

ADSORPTION OF RHODAMINE B DYE ON COMPOSITE PELLETS OBTAINED FROM PECTIN AND MONTMORILLONITE CLAY

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Abstract

Montmorillonite (MMt) clay has exhibited excellent efficiency for the adsorption of cationic dyes. However, recovery of MMt clay powder after the adsorption from the liquid body is a difficult task. To overcome this limitation, the pelletizing of these powder particles with biopolymer is one of the potential alternatives. The composite pellet was prepared by immobilization of MMt particles inside the structure of the natural pectin pellet extracted from the watermelon peel (*Citrullus lanatus*). Then, the composite pellet and MMt were characterized comparatively using N₂ adsorption-desorption isotherm at 77.4 K, Fourier Transform Infrared Spectroscopy (FTIR), and Field Emission Scanning Electron Microscopy (FESEM). The highest dye removal efficiency was 88.31%. The optimum condition was observed under a certain condition, which is the contact time of 180 min, the initial dye concentration of 250 mg/L, the initial pH of 2.0, and the temperature of 55°C. The adsorption isotherm followed the Freundlich equation revealing multilayer coverage. The kinetic data fit well with the pseudo-second order kinetic model exhibiting the chemical reaction involved. The pelletizing of MMt as the composite pellet has not only proven an effective adsorbent for the adsorption of Rhodamine B dye from wastewater, but also facilitated the recovery of the spent adsorbent.

Keywords: Adsorption, Rhodamine B, composite pellet, pectin, montmorillonite clay

Introduction

Contaminated synthetic dyes in natural streams such as creek, swamp, and canal become serious environmental pollution in the rural area of the lower northeastern region of Thailand. Villagers gather into household scale textile industries to increase the production of local textile products such as silk and cotton. Villagers can earn additional income from selling these products apart from

selling their agricultural products (Junsongduang *et al.*, 2017). Natural dyes were used in the past; however, they were easily decomposed leading to the faded colour products. Nowadays, synthetic dyes are preferentially used due to their bright, long-lasting colour, and fast dyeing. Rhodamine B dye is used as the synthetic dye in this research because it contains some functional groups such as two amino

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and one carboxyl groups which are like those of available local chemical dyes (Samchetshabam *et al.*, 2017). In the dyeing process, synthetic dyes and large amount of water are used. As a result, the used water which is contaminated by the synthetic dyes becomes effluent or wastewater since the dyestuffs are left in the water body around 60-70% of their original quantity. Due to the complex structures and resistance to heat and light of the dyes, they are severely biodegradable. Direct discharge of this effluent into the reservoirs is dangerous to aquatic life and may cause unsightly scene, prevention of sunlight penetration and reduction in oxygen solubility (Lellis *et al.*, 2019). Thus, treatment of this wastewater before being discharged into the environment is an essential task.

There are many approaches to treat the effluent contaminated by synthetic dyes, which can be divided into 3 groups: biological, chemical, and physical methods (Katheresan *et al.*, 2018). Examples of biological methods include enzymatic degradation, microbiological cultures, and biological degradation of algae. Although the biological approaches are highly efficient, additional specific nutrients and serious control under a particular condition are necessary (dos Santos *et al.*, 2007; Ali and El-Mohamedy, 2012). Chemical treatment includes advanced oxidation, electrochemical destruction, Fenton reaction, photochemical and ultraviolet irradiation, and ozonation. The chemical treatment is efficient, but it is expensive and potentially generates secondary pollution to the environment (Forgacs *et al.*, 2004; Hassaan *et al.*, 2017). Physical methods are composed of adsorption, coagulation or flocculation, ion exchange, irradiation, and membrane filtration. The adsorption is an effective method among alternatives due to relatively low cost, fast process, and simplicity. Over decades, activated carbon has exhibited its excellent dye removal efficiency. However, the activated carbon is not widely used for dye removal from large amount of wastewater because it is costly and has a high reutilization cost by heat treatment at a high temperature (Heidarinejad *et al.*, 2020). The development of low-cost adsorbent alternatives such as agricultural wastes, industrial by-products, fruit peels, natural soil, and wood materials, etc (Gisi *et al.*, 2016) while maintaining high adsorption efficiency is a challenging task.

