Kinetics, isotherm and thermodynamic modeling of liquid phase saponin sorption in soils.

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Abstract. The sorption behavior of saponin onto clay, paddy, silty loam and sandy soil was thoroughly evaluated in this study. The adsorption kinetic, isotherm and thermodynamic were conducted in batch analysis. Pseudo-first order, pseudo-second order and Elovich kinetic models were applied to evaluate the kinetics of the adsorption. Based on the models, the adsorption of saponin onto soils were mostly governed by physisorption while chemisorption also plays a role in the adsorption process in clay and paddy soil. Mechanism of adsorption was determined by adopting the intraparticle diffusion and Boyd models. The two models concluded that intraparticle diffusion is not the rate-limiting step in saponin uptake in all four soil types. Equilibrium isotherm was evaluated by using Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. The data obeys both Langmuir and Freundlich model, however, Langmuir model tends to overestimate the \( q_e \) value of the given soil. Clay soil showed highest maximum adsorption, followed by paddy, silty loam and sandy soil. Effects of temperature variation is minimal while variation in pH value was significant where optimum adsorption was achieved at near-neutral pH range. The thermodynamic study showed that the adsorption process was exothermic and spontaneous.

1. Introduction
Infestation of Golden Apple Snails (Pomacea canaliculata) is a major concern in rice industry, especially in Asian region where rice is consumed as staple food. According to a study, one Golden Apple Snail can consume up to 24 rice seedlings per day (Mohd Salleh et al., 2012). In managing the infestation of this pest, various approaches including chemical, mechanical and biological methods have been employed in rice fields (Brito and Joshi, 2016). However, chemical approach through pesticides deployment is the most popular and widely used method in addressing this problem due to the ease of handling as well as direct results post-application (Miller, 2004). Apart from effectiveness, low operating cost is another factor that drives the widespread use of chemical pesticides. According to a reported studies, pesticide application allows food supply to be cheaper and the value saved is approximately four times higher than the cost of applying pesticides (Hazra and Purkait, 2019; Pimintel et al., 1992). However, widespread utilization of pesticides may lead to unwanted side effects on the environment. Pesticides are usually applied by chemical spraying in pest control, which does not specifically target the intended target species (Miller, 2004; Pimentel, 2005). As a result of chemical spraying, the applied pesticides would reach non-targeted species or the surrounding environment, which causes various implications on natural...
biodiversity (Strandberg et al., 2017). Apart from that, depending on its composition, the applied pesticides might persist in the environment for an extended period of time.

1.1 Saponin-based biopesticides as an alternative solution

Biopesticides are nature-derived, non-chemical based pesticides. According to EPA definition, biopesticides are natural compounds or mixture that are able to demonstrate non-toxic bioactivity against pests (Leahy et al., 2014, Seiber et al., 2018). There are several other terms used in place of biopesticides such as third generation pest control agents and reduced-risk pesticides. Generally, biopesticides are considered as safe, economical and biodegradable which makes it suitable to serve as an alternative for chemical pesticides in agriculture (Goni et al., 2017; Singh and Kaur, 2018). The most extensively studied compounds in synthesizing biopesticides are terpenes and essential oils. These compounds include pyrethrins, azadirachtins, ryanodanes and saponins (Martin et al., 2011; Singh and Kaur, 2018; Cheok et al., 2014). Saponins contain several beneficial properties that can be applied in agricultural sector such as anti-fungal, anti-microbial, insecticidal and molluscicidal activities (Shen et al., 2017). Several researches have demonstrated the effectiveness of saponin as a molluscicidal agent in controlling the infestation of Golden Apple Snails, which is scientifically known as *Pomacea canaliculata* (Massaguni et al., 2017; Ramli et al., 2018). According to Ramli et al. (2018), up to 90% mortality of Golden Apple Snails was achieved through deployment of saponin-based biopesticides in a controlled environment.

1.2 Importance of the evaluation of sorption phenomena

Various studies have been documented on the effectiveness of saponin in suppressing Golden Apple Snails. However, the vast majority of the studies focused on the extraction and formulation of the biopesticides. The effectiveness of the biopesticides was commonly evaluated by applying the biopesticides directly towards the pests through spraying without taking into consideration real-life problems in pesticide applications such as pest targeting, adsorption by soil, degradation and migration.

Sorption of biopesticide plays significant roles in determining the degradation, transport, volatilization and bioaccumulation of the biopesticide in soil environment (Cederlund, 2016; Seiber et al., 2018). The probability and severity of surface water and ground water contamination are directly influenced by these factors. Furthermore, soils are rich in various organic and inorganic compounds with diverse compositions and surface activities. The bioavailability of the applied biopesticide might be reduced due to the binding activities of soil components (Kumar and Philip, 2005). Therefore, in-depth study on sorption of biopesticide in soil is crucial in understanding the biopesticide’s behavior and mobility in soil.

