Eco-friendly lake pigment from sappanwood: Adsorption study and its application as natural colorant for natural rubber toy balloon

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Abstract

Due to the awareness of the impact of synthetic dye on human health and the environment, natural dye and lake pigment have attracted considerable attention from researcher. Herein, pink−red lake pigment from sappanwood was prepared using adsorption approach. The effects of initial pH, pH and concentration of brazilein solution, dosage of aluminium hydroxide, and adsorption time on adsorption were also explored. Results showed that the maximum adsorption capacity of 30 mg·g^{-1} was achieved when 0.25%w/v of aluminium hydroxide and 100 mg·L^{-1} of brazilein solution were applied. The adsorption kinetics and adsorption isotherm fitted the pseudo second order model and Langmuir isotherm, respectively. Additionally, this lake pigment can be utilized as a natural colorant for natural rubber toy balloons, which could made toy balloon safer for children than synthetic dye. Thus, our lake pigment can be an alternative choice of safe and environmental friendly colorant for products including toys.

1. Introduction

Over the past decade, the demand for products using natural dyes significantly increase due to the fact that consumers have realized that natural colorants are safer and more environmentally friendly than synthetic dyes [1-3]. As a result, the market for natural dyes has expanded and the extensive investigation of new natural dye sources, natural dye molecule isolation, and natural dye preservation and stability control have been conducted [4-6]. Several new dyeing methods including microwave-assisted dyeing, plasma-induced coloration, supercritical carbon dioxide dyeing process were also explored [10] in order to reduce negative impacts of dyeing in the textile industry such as soil and water pollution and toxicological prospects of synthetic dyes [11,12].

Natural dyes can be derived not only from plant parts [13] including leaves [14], roots [15,16], rhizomes and bark [17], but also insects [18,19], marine organisms and microbes [20,21]. Sappanwood (*Caesalpinia sappan*) is a common source of natural red dye in Southeast Asia [22]. Sappanwood contains colorless and red pigment called brazilin and brazilein, respectively (Figure 1) [23,24. Natural dye and lake pigment from sappanwood are widely used for textile dyeing, food and cosmetics [25-28]. Sappanwood extract is also used as folk medicine in Asia [29]. Several studies of the applications of brazilin and brazilein have been reported [30-33].

Natural dyes can be transformed into lake pigments, which can impart patterns, richness, and volume to painting products, including cloth, cosmetics, and toys, resulting in the wide application of natural dyes [34,35]. Lake pigments or lake colors can be easily prepared by fixing natural dyes with a substrate using precipitation or adsorption method [36-40]. The precipitation method requires inert binders or mordants such as potassium aluminum sulfate (most frequently used), tannin, and other soluble salts of metal, including iron, tin, copper and aluminium whereas adsorption method needs adsorbents, such as clay, aluminium oxide, aluminium hydroxide, and montmorillonite [41-45]. Different mordants or adsorbents can produce different color shades from a particular natural dye [1]. Aluminium hydroxide, also known as gibbsite or hydrargillite, is a white powder mainly used as a raw material for manufacturing other aluminium compounds [46]. Aluminium hydroxide is amphoteric as it can react with both acid and base [47]. One of the most commonly known pharmaceutical applications of aluminium hydroxide is as an antacid, which can neutralize hydrochloric acid in gastric secretions [48]. Aluminium hydroxide is also employed as catalyst and adsorbent [49-52].
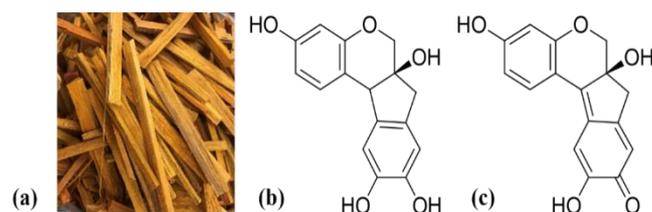
Figure 1. Sappanwood (a) and its pigments: brazilin (b) and brazilein (c).

Herein, pink–red lake pigment was prepared by adsorbing brazilein from sappanwood on the white powder of aluminium hydroxide. The effects of initial pH, pH and concentration of brazilein solution, adsorbent dosage, and adsorption time on adsorption were investigated. The adsorption kinetics and adsorption isotherm were also explored. Additionally, the application of lake pigment as a natural colorant for natural rubber toy balloons was tested. Our observations in this work could provide useful information for the preparation of lake pigment from sappanwood or other natural dyes using the adsorption method.

2. Experimental

2.1 Materials and general methods

All chemicals and solvents were of reagent grade and used without further purification. Natural rubber and hardener for toy balloon fabrication were purchased from Rubber Research Institute, Department of Agriculture, Ministry of Agriculture and Cooperatives, Thailand. The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 spectrometer using tetramethylsilane as an internal reference. Attenuated Total Reflection Fourier-Transformed Infrared (ATR FT-IR) spectra were recorded in the range of 400 cm^{-1} to 4000 cm^{-1} using Fourier-Transformed Infrared spectrophotometer (Thermo Scientific Nicolet 6700). Static volumetric N_2 gas adsorption method was employed to determine BET surface areas and average pore diameter using Micromerities, USA whereas a scanning electron microscopy (SEM, JEOL model JSM-7800F) with energy dispersive X-ray spectroscopy (EDS attached was employed for the morphologies and elemental analysis. Using a Thermogravimetric Analyzer (TGA) (Pyris 1, Perkin Elmer, USA), the thermal analysis was performed by heating samples (ca. 3-5 mg) from 50°C to 700°C with 20°C·min^{-1} heating rate. The diffuse reflectance spectra and CIELAB color space were measured using an Agilent Cary 60 UV-Vis spectrophotometer. Absorption measurements were conducted out using a Hewlett Packard 8453 spectrophotometer. A KJ–1065B Universal Testing Machine was employed to determine Young's modulus, tensile stress, and elongation at break.

2.2 Preparation of brazilein

Using reported method in 2009, brazilein was isolated from sappanwood [53]. First, 500 g of small pieces of sappanwood was soaked in 1,500 mL of methanol for 3 days and then filtrated. Afterward, using a rotary evaporator, brazilein extract was evaporated to reduce its volume to 150 mL. The brazilein extract was kept in a refrigerator at 5°C for 4 days to obtain a dark red solid of pure brazilein. After filtration under vacuum, pure brazilein was washed with cold methanol (3 × 10 mL) and then characterized with NMR. Its NMR spectrum was shown in Figure S1. Brazlein, ^{1}H NMR (DMSO–*d6*, 300 MHz) δ (ppm): 2.85 (s, 2H), 4.00 (d, *J* = 11.4 Hz, 1H), 4.46 (d, *J* = 11.7 Hz, 1H), 6.34 (d, *J* = 9.0 Hz, 2H), 6.56 (d, *J* = 8.1 Hz, 1H), 7.11 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 1H).

2.3 Preparation of brazilein solutions

Methanol:water (20:80 v/v) was used in the preparation of the brazilein solution. Stock brazilein solution at 300 mg·L^{-1} was prepared by dissolving 0.3 g of brazilein powder in 100 mL of methanol:water (20:80 v/v), and other concentrations of brazilein solution were prepared by the dilution method. The calibration curve of the plot between absorbance and concentration of the brazilein solution at pH 7 was also explored and used to convert absorbance into the concentration of brazilein solution.

