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Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash

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Abstract

Removal of acid green 25 (AG25) dye onto activated palm ash from aqueous solutions was investigated. Experiments were carried out as function of contact time, initial concentration (50–600 mg/L), pH (2–12) and temperature (30–50 °C). The equilibrium adsorption data of AG25 dye on activated palm ash were analyzed by Langmuir and Freundlich models. The results indicate that the Freundlich model provides the best correlation of the experimental data. The adsorption capacities of the activated palm ash for removal of AG25 dye was determined with the Langmuir equation and found to be 123.4, 156.3 and 181.8 mg/g at 30, 40, and 50 °C, respectively. Adsorption data were modeled using the pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetics equations. It was shown that pseudo-second-order kinetic equation could best describe the adsorption kinetics. Isotherms have also been used to obtain the thermodynamic parameters such as free energy, enthalpy and entropy of adsorption. The positive value of the enthalpy change (26.64 kJ/mol) indicates that the adsorption is endothermic process. The results indicate that activated palm ash is suitable as adsorbent material for adsorption of AG25 dye from aqueous solutions.

Keywords: Acid green 25 dye; Activated palm ash; Adsorption isotherm; Kinetics; Thermodynamics

1. Introduction

The industrial wastewater usually contains a variety of organic compounds and toxic substances which are harmful to fish and other aquatic. Dyeing wastewater discharged to natural receiving waters may make them unacceptable for public consumption. Thus, it is desirable to eliminate dyes from textile wastewater [1]. The total dye consumption of the textile industry alone is in excess of 10^7 kg/year and an estimated 90% of this total ends up on fabrics. Consequently, approximately 10^6 kg/year of dyes are discharged into waste streams by the textile industry [2].

Dyes and pigments represent one of the problematic groups; they are emitted into wastewaters from various industrial branches, mainly from the dye manufacturing and textile finishing. Dyes can be classified as anionic (direct, acid, and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) [3]. Acid dyes are organic sulphonic acids; the commercially available forms are usually sodium salts, which exhibit good water solubility. In sequence of their importance, acid dyes are mostly used with certain fiber types such as polyamide, wool, silk, modified acrylic, and polypropylene fibers, as well as blends of the aforementioned fibers with other fibers such as cotton, rayon, polyester, regular acrylic, etc. [4].

The most widely used methods for removing dyes from wastewater systems include physicochemical, chemical, and biological methods, such as flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques, ozonation, and fungal decolorization [5]. Adsorption is widely used in the removal of contaminants from wastewaters. The design and efficient operation of adsorption processes require equilibrium adsorption data. The equilibrium isotherm plays an important role in predictive modeling for analysis and design of adsorption systems [6]. Although activated carbons are among the most effective adsorbents with high surface areas and can be regenerated by thermal desorption or combustion of the toxicant in air, are still considered expensive [7].

Recently, attentions have been focused on the development of low cost adsorbent for the application concerning treatment of

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Nomenclature

A	Arrhenius factor
C_e	equilibrium liquid phase concentration (mg/L)
C_0	initial liquid phase concentration (mg/L)
E_a	Arrhenius activation energy (J/mol)
ΔG°	free energy Gibbs (kJ/mol)
ΔH°	enthalpy (kJ/mol)
k_{dif}	intra-particular diffusion rate constant (mg/h$^{1/2}$ g)
k_1	rate constant of first-order adsorption (h^{-1})
k_2	rate constant of second-order adsorption (g/g h)
K_F	Freundlich isotherm constant related to adsorption capacity ((m/g)(L/mg)$^{1/n}$)
K_L	adsorption energy constant of Langmuir adsorption isotherm (L/mg)
n	Freundlich isotherm constant related to adsorption intensity
q_e	equilibrium solid phase adsorbate concentration (mg/g)
q_{max}	the maximum surface coverage (formation of monolayer) of adsorbent (mg/g)
q_t	amount of adsorption at time t (mg/g)
R_L	dimensionless separation factor
R^2	correlation coefficient
S.D.	normalized standard deviation (%)
ΔS°	entropy (J/mol K)
t	time (h)
T	absolute temperature (°C)
V	volume of solution (L)
W	mass of adsorbent (g)