This research work presents a novel study on the behavior of saponin-based biopesticide in soils. Adsorption of saponin-based biopesticide in several agricultural soils was assessed to determine the suitability of its application on the respective soil. This study also attempted to evaluate the effects of organic matter content, clay content and interference of functional groups in soil on adsorption of saponin-based biopesticide. The outcomes of this study are useful in determining the biopesticide’s mobility, potential to cause contamination and the practicality of the biopesticide’s deployment.

2. Methodology

2.1 Soil samples

The paddy soil samples were retrieved from a paddy cultivation site at FELCRA Seberang Perak, Malaysia (4°08’30.9"N, 100°54’07.4"E). The other soil types were purchased from Semaian Seri Iskandar, Seri Iskandar, Perak, Malaysia (4°22’07.6"N, 100°58’48.6"E). The soils were sieved to remove the gravels through 2 mm sieve (IS sieve No. 10) and the fraction that passed through the sieve was collected. The clay, silt and sand component were classified according to particle size as outlined in USDA soil taxonomy standard (clay: less than 0.002 mm; silt: 0.002 – 0.05 mm; sand: more than 0.05 mm). The soil pH was measured directly by using portable pH meter with calomel electrode. Soil organic matter content was determined by Walkley-Black method (IS 2720 (part 22), 1972). The details on the soil properties are outlined in Table 1. All the soil samples were oven dried at 110°C until constant weight was reached and stored in a desiccation chamber.
Table 1. Properties of soils used for adsorption study.

| Soil properties       | Clay soil | Silty loam soil | Sandy soil | Paddy soil |
|-----------------------|-----------|-----------------|------------|------------|
| **pH value**          | 7.86 ± 0.1| 7.3 ± 0.1       | 8.68 ± 0.1 | 5.83 ± 0.1 |
| **Organic matter (%)**| 3.43 ± 0.1| 2.41            | 0.78 ± 0.1 | 10.3 ± 0.1 |
| **Clay (%)**          | 62.3      | 16.8            | 1.3        | 36.7       |
| **Moisture content (w/w %)** | 31.3 ± 2 | 12.8 ± 2       | 4.7 ± 2    | 24.7 ± 2  |

2.2 Chemicals

High purity saponin extract from Quillaja Bark and other chemical reagents and solvents were purchased from Merck Sdn Bhd, Malaysia. All the reagents used were of HPLC grade. The stock saponin solution was prepared by dissolving the saponin extract in distilled water for all experiments. The experiments were carried out in triplicates and the mean values are used in all data reporting.

2.3 Kinetic study

A 5 g of designated soil sample was placed in a screw-capped conical flask. A 100 ml of saponin solution with concentration of 100 mg/l was then added into the flask. The flask was placed in water bath shaker with temperature of 28 ± 2 °C and constant agitation was applied to allow the adsorptions of saponin compound onto the soil and prevent sedimentation. A 5 ml samples from the saponin solution were taken at 0, 0.25, 0.5, 0.75, 1, 1.5, 2, 3, 4, 6, 8, 10 and 12 h. The collected samples were filtered through HPLC grade filtration membrane and analyzed by high-performance liquid chromatography (HPLC). The results of saponin sorption were fitted with Lagergren pseudo-first order, Ho’s pseudo-second order, and Elovich kinetic models. The equations and parameters for the models are given in Table 2.

2.4 Equilibrium isotherm study

Equilibrium isotherm study was carried out for all four types of soil by using 5 g of adsorbent in conical flasks. Saponin solution with final concentrations of 0.5, 1, 2, 5, 10, 25, 50 and 100 mg/l was poured into the flask. A blank was prepared to evaluate the effect of adsorption on saponin on the glassware. The flask was placed in water bath shaker with temperature of 28 ± 2 °C and constant agitation was applied to allow the adsorptions of the saponin compound to soil and prevent sedimentation. After 5 h, 5 ml of sample was collected from each flask and the collected samples were filtered through HPLC grade filtration membrane and analyzed by high-performance liquid chromatography (HPLC). The results for sorption of saponin were fitted with Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption isotherm models. The equations and parameters for the models are given in Table 2.

Table 2. Kinetics and isotherm models, equations and parameters.