One of the natural mineral clays that is available in many regions of Thailand such as Lampang, Ranong, and Narathiwat provinces is montmorillonite clay (MMt) (Kuroda *et al.*, 2017). The commercial MMt product is cheap and available in the local area so MMt, as received, can be directly used without further purification. The physical structure of the MMt is generally

perceivable in sheets and layers. Each layer of the MMt consists of two tetrahedral sheets separated by an octahedral sheet. Naturally, the Si^{4+} in tetrahedral sheet can be substituted by lower valence cations of Al^{3+} from the neighbouring octahedral sheet while Al^{3+} in the octahedral sheet can be substituted by external lower valence cations of Mg^{2+} and Fe^{2+} . The substitution causes an excess of negatively charged oxygen atoms and the layers become a net negative charge. Each layer becomes apart due to the electrostatic repulsion between the negative charge layers. The gap between layers is also known as “interlayer”. The counter ions are allowed to deposit in the interlayer to compensate for the excess negative charge of each layer (Krupskaya *et al.*, 2017). Besides, the water molecules can intervene in the interlayer, causing the gap to swell which is beneficial for capturing macromolecules. Due to the hydroxyl groups and oxide-type functional groups on the MMt edge surfaces, the MMt has exhibited high effectiveness for adsorbing cationic dyes, such as methylene blue, Rhodamine B, basic yellow 2 and methyl green, etc (Kausar *et al.*, 2018; Sukboonyasatit *et al.*, 2018). However, recovery of the MMt particles after the adsorption such as centrifugation, sedimentation, and filtration is a still challenging task for the high volume of the wastewater. The enlargement of the MMt is a potential approach to overcome this limitation.

Pectin is a structural heteropolysaccharide, a natural biopolymer. Pectin can be extracted from the cell walls of citrus fruits, e.g. lime shells, banana peels, passion fruit, and watermelon rinds, etc. (Sandarani, 2017; Lichanporn *et al.*, 2020). The physical structure of pectin consists of α -1,4-linked d-galacturonic acid. The carboxyl groups along the chain are largely esterified with methoxy groups and some can also be acetyl groups existing on the free hydroxy groups. In food processing, it is a gelling agent in jams and jellies, being used as edible packaging, film, and coating. Pectin membrane can be used as an adsorbent for removing methylene blue, a cationic dye, from wastewater (Hastuti *et al.*, 2020). Watermelon rinds (*Citrullus lanatus*) can be the potential sources of pectin as they are solid waste that is locally available all year round. The extraction of pectin from watermelon rinds is an interesting option. Pectin is not solely formed in pellets but combines with other materials to form composite pellets. The preparation of nanocomposite pellets can be performed in two steps: entrapment of the MMt in the network of the natural pectin film using sodium alginate as a crosslinking agent (Saha *et al.*, 2015) and slicing the composite film into identical size and shape pieces. An effective approach to handle the difficulty of recovering small MMt particles is expected.

In this study, the composite film prepared by MMt and pectin was used as an adsorbent for removing Rhodamine B dye (RB), from synthetic wastewater. The pectin pellets, MMt, and the composite pellets were then characterized by N₂ adsorption-desorption at 77.4 K, FTIR, and FESEM. After that, the influencing factors on dye removal efficiency such as contact time, initial dye concentration, initial solution pH, and temperature were investigated. Finally, well-established adsorption isotherms such as Langmuir and Freundlich isotherms and kinetic models were used for predicting the adsorption behaviour and mechanisms, respectively.

Materials and Methods

Dye and Chemicals

The cationic dye used was Rhodamine B (RB: C₂₈H₃₁ClN₂O₃) which was bought from Sigma Aldrich Chemie GmbH, Germany. The as-received montmorillonite clay (MMt) with a cation exchange capacity (CEC) of 0.80 milliequivalent/g was purchased from Nippon-Chemical Thailand Ltd, Thailand. From the supplier datasheet, alumina (Al₂O₃) and silica (SiO₂) are the main compositions of the MMt. The watermelon rinds (Jintara varieties) were obtained from local places near Ubon Ratchathani University. Citric acid, calcium chloride, and glycerol (99.5%) were purchased from Ajax Finechem Pty Ltd, New Zealand. 95% ethanol and 50% acetone were purchased from Merk, USA. The sodium alginate was obtained from Sierra-Aldrich Co., Ltd, Norway. All chemicals were analytical grade and used without further purification.

