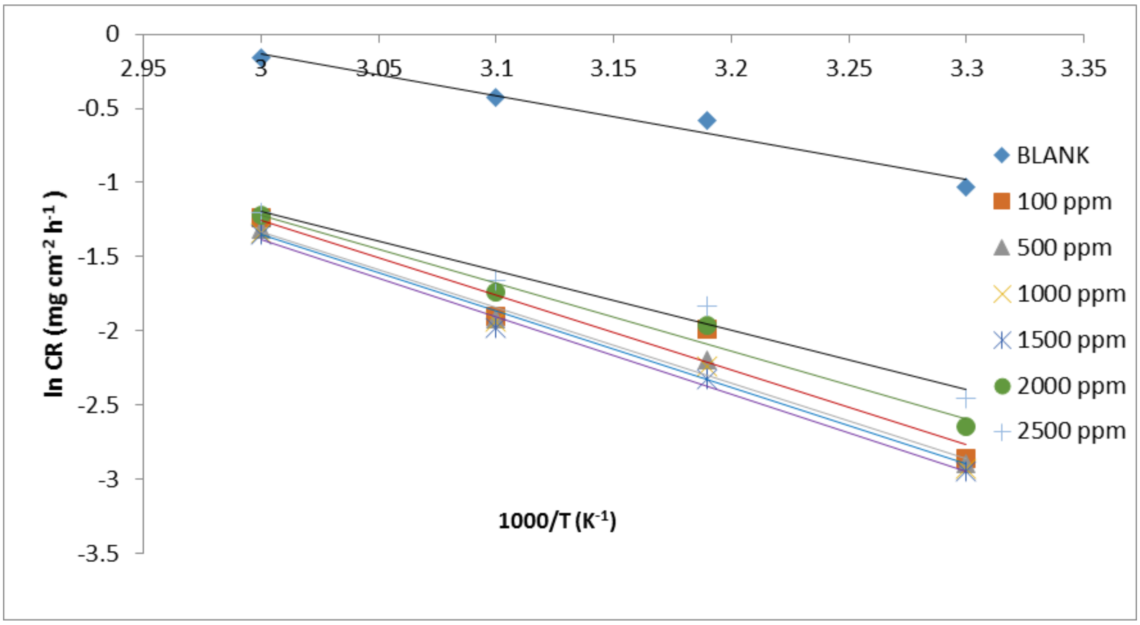


Figure 2: Arrhenius plot for ln CR vs 1000/T for aluminium in 1 M phosphoric acid at various concentration of stingless bee honey

