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Original Article

Adsorption of cationic and anionic dye using modified pineapple peel

Chompoonut Chaiyaraksa*, Chanyapat Ruenroeng, Bunyisa Buaphuan,
and Sidaporn Choksakul

*Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang,
Lat Krabang, Bangkok, 10520 Thailand*

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Abstract

This research used leftover pineapple peel from a fruit shop to adsorb Basic Red 9 dye and Direct Red 83 dye. Pineapple peel was modified with 1.25 M calcium chloride before conducting adsorption experiments. The studied parameters that affect adsorption efficiency included time, pH, adsorbent quantity, dye concentration in the wastewater, and temperature. Both dyes showed the best adsorption at pH 7. Basic Red 9 and Direct Red 83 took 60 and 90 min, respectively, to reach equilibrium reactions. As the quantity of pineapple peel increased, the adsorption capacity increased. Temperature slightly affected the dye adsorption. The adsorption isotherms of Basic Red 9 and Direct Red 83 followed the Temkin and Freundlichad sorption models, whereas the adsorption kinetics of the two were consistent with the pseudo-second-order equation. The adsorption was endothermic and spontaneous.

Keywords: adsorption, Basic Red 9, Direct Red 83, calcium chloride, pineapple peel

1. Introduction

Currently, the Thai government has a campaign to encourage people to wear silk and cotton costumes, which are an export product of Thailand. Therefore, Thailand's textile and apparel industry has expanded and has a significant role in foreign currency import. As a result, the bleaching and dying industry, which is an intermediate industry in the textile industry, has expanded as well. The production process in the bleaching and dying industry uses chemicals in order to produce colourful fabrics and thread that are durable and satisfy the demands of consumers. Wastewater from these industries contains alkaline salts at a high temperature with a strong smell and unpleasant color. When discharged into the public water sources, it destroys the beauty of nature and causes an imbalance in nature. In addition, some dyes are toxic (Ratna & Padhi, 2012). The main chemicals used in the bleaching and dyeing process are synthetic dyes. They can be organic or inorganic compounds with complex molecules and are difficult to dispose of (Album & Rani, 2016). Basic dye is widely used in the industry. It has a colourful hue which can be clearly seen in a solution even at low concentrations. Another type of dye is direct dye, which is an anionic dye.

Recently, research was conducted on dye removal. The removal mechanisms can be physical, chemical or biological. Various techniques are used to remove dyes such as flocculation (Rodrigues, Madeira, & Boaventura, 2013), oxidation (Navarro, Gabaldón, & Gómez-López, 2017), and electrolysis (Han *et al.*, 2016). These techniques have limitations because they use chemicals in the disposal process. This is not only expensive but also leaves a huge quantity of sediment and increases the amount of chemical substances in the environment.

The best alternative method for removal of dyes is adsorption. This method reduces costs and is environmentally friendly. Different low-cost materials to adsorb dyes have been studied. Those materials can be divided into three classes: inorganic materials, e.g., bentonite, gypsum, zeolite, and kaolin; industrial by-products, e.g., metal hydroxide

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*Corresponding author
Email address: kcchompoonut@gmail.com

sludge, sewage sludge, fly ash, and red mud; and agricultural solid waste, e.g., sawdust, chitosan, pine cones, rice husks, and coconut coir (Seow & Lin, 2016; Yagub, Sen, Afroze, & Ang, 2014). This current research used pineapple peel as the adsorbent. Thailand is one of the top five producers of pineapple in the world and has a total production of 2.3-2.5 million tons a year. For this reason, pineapple peel is an agricultural leftover. The peel is 30% of the whole pineapple or about 600,000 tons per year. If pineapple peels are left behind, it produces methane, which has a strong smell. Moreover, methane is one type of greenhouse gas that causes global warming. Without modification, the dye adsorption efficiency is not sufficiently effective. Previously, calcium chloride was successfully used to modify sawdust and sugarcane bagasse (Batzias & Sidiras, 2004; Kadam, Lade, Patil, & Govindwar, 2013). Most researchers have worked on either cationic or anionic dyes, but the content of textile wastewater is normally complicated, and adsorption using only one type of ionic group is usually incapable of eliminating various ionic dyes. The purpose of this study was to investigate modification of pineapple peel by calcium chloride and the use of pineapple peel as an adsorbent to adsorb both a cationic dye (Basic Red 9) and an anionic dye (Direct Red 83). The investigated factors that affect dye adsorption were pH, contact times, adsorbent amount, dye concentration, and system temperature. The adsorption isotherms, kinetics, and thermodynamics were also evaluated.