Pectin Extraction

The watermelon rinds were washed several times with drinking water. The deep red juicy flesh of the rinds was removed and the residuals which are green and white parts were further used. Then, they were cut into small pieces with the size of 1 cm × 1 cm × 1 cm then boiled in distilled water for 10 min to inhibit enzyme activities. The liquid was removed by a microfilter, and size reduction was employed using a blender. The solid powder was obtained by placing it in an oven at 50°C until the weight is constant. The pectin extraction procedure was modified from Petkowicz *et al.* (2019). The dried powder was mixed with 0.05 M HCl in a beaker for a given ratio of 1 g: 12 mL and then boiled at 95°C for 1 h. The solid was removed by a filter cloth. The filtrate was well mixed with ethanol at the ratio of 1:1 (v/v) and left at room temperature for 15 h to facilitate crystallization of pectin. The crystals were harvested by the filter

cloth and then triplicate rinsed with ethanol (95%) following by acetone (50%). The crystals were dried in the oven at 50°C until their weight was constant. Then, they were blended and sieved to obtain the particle size under 212 microns and kept in a desiccator.

Preparation of the Composite Pellet

The procedure of preparing composite pellets from the MMt and pectin was modified from that developed by Lini *et al.* (2014). The MMt (0.5 g) was continuously stirred in 100 mL deionized water. Then, 1.0 g of pectin, 1.0 g of sodium alginate, and 0.6 ml of glycerol were added, and the temperature was raised to 65°C for 6 h. After that, 30 ml of 0.4 M CaCl₂ was added, and the mixture was stirred for another 6 h. The mixture was transferred into a Petri plate at room temperature. A thin film with a thickness of 2±0.5 mm was obtained after the evaporation of water. The film was cut into small pellet-like pieces. The pellets were put through a sieve with mesh number 10 to retain particles greater than 2 mm and then put through mesh number 5 to obtain the particles in the range of 2-4 mm. The pellets were stored in a desiccator for further use. They were also prepared in a similar manner as described but without the MMt.

Characterizations of the Adsorbents

The composite pellets and MMt were examined by Automatic Surface Analyzer (ASI-C-8, Quantachrome Instrument) at 77.4 K for the determination of N₂ adsorption-desorption isotherm. Then, the specific surface area, average pore size, and total pore volume were determined using the BET method, t-plot, and the amount of N₂ adsorbed at P/P₀ of 0.99, respectively (De Lange *et al.*, 2014). To determine the functional groups presenting on the adsorbent surfaces, the IR spectra of the composite pellets, pectin pellets, and MMt were analysed by Fourier Transform Infrared Spectrophotometer: FTIR (Spectrum RX1, Perkin Elmer) using KBr. The wavenumber scan is in the range of 4,000-400 cm⁻¹ (Akpomie and Dawodu, 2016). To study the morphology of the adsorbents, SEM images were obtained by Field Emission Scanning Electron Microscope: FESEM (JSM-5410LV, LEO) at 20 kV with 5,000x magnification (Mouzon *et al.*, 2016). Point of zero charge (pHpzc) was also determined. An amount of 0.1 g adsorbent was added into the NaCl solution with 0.01 M. The pH solution was adjusted to 2, 4, 6, 8, and 10 using 0.1 M HCl and/or NaOH. The initial pH (pH₀) was measured. Then, the suspension was agitated at 200 rpm for 24 h under 30°C. Then finally, the pH of the suspension was determined. The plot of pH₀-pH_f versus pH₀ was made and the pHpzc of the

composite pellets was located at the abscissa - intercept.

Batch Adsorption Tests

Preliminary study was carried out to compare the dye removal efficiency between the composite pellets and MMt under a certain condition (initial dye concentration (C_0) of 50 mg/L, initial pH solution (pH_0) of 4.0, contact time (t) of 24 h, temperature (T) of 35°C, adsorbent dose (m) of 0.3 g).

Then, the batch adsorption tests were investigated to study the effects of operating factors i.e. contact time, initial pH solution, initial dye concentration, and temperature on the adsorption. Firstly, the effect of contact time was studied. A set of 250 mL Erlenmeyer flasks was filled with 100 mL of 50 mg/L dye solutions. The initial pH solutions were adjusted by adding 0.1 M NaOH and/or 0.1 M HCl and kept at 4.0 in this set of experiments (original pH solution of RB). A given quantity of composite pellets (0.3 g) was added to the solution. Then, it was horizontally shaken at 200 rpm under a controlled temperature of 35°C. The samples were measured at time intervals of 10-240 min. The composite pellets were removed from the suspension by a filter cloth and the filtrate was brought to the UV-Vis Spectrophotometer for absorbance measurement at a maximum absorbance wavelength (λ_{max}) of 530 nm. The dye concentration in the liquid phase was evaluated by conversion of absorbance to the dye concentration using the calibration curve (a plot between absorbance vs. dye concentration).