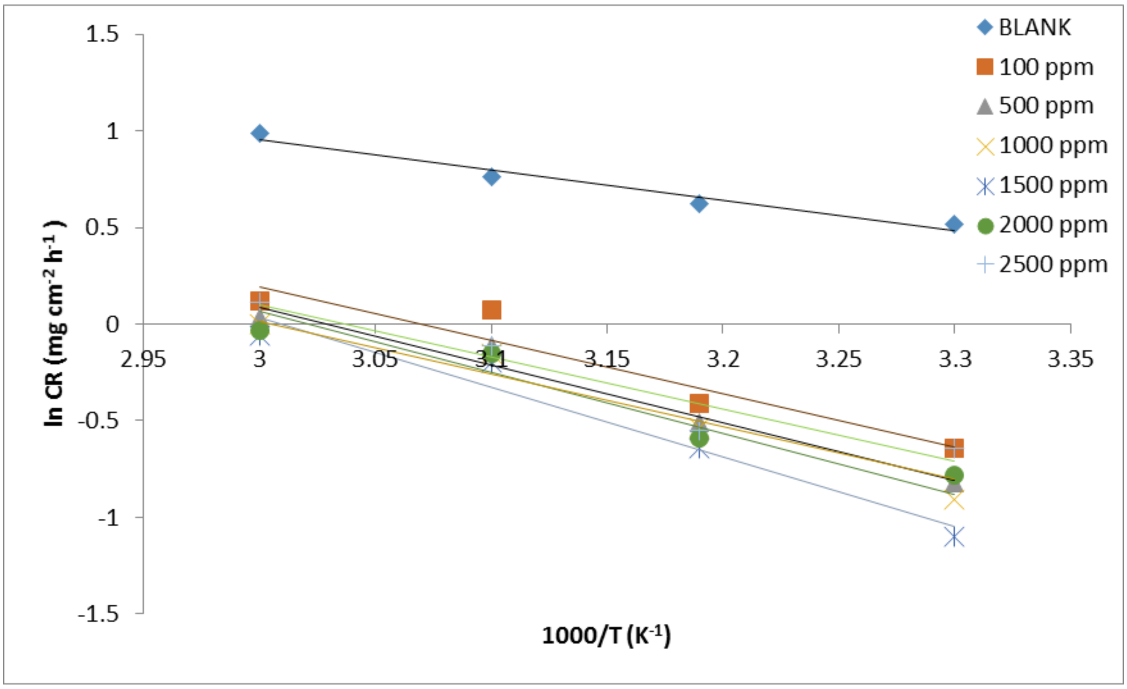


Figure 3: Arrhenius plot for ln CR vs 1000/T for aluminium in 1 M phosphoric acid at various concentration of natural honey

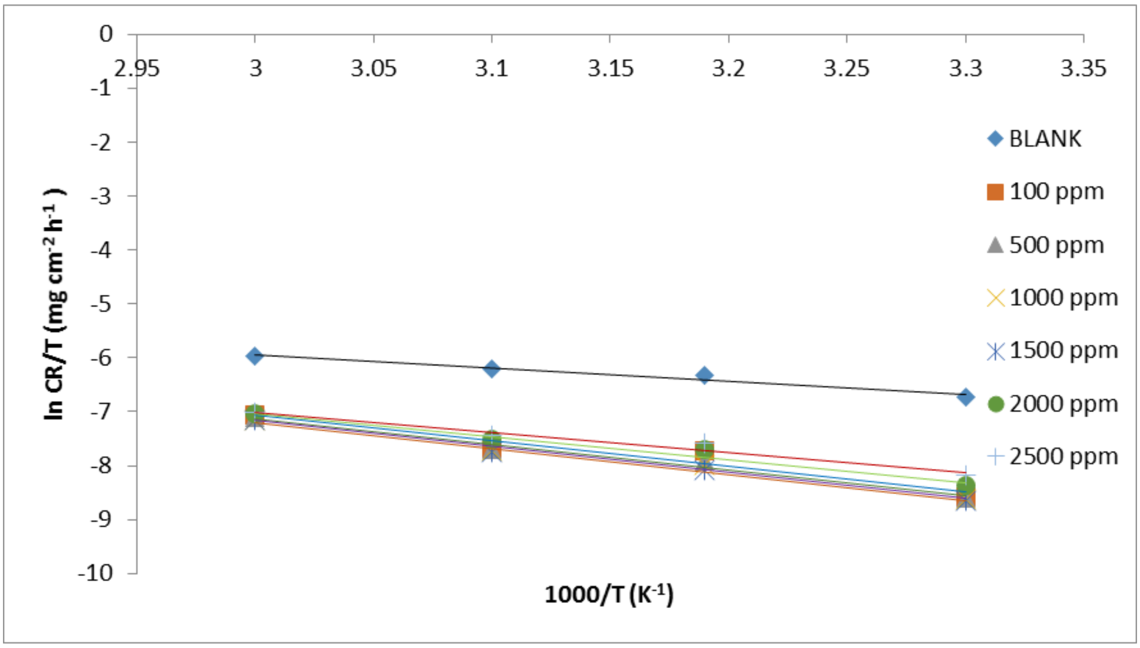


Figure 4: Transition state plot for ln CR/T vs 1000/T for aluminium in 1M phosphoric acid at various concentration of stingless bee honey.