2. Materials and Methods

2.1 Preparation of adsorbent and dye solutions

Pineapple peel (PP) was collected from a nearby fruit shop. The pineapple peel was washed with tap water to remove dirt, sliced into small pieces, and then dried under sunlight for several days. The dried pineapple peel was ground into a fine powder and put in an oven for 24 h at 100 °C. Preparation of the modified pineapple peel was carried out by mixing PP powder with 50 mL of 95% ethanol and 25 mL of 1.25 M calcium chloride. Pectin acid of lignocellulosic materials can be precipitated by treating with calcium chloride. Moreover, treatment with calcium prevents the leaching of some organic components from the biomass and increases the stability of the biosorbent. The mixture was left for 24 h at room temperature and then filtered. The excess calcium chloride was removed by washing several times with deionized water. The modified pineapple peel (M-PP) was dried in the oven for 24 h at 100 °C and kept in a desiccator for further use. This method was modified from the method of Feng and Guo (2012).

Stock dye solutions were prepared at a concentration of 1,000 ppm. Various concentrations were prepared by diluting this stock solution with deionised water. All of the chemicals used in the experiments were AR grade.

2.2 Adsorbent characterization

The physical characteristics of the unmodified pineapple peel (PP) and modified pineapple peel (M-PP) before and after adsorption were analysed using a Spectrum GX Fourier Transform Infrared Spectrometer (Perkin-Elmer) and a scanning electron microscope (Leo 1455 VP).

2.3 Adsorption experiments

Adsorption experiments were carried out in a batch process. A double beam UV spectrophotometer (Thermo Scientific, model Genesis 10S UV-Vis, England) at the maximum absorption wavelength (545 nm) was used to determine dye concentrations. A calibration curve was obtained using the five known concentrations of standard dye solution.

2.3.1 Determination of the optimum pH

The M-PP (0.25 g) was added into 25 mL of a 100 mg/L dye solution at various pH levels (2 to 10). A solution of 0.10 M HCl or NaOH was added to adjust the pH of all samples. The sample was agitated at 100 rpm for 150 min. The optimum pH was determined and used throughout all adsorption experiments.

2.3.2 Effects of adsorbent dosage, solution concentration, and system temperature

In each experiment, an accurate adsorbent dose was added to 500 mL of a 100 mg/L dye solution with the optimum pH observed previously in a 1 liter beaker. The mixture was agitated at a constant temperature. An amount of 5 mL of dye solution was continuously collected and its concentration measured over a period of 150 min. To determine the effect of dye concentration to the adsorption at room temperature, the optimum pH and adsorbent dosage were used.

2.3.3 Isotherm, kinetic, and thermodynamic studies

Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherms were considered in this study. The kinetic models were applied mainly by pseudo-first-order, pseudo-second-order, the Elovich model, and the intraparticle diffusion model. The free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) changes during adsorption were evaluated for the thermodynamic study.

3. Results and Discussion

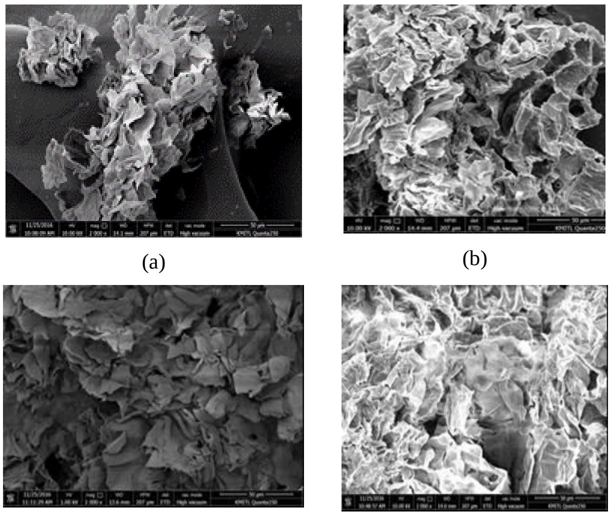
3.1 Adsorbent characterization

3.1.1 Scanning electron microscopy (SEM)

The SEM images at a magnification at x2,000 are shown in Figure 1. Figure 1 (a) shows that the surface of PP was dense, while the pineapple peel had more porosity after modification with $CaCl_2$. There were significant differences between the modified and unmodified samples. After adsorption, the surface of the pineapple peel became less porous.