| Model                        | Equation                                                                 |
|------------------------------|--------------------------------------------------------------------------|
| Pseudo-first order           | \( \ln (q_e - q_t) = \ln q_e - k_1 t \)                                  |
| Pseudo-second order          | \( t/q_t = (1/k_2 q_e^2) + t/q_e \)                                      |
| Elovich                      | \( q_t = 1/\beta \ln (\alpha \beta) + 1/\beta \ln t \)                  |
| Intraparticle diffusion      | \( q_t = k_{id} t^{1/2} + C \)                                          |
| Boyd                         | \( Bt = -\ln \pi^2/6 - (\ln (1-F(t)) \)                                 |
| Langmuir                     | \( 1/q_e = (1/q_{max} K_t)/(1/C_e) + 1/ q_{max} \)                       |
| Freundlich                   | \( \ln q_e = \ln K_f + (1/n_f) \ln C_e \)                              |
| Dubinin-Radushkevich        | \( \ln q_e = \ln q_0 - \beta e^2 \)                                    |
qt and qe are the sorption amount at time t and at equilibrium respectively (mg/g); t is the sorption time (h); k1 (h⁻¹) and k2 (mg/g/h) are the rate constants for pseudo-first order and pseudo second order respectively. K and v are constants in fractional power kinetics model. In Elovich kinetic models, α is a constant that explains chemisorption rate and β is a constant that explains adsorbent’s surface coverage. For intraparticle diffusion model, ked (mg g⁻¹ h¹/2) is the rate constant for intraparticle diffusion while C is the intercept (mg/g) which correlates with thickness of boundary layer. qmax and q0 are maximum adsorption capacity while KL and KF are Langmuir and Freundlich constants respectively. nF is another constant in Freundlich isotherm model that reflects the intensity of the adsorption process. In Dubinin-Radushkevich model, β is a coefficient to determine the sorption energy E (kJ/mol) and ε is Polanyi potential which can be calculated as follow:

\[ ε = RT \ln (1 + 1/C_e) \]  
\[ E = \sqrt{\frac{1}{2 \beta}} \]  

3. Results and Discussion

3.1 Adsorbent – Soil samples

The four soil samples displayed distinct characteristics. Clay soil contained highest clay content with 62.3 w/w% while sandy soil showed the lowest with approximately 1.3 w/w%. In term of organic matter content, variation from 0.78 w/w% to 10.3 w/w% was observed amongst the soil types. Moisture content varies from 4.7 w/w% to 31.3 w/w%. There was no significant variation in pH value for the different soil types.

3.2 Kinetics study

The adsorption kinetics demonstrated a non-linear relationship between saponin adsorption onto soil surface with time in all four soil types. As shown in Figure 1A, an immediate rapid adsorption was observed as saponin uptake was rapid in the initial phase and gradually achieved a near-steady state with increased time. In this study, pseudo-equilibrium point was decided when there is less than 2.5% variation in concentration of saponin after 8 hours. Pseudo-equilibrium was first achieved in sandy soil after 1.5 hours followed by silty loam soil and paddy soil and clay soil at 4 h time point. The rapid initial adsorption of saponin onto these soils was due to the abundance of vacant sites in the soil during the initial stage and the rate decrease over time due to saturation. Slower mass transfer and diffusion of compounds was depicted by the slow rate of saponin uptake until a near steady state was achieved, which was referred to as pseudo-equilibrium point (Remya et al., 2019). Based on the observed trend, the long term behavior of saponin uptake by all four soil types was less significant to be evaluated as compared to the amount adsorbed in the initial phase. The sorption kinetic were further analyzed by using other kinetic models.

Figure 1A. Concentration of saponin in solution against time.
The kinetic rates of saponin adsorption onto the four tested soils were estimated by using pseudo-first order, pseudo-second order and Elovich kinetic models. Based on the plots of kinetic models given in Figure 1B-1F and the calculated parameters in Table 3, the adsorption of saponin onto the four different soil types are governed by more than a single mechanism and varied across the four soil types. Based on the experimental data in Figure 1B and Table 3, the plot of log \( q_e - q_t \) against time gives a straight line with a good fitting \((R^2 > 0.97)\) for all four soil types. Furthermore, the estimated \( q_e \) values given by Lagergren pseudo-first order model were relatively accurate especially for sandy soil where difference between theoretical and actual value is less than 5%. The deviation of calculated \( q_e \) from actual value for the other three soil types were not more than 10%. These findings demonstrated that the experimental data fits well with Lagergren pseudo-first order model. This model suggests the adsorption process mimics the first order reaction. Since the experimental data obeys the pseudo-first order, it can be concluded that the majority of the adsorption process was achieved through physisorption (Lagergren, 1898; Ho and McKay, 1999).

On the other hand, Ho’s pseudo-second order model gives similar correlation coefficients \((R^2)\) with Lagergren pseudo-first order model except for adsorption of saponin onto sandy soil where the model showed a poor fitting with experimental data. Despite the high correlation coefficients, this model was not able to accurately estimate the value of \( q_e \), where the estimated theoretical value often overestimates the maximum adsorption capacity as shown in Table 3. The huge variation in the value of \( q_e \) indicates that the experimental data cannot be explained by this model.