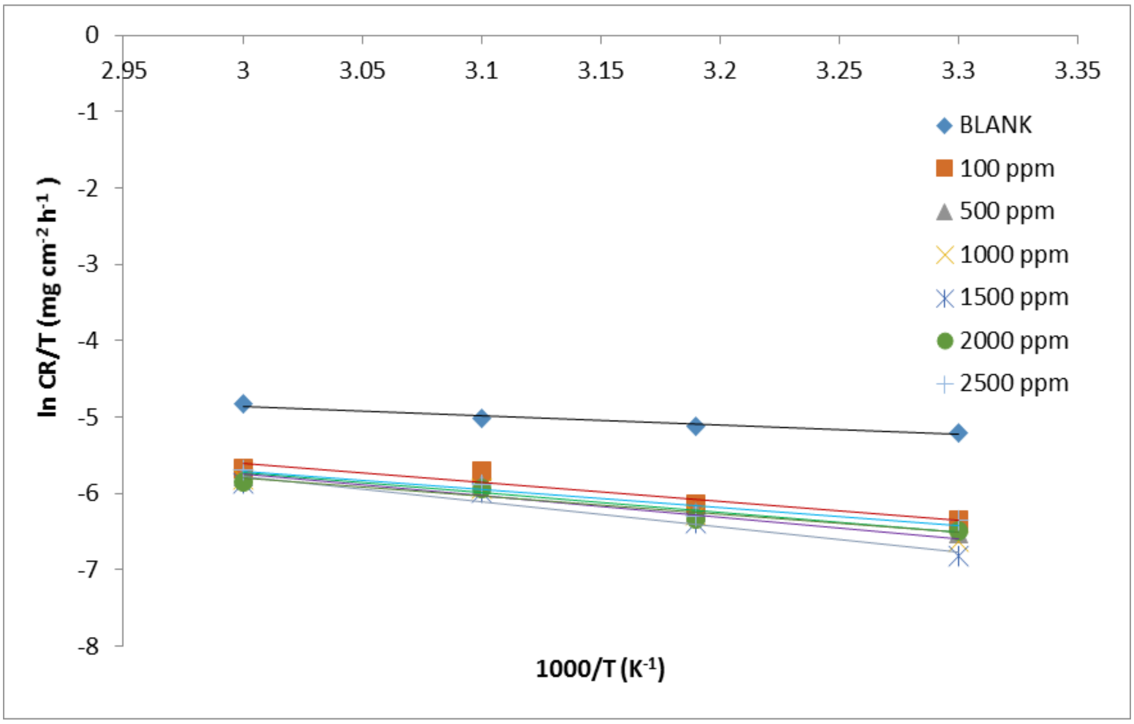
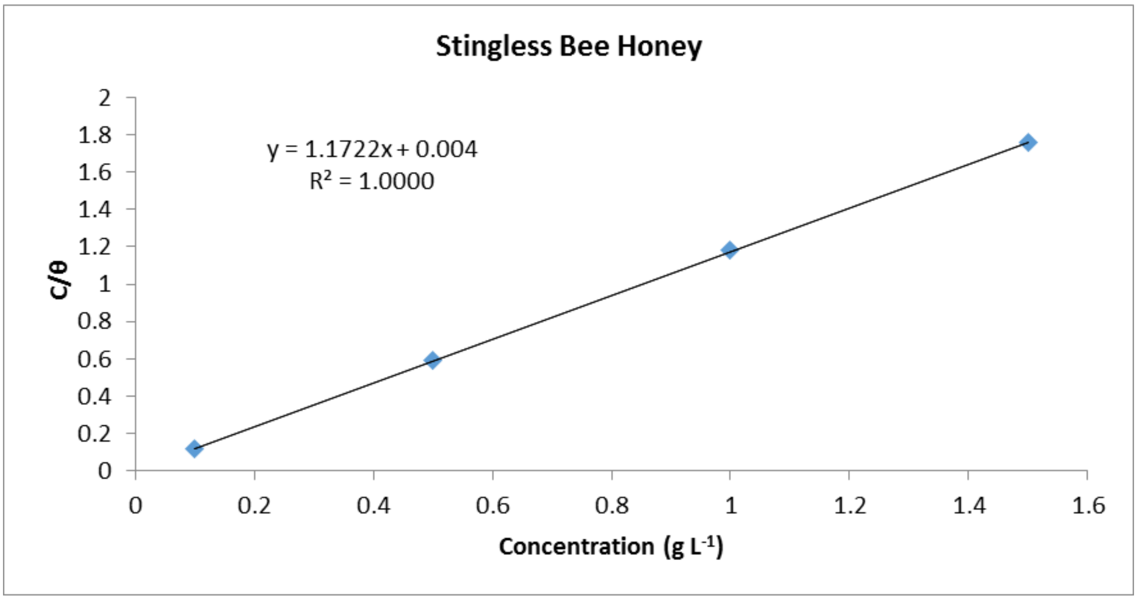