3.1.2 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were performed in a range of 400 to 4,000 cm^{-1} in order to investigate the surface characteristics of PP and M-PP. The broadest band in the region of 3331.82 cm^{-1} represents the O-H stretching vibrations of cellulose, pectin, hemicellulose, and lignin (Figure 2). The peak at 2916.61 cm^{-1} can be attributed to the C-H stretching vibrations of methyl,



(a) (b)

(c) (d)

Figure 1. SEM photograph of (a) PP before adsorption (b) M-PP before adsorption (c) M-PP after Basic Red 9 adsorption and (d) M-PP after Direct Red 83 adsorption.

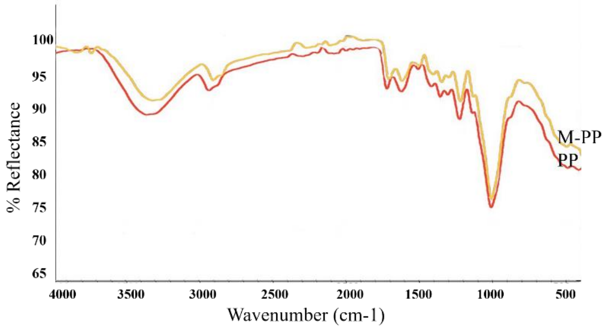


Figure 2. FTIR spectra of PP and M-PP.

methylene, and methoxy groups. The peaks at 1724.77 cm^{-1} and 1629.48 cm^{-1} represent the C=O and COO^- stretching vibrations of pectin. The peaks at 1367.77-1240.08 cm^{-1} were attributed to C-H (methyl), C-O (alcohol), and OH (carboxylic acid) group bonding. The FTIR spectra showed that carboxyl, carbonyl, and hydroxyl groups were very prominent functional groups on the surface of the pineapple peel, which could play a major role in dye adsorption. The FTIR spectra of M-PP showed a lower intensity of the bands at 3331.82 cm^{-1}, 1724.77 cm^{-1}, and 1629.48 cm^{-1}. This may be caused by the reduction of pectin (Feng & Guo, 2012; Utomo, Phoon, Shen, Ng, & Lim, 2015).

3.2 Adsorption experiments

3.2.1 Effects of initial solution pH

The highest adsorption capacity of Basic Red 9 (79.62%) was at pH 4 (Figure 3). The adsorption efficiency between pH 4-7 did not differ significantly. The best adsorption efficiency of Direct Red 83 (53.66%) was at pH 2 of the synthetic dye wastewater. Direct Red 83 is an anionic dye. Therefore, when the wastewater was in an acidic condition, there was a high concentration of H^+. Since the adsorbent surface was positive, it was able to adsorb the anionic dye. The adsorption capacities between pH 3 and 7 did not differ significantly for Direct Red 83. The adsorption efficiency obviously decreased after pH 7 because in the basic condition the adsorbent surface became negatively charged and push away the anionic dye (Ramachandran, Vairamuthu, & Ponnusamy, 2011). Therefore, pH 7 was considered to be the best condition since it enhanced the adsorption efficiency of Basic Red 9 and Direct Red 83 without using a chemical substance to adjust the pH of the wastewater.

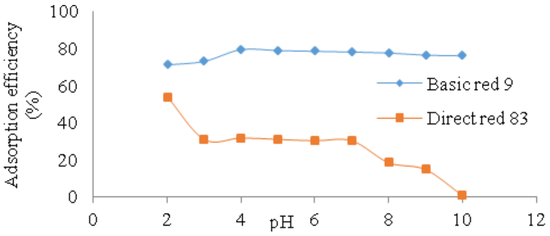


Figure 3. Effects of initial solution pH on the adsorption.