2.4 Adsorption experiment

For the adsorption experiments, aluminium hydroxide was mixed with brazilein solution under magnetic stirring for 3 h, followed by filtration. Then, the lake pigment powder was dried in an oven at 70°C for 24 h, and the UV-Vis absorption of the filtrate was observed. Moreover, the diffuse reflectance spectra and CIELAB color space of the lake pigments were measured. The effects of initial pH (pH 5 to pH 9), (pH 5 to pH 9, dosage of aluminium hydroxide (0.1%w/v to 2%w/v), and concentration of brazilein solution (10 mg·L^{-1} to 100 mg·L^{-1}) on the adsorption and color of lake pigments were also explored. HCl and NaOH (0.1 mM) were used to adjust the pH of the brazilein solution and Tris buffer was employed. Using Equation 1 and 2, the adsorption percentages and adsorption capacities at equilibrium were calculated, respectively. Additionally, the CIELAB color space and diffuse reflectance spectra of lake pigments were determined and compared.

$$\% Adsorption = \frac{(C_0 - C_t) \times 100}{C_0} \tag{1}$$

$$q_e = \frac{(C_0 - C_e) \cdot V}{W} \tag{2}$$

Where C_0 is the initial concentration of brazilein solution (mg·L^{-1})
       C_t is the concentration of brazilein solution at time *t* (mg·L^{-1})
       C_e is the equilibrium concentration of brazilein solution (mg·L^{-1})
       W is the amount of aluminium hydroxide (mg)
       V is the volume of brazilein solution (L)

To perform the adsorption kinetic studies, 0.25%w/v of aluminium hydroxide was mixed with 250 mL of brazilein solution. At different time intervals (1, 3, 5, 10, 15, 20, 25, 30, 40, 50, 60, 80, 100, 120, 150, and 180 min), 200 μL of the mixture was diluted with distilled water (2.8 mL, pH 7) and centrifuged for 1 min at 5,000 rpm. Afterward, UV-Vis absorption of solution was observed and compared. Then, the data were fitted to the pseudo first order (Equation 3), pseudo second order (Equation 4) and intraparticle diffusion models (Equation 5). Additionally, the Langmuir (Equation 6) and Freundlich (Equation 7) isotherm models were used to analyze the adsorption isotherm.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (4)$$

$$q_t = k_p t^{1/2} + C \qquad (5)$$

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}K_L} + \frac{C_e}{Q_{max}} \qquad (6)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (7)$$

Where K_1 is pseudo first order rate constant (mg·g^{-1}·min)

K_2 is pseudo second order rate constant (mg·g^{-1}·min)

K_P is the intraparticle diffusion rate constant (g·mg^{-1}·min$^{1/2}$)

K_L is Langmuir constant (L·mg^{-1})

K_F is Freundlich constant (L·mg^{-1})

Q_{max} is the adsorption capacity (mg·g^{-1})

n is adsorption intensity.

2.5 Dye fixation studies

Dye fixation was also studied by monitoring the release of brazilein from the lake pigment. 0.25%w/v of lake pigment prepared from aluminium hydroxide (0.25% w/v) and brazilein solution (100 mg·g^{-1}, pH 7) was stirred in distilled water for 0.25, 0.5, 1, 3, 6, 24 and 48 h at room temperature followed by filtration. The UV-Vis absorption filtrates were then recorded and the amount of released brazilein at each time was calculated. Finally, the percentage of released dye were calculated and compared.

2.6 Preparation of natural rubber toy balloon samples

Lake pigment was added to 50 mL of natural rubber. The mixture was stirred for 30 min and left to stand until the bubbles disappeared. To investigate the effect of the amount of lake pigment on natural rubber toy balloon samples, different percentages of lake pigment (1%w/v, 5%w/v and 10%w/v) in natural rubber were tested. 4 mL of the colored natural rubber sample was slowly poured into a petri dish and left to stand for 24 h. Later, the samples were dried in an oven at 60°C for 24 h. Then, the CIELAB color space, diffuse reflectance spectra, and mechanical properties, including tensile stress, Young's modulus, and elongation at break of the samples were measured and compared.

3. Results and discussion

3.1 Characterization of aluminium hydroxide and lake pigment from sappanwood

As can be seen in Figure 2, aluminium hydroxide and lake pigment from sappanwood were white and pink-red, respectively. Their morphologies and element compositions evaluated by SEM technique and EDS analysis demonstrated that both of their structures are flaky with large agglomeration, indicating that brazilein loading did not affect the morphologies of aluminium hydroxide. The elements with their % weight observed in aluminium hydroxide and lake pigment were shown in Table 1.
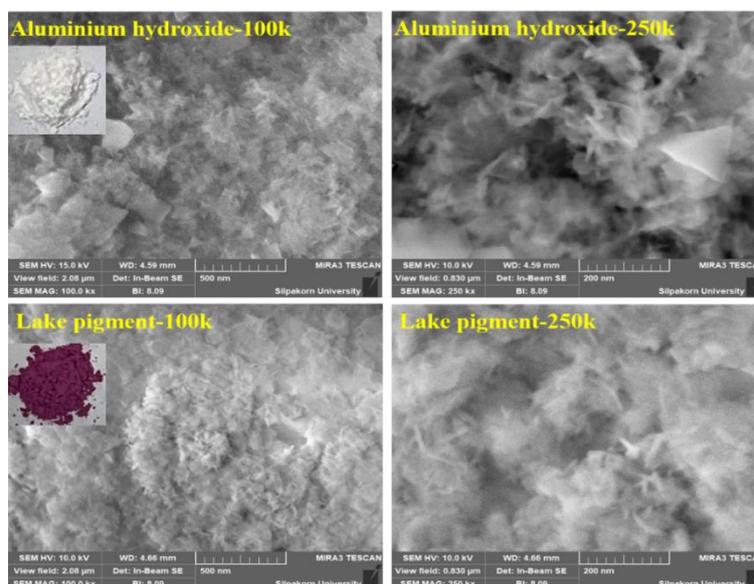
Figure 2. SEM images of aluminium hydroxide and lake pigment from sappanwood.

Table 1. Elements and their weight % observed in aluminium hydroxide and lake pigment from sappanwood.

Element	Weight %	
	Aluminium hydroxide	Lake pigment
C	3.32±0.41	4.88±0.62
O	54.99±2.26	56.03±0.51
Al	41.69±2.66	39.09±0.99

The surface chemical compositions of aluminium hydroxide and lake pigment were explored by using FT-IR spectrophotometer. As shown in Figure 3 and Table 2, it was found that the FT-IR spectra of aluminium hydroxide and lake pigment were dominated by a broad band at 480 cm^{-1} to 485 cm^{-1} and 3300 cm^{-1} to 3500 cm^{-1}, which were corresponded to the Al-O stretching and OH streching, respectively. Moreover, aliphatic C–H band at 2925 cm^{-1} and CH$_2$ stretching at 2963 cm^{-1} characteristic peaks of brazilein were observed in the FT-IR spectra of lake pigment, confirming that brazilein was adsorbed on the surface of lake pigment.
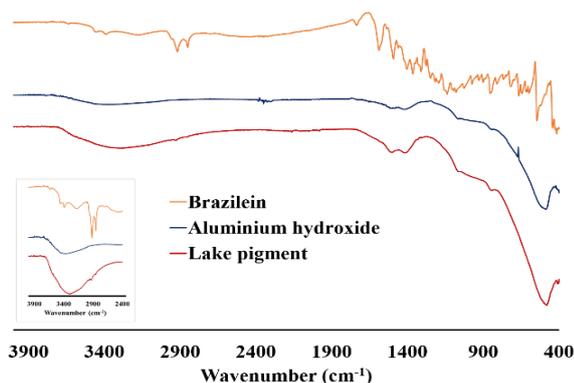
Figure 3. FT-IR spectra of brazilein, aluminium hydroxide and lake pigment from sappanwood.