Figure 5: Transition state plot for ln CR/T vs 1000/T for aluminium in 1 M phosphoric acid at various concentration of natural honey.



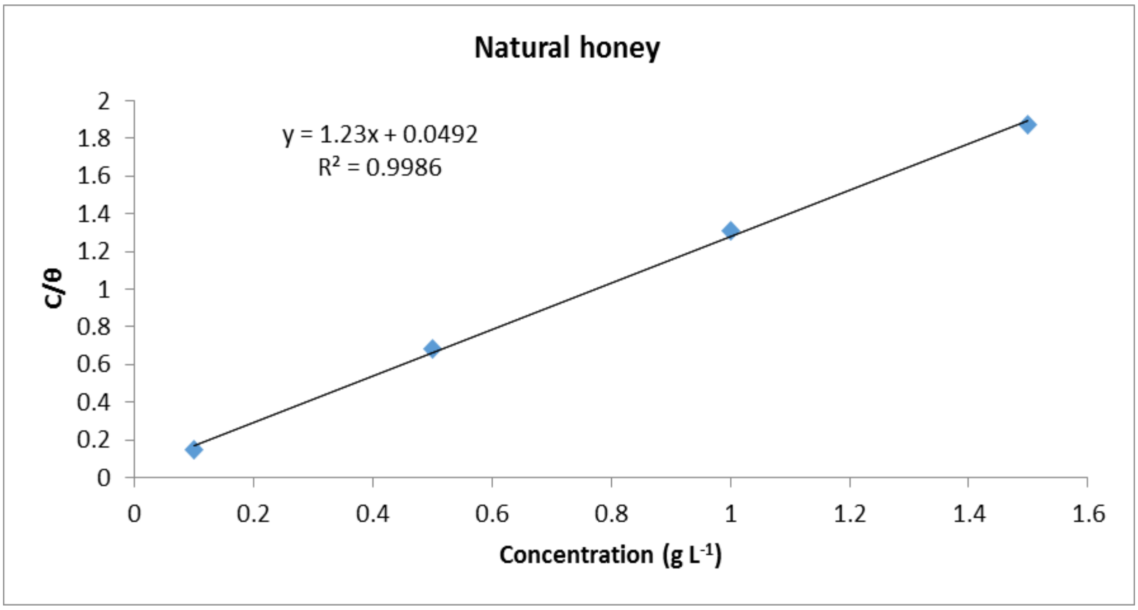


Figure 5: Langmuir adsorption isotherm plot for stingless bee honey and natural honey in 1 M phosphoric acid at 303 K.

Table 1: The effect of temperature for stingless bee honey in various concentrations on aluminium in 1M phosphoric acid.