3.2.2 Effects of adsorbent dosage

The adsorption equilibrium time of Basic Red 9 was at 60 min (Figure 4a). An increase of the adsorbent dosage increased the percentage of Basic Red adsorption because there was more surface area of the adsorbent (Sen, Afroze, & Ang, 2011). The surface area was directly proportional to the amount of adsorbent. To carry out all experiments in the next step, 7.5 g of M-PP was used. The adsorption equilibrium time of Direct Red 83 using 5.00-7.50 g of adsorbent was at 90 min (Figure 4b). However, when 1.25-3.75 g of adsorbent was used to remove Direct Red 83, the equilibrium could not be reached within 150 min. More time was required for the test.

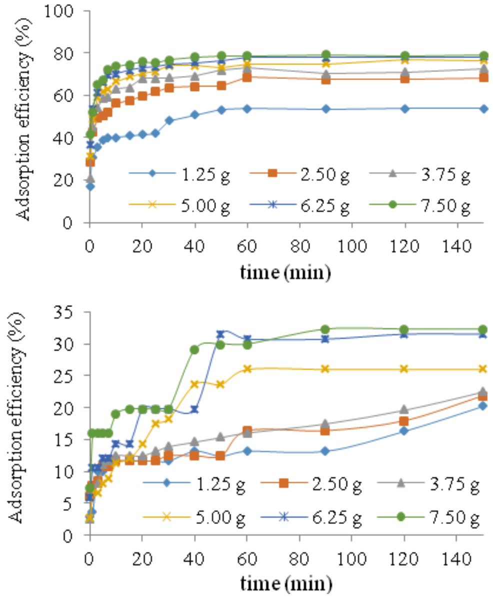
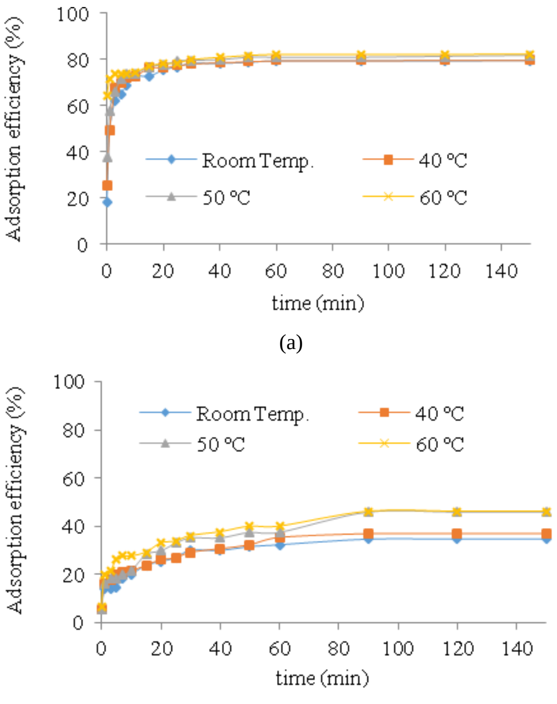


Figure 4. Effects of adsorbent dosage on the adsorption of (a) Basic Red 9 (b) Direct Red 83.

3.2.3 Effects of temperature

Maximum dye removal was obtained at 60 °C. The Basic Red 9 adsorption increased from 79.28% to 82.03% as the solution temperature increased from 33.5 °C (room temperature) to 60 °C (Figure 5a). Furthermore, adsorption of Direct Red 83 increased from 34.62% to 46.15% (Figure 5b). This was possibly due mainly to the increased surface activity, which suggested that the adsorption was an endothermic process (Roy, Chakraborty, Kundu, Adhikari, & Majumder, 2012; Üner, Geçgel, & Bayrak, 2016).



(a)

(b)

Figure 5. Effects of temperature on the adsorption of (a) Basic Red 9 and (b) Direct Red 83.