wastewater. Oil palm ash, being a low-cost and easily available adsorbent, could be an alternative for more costly wastewater treatment processes. Currently, Malaysia is the largest exporter of palm oil in the international market. Beside the production of crude palm oil, a large amount of solid waste is also an output from the palm oil industry. For example, 2.6 million tonnes of solid waste in form of oil palm shells are produced annually [8]. This waste is usually used as fuel in palm oil mill factories. The ash is produced after the combustion of oil palm fibers and shells as boiler fuel for the steam generation for palm oil mill consumption. Around 200 palm oil mills are in operation in Malaysia where thousands of tonnes of ash are produced annually and are simply disposed of without any commercial return [9]. In our previous study activated palm ash showed remarkable efficiency for the removal of direct dye from aqueous solution [10]. Hence a further attempt of the feasibility of applying activated palm ash for the removal of acid dye from aqueous solution was approached.

Therefore, the objective of this study was to evaluate the adsorption potential of palm ash for acid green 25 (AG25) dye. The equilibrium and kinetic data of adsorption studies were processed to understand the adsorption mechanism of acid green 25 (AG25) dye onto the activated palm ash.

2. Materials and methods

2.1. Preparation and characterization of activated palm ash

In the present study, palm ash was collected from United Oil Palm Mill, Penang, Malaysia. Palm ash was activated by the procedure reported in our previous work [10]. Initially, palm ash was washed doubly with water and oven dried at 110 °C overnight and sieved through sieve no. 100 (150 μm) to remove any foreign materials and large ash particles. Forty grams of palm ash was activated by refluxing with 250 mL of 40 wt% H_2SO_4 at 60 °C for 4 h in a round-bottom flask. The suspension was cooled in air and filtered off and then washed several times with double-distilled water and dried in an oven at 110 °C for 2 h prior to use.

The values of Brunauer–Emmett–Teller (BET) surface area, average pore diameter and pore volume were obtained from adsorption of N_2 at 77 K using Autosorb I, supplied by Quantachrome Corporation, USA. Prior to measurements, the sample was outgases under vacuum at 200 °C for 3 h. The chemical composition of activated palm ash was determined using Rigaku RIX 3000 X-ray Fluorescence (XRF) spectrometer.

The BET specific surface area, average pore diameter and pore volume of activated palm ash were found to be 5.356 m^2/g, 2.26 nm and 0.0030 cm^3/g, respectively. The chemical composition of activated palm ash was determined using Rigaku RIX 3000 X-ray Fluorescence (XRF) spectrometer. It was found to have the composition: SiO_2 40%, K_2O 12.1%, CaO 10.0%, Al_2O_3 6.1%, MgO 6.4%, P_2O_5 8.32%, C 5.4%, others 4.38% and its ignition loss 7.3%. The high oxides contents in activated palm ash give its structure credibility as a good adsorbent.

2.2. Adsorbate: acid green 25 dye

Acid green 25 (AG25) dye was purchased from Sigma–Aldrich (M) Sdn Bhd, Malaysia and used without purification. The dye was chosen as adsorbate because it is commonly used in dye houses nowadays and is regarded as dye contaminant in the discharged effluent. The characteristics and chemical structure of the dye is listed in Table 1 and Fig. 1, respectively.