Elovich kinetic model fits relatively well with the experimental data obtained across all four soil types which indicates the occurrence of chemisorption. The initial rate of chemisorption, denoted by the constant \( \alpha_{EL} \), was the highest in clay soil, followed by paddy soil, silty loam soil and sandy soil. Low \( \alpha_{EL} \) for adsorption of saponin onto silty loam and sandy soil suggest low occurrence of chemisorption activity in these soil. Therefore, it can be concluded that chemisorption is more prevalent in clay soil and paddy soil. The extension of surface coverage, \( \beta_{EL} \), is the highest in sandy soil, followed by silty loam soil, paddy soil and clay soil. Low \( \beta_{EL} \) indicates that the uptake of saponin was more likely achieved through functional groups. This further supports the assumption of high chemisorption activity in clay soil and paddy soil as stated earlier. In order to further evaluate the mechanism of saponin adsorptivity, further analysis with intraparticle diffusion and Boyd kinetic models was carried out.
Intraparticle diffusion model was applied in this study to evaluate the diffusion mechanism of saponin sorption onto soils. Based on the model, a linear relationship between $q_t$ and $t^{1/2}$ indicates the influence and involvement of intraparticle diffusion. The plot of $q_t$ against $t^{1/2}$ for different soil types is presented in Figure 1E. Based on the plot, there is no single, linear line observed in all four soil types. Instead, the plotted data resembles a multi-linearity where each plot can be divided into two linear lines. The observed multi-linearity indicates that multiple processes were involved in the sorption of saponin onto the soils (Lorenc-Grabowska and Gryglewicz, 2007; Sieczka and Koda, 2016). The first stage is described as the depiction of external mass transfer where the adsorption process was instantaneous. This is followed by the gradual adsorption stage where intraparticle diffusion is dominant assuming if intraparticle diffusion is the rate limiting step. The final stage indicates equilibrium where intraparticle diffusion has declined as the adsorbate concentration declined in the solution (Noroozi et al., 2007; Betianu et al., 2009). The first stage is not observable in the plot as this step should take place within the first few minutes of the adsorption process. Therefore, the first linear lines, at $t^{1/2}<2$, was attributed to intraparticle diffusion effects. The second linear lines, at $t^{1/2}>2$, were not considered as the adsorption had reached pseudo-equilibrium point. The linear regression observed in Figure 1E suggests that intraparticle diffusion was prevalent prior to pseudo-equilibrium point. However, the linear line deviates from the origin suggesting that intraparticle diffusion might play a role in the uptake of saponin. Similar findings have been reported by Betianu et al., (2009) for adsorption of AO7 in soils and Wei et al., (2017) for adsorption of PFOS in soils.

In Boyd kinetic model, a linear plot passing through the origin indicates that intraparticle diffusion is the rate limiting step for the sorption activity. Based on the Figure 1F, linear regression can be observed in all studied cases, however, none of them passes through the origin. Non-linear plot or linear plot that does not passes through the origin is an indication that the rate-limiting step is film diffusion or chemical reaction (Malash and El-Khaiary, 2010; Sharma and Das 2012). Similar finding was reported by Yakubu and Owabor (2018) in the study of adsorption of phenol onto soil sediments. Therefore, it can be concluded that external mass transfer plays a major role in saponin sorption in soils and more prominent than the internal transport (Viegas et al., 2014). This finding is in agreement with the previous finding where the experimental data obeys the pseudo-first order model, which indicates that physisorption is dominant and film diffusion is more likely to be the rate-limiting step.
Table 3. List of calculated parameters for kinetic models.

| Model                  | Constant         | Clay     | Paddy    | Silty loam | Sandy   |
|------------------------|------------------|----------|----------|------------|---------|
|                        | $q_e \text{ exp (mg/g)}$ | 1.731    | 1.626    | 1.065      | 0.754   |
|                        | $k_1 \text{ (h}^{-1}\text{)}$ | 1.135    | 1.287    | 1.314      | 1.940   |
|                        | $q_e \text{ cal (mg/g)}$      | 1.580    | 1.741    | 1.227      | 0.719   |
|                        | $R^2$                      | 0.978    | 0.969    | 0.986      | 0.965   |
|                        | $q_e \text{ cal (mg/g)}$      | 2.159    | 2.080    | 1.502      | 1.150   |
|                        | $k_2 \text{ (mg/g.h)}$       | 0.539    | 0.496    | 0.557      | 1.077   |
|                        | $h \text{ (mg/g.h)}$         | 2.510    | 2.146    | 1.256      | 1.426   |
|                        | $R^2$                      | 0.975    | 0.966    | 0.987      | 0.8696  |
|                        | $\alpha_{EL} \text{ (mg.g.h)}$ | 5.422    | 4.404    | 2.654      | 2.582   |
|                        | $R^2$                      | 0.938    | 0.953    | 0.993      | 0.960   |
|                        | $k_{id} \text{(mg/g.h}^{1/2}\text{)}$ | 1.234    | 1.178    | 0.660      | 0.708   |
|                        | $C \text{ (mg/g)}$           | -0.065   | -0.094   | -0.008     | -0.035  |
|                        | $R^2$                      | 0.952    | 0.955    | 0.970      | 0.958   |