Secondly, the effect of the initial pH solution was studied. The procedure was almost the same as the first set of experiments but the initial pH of the 50 mg/L dye solution in each flask was adjusted to obtain different pH values between 2.0-10.0 and horizontally shaken for 180 min.

Thirdly, the influence of initial dye concentrations was investigated. The experiments were also conducted in the same manner as the first experiment, but the initial dye solutions were varied between 50-250 mg/L and the horizontal agitation was allowed for 180 min.

Finally, the factor affecting the adsorption which is the operating temperature was conducted. The first and third sets of experiments were repeatedly carried out, but the temperatures were raised from 35°C to 45°C and 55°C, respectively.

Results and Discussion

Characteristics of the Adsorbents

The N_2 adsorption-desorption isotherms of the composite pellets and MMt are depicted in Figure 1.

The composite pellets' isotherm was classified as type I isotherm by the International Union of Pure and Applied Chemistry (IUPAC). It revealed that the surface of composite pellets was nonporous. The isotherm of MMt, on the other hand, showed the hysteresis loop, which was classified as type IV by IUPAC, indicating that the MMt had a mesoporous surface (Cychosz and Thommes, 2018).

The specific surface area of the composite pellets was $5.04 \times 10^{-2} \text{ m}^2/\text{g}$, which was significantly lower than that of the MMt ($41.91 \text{ m}^2/\text{g}$). The lower surface area results from the fact that the MMt molecules are trapped in the layer of pectin resulting in loss of the internal surface due to pore blockage which inhibits the transferring of N_2 molecules to the interior of the MMt (Namdaung and Umpuch, 2019). The average pore size of the composite pellets (41.31 nm) was wider than that of the MMt (4.80 nm). The small pores on the surface of the MMt embedded inside the composite pellets were screened and left only the large pore on the surface. Likewise, the total pore volume of the composite pellets ($9.356 \times 10^{-4} \text{ cm}^3/\text{g}$) was lower than that of the MMt ($0.6115 \text{ cm}^3/\text{g}$). The loss of internal surface area causes the smaller pore volume. The results were in accordance with a lower specific surface area of the composite pellets.

To investigate functional groups, FTIR spectra of the pectin pellet, composite pellet, and MMt were analysed and the results are summarized in Table 1. The characteristic absorption peaks of the MMt are discussed first. The broadband was detected at $3,624 \text{ cm}^{-1}$ representing O-H stretching which is according to the stretching vibration of AlOH and SiOH. The absorption band at $1,641 \text{ cm}^{-1}$ was possibly due