Table 1
The physical and chemical characteristic of AG25 dye

Generic name	C.I. Acid Green 25
Color index number	61570
Abbreviation	AG25
Commercial name	Acid Green 25
Molecular formula	$C_{28}H_{20}N_2Na_2O_8S_2$
Purity (%)	75
Chromophore	Anthraquinone
Molecular weight	622.59
λ_{max} (nm)	642
Appearance	Dark blue-green to black powder
Chemical name (IUPAC)	Disodium 2,2′-(9,10-dioxoanthracene-1,4-diyldiimino)bis(5-methylsulphonate)

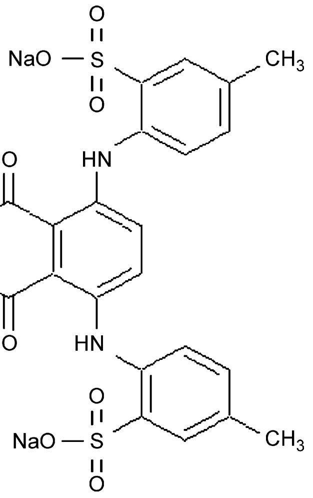

Fig. 1. Chemical structure of acid green 25 dye.

2.3. Batch equilibrium and kinetic studies

Adsorption experiments were carried out by adding a fixed amount of adsorbent (0.3 g) to a series of 250 mL conical flasks filled with 200 mL diluted solutions (50–600 mg/L). The conical flasks were then sealed and placed in a water bath shaker and shaken at 125 rpm with a required adsorbent time at 30, 40 and 50 °C and natural pH. The effect of pH was investigated at temperature 30 °C and initial concentration 200 mg/L. pH adjustments have been done using solutions of 0.1 M NaOH and 0.1 M HCl. The flasks were then removed from the shaker, and the final concentration of dye in the solution was measured at maximum wavelengths of acid green 25 (642 nm) using UV/vis spectrophotometer (Shimadzu UV/vis1601 Spectrophotometer, Japan). The amount of dye at equilibrium q_e (mg/g) on activated palm ash was calculated from the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e (mg/L) are the liquid phase concentrations of dye at initial and equilibrium, respectively, V the volume of the solution (L) and W is the mass of adsorbent used (g).

The procedure of kinetic tests was basically identical to those of equilibrium tests. The aqueous samples were taken to preset time intervals and the concentrations of dye were similarly measured. The amount of adsorption at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{2}$$

where C_0 and C_t (mg/L) are the liquid phase concentrations of dye at initial and any time t, respectively, V the volume of the solution (L) and W is the mass of adsorbent used (g).

3. Results and discussion

3.1. Effects of initial concentration and contact time

The adsorption of AG25 dye by activated palm ash increases as the initial dye concentration increased as shown in Fig. 2. It indicated that the contact time needed for AG25 solutions with initial concentrations of 50–200 mg/L to reach equilibrium was less than 10 h. For AG25 solutions with initial concentrations of 300–600 mg/L, equilibrium time of 30 h was required. However, the experimental data were measured at 48 h to make sure that full equilibrium was attained. At lower concentration, the ratio of the initial number of AG25 dye molecules to the available surface area is low and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentration the available sites of adsorption becomes fewer and hence the percentage removal of AG25 is dependent upon initial concentration. The removal of AG25 (mg/g) increased with increase in agitation time and concentration and remained nearly constant after equilibrium time. The time required to attain this state of equilibrium is termed equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operation conditions. At the beginning, the dye ions were adsorbed by the exterior surface of palm ash, the adsorption rate was fast. When the adsorption of the exterior surface reached saturation, the dye ions entered into the pores of palm ash and were adsorbed by the interior surface of the particles. This phenomenon takes relatively long contact time. These results are in agreement with the finding reported by Tsai et al. [11] for the adsorption of acid orange 51, acid blue 9, and acid orange using activated bleaching earth.

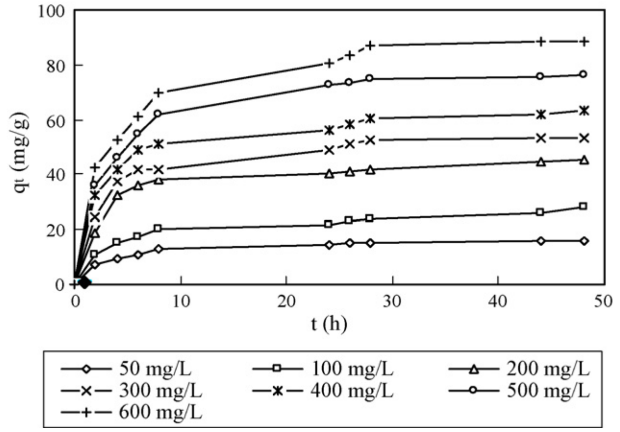

Fig. 2. The variation of adsorption capacity with adsorption time at various initial acid green 25 dye concentrations ($T = 30$ °C; adsorbent dose = 1.5 g/L; pH 7).