3.3 Equilibrium isotherm

Table 4 shows various investigated parameters obtained from plot of the three isotherms. Langmuir adsorption isotherm model gives the best fit for the experimental data with high correlation coefficient in all four soil types ($R^2>0.99$). This model assumes that at maximum coverage, only monolayer and uniform adsorption occurs in the adsorption of saponin onto these soil types. However, soil is known to be a heterogenous material where stacking of adsorbed molecules is likely to occur. The good correlation obtained in the plots might be due to low adsorbate availability making it unable to compete with the overabundance of sorption sites available on the adsorbent. This phenomenon mimics the occurrence of monolayer adsorption despite the possibility of a multilayer adsorption. Similar finding and assumption were reported by Kumar and Philip (2005) where the uptake of endosulfan by soil obeyed the Langmuir isotherm model. Based on the plot and calculated parameters, the highest monolayer saturation capacity ($q_{max}$) for saponin uptake was obtained in clay soil, followed by paddy soil, silty loam soil and sandy soil. Clay particles contains higher number of vacant sites and surface area compared to sand particles.
(Gao et al., 1998). As shown in Table 1, clay soil has higher amount of clay content compared to the other three soil types. Despite the high correlation coefficients value, this model was not able to accurately estimate the value of $q_e$, where the estimated theoretical value often overestimates the maximum adsorption capacity as shown in Table 4.

Freundlich adsorption isotherm model also gives a good fit as the experimental data with high correlation coefficient as shown in Table 4. This model assumes that stronger binding sites are first occupied and the surface is continuously filled until the weakest binding sites are occupied. This finding indicates that the concentration of saponin on the soil surface increases as the concentration of saponin increases. The process is considered as favourable and physical since the calculated value of $n$ in all studied cases are above unit.

Dubinin-Radushkevich (D-R) model was applied to distinguish between the physical and chemical adsorption that governs the uptake of saponin in soils. The low adsorption energy ($E$) obtained from Dubinin-Radushkevich (D-R) isotherm indicated that the uptake of saponin was mainly through physisorption. This is in agreement with the previous findings in kinetic analysis where physisorption was determined to be dominant especially in sandy soil. However, Dubinin-Radushkevich (D-R) model resulted in a poor fit with the experimental data with low correlation coefficient ($R^2$) in all studied cases, thus making the model and its assumptions unreliable in explaining the behavior of saponin adsorption onto soil.

### Table 4. List of calculated parameters from Langmuir, Freundlich and Dubinin-Radushkevich isotherm.

| Isotherm   | Constant          | Soil types         | Clay  | Paddy | Silty loam | Sandy |
|------------|-------------------|--------------------|-------|-------|------------|-------|
|            | $q_e$ exp (mg/g)  |                    | 1.731 | 1.626 | 1.065      | 0.754 |
| Langmuir   | $q_{max}$ (mg/g)  |                    | 2.332 | 1.896 | 1.366      | 0.832 |
|            | $K_L$             |                    | 0.046 | 0.037 | 0.020      | 0.014 |
|            | $R^2$             |                    | 0.9968| 0.9949| 0.9973     | 0.9959|
| Freundlich | $K_F$             |                    | 0.118 | 0.068 | 0.026      | 0.011 |
|            | $n$               |                    | 0.934 | 0.994 | 1.004      | 0.986 |
|            | $R^2$             |                    | 0.9978| 0.9892| 0.994      | 0.9871|
| D-R        | $q_0$ (mg/g)      |                    | 0.369 | 0.314 | 0.202      | 0.120 |
|            | $\beta$           |                    | 0.105 | 0.134 | 0.226      | 0.331 |
|            | $E$               |                    | 2.182 | 1.932 | 1.487      | 1.229 |
|            | $R^2$             |                    | 0.729 | 0.706 | 0.649      | 0.599 |
3.4 Effect of organic matter
Based on Table 1, clay soil and paddy soil showed considerably similar properties except for the organic matter content and clay percentage. Although clay soil has higher percentage of clay content, the difference in the amount of adsorbed saponin does not differ greatly from each other, 2.332 mg/g in clay soil and 1.896 mg/g in paddy soil. The low clay content in paddy soil might be compensated by the high organic matter content, which might play a role in the adsorption of saponin onto the soil (Yu and Zhou, 2005). Similar result was demonstrated by Kumar and Philip (2005) in which the reduction in organic matter content decreased the rate of adsorption and adsorption capacity of alpha and beta endosulphan onto clay soil. From this result, it was shown that the adsorption onto soil minerals is not only dependent on the clay ratio but also dependent on carbon content. Therefore, paddy soil with high organic matter content would be ideal for saponin retention in soil and reduce the risk of contamination.