3.3 Adsorption isotherm study

The general equations used in the adsorption isotherm study were equations 1, 2 and 3 (Dada, Ojediran, & Olalekan, 2013; Dada, Olalekan, Olatunya, & Dada, 2012; Rangabhashiyam, Anu, GiriNandagopal, & Selvaraju, 2014)

$$q_t = \frac{(C_0 - C_t)}{W} \text{x V} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)}{W} \text{x V} \quad (2)$$

$$\%\text{removal} = \frac{(C_0 - C_e)}{C_0} \text{x100} \quad (3)$$

where q_t, and q_e = the amount of adsorbed dye per unit mass of adsorbent at time t and at equilibrium (mg/g), respectively, C_0, C_t, C_e = dye concentration at initial, at time t and at equilibrium (mg/L), respectively, V = solution volume (L), and W = dry adsorbent mass (g).

3.3.1 Langmuir isotherm

$$q_e = \frac{q_m.K_L.C_e}{1 + K_L.C_e} \quad (4)$$

$$R_L = \frac{1}{1 + K_L.C_0} \quad (5)$$

where q_m = the maximum amount of the adsorbed dye per unit mass of sorbent (mg/g), K_L = Langmuir constant (L/mg), And R_L = a dimensionless separation factor or equilibrium parameter. (The value indicates the type of adsorption to be irreversible, favourable or unfavourable).

3.3.2 Freundlich isotherm

$$q_e = K_f.C_e^{1/n} \quad (6)$$

where K_f = the Freundlich constant and 1/n = value related to the adsorption intensity.

3.3.3 Temkin isotherm

$$q_e = \frac{RT}{b_0} \ln(AC_e) \quad (7)$$

where A = Temkin isotherm constant (L/g), b_0 = Temkin constant related to heat of sorption (J/mol), R = gas constant (J/mol.K), and T = absolute temperature (K).

3.3.4 Dubinin-Radushkevich isotherm

$$q_e = q_D e^{-K_{DR}\left[RT \ln\left(1+\frac{1}{C_e}\right)\right]^2} \quad (8)$$

where q_D = Adsorption capacity (mg/g) and K_{DR} = A constant related to mean free energy of adsorption per mole of the adsorbate (mol^2/kJ^2).

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (9)$$

where E = the mean adsorption energy (kJ/mol) of the adsorbate.

The study on the adsorption isotherm of Basic Red 9 in comparison with the Langmuir adsorption isotherm model and the Freundlich adsorption isotherm model indicated that the correlation coefficient (R^2) of the Freundlich adsorption isotherm was 0.9625, which was higher than the Langmuir adsorption isotherm, which was 0.9311. Thus, adsorption of Basic Red 9 was in accordance with the Freundlich adsorption isotherm model. That is to say, the surface of adsorbent was not integrated and it had multi-layer adsorption. The adsorption constant from the Freundlich adsorption isotherm (K_f) was 0.0239 L/g and 1/n was 0.7973. This implied that this isotherm was favourable. The study on the Temkin isotherm of Basic Red 9 showed that R^2 was close to 1. Therefore, it was suitable to explain the adsorption of Basic Red 9. The hypothesis of this isotherm was that the adsorption would decrease to a straight line when the amount of adsorbent surface was covered with the adsorbent. When the Dubinin-Radushkevich isotherm was used for the calculation, the independent energy (E) was 1.0954, which was less than 8 kJ/mol. It could be explained that the adsorption mechanism of the two dyes was physical adsorption. Üner, Geçgel, and Bayrak (2016) also found physical adsorption when an activated carbon was prepared from *Citrullus lanatus* rind to adsorb methylene blue. When considering the Direct Red 83 adsorption model, it was found that all models had a low R^2; therefore, none of them were appropriate for explanation of the adsorption.

3.4 Kinetic study

3.4.1 The pseudo-first-order kinetic

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \tag{10}$$

where k_1 = the rate constant for pseudo-first order adsorption (1/min) (Yakout & Elsherif, 2010)

3.4.2 The pseudo-second-order kinetic

$$\frac{1}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{11}$$

where k_2 = the rate constant for pseudo-second order adsorption (g/[mg.min]).