3.2. Effect of solution pH

The effect of solution pH was studied for adsorption of acid green 25 on activated palm ash at temperature 30 °C, constant initial concentration of 200 mg/L, amount of adsorbent (0.3 g) and 125 rpm agitation speed. The range of solution pH was adjusted between 2 and 12. Fig. 3 shows the Effect of pH on the adsorption of AG25 dye onto activated palm ash. A lower adsorption at higher pH values may be due to the abundance of OH^- ions and because of ionic repulsion between the negatively charged surface and the anionic dye molecules. There are also no more exchangeable anions on the outer surface of the

Table 2
Langmuir, Freundlich isotherm constants and separation factors (R_L) for adsorption of acid green 25 dye on activated palm ash

Temperature (°C)	Langmuir isotherm model				Freundlich isotherm model		
	q_{max} (mg/g)	K_L (L/mg)	R^2	R_L	K_F (mg/g)(L/mg)$^{1/n}$	n	R^2
30	123.4	0.50	0.95	0.25	1.25	1.71	0.98
40	156.3	0.17	0.93	0.49	1.65	1.27	0.99
50	181.8	0. 02	0.76	0.46	2.58	1.26	0.99

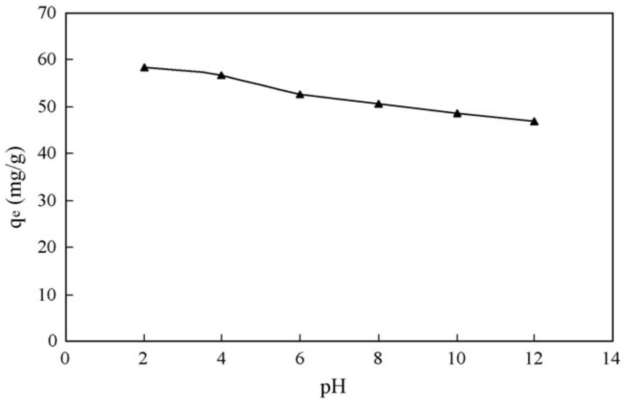

Fig. 3. Effect of solution pH on the adsorption of acid green 25 dye onto activated palm ash (C_0 = 200 mg/L; T = 30 °C; adsorbent dose = 1.5 g/L).

adsorbent at higher pH values and consequently the adsorption decreases. At lower pH, more protons will be available, thereby increasing electrostatic attractions between negatively charged dye anions and positively charged adsorption sites and causing an increase in dye adsorption. Similar results were reported for the adsorption of acid red 57 from aqueous solutions onto surfactant-modified sepiolite [12] and also adsorption of acid yellow 36 on activated carbons prepared from sawdust and rice-husk [13].

3.3. *Effect of temperature*

The adsorption studies were carried out at three different temperatures 30, 40 and 50 °C, and the results of these experiments are shown in Fig. 4. The adsorption capacity increases with the increasing temperature, indicating that the adsorption is an endothermic process (Table 2). This may be a result of increase in the mobility of the dye with increasing temperature [14]. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the activated palm ash enabling large dye to penetrate further [15]. Bouberka et al. [16] reported that the amount of yellow 4GL (acid dye) adsorbed on modified clays increases with the increasing of temperature from 30 to 50 °C. Alkan et al. [17] also reported that the adsorption capacity of sepiolite for acid blue 62 dye at 55 °C is higher than that of 25 °C. Table 2 also shows the maximum adsorption capacity of activated palm ash were determined as 123.4, 156.3 and 181.8 mg/L at 30, 40 and 50 °C, respectively.