The nitrogen adsorption-desorption isotherms and pore size distribution of aluminium hydroxide and lake pigment were also investigated. It was found that aluminium hydroxide and lake pigment was type IV (BDDT classification, indicating mesoporous structure. Table 3 revealed that the calculated specific surface area of aluminium hydroxide (141.83 m^2·g^{-1}) was much higher than that of lake pigment (55.18 m^2·g^{-1}) due to the adsorption of brazilein inside the pore of aluminium hydroxide. Pore volume and average pore diameter of aluminium hydroxide were 0.495 cm^3·g^{-1} and 140.681 Å, respectively, while those of lake pigment were 0.292 cm^3·g^{-1} and 211.665 Å, respectively. Moreover, pH$_{pzc}$ values of aluminium hydroxide was determined using pH drift method. According to the interception point between the data curve and the straight line of pH$_i$ = pH$_f$, pH$_{pzc}$ value of aluminium hydroxide was 7.8.

Figure 4. Thermogravimetric curves of aluminium hydroxide and lake pigment from sappanwood.

3.2 Adsorption experiment results

3.2.1 Effect of initial pH on adsorption

Initial pH is referred to the pH of brazilien solution before addition of the aluminium hydroxide adsorbent. Addition of the adsorbent can lead to pH change, which affects the structure of brazilien, and results in change of its color in solution and adsorption. To explore the effect of the initial pH of brazilein solution on adsorption, the adsorption of brazilein on aluminuim hydroxide was observed at different initial pH values (pH 5 to pH 9) of brazilein solution (20 mg·L^{-1}). Using NaOH and HCl, the pH of brazilein solution (0.10 mM) was adjusted and 0.25%w/v of aluminium hydroxide was used. As shown in Figure 5, the adsorption of brazilein on aluminum hydroxide using brazilein solutions with different initial pH values (pH 5 to pH 9) exhibited similar adsorption efficiencies of more than 98%. Moreover, the lake pigments prepared by using brazilein solutions with different initial pH values have a simiar pink color and CIELAB with maximum absorption at 554 nm (Figure 6 and Table 4). This indicates that the different initial pH values of brazilein solution (pH 5 to pH 9) do not affect the adsorption and color of lake pigments, which can be attributed to the fact that aluminium hydroxide is amphoteric and can react as both acid and base. After aluminium hydroxide was added to brazilein solutions with different initial pH values, the pH of brazilein solutions became silimar (~7.5), resulting in the similar adsorption and color of lake pigments.

Table 2. FT-IR vibration assignment of aluminium hydroxide and lake pigment from sappanwood.

Vibration assignment	Wavenumber (cm^{-1})		
	Aluminium hydroxide	**Brazilein**	**Lake pigment**
Al-O stretching	483, 846, 1061	-	480, 846, 1063
C=C(=O)-C=C stretching	-	1365	1398
C=C stretching	-	1587	-
aliphatic C–H band	-	2850, 2918	2925
CH$_2$ stretching	-	2940	2963
OH stretching	3462	3390, 3450	3293
C=O band	-	1364	1415

Table 3. The textural properties of aluminium hydroxide and lake pigment from sappanwood.

Samples	Surface area (m^2·g^{-1})	Pore volume (cm^3·g^{-1})	Average pore diameter (Å)
Aluminium hydroxide	141.826	0.495	140.681
Lake pigment	55.181	0.292	211.665

Figure 5. Adsorption efficiencies of the adsorption of brazilein on aluminum hydroxide using brazilein solution with different initial pH values.
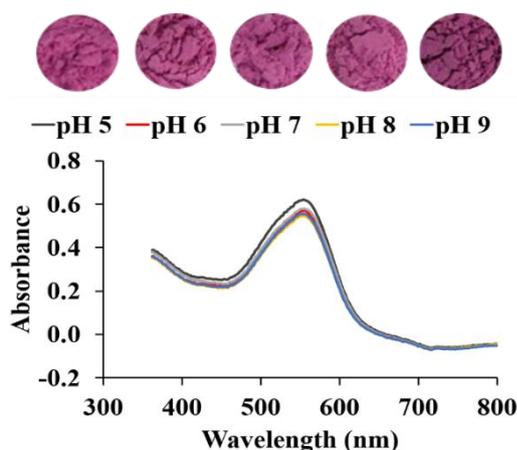
Figure 6. Lake pigments and their diffuse reflectance spectra prepared by the adsorption method using brazilein solution with different initial pH values.

3.2.2 Effect of pH on adsorption

To systematically study and investigate effects of pH on adsorption of brazilien, the pH buffer solutions were utilized to maintain the pH of brazilien solution after addition of the adsorbent, thus pH of brazilien solution before and during adsorption remains unchanged due to addition of the buffers. The adsorption of brazilein on aluminium hydroxide using 0.25% w/v of adsorbent and brazilein solution (20 mg·L^{-1}) containing Tris buffer with different pH values (pH 5 to pH 9) was investigated. Notably, high adsorption efficiencies of ~98% to 99% were observed at pH 5 to pH 7. The adsorption efficiency was reduced to 42% and 30% for the adsorption at pH 8 and pH 9,

respectively (Figure 7). This is because pH 8 and pH 9 are higher than pH–point of zero charge (pH$_{pzc}$) of aluminium hydroxide (pH 7.8). The surface of the adsorbent become negatively charged, resulting in less adsorption of negatively charged brazilein on the surface. Additionally, adsorption using brazilein solution with dufferent pH values exhibited similar pink lake pigments with maximum absorption at 554 nm. However, the pink color of lake pigments obtained at pH 8 and pH 9 (maximum absorbance of 0.38 and 0.08, a* of 38 and 17, respectively) was paler than that of lake pigments obtained at (pH 5 to pH 7) (maximum absorbance of 0.6-0.7, a* of 46-49) as illustrated in Figure 8 and Table 5.
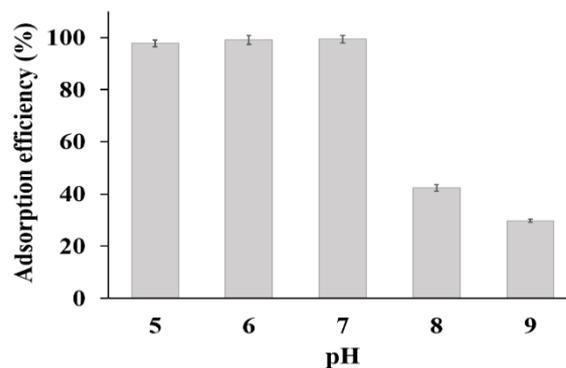
Figure 7. Adsorption efficiencies of the adsorption of brazilein on aluminum hydroxide using brazilein solution with different pH values.
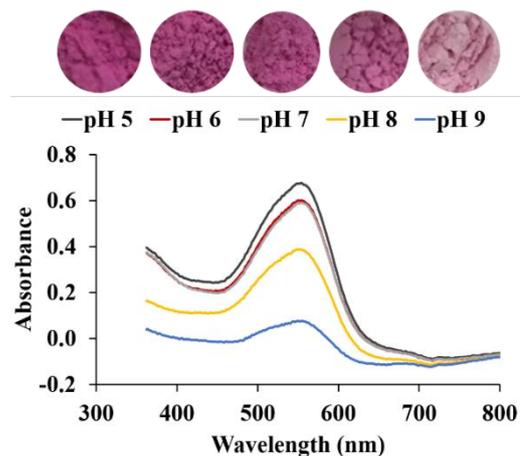
Figure 8. Lake pigments and their diffuse reflectance spectra prepared by the adsorption method using brazilein solution with different pH values.