3.5 Effect of temperature and pH
Changes in temperature did not significantly affect the adsorption of saponin onto paddy soil. From Figure 3A, the largest difference between amount of adsorbed saponin at highest and lowest temperature is approximately 16.5 %, which was achieved at pH 8. Furthermore, saponins are generally thermostable compounds (Savage, 2003). Low susceptibility to structural changes due to heat influence might contribute to the minimal effect of temperature on the adsorption of saponin onto soil.
Soil pH plays an important role in the adsorption of saponin paddy soil by determining the surface charge and crystal lattice structure in clay particles. Effects of pH on the uptake of saponin onto paddy soil was investigated. The amount of saponin adsorbed at different pH value is shown in Figure 3A. Based on the figure, minimal adsorption was achieved at pH 1.5 and pH 2 with 0.036 g and 0.057 g of saponin adsorbed per gram of soil at 28˚C. From pH 4 to pH 6, the amount of adsorbed saponin gradually increased from 0.992 mg/g to 1.487 mg/g as the pH increased. From pH 6 to pH 10, notable reduction in saponin adsorption was observed where the recorded amount of adsorbed saponin at pH 8 and pH 10 was 1.306 mg/g and 0.817 mg/g respectively.

**Figure 3A.** Effect of temperature and pH on adsorption of saponin onto paddy soil.

Based on the observation, acidic condition leads to poor adsorption of saponin onto paddy soil. This phenomenon might be due to the destruction of soil crystal lattice structure in clay particles (Kumar and Philip, 2005). Paddy soil has a relatively high clay content (Table 1) which plays important role in saponin adsorption. In order to verify the assumption, the effect of temperature and pH was also experimented by using sandy soil which was known to have low clay content. In sandy soil, the variation between highest and lowest saponin adsorption at 28˚C was approximately 28.2% while in paddy soil, the variation was approximately 97.6%. This finding implies that sandy soil is less vulnerable to changes in pH compared to paddy soil due to the lack of clay particles in sandy soil. For further verification, adsorption kinetic study was conducted by using one sample of acid treated soil (pH 2) that was...
neutralized to pH 7 as adsorbent. The obtained amount of adsorbed saponin in the neutralized soil at 28˚C was 0.304 mg/g, approximately 78% lower in comparison to the estimated amount at pH 7 given in Figure 3A. This finding supported the assumption that the minimal adsorption at very low pH was due to the destruction of soil crystal lattice structure which might play an important role in the adsorption of saponin onto paddy soil. Furthermore, these findings also demonstrated that regaining of crystal lattice in clay particles is not achievable through pH adjustment. In Malaysia, optimum soil pH range for wetland paddy cultivation is between 5.5 to 6.5 as outlined by Malaysian Agricultural Research and Development Institute (Abd Rani et al., 2015). Therefore, high saponin uptake of saponin at near-neutral pH is advantageous for the application of saponin-based biopesticide as the risk of contamination will be minimized.

3.6 Thermodynamic analysis
Calculated thermodynamic parameters for the adsorption of saponin onto paddy soil are provided in Table 5. Based on the table, negative value of ΔH° for saponin adsorption indicated that the adsorption process was exothermic in nature. Positive ΔS° indicates the increase in the randomness at the solid-liquid interface in the adsorption process. This observation might be due to the acquired translational entropy from displaced water was higher than the loss of translational entropy from saponin uptake (Inyinbor et al., 2016). Negative value of ΔG° suggests that the adsorption was spontaneous. Lower negative values were obtained as temperature increased which indicated lower spontaneity at high temperature.

4. Conclusion
In conclusion, saponin was mainly taken up by soil through physisorption and film diffusion is the rate limiting step. However, chemisorption also took place at lower rate especially in clay soil and paddy soil as soil is a heterogenous material. Soils with higher clay content and organic matter content had higher adsorption capacity and higher rate of saponin adsorption. Out of the four soil types evaluated in this study, clay soil is the most suitable soil type for saponin-based biopesticide application. Paddy soil also displayed high suitability for the biopesticide’s application. This is attributed to their high retention of saponin in soil which can prevent leaching activities and undesired contamination of biopesticide in the environment. Furthermore, soil pH is an important factor to be considered when applying saponin-based biopesticide as soil with high acidity or base will affect the adsorption of saponin especially in soil with high clay content.

Table 5. Thermodynamic parameters for adsorption of saponin onto paddy soil.

| Adsorbent | ΔH° (kJ/mol) | ΔS° (J/mol/K) | ΔG° (kJ/mol) |
|-----------|-------------|--------------|--------------|
| Saponin   | -11.74      | 49.23        | -4.6         | -4.3         | -3.7         | -3.1         |

References
[1] Abd Rani MNF, Yusof MNM, Hashim S, Sulaiman E and Ramli A 2015 Soil fertility and nutrient management for rice crop in Malaysia Buletin Teknologi MARDI 8 37-44.
[2] Abdullah NS, Aziz NA and Mailon R 2017 Molluscicidal activity of Entada rheedi stem bark methanolic extract against paddy pest Pomacea canaliculata (Golden Apple Snails) Malaysian Journal of Analytical Sciences 21 46-51.
[3] Ayawei N, Abelegi AN and Wankasi D 2017 Modelling and Interpretation of Adsorption Isotherms Journal of Chemistry 2017.
[4] Betianu C, Bulgariu D and Gravilescu M 2009 An investigation of the sorption of acid orange 7 from aqueous solution onto soil Environmental Engineering and Management Journal 8 1391-1402.
[5] Brito F and Joshi RC 2016 The golden apple snail Pomacea canaliculata: A review on invasion,
dispersion and control *Outlooks on Pest Management* 27 157-163.