3.4.3 Elovich model

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{12}$$

where α = the initial adsorption rate (mg/g.min) and β = the constant related to the extent of surface coverage and the activation energy for chemisorptions (g/mg). (Wua, Tsengb, & Juang, 2009)

3.4.4 The intraparticle diffusion model

$$q_t = K_{id}(t)^{\frac{1}{2}} + C \tag{13}$$

where K_{id} = the intraparticle diffusion rate constant (mg/g $\min^{1/2}$).

Kinetic adsorption parameters of Basic Red 9 and Direct Red 83 are shown in Table 2 and Table 3.

Table 1. Isotherm parameters of Basic red 9 and Direct red 83.

Langmuir isotherm			Dubinin-Radushkevich isotherm		
	Basic red 9	Direct red 83		Basic red 9	Direct red 83
q_{max}(mg/g)	11.3895	2.9070	q_D(mg/g)	0.4649	0.0174
K_L (L/mg)	0.0158	0.0064	E (kJ/mol)	1.0954	0.3437
R_L	0.3876	0.6116	R^2	0.9500	0.5377
R^2	0.9311	0.5521			
Freundlich isotherm			**Temkin isotherm**		
	Basic red 9	Direct red 83		Basic red 9	Direct red 83
K_F (mg/g) $(L/mg)^{1/n}$	0.0239	0.0001	b_0 (kJ/mol)	0.1193	0.3217
1/n	0.7973	2.3015	A (L/g)	0.0595	0.0191
R^2	0.9625	0.5339	R^2	0.9899	0.4920

Table 2. Kinetic parameters of Basic Red 9.

	Concentration (mg/L)				Temperature (°C)			
	60	80	100	120	33.5	40	50	60
The pseudo-first-order								
K_1 (1/min)	0.0544	0.0986	0.0739	0.0615	0.0831	0.0845	0.0859	0.0636
q_e (mg/g)	0.5992	1.1882	1.2459	1.3709	1.6118	1.3125	1.2871	0.8784
R^2	0.6471	0.9383	0.9000	0.8883	0.9082	0.9081	0.8983	0.9622
The pseudo-second-order								
K_2 (g/mg. min)	0.3258	0.2895	0.1798	0.1108	0.2125	0.2762	0.2375	0.2577
q_e (mg/g)	2.9028	4.1118	5.3619	6.5963	5.3305	5.3476	5.4526	5.5036
R^2	0.9998	0.9999	0.9999	0.9996	0.9999	1.0000	1.0000	0.9999
Elovich model								
α (mg/g. min)	1.1510	2.7704	2.4809	6.6011	8.0200	5.2110	4.5108	1.5616
Β (g/mg)	5.2966	4.4783	3.3829	2.9146	2.6695	3.0157	3.4072	5.8685
R^2	0.8445	0.9021	0.9277	0.9591	0.8732	0.7854	0.8862	0.9334
Intraparticle diffusion model								
K_{id} (mg/g. $\min^{1/2}$)	0.1018	0.1294	0.1636	0.1576	0.2089	0.1818	0.1560	0.0823
R^2	0.4975	0.4975	0.5408	0.7419	0.4875	0.4546	0.5258	0.7671

Table 3. Kinetic parameters of Direct Red 83.

	Concentration (mg/L)				Temperature (°C)			
	60	80	100	120	33.5	40	50	60
The pseudo-first-order								
K_1 (1/min)	0.0219	0.0332	0.0327	0.0159	0.0408	0.0389	0.0256	0.0276
q_e (mg/ g)	1.0819	0.9175	1.1460	1.1929	1.4900	1.5860	2.0100	1.7239
R^2	0.9267	0.9301	0.8262	0.8974	0.9658	0.9396	0.9068	0.9206
The pseudo-second-order								
K_2 (mg/g. min)	0.0437	0.0892	0.1028	0.0568	0.0704	0.0631	0.0344	0.0495
q_e (mg/g)	2.1102	2.2183	2.8572	2.9904	2.3987	2.5549	3.2196	3.1736
R^2	0.9741	0.9956	0.9978	0.9902	0.9971	0.9949	0.9889	0.9937
Elovich model								
α (mg/g. min)	2.3869	12.3049	24.7790	60.9467	2.2034	4.0551	1.8673	6.0497
β (mg/g)	3.9078	4.1271	3.2185	3.7566	2.8345	3.0193	2.0942	2.5259
R^2	0.8276	0.9579	0.9451	0.7503	0.9398	0.9444	0.9277	0.9555
Intraparticle diffusion model								
K_{id} (mg/g. min)	0.1231	0.1015	0.1316	0.1259	0.1565	0.1567	0.2172	0.1890
R^2	0.9604	0.9323	0.8023	0.9078	0.8547	0.8797	0.9191	0.8811