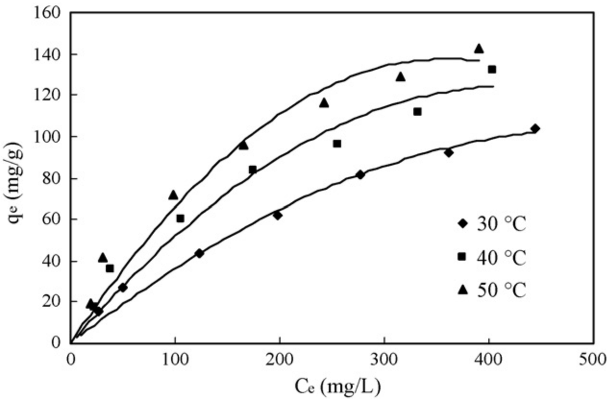

Fig. 4. Adsorption isotherms for acid green 25 dye on activated palm ash at different temperatures.

3.4. *Adsorption isotherms*

The Langmuir equation is given in the following equation [18]:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (3)$$

where q_e is the solid phase adsorbate concentration in equilibrium (mg/g), q_{max} the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g), C_e the concentration of adsorbate at equilibrium (mg/L) and K_L is the Langmuir constant (L/mg). Eq. (3) can be rearranged to a linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \qquad (4)$$

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e (Fig. 5). It was observed that the equilibrium adsorption data followed Langmuir's isotherm. Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of activated palm ash surface, i.e. each dye molecule/activated palm ash adsorption has equal adsorption activation energy and demonstrates the formation of monolayer coverage of dye molecule on the outer surface of activated palm ash. Langmuir parameters calculated from Eq. (4) are listed in Table 2.

The essential characteristics of the Langmuir equation can be expressed in term of a dimensionless separation factor, R_L, defined as [19]:

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

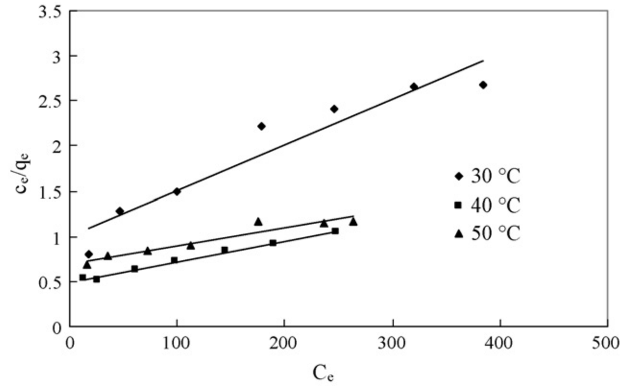

Fig. 5. Langmuir isotherm for acid green 25 dye adsorption onto activated palm ash at different temperatures.

where C_0 is the highest initial solute concentration and K_L is the Langmuir's adsorption constant (L/mg). Table 2 shows the values of R_L (0.25–0.49) were in the range of 0–1 at all temperatures studied which confirm the favorable uptake of the AG25 dye (Table 3).

The Freundlich equation is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor 1/n. Hence, the empirical equation can be written [20]:

$$q_e = K_F C_e^{1/n} \tag{6}$$

where q_e is the solid phase adsorbate concentration in equilibrium (mg/g), C_e the equilibrium liquid phase concentration (mg/L), K_F the Freundlich constant (mg/g)(L/mg)$^{1/n}$ and 1/n is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of Eq. (6):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ (Fig. 6) enables the constant K_F and exponent 1/n to be determined. The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of the monolayer. The Freundlich equation predicts that the dye concentration on the adsorbent will increase so long as there is an increased in the dye concentration in the liquid. It is clear from Table 2 that the values of the Freundlich exponents n were greater than 1 values, $n > 1$ represent favorable adsorption condition [21]. The result shows that Freundlich isotherm best-fit the equilibrium data for adsorption of AG25 dye on activated palm ash.