Temperature (K)	**Concentration (ppm)**	**Weight loss (g)**	**CR (mg cm^{-2} h^{-1})**	**IE%**	**θ**
303	0	0.1028	0.3569	-	-
	100	0.0164	0.0570	84.0	0.840
	500	0.0159	0.0552	84.5	0.845
	1000	0.0154	0.0535	85.0	0.850
	1500	0.0151	0.0524	85.3	0.853
	2000	0.0203	0.0705	80.3	0.803
	2500	0.0245	0.0851	76.2	0.762
313	0	0.1612	0.5598	-	-
	100	0.0406	0.1410	74.8	0.748
	500	0.0318	0.1104	80.3	0.803
	1000	0.0308	0.1069	80.9	0.809
	1500	0.0280	0.0972	82.6	0.826
	2000	0.0406	0.1410	74.8	0.748
	2500	0.0460	0.1597	71.5	0.715

323	0	0.1878	0.6521	-	-
	100	0.0432	0.1500	77.0	0.770
	500	0.0422	0.1465	77.5	0.775
	1000	0.0414	0.1438	77.9	0.779
	1500	0.0397	0.1378	78.9	0.789
	2000	0.0503	0.1747	73.2	0.732
	2500	0.0549	0.1906	70.8	0.708
333	0	0.2466	0.8563	-	-
	100	0.0832	0.2889	66.3	0.663
	500	0.0772	0.2681	68.7	0.687
	1000	0.0751	0.2608	69.5	0.695
	1500	0.0747	0.2594	69.7	0.697
	2000	0.0850	0.2951	65.5	0.655
	2500	0.0868	0.3014	64.8	0.648

Table 2: The effect of temperature for natural honey in various concentrations on aluminium in 1 M phosphoric acid.

Temperature (K)	**Concentration (ppm)**	**Weight loss (g)**	**CR (mg cm^{-2} h^{-1})**	**IE%**	**θ**
303	0	0.4830	1.6771	-	-
	100	0.1525	0.5295	68.4	0.684
	500	0.1270	0.4410	73.7	0.737
	1000	0.1155	0.4010	76.1	0.761
	1500	0.0962	0.3340	80.1	0.801
	2000	0.1322	0.4590	72.6	0.726
	2500	0.1518	0.5271	68.6	0.686
313	0	0.5368	1.8639	-	-
	100	0.1920	0.6667	64.2	0.642
	500	0.1735	0.6024	67.7	0.677
	1000	0.1685	0.5851	68.6	0.686
	1500	0.1515	0.5260	71.8	0.718
	2000	0.1594	0.5535	70.3	0.703
	2500	0.1827	0.6344	66.0	0.660

323	0	0.6134	2.1299	-	-
	100	0.2787	0.9677	54.6	0.546
	500	0.2570	0.8924	58.1	0.581
	1000	0.2475	0.8594	59.7	0.597
	1500	0.2350	0.8160	61.7	0.617
	2000	0.2747	0.9538	55.2	0.552
	2500	0.3045	1.0573	50.4	0.504
333	0	0.7733	2.6851	-	-
	100	0.3836	1.3319	50.4	0.504
	500	0.3546	1.2313	54.1	0.541
	1000	0.3364	1.1681	56.5	0.565
	1500	0.3123	1.0844	59.6	0.596
	2000	0.3568	1.2389	53.9	0.539
	2500	0.3927	1.3635	49.2	0.492

Table 3: Activation parameters of the dissolution reaction of aluminium in 1 M H_3PO_4 in the absence and presence of stingless bee honey.

Concentration (ppm)	**E_a (kJ mol^{-1})**	**ΔH (kJ mol^{-1})**	**-ΔS (J mol^{-1})**
0	12.96	10.11	207.61
100	41.73	39.22	138.54
500	42.33	39.80	137.49
1000	42.73	39.89	137.47
1500	43.33	40.55	135.73
2000	38.09	35.58	149.25
2500	33.39	31.20	162.10

Table 4: Activation parameters of the dissolution reaction of aluminium in 1 M H_3PO_4 in the absence and presence of natural honey

Concentration (ppm)	**E_a (kJ mol^{-1})**	**ΔH (kJ mol^{-1})**	**-ΔS (J mol^{-1})**
0	12.96	10.11	207.61
100	26.50	23.65	172.66
500	29.22	26.38	164.98
1000	30.19	27.60	161.58
1500	33.42	30.64	152.88
2000	31.75	29.05	156.31
2500	27.86	25.73	165.93