From the kinetic studies on pseudo-first-order, pseudo-second-order, the Elovich model, and the intraparticle diffusion model, it was found that pseudo-second-order had the R^2 close to 1. This revealed that the interaction between the adsorbate and adsorbent on the external surface of the adsorbent was the rate limiting step (Khalfaoui, Meniai, & Derbal, 2012). It also indicated that a higher initial dye concentration resulted in a higher rate constant, and a higher system temperature resulted in a higher amount of adsorbed Basic Red 9 per unit mass of M-PP at equilibrium. The Elovich plots for the adsorption of Direct Red 83 by M-PP at various initial dye concentrations and at various temperatures were linear with a rather good correlation coefficient. The Elovich model is better used to describe the adsorption kinetics of an ion exchange system. The equation is often valid for systems in which the adsorbing surface is heterogeneous (Mi, Li, Zhu, & Liu, 2016).

3.5 Thermodynamic study

Gibbs energy can be calculated from Equations 14 and 15 (Miyaha, Lahrichib, & Idrissi, 2016).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (14)$$

$$\Delta G^0 = -RT \ln K_C \qquad (15)$$

where K_c = the equilibrium constant which represents the ability of the adsorbent to retain the adsorbate and the extent of movement of the adsorbate within the solution.

$$K_C = \frac{q_e}{C_e} \qquad (16)$$

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (17)$$

ΔG° was negative, which explained that the adsorption could happen independently (Table 4). The change of Gibbs free energy of the synthetic dye wastewater adsorption decreased as the temperature increased. This implied that the temperature influenced the adsorption. Increasing the temperature caused a greater force, which fostered the adsorption. The change of enthalpy of the adsorbent in Basic Red 9 and Direct Red 83 was 57.79J/mol and 175.45 J/mol, respectively. The positive value showed that the adsorption process was endothermic and physisorption in nature. A similar observation was reported for the adsorption of textile dye (Fontana *et al.*, 2013; Geçgel, Üner, Goekara, & Bayrak, 2016). The changes of entropy were 45.67 J/mol.K and 67.71 J/mol.K, which were positive values. This showed that the randomness at the sorbent/solution interface increased during the sorption process of the evaluated dye onto the M-PP. When the value of ΔS is more than 0 and that of ΔH is also more than 0, the process is spontaneous at high temperatures and non-spontaneous at low temperatures.

4. Conclusions

This study showed that $CaCl_2$ treated pineapple peel could be a rather effective adsorbent for the removal of Basic Red 9 from aqueous solutions, but was found to be inferior for Direct Red 83. The adsorption was high at pH 7. At a higher contact time, adsorbent dosage, and temperature, the level of adsorption was higher. The adsorption of Basic Red 9 and Direct Red 83 on M-PP reached equilibrium in 60 min and 90 min,

Table 4. Thermodynamic parameters.

	ΔG° (KJ/mol)				ΔH° (J/mol)	ΔS° (J/mol.K)
	33.5 °C	40 °C	50 °C	60 °C		
Basic Red 9	-13.95	-14.24	-14.69	-15.16	57.79	45.67
Direct Red 83	-20.56	-20.99	-21.67	-22.35	175.45	67.71

respectively. The best-fitting isotherms for Basic Red 9 were the Temkin and Freundlich equations. For Direct Red 83, the R^2 values were too low, so no isotherm could be used to explain the adsorption of Direct Red 83. The best-fitting kinetic model was the pseudo-second-order kinetic model. The change of enthalpy was positive, which indicated that the adsorption process was endothermic. The change of entropy was more than 0. The process was spontaneous at low temperatures and non-spontaneous at high temperatures. The change of Gibbs free energy of the adsorption was negative, which indicated that the absorption can occur naturally.

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