Table 3
The parameter R_L indicated the shape of isotherm [19]

Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

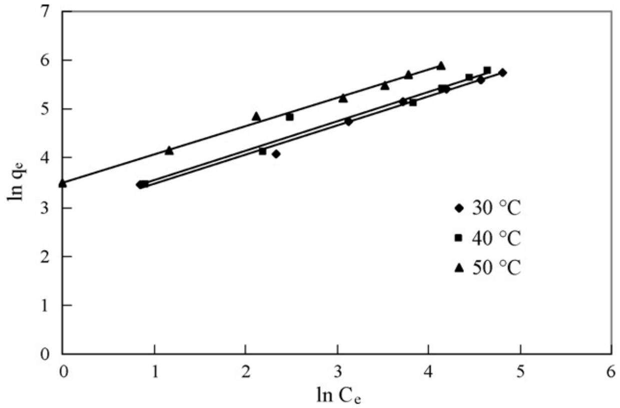

Fig. 6. Freundlich isotherm for acid green 25 dye adsorption onto activated palm ash at different temperatures.

4. Adsorption kinetics

To investigate the mechanism of AG25 dye adsorption on activated palm ash, the pseudo-first-order, pseudo-second-order and intra-particle diffusion equations were used to find out the adsorption mechanism.

4.1. Pseudo-first-order kinetic model

A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form [22]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{8}$$

where k_1 is the rate constant of pseudo-first-order adsorption and q_e represents adsorption capacity (i.e. the amount of adsorption corresponding to monolayer coverage). After definite integration by applying the initial conditions $t = 0$ to t and $q_t = 0$ to q_t, Eq. (8) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{9}$$

where q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and at any time t, k_1 is the rate constant (h^{-1}). The plot of $\log(q_e - q_t)$ versus t gives a straight line for the pseudo-first-order adsorption kinetics (Fig. 7). The values of the pseudo-first-order rate constant k_1 were obtained from the slopes of the straight lines. The k_1 values, the correlation coefficients, R^2, and the predicted and experimental q_e values are given in Table 4.

4.2. Pseudo-second-order kinetic model

The pseudo-second-order model can be represented in the following form [23]:

$$\frac{dq_t}{dt} = k_2(q_{e2} - q_t)^2 \tag{10}$$

where k_2 is the rate constant of pseudo-second-order adsorption. Integration of Eq. (10) and applying the initial conditions [23],

Table 4
Comparison of the pseudo-first-order and pseudo-second-order models for different initial acid green 25 dye concentrations at 30 °C

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model			
		$q_{e,cal}$ (mg/g)	k_1 (h^{-1})	R^2	S.D. (%)	$q_{e,cal}$ (mg/g)	k_2 (g/mg h)	R^2	S.D. (%)
50	16.13	13.41	0.049	0.93	6.88	16.63	0.023	0.99	1.26
100	27.92	27.79	0.058	0.90	2.19	29.15	0.007	0.98	1.79
200	45.11	60.25	0.068	0.89	13.71	47.6	0.003	0.99	1.25
300	58.13	65.91	0.067	0.91	5.46	58.82	0.007	0.99	0.48
400	67.92	67.71	0.062	0.90	2.12	69.93	0.002	0.97	1.21
500	81.77	83.23	0.066	0.93	0.73	81.96	0.004	0.99	0.09
600	88.46	85.19	0.054	0.95	1.51	93.45	0.004	0.99	1.21

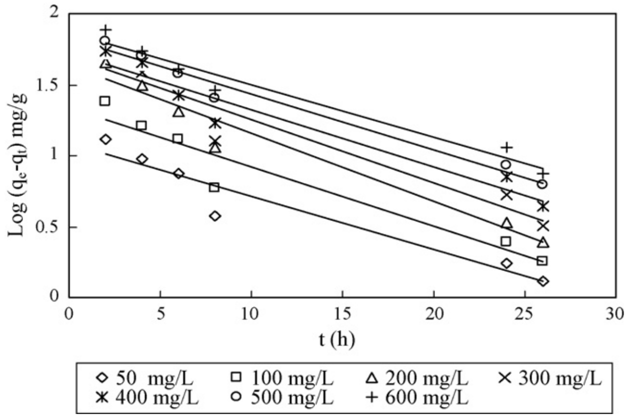

Fig. 7. Pseudo-first-order kinetics for adsorption of acid green 25 dye onto activated palm ash at 30 °C.