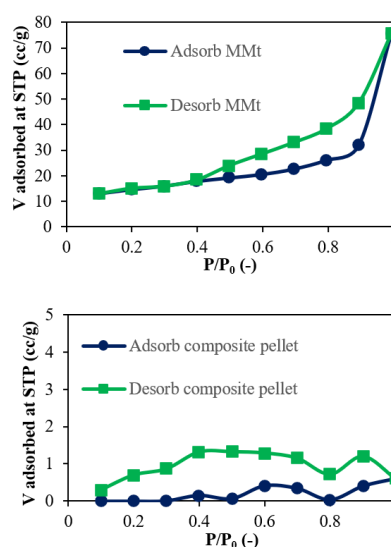


Figure 1. N_2 adsorption-desorption isotherm of the MMt at 77.4 K

Table 1. IR spectra of the pectin pellets, composite pellets and MMt

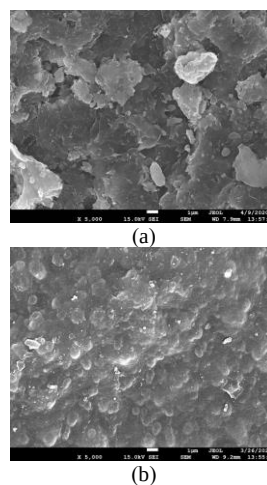
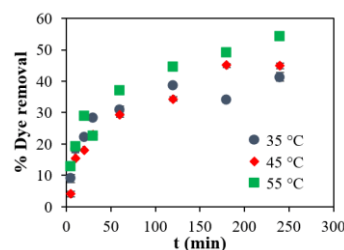
FT-IR peaks (cm ⁻¹)			Vibrational mode
Pectin pellet	Composite pellet	MMt	
-	-	3,624	O-H stretching
3,274	3,332	3,460	O-H stretching, hydration
2,923	2,922	-	C-H stretching
1,733	-	1,640	O-H stretching, hydration
1,600	1,600	-	N-H bending
1,417	1,419	-	CH ₂ methylene bridge
1,080	1,004	1,034	Si-O stretching

to the O-H stretching vibration mode. The peak at 1,034 cm⁻¹ was likely to be Si-O stretching vibration of SiO (Umpuch and Sakaew, 2013). The absorption peaks of the composite pellet were mostly similar to those of the pectin pellet i.e. the absorption band at 2,922 cm⁻¹ was detected due to C-H stretching representing the stretching vibration of CH groups. On the other hand, there were only two peaks (3,460 and 1,004 cm⁻¹) which were similar to that of the MMt. The results demonstrated that the peaks appeared on IR-spectra of the composite pellet *also* exists on those of the MMt and the pectin pellets. Additionally, the adsorptive functional groups on the composite pellet surface for interacting with the RB are carboxylic and hydroxyl groups.

To investigate the morphology, SEM images at 5,000x magnification of the MMt and composite pellet are depicted in Figure 2. The numerous pores distributed along the surface were observed on the SEM image of the MMt (Figure 2(a)). Compared with the composite pellet, the mesoporous surface of the MMt is more dense which causes a higher specific surface area. When dissolving in water, these pores of the MMt directly allow the solute penetrated. On the other hand, the less dense of mesopores on surface of the composite pellet (Figure 2(b)) cause lower specific surface area of the composite pellets. It was attributed to the coverage of pectin layer over the MMt particles. The solute molecules must diffuse through the external layer of pectin and then penetrate the pores of the entrapped MMt particle. The result was in accordance with those presented in the literature (Fishman *et al.*, 2004; Sabka *et al.*, 2019).

Batch Adsorption Result

Besides, the percent dye removals of the composite pellet and MMt were 51.26% and 68.54%, respectively. The loss of specific surface area of the composite pellet causes lower dye removal efficiency.

**Figure 2. SEM images with magnitude 5,000x of the MMt (a) and the composite pellet (b)****Figure 3. Percent dye removal versus contact time for the adsorption of RB molecules on composite pellets at different temperatures**

Besides, the percent dye removals of the composite pellet and MMt were 51.26% and 68.54%, respectively. The loss of specific surface area of the composite pellet causes lower dye removal efficiency.

To investigate the adsorption rate and evaluate equilibrium duration, the batch adsorption experiments with the contact time from 0 to 240 min were investigated. The other operating factors were controlled constant i.e. pH₀ of 4.06±0.2, C₀ of 50 mg/L, and T of 35°C. The results are presented in Figure 3. It was found that the percent dye removal slightly increased with running contact time from 0 to 20 min, then increased from 20 to 180 min, and then became level off. The slight increase in the first stage can be explained that the RB molecules mostly adsorb on the external surface of the composite pellets and some of them penetrate through the pectin layer, entrapping the MMt molecules beneath. Then, the accumulation of RB molecules on the external surface of the composite pellets causes a higher concentration gradient between the outer surface and the interior surface

of the composite pellets. A higher number of RB molecules can transport by diffusion through the thin layer of pectin into the internal surface which is surface of MMt particle entrapped. The transport of RB molecules inside the micropore and mesopore of MMt particle is expected to be more rapid due to convective transport. This results in a more rapid adsorption rate in the second stage compared with the first stage (Girish and Murty, 2016). In the final stage, the percent dye removal became level off due to the adsorbent surface saturated by the RB molecules. The equilibrium time was expected at 180 min because the difference between the percent dye removal at 180 and 240 min was less than 5%.