Table 4. CIELAB color space of the lake pigments prepared by the adsorption method using brazilein solution with different initial pH values.

Initial pH	5	6	7	8	9
L*	68.59	71.08	70.30	72.14	71.75
a*	42.19	40.90	40.13	39.43	39.95
b*	-15.69	-15.11	-15.17	-14.66	-14.74

Table 5. CIELAB color space of the lake pigments prepared by the adsorption method using brazilein solution with different pH values.

pH	5	6	7	8	9
L*	67.19	70.57	71.09	80.77	98.39
a*	49.26	46.37	45.60	37.87	16.63
b*	-18.29	-17.54	-17.76	-13.75	-4.22

3.2.3 Effect of adsorbent dosage on adsorption

The effect of the amount of aluminium hydroxide on adsorption was investigated by monitoring the adsorption capacities using different adsorbent dosages (0.1%w/v to 2%w/v) in brazilein solution (20 mg·L^{-1}) at pH 7. The results showed that the adsorption capacities at equilibrium (q_e) decreased from 17.69 mg·g^{-1} to 0.92 mg·g^{-1} with the increase in the adsorbent dosage (Figure 9). When high dosages of aluminium hydroxide were used, the pink lake pigments with maximum absorption at 554 nm became pale and the maximum of the absorbance decreased from 0.91 to 0.17 (Figure 10). Additionally, Table 6 showed that a* values were also reduced from 52 to 26 with the increase of adsorbent dosages. This observation could be attributed to higher surface area when higher dosage of aluminium hydroxide were added, which led to lower density of adsorbed brazilein per unit of surface area. Consequently, paler color of the lake pigment was observed.

3.2.4 Effect of adsorption time and concentration of brazilein solution on adsorption

According to the results of the study of the effect of adsorption time and concentration of brazilein solution on the adsorption of brazilein on aluminium hydroxide shown in Figure 8, the adsorption capacities increased sharply in the first 20 min and reached the adsorption equilibrium within 50 min (Figure 11(a)). Upon the increase of concentrations of brazilein solutions, the adsorption capacities at equilibrium increased from 3.97 mg·g^{-1} to 29.84 mg·g^{-1} (Figure 11(b)) because higher initial concentration gave larger necessary driving force to overcome the resistances to the mass transfer of brazilein between the aqueous and the solid phases [54]. Moreover, the lake pigments obtained from the adsorption process were pink with maximum absorption at 554 nm. However, the increase in the concentration of brazilein solution from 20 mg·L^{-1} to 100 mg·L^{-1} resulted in the deeper pink color of lake pigments and the increase in the maximum absorbance from 0.39 to 1.12 and a* values from 43 to 56 (Figure 12 and Table 7). Comparison with the other reported adsorbents for preparation of lake pigment from sappanwood [40,55,56] as shown in Table 8 demonstrated that the colors of lake pigment were varied when the different adsorbent were used. Importantly, using aluminium hydroxide as the adsorbent for brazilein exhibited highest adsorption capacities.

3.2.5 Adsorption kinetics

To explore the adsorption kinetics of the adsorption of brazilein on aluminium hydroxide, three models of adsorption kinetics, namely, pseudo first order kinetic, pseudo second order kinetic, and intraparticle diffusion models, were tested. The results were showned in Figure 13 and Table 9. Notably, a high R^2 of 0.9986 (on average) was obtained from the pseudo second order kinetic model. The calculated adsorption capcities of pseudo second order kinetic model were also the most similar to the experimental data, compared with those of other models. This indicates that the adsorption kinetics of the adsorption of brazilein on aluminium hydroxide fit the pseudo second order kinetic model well.
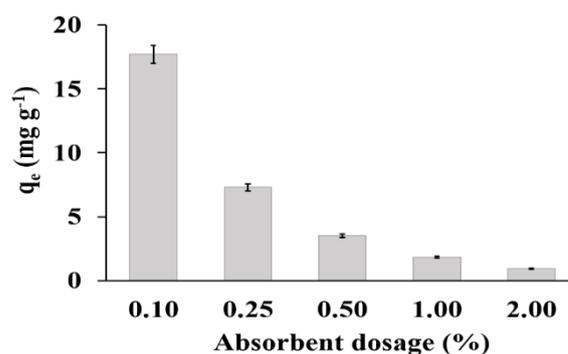
Figure 9. Adsorption capacities at equilibrium (q_e) of the adsorption of brazilein on aluminum hydroxide with different adsorbent dosages.
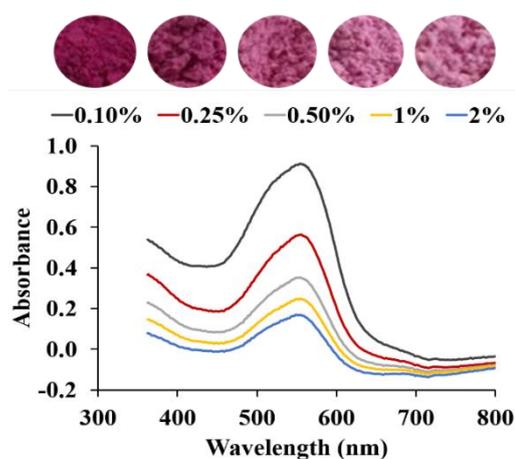
Figure 10. Diffuse reflectance spectra of lake pigments prepared by the adsorption method using brazilein solution with differnet adsorbent dosages.

Table 6. CIELAB color space of the lake pigments prepared by the adsorption method using brazilein solution with different adsorption dosages.

% Adsorbent dosage (w/v)	0.1	0.25	0.5	1	2
L*	55.71	72.19	82 .78	88.94	93.80
a*	52.40	43.49	34.68	29.48	26.17
b*	-17.51	-17.61	-14.21	-12.24	-10.23

Table 7. CIELAB color space of lake pigments prepared by the adsorption method using brazilein solution with different concentrations.

Concentrations of brazilein solutions (mg·L^{-1})	10	20	40	80	100
L*	82.02	71.76	59.68	50.50	47.06
a*	43.27	52.92	57.20	56.64	56.38
b*	-17.24	-20.04	-19.33	-16.17	-14.47

Table 8. Comparison of lake pigment from sappanwood prepared by different adsorbents.