we have:

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

where k_2 (h g/mg) is the rate constant for the pseudo-second-order adsorption kinetics. The slopes of the plots t/q_t versus t give the value of q_e, and from the intercept k_2 can be calculated. Fig. 8 shows the pseudo-second-order plots for AG25 onto activated palm ash at 30 °C. The pseudo-second-order rate constants k_2, the calculated q_e values and the corresponding linear regression correlation coefficients values R^2 are given in Table 4. The calculated q_{e2} values agree with experimental $q_{e,exp}$ values, and also, the correlation coefficients for the pseudo-second-order kinetic plots at all the studied concentrations were higher $R^2 \geq 0.97$. Similar kinetic results have also been reported for the adsorption of acid blue 193 onto BTMA-bentonite [24].

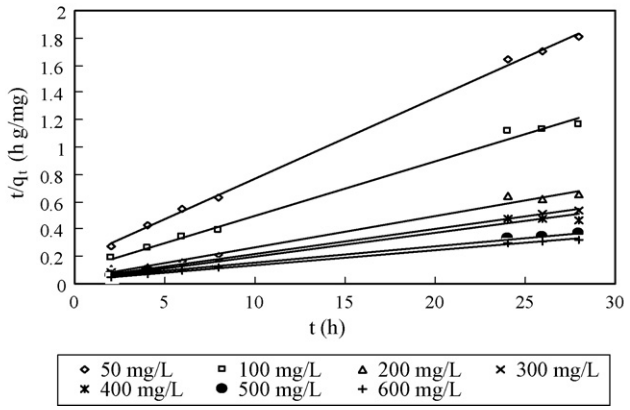

Fig. 8. Pseudo-second-order kinetics for adsorption of acid green 25 dye onto activated palm ash at 30 °C.

4.3. Intra-particle diffusion model

In adsorption systems where there is the possibility of intra-particle diffusion being the rate-limiting step, the intra-particle diffusion approach described by Weber and Morriss is used. The rate constants, for intra-particle diffusion (k_{dif}) are determined using equation given by Weber and Morriss [25]:

$$q_t = k_{dif}\sqrt{t} + c \tag{12}$$

where k_{dif} is intra-particular diffusion rate constant (mg/g $h^{1/2}$). If intra-particle diffusion is rate-limited then plots of adsorbate uptake q_t versus the square root of time ($t^{1/2}$) would result in a linear relationship and k_{dif} and C values can be obtained from these plots (Fig. 9) and (see Table 5). Fig. 9 shows two separate regions at high initial concentration. The first step in diffusion model is the mass transfer of adsorbates molecule from the bulk solution to the adsorbent surface or instantaneous stage and sec-

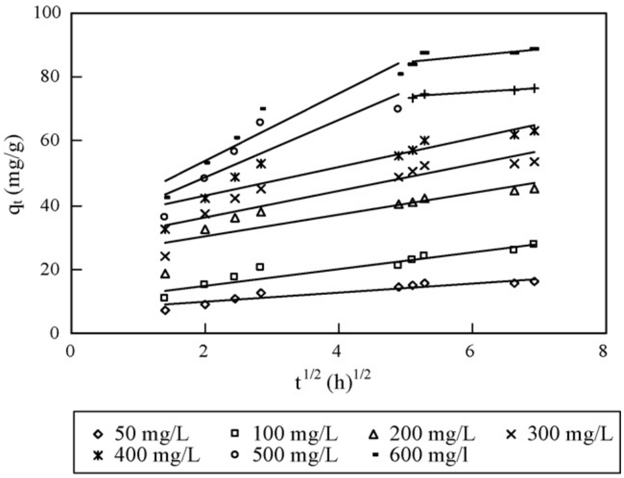

Fig. 9. Intra-particle diffusion kinetics for adsorption of acid green 25 dye on to activated palm ash at 30 °C.