[6] Brunauer S, Emmett PH and Teller E 1938 Adsorption of gases in multi molecular layers *J Amer. Chem. Soc.* 60 309–319.

[7] Cederlund H, Borjesson E, Lundberg D and Sternstrom J 2016 Adsorption of pesticides with different chemical properties to a wood biochar treated with heat and iron *Water, Air & Soil Pollution* 227.

[8] Cestari A, Vieira E, Vieira G and Almeida L 2006 The removal of anionic dyes from aqueous solutions in the presence of anionic surfactant using aminopropylsilica—A kinetic study *Journal of Hazardous Material* 138 133-141.

[9] Cheok CY, Salman HAK and Sulaiman R 2014 Extraction and quantification of saponins, a review *Food Res. Int.* 59 16-40.

[10] Choppala G, Kunhikrishnan A, Seshadri B, Park JH, Bush R and Bolan N 2018 Comparative sorption of chromium species as influenced by pH, surface charge and organic matter content in contaminated soils *Journal of Geochemical Exploration* 184 255-260.

[11] Elshafei GS, Nasr IN, Hassan ASM and Mohammad SGM 2009 Kinetics and thermodynamics of adsorption of cadusafos on soils *Journal of Hazardous Materials* 172 1608-16.

[12] Freundlich HMF 1906 Over the adsorption in solution *J Physic. Chem.* 57 385–471.

[13] Goni ML, Ganan NA, Herrera JM, Strumia MC, Andreatta AE and Martini RE 2017 Supercritical CO2 iof LDPE films with terpene ketones as biopesticides against corn weevil (Sitophilus zeamais) *The Journal of Supercritical Fluids* 122 18-26.

[14] Hazra DK and Purkait A 2019 Role of pesticide formulations for sustainable crop protection and environment management: A review *Journal of Pharmacognosy and Pharmacology* 8 686-693.

[15] Ho YS and McKay G 1999 Pseudo-second order model for sorption processes *Process Biochem.* 34 451–465.

[16] Inyinbor AA, Adekola FA and Olatunji GA 2016 Kinetics, isotherms and thermodynamic modelling of liquid phase adsorption of Rhodamine B dye onto Raphia hookerie fruit epicarp *Water Resources and Industry* 15 14-27.

[17] Kakavandi B, Jafari AJ, Kalantary RR, Nasseri S, Ameri A and Esrafily A 2013 Synthesis and properties of Fe3O4-activated carbon magnetic nanoparticles for removal of aniline from aqueous solution: equilibrium, kinetic and thermodynamic studies *Iran. J Environ. Health Sci. Eng.* 10.

[18] Kumar M and Philip L 2005 Adsorption and desorption characteristics of hydrophobic pesticide endosulphan in four Indian soil *Chemosphere* 62 1064-77.

[19] Lagergren S, 1898, About the theory of so-called adsorption of soluble substances *Kungliga Svenska Vetenskapsakademiens Handlingar* 24 1–39.

[20] Langmuir I 1918 The adsorption of gases on plane surfaces of glass, mica and platinum *J Amer. Chem. Soc.* 40 1361–1403.

[21] Leahy J, Mendelsohn M, Kough J, Jones R and Berekes N 2014 Biopesticide oversight and registration at the U.S. Environmental Protection Agency *ACS Symposium Series*.

[22] Lopes E, dos Anjos F, Vieira E and Cestari A 2003 An alternative Avrami equation to evaluate kinetic parameters of the interaction of Hg(II) with thin chitosan membranes *Science* 236 542-547.

[23] Lorenc-Grabowska E and Gryglewicz G 2007 Adsorption characteristics of congo red on coal-based mesoporous activated carbon *Dyes and Pigments* 74 34-40.

[24] Malash GF and El-Khaiary MI 2010 Piecewise linear regression: a statistical method for the analysis of experimental adsorption data by the intraparticle-diffusion models *Chem. Eng. J.* 163 256-263.

[25] Martin L, Marques JL, Gonzalez-Coloma A, Mainar AM, Palavra AMF and Urieta JS 2012 Supercritical methodologies applied to the production of biopesticides: a review *Pythochemistry Reviews* 11(4) 413-431.
[26] Massaguni R and Md Latip NH 2015 Assessment the molluscicidal properties of Azadirachtin against Golden Apple Snail, Pomacea canaliculata Malaysian Journal of Analytical Sciences 781-789.