Adsorbent	Dye	Color	Maximum adsorption capacity (mg·g⁻¹)
Munpoo clay	Sappanwood extract	Reddish-brown	-
Dindang clay	Sappanwwod extract	Reddish-brown	-
Montmorillonite	Brazilein	Pink-purple	17.40
Aluminium oxide	Brazilein	Pink	10.48
Aluminium hydroxide	Brazilein	Pink-red	29.84

Table 9. Pseudo first order and pseudo second order kinetic constants for the adsorption of brazilein on aluminium hydroxide.

Concentrations (mg·L⁻¹)	q_e (exp)	Pseudo first order kinetic			Pseudo second order kinetic			Intraparticle diffusion model	
		R^2	K_1 (min⁻¹)	q_e (cal)	R^2	K_2 (mg·g⁻¹·min⁻¹)	q_e (cal)	R^2	K_2 (g·mg⁻¹·min⁻¹/²)
10	3.97	0.5834	0.1702	0.74	0.9979	0.6931	4.00	0.2064	0.0888
20	6.87	0.4447	0.0104	0.59	0.9976	-0.1220	6.83	0.1702	0.1493
40	14.53	0.2771	0.0147	0.83	0.9982	-0.5324	14.66	0.2702	0.3804
80	26.86	0.7126	0.0739	7.13	0.9998	0.0225	28.25	0.3803	0.8333
100	29.84	0.8419	0.0469	7.11	0.9997	0.0192	30.96	0.3802	0.9062
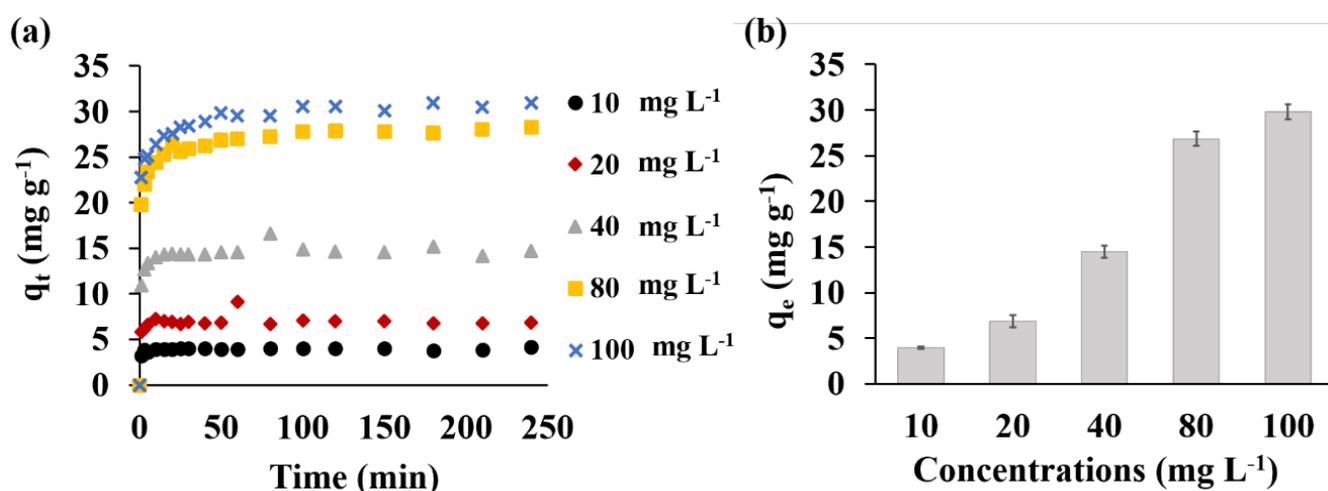
Figure 11. Adsorption capacities at different adsorption times (a) and adsorption capacities at equilibrium (b) of the adsorption of brazilein on aluminum hydroxide using brazilein solution with different concentrations.
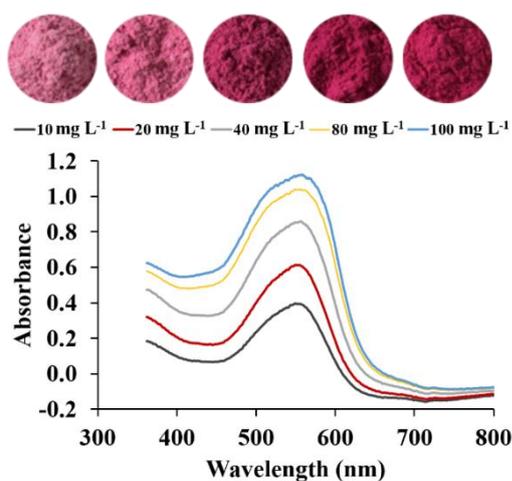
Figure 12. Diffuse reflectance spectra of lake pigments prepared by adsorption method using various concentrations of brazilein solution.

Table 10. Langmuir and Freundlich constants for the adsorption of brazilein on aluminium oxide.

Langmuir isotherm		Freundlich isotherm	
R_2	= 0.9960	R_2	= 0.9468
K_L	= 0.2262	K_F	= 1.2069
Q_{max}	= 37.19	n	= 1.75

3.2.6 Adsorption isotherms

Two adsorption isotherm models, namely, Langmuir isotherm and Freundlich isotherm were tested in this work to obtain a better understanding of the adsorption behavior of the adsorption of brazilein on aluminium hydroxide. As represented in Figure 14 and Table 10, the Langmuir isotherm model showed a better fit to the expermental data than the Freundlich isotherm model, indicating that brazilein adsorbed on the surface of aluminium hydroxide with a monolayer adsorption with the maximum adsorption capacity of 37.19.
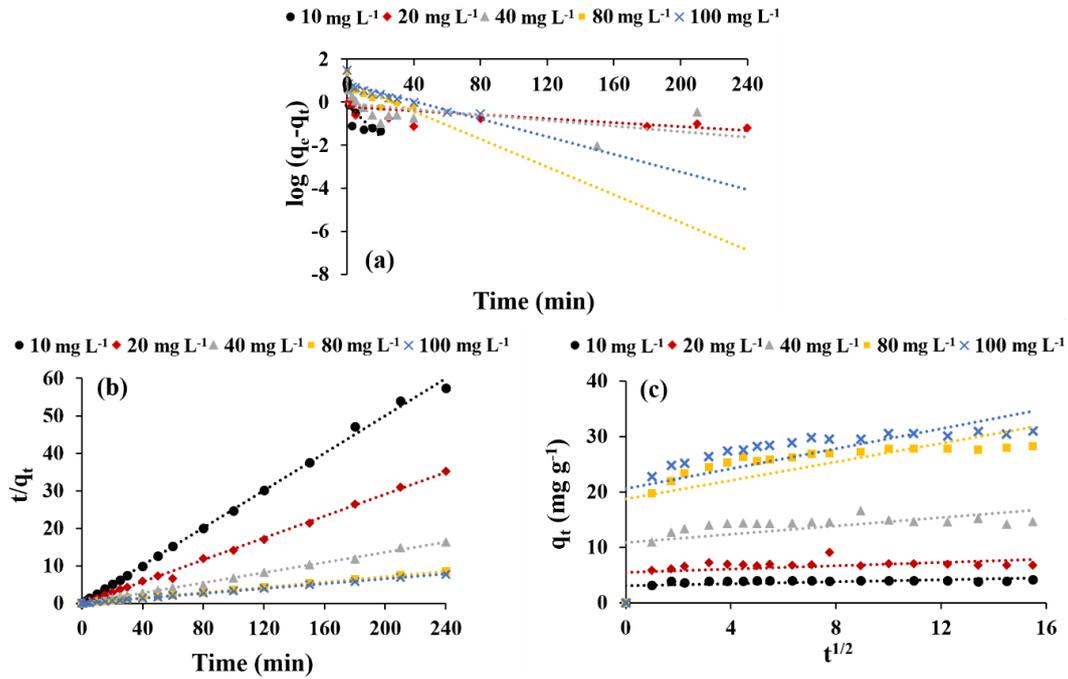
Figure 13. (a) Pseudo first order kinetic model, (b) pseudo second order kinetic model and (c) intraparticle diffusion model of the adsorption of brazilein on aluminium hydroxide.\
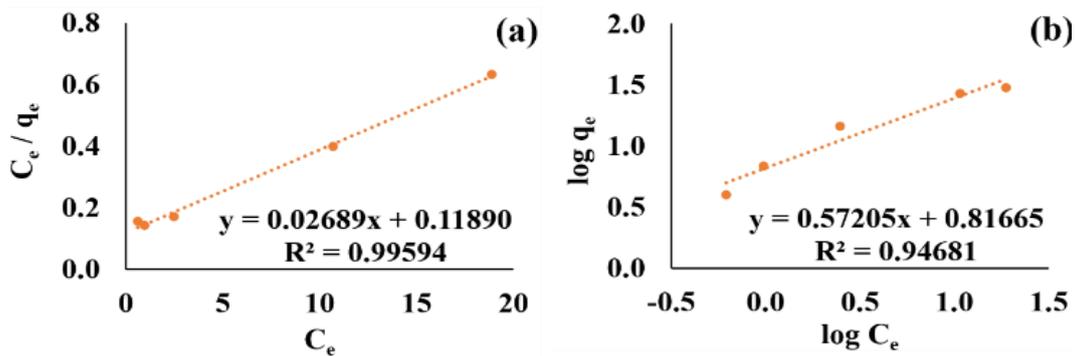
Figure 14. (a) Langmuir and (b) Freundlich isotherms for the adsorption of brazilein on aluminium hydroxide.