One of the most important factors that can influence the dye removal efficiency in terms of the degree of ionization and surface properties of the adsorbent is the initial pH solution (Inyinbor *et al.*, 2015). In this part, the initial pH was varied from 2.0 to 10.0 whereas other parameters i.e. C_0 of 50 mg/L, T of 35°C, and t of 180 min were kept constant. The percent dye removal depended on the initial pH solution because the percent dye removal decreased significantly from 88.31% to 54.46% with an increase in the initial pH from 2.0 to 6.0 as shown in Figure 4. The highest dye removal was found at the initial pH of 2.0 and the adsorption was favourable at this pH. The pH_{pzc} of the composite pellets was found at the pH of 6.0. The pH solution below 6.0 causes the adsorbent surface to be positively charged which can interact with the negatively charged RB molecules via electrostatic attraction. On the other hand, the pK_a of the RB is 3.7 and the carboxyl groups on RB molecules dissociate. The RB molecules contain both positively charged xanthane groups and negatively charged of carboxyl groups, known as zwitterion. The attraction between the carboxyl groups of the RB monomer and xanthane groups of the other RB monomer results in the formation of dimers, hence adsorption of the RB molecules becomes more difficult yielding a decrease in the RB uptake. The highest adsorption of RB molecules at a pH between 3 and 4 was previously reported (Birtalan *et al.*, 2011; Oyekanmi *et al.*, 2019).

The percent dye removal decreased with an increase in the initial dye concentration as shown in Figure 5. In this experiment, the initial dye concentration ranging from 50-250 mg/L was investigated while other parameters i.e. pH_0 of 4.06 ± 0.2 , $T = 35^\circ\text{C}$, and $t = 24$ h were kept constant. The percent dye removal is dye concentration stripping from the liquid phase. At the low initial dye concentration, the fraction of the dye concentration compared with the adsorbent surface was low, so the high value of percent dye removal was observed. When the initial dye concentration increased, the

fraction of the dye concentration compared with the adsorbent surface was high. As a result, the low value of percent dye removal was found. The highest percent dye removal of 64.35% was observed at the initial dye concentration of 50 mg/L. The results were also found in some literature (Postai *et al.*, 2016; Abbas, 2017).

Temperature is one of the important factors affecting the adsorption. The percent dye removal increased with the rise of temperature as illustrated in Figures 3 and 5. More dye molecules were removed from the solution when the temperature was raised. It can be explained by two hypothetical assumptions. Firstly, the adsorption of RB molecules on the composite pellets involves the chemical reaction and endothermic process. When the system absorbs more energy, the chemical reaction is further forward and the equilibrium constant increases (Postai *et al.*, 2016; Bello *et al.*, 2019). Secondly, the composite pellets are physically changed due to an increase in the temperature. The higher number of RB molecules can diffuse through the barrier on the external surface and can access the internal surface in the pores of the composite pellets.

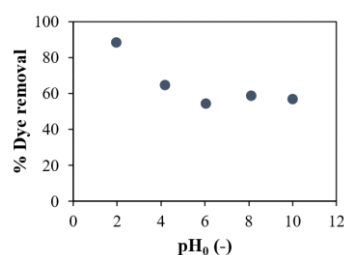


Figure 4. Percent dye removal versus initial pH solution for the adsorption of RB molecules on the composite pellets

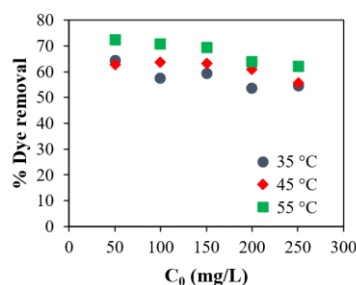


Figure 5. Percent dye removal versus initial pH solution for the adsorption of RB molecules on the composite pellets

Adsorption Kinetic Models

To understand the mechanisms of the RB molecules adsorbed on the composite pellets, the

experimental data were fitted to the well-established adsorption kinetic models such as pseudo-first order reaction and pseudo-second order reaction models. Besides, the slowest or longest step that controls the adsorption process known as the rate-limiting step can be interpreted from the two models. The rate-limiting step is an important aspect of the adsorption process design because this step governs the overall rate.

The pseudo-first order reaction model was developed by Lagergren *et al.* (1898). The rate equation of homogeneous reaction was used to fit the kinetic experimental results which involve the heterogeneous reaction. Therefore, the 'pseudo' is addressed as a prefix. The pseudo-first order reaction equation in the linear form is expressed as:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (1)$$

where q_e and q_t (mg/g) are the adsorption at equilibrium stage and instantaneous time t , respectively. k_1 is the rate constant of the first order reaction (1/min) and t is the contact time (min).