[27] Meissner J, Prause A, Bharti B and Findenegg GH 2015 Characterization of protein adsorption onto silica nanoparticles: influence of pH and ionic strength Colloid and Polymer Science 293 (11) 3381-91.

[28] Miller GT 2004 Sustaining The Earth 6th ed. Thompson Learning, Inc Pacific Grove, California.

[29] Mohd Salleh NH, Arbain D, Mohamed Daud MZ, Pilus N and Nawi R 2012 Distribution and management of Pomacea canaliculata in the Northern Region of Malaysia: Mini review APCBEE Procedia 2 129-134.

[30] Noroozi B, Sorial GA, Bahrami H and Arami M 2007 Equilibrium and kinetic adsorption study of a cationic dye by a natural adsorbent – Silkworm pupa, Journal of Hazardous Material 139 303-312.

[31] Pimentel D 2005 Environmental and Economic Costs of the Application of Pesticides Primarily in the United States Environ., Dev. Sustain. 7 229–252.

[32] Pimintel D, Acquay H, Biltonen M, Rice P, Silva M, Nelson J, Lipner V, Giordano S, Horowitz A and D’Amore M 1992 Environmental and Economic Costs of Pesticide Use Bioscience 42 750-760.

[33] Ramli NH, Yusup S, Quitain AT, Johari K and Kueh BWB 2019 Optimization of saponin extracts using microwave-assisted extraction as a sustainable biopesticide to reduce Pomacea canaliculata population in paddy cultivation Sustainable Chemistry and Pharmacy 11 23-35.

[34] Ramli NH, Yusup S, Johari K and Abd Rahim M 2017 Selection of potential plants for saponin extract using supercritical-CO2 extraction against Golden Apple Snails (Pomacea canaliculata) for paddy cultivation Archives of Crop Science 1.

[35] Remya N, Roshni T, Yadav RR and Shukla N 2019 Experimental investigation of groundwater contamination by surface sources: Determination of adsorption capacity, diffusion, and sorption potential of selected anions in different soils Environmental Quality Management 29 139-148.

[36] Sieczka A and Koda E 2016 Kinetic and equilibrium studies of sorption of ammonium in the soil-water environment in agricultural areas of central Poland Applied Sciences 6(10) 269.

[37] Singh A and Kaur J 2016 Toxicity of leaf extracts of Ricinus communis L. (Euphorbiaceae) against the third instar larvae of Musca domestica L. (Diptera: Muscidae) American Journal of Bioscience 4 5-10.

[38] Seiber JM, Coats J, Duke SO and Gross AD 2018 Pest management with biopesticides Front. Agr. Sci. Eng. 5(3) 295-300.

[39] Serna-Guerrero S and Sayari A 2010 Modeling adsorption of CO2 on amine-functionalized mesoporous silica. 2: Kinetics and breakthrough curves Chemical Engineering Journal 161 182-190.

[40] Sharma P and Das MR 2012 Removal of a cationic dye from aqueous solution using graphene oxide nanosheets: investigation of adsorption parameters J. Chem. Eng. Data 58 151-158.

[41] Sha W, Wu X, Keong KG 2011 Modelling the thermodynamics and kinetics of crystallisation of nickel–phosphorus (Ni–P) deposits, electroless copper and nickel–phosphorus plating Woodhead Publishing Series in Metals and Surface Engineering 183-217.

[42] Shen X, Shi L, Pan H, Li B, Wu Y, and Tu Y 2017 Identification of triterpenoid saponins in flowers of four Camelia sinensis cultivars from Zheijiang province: differences between cultivars, developmental stages, and tissues Ind. Crops. Prod. 95 140-147.

[43] Strandberg B, Boutin C, Mathiassen SK, Damgaard C, Dupont YL, Carpenter DJ and Kudsk P 2017 Effects of herbicides on non-target terrestrial plants, Pesticide dose: Effects on the environment and target and non-target organisms ACS Symposium Series 1249 149-166.

[44] Tempkin MI, Pyzhev V 1940 Kinetics of ammonia synthesis on promoted iron catalyst Acta Phys. Chim. Sin. 12 327–356.
[45] Viegas RNC, Campinas M, Costa H and Rosa MJ 2014 How do the HSDM and Boyd’s model compare for estimating intraparticle diffusion coefficients in adsorption processes Adsorption 20 737-746.

[46] Wei C, Song X, Wang Q and Hu Z 2017 Sorption kinetics, isotherms and mechanisms of PFOS on soils with different physicochemical properties Ecotoxicology and Environmental Safety 142 40-50.

[47] Yakubu EE and Owabor C 2018 The effect of mass transfer resistance on the adsorption rate of phenol in soil sediments American Journal of Environmental Science and Engineering 2 56-64.

[48] Zhao Y, Liu F and Qin X 2017 Adsorption of diclofenac onto goethite: Adsorption kinetics and effects of pH Chemosphere 180 373-378.

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