3.3 Dye fixation results

As can be seen in Figure 15, less than 1% of brazilein was released from lake pigment in water after 48 h, indicating that brazilein were strongly adsorbed on the surface of aluminium hydroxide.

3.4 Application as colorants for natural rubber toy balloon

To explore the application of lake pigments prepared in this work, they are utilized as natural colorants for natural rubber toy balloon, which is one of the most popular toys for kids. Figure 16 shows that natural rubber toy balloon samples colored with lake pigments have pink–red color with the maximum absorption at 570 nm. Lake pigments also mixed well with the natural rubber. Moreover, with a higher amount of lake pigments added, deeper pink–red color with higher a*value and lower L*value observed (Table 11). In addition, higher percentages of lake pigments lead to the slightly higher values of Young's modulus, tensile stress, and elongation at break of natural

rubber toy balloon samples (Table 12). This can be implied that coloring natural rubber for toy balloon with lake pigments shows no affect the mechanical properties of natural rubber.
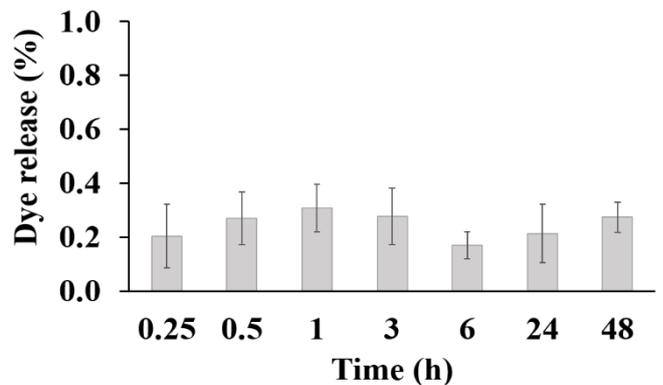
Figure 15. The percentage of the released brazilein of the lake pigment in distilled water vs various time.

Table 11. Natural rubber toy balloon samples colored with lake pigments prepared by the adsorption of brazilein on aluminium hydroxide and their CIE LAB color space.

% Lake pigment (w/v)	0	1	5	10
L*	95.59	86.38	68.03	62.67
a*	-3.54	11.80	27.45	30.70
b*	13.24	4.45	-7.73	-9.55

Table 12. List of values of Young's modulus, tensile stress, and elongation at break of natural rubber toy balloon samples colored by lake pigment prepared with the adsorption of brazilein on aluminium hydroxide.

% Lake pigment (w/v)	Tensile strength (MPa)	Elongation at break (%)	Young's Modules (MPa)
0	0.766 ± 0.147	948.515 ± 91.870	0.054 ± 0.010
1	0.865 ± 0.217	939.345 ± 68.898	0.059 ± 0.018
5	0.909 ± 0.189	891.172 ± 92.827	0.062 ± 0.012
10	1.019 ± 0.205	851.225 ± 90.832	0.080 ± 0.014
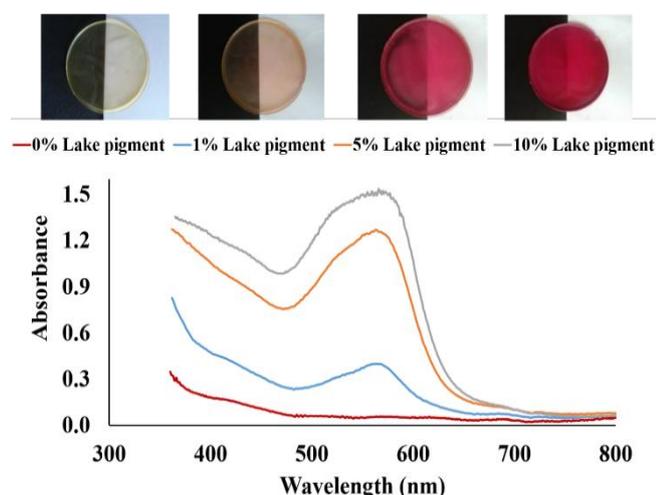
Figure 16. Natural rubber toy balloon samples colored with lake pigment from sappanwood (a) and their diffuse reflectance spectra (b).

4. Conclusions

Herein, the adsorption of natural pigment called brazilien on aluminium hydroxide was thoughly explored. The results showed that the initial pH of brazilein solution in the range of 5 to 9 did not affect the adsorption and more than 98% adsorption efficiency was obtained. The highest adsorption capacity of 30 mg·g^{-1} was acheived when 0.25%w/v of aluminium hydroxide and 100 mg·L^{-1} of brazilein solution were applied. The adsorption kinetics fitted with pseudo second order model well, whereas the adsorption isotherm fitted with Langmuir isotherm model well. Additionally, the pink–red lake pigment prepared in this work mixed well with the natural rubber for toy balloon fabrication and yielded a pink–red colored natural rubber toy balloon. Our method to produce lake pigment from brazilein by aluminium hydroxide adsorbent shall benefit and add value to the specific product that required safety for human and environmental-friendly such as toys, food, food containers, and cosmetics. Furthermore, pilot scale production for practical industrial use and using of stabilizing agent to prevent color degradation will be considered in our future work to broaden the utilization of lake pigment from sappanwood.