The pseudo-second order reaction model was developed by Ho and McKay (1999). This is similar to the pseudo-first order reaction model but the order of the reaction is second order. The pseudo-second order reaction equation in the linear form is given by:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{t}{k_2 q_e^2} \quad (2)$$

where k_2 is a rate constant for the second order reaction (g/(mg·min)). The experimental data that follows the pseudo-first order reaction and/or pseudo-second order reaction models indicating the chemical reaction is the rate-controlling step.

The parameters of the pseudo-first order reaction and pseudo-second order reaction equations are listed in Table 2. The R^2 of the pseudo-second order reaction equation was closer to 1.0 compared with that of the pseudo-first order reaction equation so the experimental data were in good agreement with the pseudo-second order reaction equation. Additionally, the experimental adsorption capacities,

$q_{e, \text{exp}}$ at different temperatures were closed to those values predicted from the models, $q_{e, \text{cal}}$. This indicates that one of mechanism is the chemical reaction which is the rate-controlling step in this study.

Adsorption Isotherm

To understand the behaviour of RB molecules adsorbed on the surface of the composite pellets, two well-known adsorption isotherms such as Langmuir isotherm and Freundlich isotherm were used to fit the experimental data at the equilibrium stage.

The assumption of the Langmuir isotherm (Langmuir, 1918) involves homogeneous or a finite number of identical sites present on the adsorbent surface. The data follow the Langmuir isotherm indicating monolayer coverage on the adsorbent surface. The linear form of the Langmuir isotherm equation is expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L q_m} \quad (3)$$

where k_L is Langmuir constant (L/g) and q_m is the maximum monolayer dye uptake (mg/g). Besides, R_L is a separation factor or equilibrium parameter which can be calculated using the k_L from Equation (2). The parameter suggests the type of isotherm is irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavourable ($R_L > 1$). The R_L is defined as:

$$R_L = \frac{1}{1 + k_L C_0} \quad (4)$$

The assumption of Freundlich isotherm (Freundlich, 1906) relates the heterogeneous or various adsorptive sites that exist on the adsorbent surface. The data follow the Freundlich isotherm indicating multilayer coverage on the adsorbent surface. The linear form of the Freundlich isotherm equation is expressed:

$$\ln(q_e) = \ln(k_F) + \frac{1}{n} \ln(C_e) \quad (5)$$

where k_F is the measure of adsorption capacity (($\text{mg}^{1-1/n} \cdot \text{L}^{1/n} / \text{g}$)) and constant n is the adsorption intensity.

The isotherm parameters interpreted from the two adsorption isotherms are summarized in Table 3. The experimental data were better fitted to the Freundlich isotherm by considering the linear regression, R^2 values that were closer to 1.0. Thus, the RB molecules adsorb on the surface of the composite pellets in multilayer coverage. In addition, the R_L values obtained from the Langmuir isotherm

Table 2. Parameters of two kinetic adsorption models

Temp.	35°C	45°C	55 °C
$q_{e, \text{exp}}$ (mg/g)	9.75	9.58	11.08
Pseudo-first order reaction			
k_1 (1/min)	0.024	0.034	0.026
$q_{e, \text{cal}}$ (mg/g)	11.62	16.44	15.74
R^2	0.8672	0.8629	0.8085
Pseudo-second order reaction			
k_2 (g/(mg·min))	0.0031	0.0020	0.0070
$q_{e, \text{cal}}$ (mg/g)	10.11	11.24	11.82
R^2	0.9958	0.9648	0.9760

were in the range of 0.56-0.92 revealing that the adsorption of RB molecules on the composite pellets is favourable.

Activation Energy

Activation energy is the minimum energy gained by the system to cause a chemical reaction. The activation energy for the chemical reaction involves the adsorption of RB molecules on the composite pellets evaluated from the Arrhenius equation which is written in Equation (6). The parameter k_F interpreted from the Freundlich isotherm was used as the equilibrium constant.

$$\ln(k_2) = \ln(A) - \frac{E_a}{RT} \quad (6)$$

where k_2 is the rate constant for pseudo-second order reaction (g/(mg.min)), E_a is the Arrhenius activation energy (kJ/mol), and A is the Arrhenius factor, R is the gas constant which is 8.314 J/(mol.K), and T is the system temperature (K).