References

[1] H. Rymbai, R. R. Sharma, and M. Srivastav, "Bio-colorants and its implications in health and food industry–A review," *International Journal of Pharmacological Research*, vol. 3(4), pp. 2228-2244, 2011.

[2] M. Yusuf, M. Shabbir, and F. Mohammad, "Natural colorants: Historical, processing and sustainable prospects," *Natural Products and Bioprospecting*, vol. 7(1), pp. 123-145, 2017.

[3] B. Lellis, C. Z. Fávaro-Polonio, J. A. Pamphile, and J. C. Polonio, "Effects of textile dyes on health and the environment and bioremediation potential of living organisms," *Biotechnology Research and Innovation*, vol. 3, pp. 275-290, 2019.

[4] P. S. Vankar, and D. Shukla, *New Trends in Natural Dyes for Textiles*, Woodhead Publishing, United Kingdom, 2019.

[5] A. Guha, "A review on sources and application of natural dyes in textiles," *International Journal of Textile Science*, vol. 8(2), pp. 38-40, 2019.

[6] M. Shahid, F. Mohammad, and S. -u. Islam, "Recent advancements in natural dye applications: A review," *Journal of Cleaner Production*, vol. 53, pp. 310-331, 2013.

[7] M. Yusuf, A. Ahmad, M. Shahid, M. I. Khan, S. A. Khan, N. Manzoor, and F. Mohammad, "Assessment of colorimetric, antibacterial and antifungal properties of woollen yarn dyed with the extract of the leaves of henna (Lawsonia inermis)," *Journal of Cleaner Production*, vol. 27, pp.42-50, 2012.

[8] S. A. Khan, M. I. Khan, M. Yusuf, M. Shahid, F. Mohammad, and M.A. Khan, Handbook of renewable materials for coloration and finishing. Yusuf, ed., John Wiley & Sons, 2011.

[9] S. A. Khan, M. I. Khan, M. Yusuf, M. Shahid, F. Mohammad, and M.A. Khan, "Natural dye shades on woollen yarn dyed with Kamala (Mallotus philippinensis)using eco-friendly metal

mordants and their combination," *Colourage*, vol. 58(11), pp. 38-44, 2011.

[10] A. P. Periyasamy, and J. Militky, "Sustainability in textile dyeing: Recent developments," *Sustainability in the Textile and Apparel Industries*, pp.37-79, 2020.

[11] M. Yusuf, "Synthetic dyes: A threat to the environment and water ecosystem," in Textiles and Clothing, M. Shabbir (Ed.), 2019, pp. 11-26.

[12] H. Ali, "Biodegradation of synthetic dyes—A review," *Water, Air, & Soil Pollution*, vol. 213(1), pp. 251-273, 2010.

[13] K. Prabhu, and A. S. Bhute, "Plant based natural dyes and mordants: A Review," *Journal of Natural Product and Plant Resources*, vol. 2, pp. 649-664, 2012.

[14] M. Yusuf, M. Shahid, M. I. Khan, S. A. Khan, M. A. Khan, and F. Mohammad, "Dyeing studies with henna and madder: A research on effect of tin (II) chloride mordant," *Journal of Saudi Chemical Society*, vol. 19(1), pp. 64-72, 2015.

[15] M. Yusuf, S. A. Khan, M. Shabbir, and F. Mohammad, "Developing a shade range on wool by madder (Rubia cordifolia) root extract with gallnut (Quercus infectoria) as biomordant," *Journal of Natural Fibers*, vol. 14(4), pp. 597-607, 2017.

[16] M. Yusuf, M. A. Khan, and F. Mohammad, "Investigations of the colourimetric and fastness properties of wool dyed with colorants extracted from Indian madder using reflectance spectroscopy," *Optik*, vol. 127(15), pp. 6087-6093, 2016.

[17] R. Naveed, I. A. Bhatti, S. Adeel, A. Ashar, I. Sohail, M. U. H. Khan, N. Masood, M. Iqbal, and A. Nazir, "Microwave-assisted extraction and dyeing of cotton fabric with mixed natural dye from Pomegranate Rind (Punica Granatum L.) and Turmeric Rhizome (Curcuma Longa L.)," *Journal of Natural Fibers*, pp.1-8, 2020.

[18] M. Shahid, A. Ahmad, M. Yusuf, M. I. Khan, S. A. Khan, N. Manzoor, and F. Mohammad, "Dyeing, fastness and anti-microbial properties of woolen yarns dyed with gallnut (Quercus infectoria Oliv.) extract," *Dyes and Pigments*, vol. 95(1), pp.53-61, 2012.

[19] M. I. Khan, S. A. Khan, M. Yusuf, M. Shahid, F. Mohammad, and M. A. Khan, "Eco-friendly shades on wool using mixed mordants with Acacia catechu (Cutch)," *Colourage*, vol. 57(8), pp.81-88, 2010.

[20] J. G. Krishna, S. M. Basheer, P. S. Beena, and M. Chandrasekaran, "Marine bacteria as source of pigment for application as dye in textile industry," *In Proc Internatl Conf Biodiv Conserv Mgt*, vol. 1, pp. 743-744, 2008.

[21] M. Norman, P. Bartczak, J. Zdarta, H. Ehrlich, and T. Jesionowski, "Anthocyanin dye conjugated with Hippospongia communis marine demosponge skeleton and its antiradical activity," *Dyes and Pigments*, vol. 134, pp.541-552, 2016.

[22] K. Mekala, and R. Radha, "A review on sappan wood-a therapeutic dye yielding tree," *Research Journal of Pharmacognosy and Phytochemistry*, vol. 7(4), pp. 227-231, 2015.

[23] R. Rondão, J. S. R. Seixas de Melo, J. O. Pina, M. J. Melo, T. Vitorino, and A. J. Parola, "Brazilwood reds: the (photo) chemistry of brazilin and brazilein", *Journal of Physical Chemistry A*, vol. 117 (41), pp. 10650-10660, 2013.

[24] L. F. de Oliveira, H. G. Edwards, E.S. Velozo, and M. Nesbitt, "Vibrational spectroscopic study of brazilin and brazilein, the main constituents of brazilwood from Brazil," *Vibrational Spectroscopy*. vol. 28, pp. 243-249, 2002.

[25] D-K. Lee, D-H. Cho, J-H. Lee, and H Y. Shin, "Fabrication of nontoxic natural dye from sappan wood," *Korean Journal of Chemical Engineering*, vol. 25, pp. 354-358, 2008.

[26] P. Ohama, and N. Tumpat, "Textile dyeing with natural dye from Sappan tree (Caesalpinia sappan Linn) extract," International Journal of Chemical, Biomolecular, Metallurgical, Materials Science and Engineering, vol. 8, pp. 432-435, 2014.

[27] R. Carle, and R. Schweiggert, *Handbook on natural pigments in food and beverages: Industrial applications for improving food color*, Woodhead Publishing, United Kingdom, 2016.

[28] H. De Clermont-Gallerande, C. Dacruz, C. Brunet, and A. De La Sayette- Saby, " Cosmetic material comprising a sappan wood extract on a clay substrate," Google Patents, 2013.

[29] R. Dapson, and C. Bain, "Brazilwood, sappanwood, brazilin and the red dye brazilein: From textile dyeing and folk medicine to biological staining and musical instruments," *Biotechnic & Histochemistry*, vol. 90(6), pp. 401-423, 2015.