The E_a and A were obtained from the slope and intercept of the plot $\ln(k_2)$ versus $1/T$, respectively, as shown in Figure 6. The E_a was +33.45 kJ/mol. It is classified as physisorption when the activation energy is lower than 40 kJ/mol and defined as chemisorption when the energy is higher than 40 kJ/mol (Huang *et al.*, 2017). Therefore, physical sorption seems to be dominant in this adsorption process. However, the R^2 in the Figure 6 is very far from 1.0 which reveals the result, and the Arrhenius equation are inconsistency. The results expressed in Figures 3 and 5 shows the adsorption of dye increased with an increase of temperature, and the adsorption of RB molecules on the composite pellets involves the chemical reaction and endothermic process. So, the chemisorption is dominant in this study.

Thermodynamic Study

To study thermodynamics involving in the adsorption process, some parameters including Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) were determined using Equations (7) and (8), respectively.

$$\Delta G^\circ = -RT \ln(k_L) \quad (7)$$

$$\ln(k_L) = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

where R is the universal gas constant (8.314 J/(mol.K)), T is the absolute solution temperature (K), and k_L is the Langmuir equilibrium constant. The value of ΔH° and ΔS° were interpreted from the slope and intercept of the van't Hoff plot

Table 3. Parameters of adsorption isotherms

Temp.	35°C	45°C	55°C
Langmuir isotherm			
k_L (L/g)	0.0020	0.0017	0.0032
q_m (mg/g)	65.42	93.53	66.55
R_L	0.67-0.91	0.70-0.92	0.56-0.86
R^2	0.5277	0.6115	0.6760
Freundlich isotherm			
k_F	1.03	1.05	1.20
(mg ^{1-1/n} · L ^{1/n} /g)			
n	1.24	1.14	1.24
R^2	0.9901	0.9809	0.9844

Table 4. Thermodynamics parameters

Temp.	35°C	45°C	55°C
ΔG° (kJ/mol)	-15.91	-16.86	-15.67
ΔH° (kJ/mol)	+19.38		
ΔS° (J.mol.K)	+10.17		

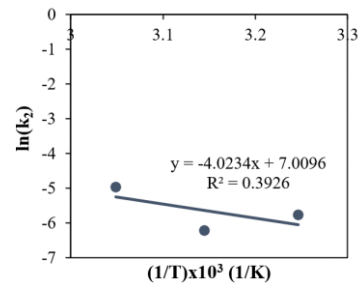


Figure 6. Plot $\ln(k_2)$ versus $1/T$ (1/K) for the adsorption of RB molecules on the composite pellets

(relationship between $\ln(k_L)$ and $1/T$). The thermodynamic parameters are summarized in Table 4.

The negative standard Gibbs free energy change (ΔG°) reveals the spontaneous nature of the adsorption. The positive standard enthalpy change (ΔH°) of +19.38 kJ/mol confirms the endothermic process. Besides, the standard enthalpy change (ΔH°) that is less than 80 kJ/mol is classified as physisorption, whereas one over this limit is chemisorption. Therefore, this exhibits that the physisorption is substantiated. The standard enthalpy change (ΔH°) in this work substantiated the physisorption. The small positive standard entropy change (ΔS°) of +10.17 J/mol. K indicates the randomness slightly increases in the system. The adsorbent is slightly changed during the adsorption process taken place (Al-Ghouti and Al-Absi, 2020).

Conclusions

The composite pellets made from pectin extracted from watermelon rinds (*Citrullus lanatus*) and MMT showed the high efficiency of RB removal from the

liquid. The characterizations of the composite pellet showed that the surface of the composite pellets could be nonporous or microporous. The specific surface area and total pore volume of the composite pellets were less than those of the MMt while the mean pore size was wider. The negatively charged functional groups present on the adsorbent surface were carboxylic and hydroxyl groups which were affinities to the cationic molecules. The RB removal increased with an increase in the contact time and temperature while decreased with an increase in the initial pH, and initial dye concentration. The optimal operating condition was suggested at a certain condition i.e. contact time of 180 min, initial pH of 2.0, initial dye concentration of 250 mg/L, and temperature of 55°C. The experimental data followed the pseudo-second order reaction model. The adsorption isotherm was better fitted to the Freundlich isotherm. Although, the activation energy confirmed physical adsorption is dominant, the consistency between the result and Arrhenius equation is low. So, the chemisorption was dominant by considering the thermodynamic study.

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