[30] N. P. Nirmal, M. S. Rajput, R. G. Prasad, and M. Ahmad, "Brazilin from Caesalpinia sappan heartwood and its pharma-cological activities: A review," *Asian Pacific Journal of Tropical Medicine*, vol. 8(6), pp. 421-430, 2015.

[31] H. Hridya, A. Amrita, M. Sankari, C. G. P. Doss, M. Gopalakrishnan, C. Gopalakrishnan, and R. Siva, "Inhibitory effect of brazilein on tyrosinase and melanin synthesis: Kinetics and in silico approach," *International Journal of Biological Macromolecules*, vol. 81, pp. 228-234, 2015.

[32] L-Y. Tao, J-Y. Li, and J-Y. Zhang, "Brazilein, a compound isolated from Caesalpinia sappan Linn, induced growth inhibition in breast cancer cells via involvement of GSK-3β/ β-Catenin/cyclin D1 pathway," *Chemico- Biological Interactions*, vol. 206(1), pp. 1-5, 2015.

[33] A. Petdum, T. Sooksimuang, N. Wanichacheva, and J. Sirirak, "Natural colorimetric sensor from sappanwood for turn-on selective Fe^{2+} detection in aqueous media and its application in water and pharmaceutical samples," Chemistry Letters, vol. 48(7), pp. 678-681, 2019.

[34] J. Kirby, M. van Bommel, and A. Verhecken, *Natural colorants for dying and lake pigments: practical recipes and their historical sources*, Archetype Publications Ltd, London, United Kingdom, 2014.

[35] S. Marras, "Natural colorants for dyeing and lake pigments", *Ge-conservación*, pp. 61-62, 2015.

[36] S. V. Berbers, D. Tamburini, M. R. van Bommel, and J. Dyer, "Historical formulations of lake pigments and dyes derived from lac: A study of compositional variability," *Dyes and Pigments*, vol. 170, pp. e107579, 2019.

[37] A. Jimtaisong, "Aluminium and calcium lake pigments of Lac natural dye," *Brazilian Journal of Pharmaceutical Sciences*, vol. 56, pp. e18140, 2020.

[38] T. Vitorino, M. J. Melo, L. Carlyle, and V. Otero, "New insights into brazilwood lake pigments manufacture through the use

of historically accurate reconstructions," *Studies in Conservation*, vol. 61, pp. 255-273, 2016.

[39] C. Clementi, B. Doherty, P. L. Gentili, C. Miliani, A. Romani, B. G. Brunetti, and A. Sgamellotti, "Vibrational and electronic properties of painting lakes," *Applied Physics A*, vol. 92, pp. 25-33, 2018.

[40] J. Sirirak, N. Worawannotai, C. Suwanchawalit, and S. Chayabutra, "Preparation and characterization of lake pigments from sappan wood using Thai local clays," *Journal of Metals, Materials and Minerals*, vol. 30(1), pp. 20-28, 2020.

[41] S. Girdthep, J. Sirirak, D. Daranarong, R. Daengngern, and S. Chayabutra, "Physico-chemical characterization of natural lake pigments obtained from Caesalpinia Sappan Linn. and their composite films for poly (lactic acid)-based packaging materials," *Dyes and Pigments*, vol. 157, pp. 27-39, 2018.

[42] C. Vadeesirisak, S. Chayabutra, and J. Sirirak, "Effect of species and preparation of mango leaves on lake pigments from mango leaves prepared by adsorption Method," *Burapha Science Journal*, vol. 25(2), pp. 545-562, 2020.

[43] S. Singla, M. Mathur, C. S. Chauhan, S. Goyal, and M. Junaid, "Formulation and charcterization of lake color obtained from red cabbage," *Indian Journal of Pharmaceutical and Biological Research*, vol. 4(01), pp. 50-56, 2016.

[44] F. Fournier, L. de Viguerie, S. Balme, J.-M, Janot, P. Walter, and M. Jaber, "Physico-chemical characterization of lake pigments based on montmorillonite and carminic acid," *Applied Clay Science*, vol. 130, pp. 12-17, 2016.

[45] S. Shivali, S. Goyal, H. Paliwal, M. Mathur, C. C. Singh, and D. Shashi, "Lake color formulation of beet root extract and its optimization," *International Journal of Pharmaceutical Sciences Review and Research*, vol. 40, pp. 86-91, 2016.

[46] D. Krewski, R. A. Yokel, E. Nieboer, D. Borchelt, J. Cohen, J. Harry, S. Kacew, J. Lindsay, A.M. Mahfouz, and V. Rondeau, "Human health risk assessment for aluminium, aluminium oxide, and aluminium hydroxide," *Journal of Toxicology and Environmental Health, Part B*, vol. 10, pp. 1-269, 2007.

[47] R. A. Robinson, and H. T. S. Britton, "CCCXCII.—The amphoteric nature of aluminium hydroxide," *Journal of the Chemical Society (Resumed)*, pp. 2817-2820, 1931.

[48] C. M. Reinke, J. Breitkreutz, and H. Leuenberger, "Aluminium in over-the-counter drugs," *Drug Safety*, vol.26(14), pp.1011-1025, 2003.

[49] H. Kathyayini, I. Willems, A. Fonseca, J. B. Nagy, and N. Nagaraju, "Catalytic materials based on aluminium hydroxide, for the large scale production of bundles of multi- walled (MWNT) carbon nanotubes," *Catalysis Communications*, vol. 7(3), pp. 140-147, 2006.

[50] B. Uçar, A. Güvenç, and Ü. Mehmetoglu, "Use of aluminium hydroxide sludge as adsorbents for the removal of reactive dyes: equilibrium, thermodynamic, and kinetic studies," *Hydrology: Current Research*, vol. 2(2), pp. e1000112, 2011.

[51] L. Gianfreda, M. Rao, and A. Violante, "Adsorption, activity and kinetic properties of urease on montmorillonite, aluminium hydroxide and AL (OH) x-montmorillonite complexes," *Soil Biology and Biochemistry*, vol. 24(1), pp. 51-58, 1992.

[52] G. Micera, C. Gessa, P. Melis, A. Premoli, R. Dallocchio, and S. Deiana, "Zinc (II) adsorption on aluminium hydroxide", *Colloids and Surfaces*, vol. 17(4), pp. 389-394, 1986.

[53] S. Berger, and D. Sicker, *Classics in spectroscopy: isolation and structure elucidation of natural products*, John Wiley & Sons, New York, 2009.

[54] M. Fatiha, and B. Belkacem, "Adsorption of methylene blue from aqueous solutions using natural clay," *Journal of Materials and Environmental Science*, vol. 7(1), pp. 285-292, 2016.

[55] P. Suppharatthanya, S. Chaneam, P. Limpachayaporn, and J. Sirirak, " Kinetics and isotherm study of the adsorption of brazilien from sappanwood on montmorillonite," *Thai Science and Technology Journal,* vol 27(6), pp. 989-1001, 2018.

[56] P. Suppharatthanya, S. Chayabutra, and J. Sirirak, "Adsorption kinetics of natural dye (sappanwood) on aluminium oxide," *Proceeding the 13th International Conference on Ecomaterials (ICEM2017)*, 2017, pp. 88-92.