Table 5
Intra-particle diffusion constants for different initial acid green 25 dye concentrations at 30 °C

C_0 (mg/L)	Intra-particle diffusion			
	k_{dif} (mg/h$^{1/2}$ g)	C	R^2	S.D. (%)
50	1.64	5.80	0.93	3.91
100	2.85	7.95	0.97	2.86
200	4.09	18.84	0.85	4.67
300	4.79	23.68	0.87	2.49
400	5.29	28.82	0.94	3.68
500	7.25	31.43	0.91	1.13
600	8.54	35.32	0.92	2.77

ond stage is the intra-particle diffusion on activated palm ash. Moreover, the particle diffusion would be the rate-controlling step if the lines pass through the origin. Similar results were reported for the adsorption of basic dye onto zeolite MCM-22 [26].

4.4. Test of kinetic models

Normalized standard deviation, S.D. (%), is used to find the most applicable model that could describe the kinetic study of adsorption of AG25 dye on activated palm ash. The normalized standard deviation S.D. (%) was calculated using the following equation:

$$\text{S.D.}\,(\%) = 100 \times \left\{ \sum \frac{[(q_{\text{e,exp}} - q_{\text{e,cal}})/q_{\text{e,exp}}]^2}{N-1} \right\}^{1/2} \quad (13)$$

where n is the number of data points, $q_{t,\text{exp}}$ the experimental values and $q_{\text{e,cal}}$ is the calculated value by both models. Based on the values of S.D. (%) given in Tables 4 and 5, it is clear that pseudo-second-order equation was better in describing the adsorption kinetics of AG25 dye using activated palm ash.

5. Thermodynamic studies

The pseudo-second-order rate constant of dye adsorption is expressed as a function of temperature by the Arrhenius type relationship:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (14)$$

where E_a is the Arrhenius activation energy (kJ/mol), A the Arrhenius factor, R the gas constant (8.314 J/mol K) and T is the solution temperature. When $\ln k_2$ is plotted versus $1/T$ a straight line with slope $-E_a/R$ is obtained (Fig. 10). The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. The physisorption processes usually have energies in the range of 5–40 kJ/mol while higher activation energies (40–800 kJ/mol) suggest chemisorption [27]. The value of activation energy (33.09 kJ/mol) given in Table 6 confirm the nature of physisorption processes of AG25 onto activated palm ash. Similar result was reported for adsorption of acid red 57 and acid blue 294 onto acid-activated bentonite in which the activation energies obtained were 29.3 and 14.6 kJ/mol, respectively [28].

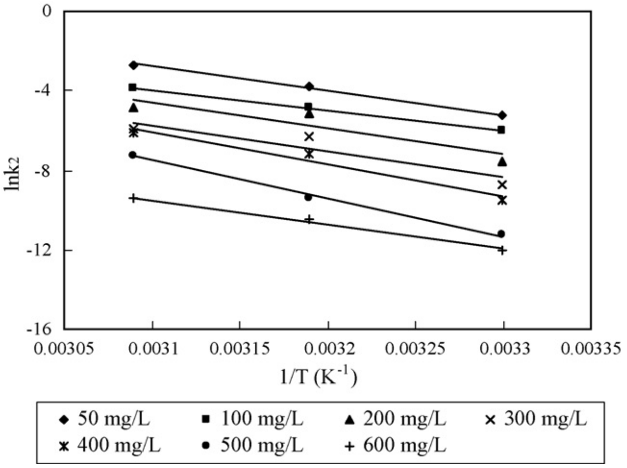

Fig. 10. Plots $\ln k_2$ vs. $1/T$ for adsorption of acid green 25 dye.

The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined by using the following equations:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\,\Delta S_{\text{ads}} \quad (16)$$

where R (8.314 J/mol K) is the gas constant, T (K) the absolute temperature and K_c (L/g) is the standard thermodynamic equilibrium constant defined by q_e/C_e. By plotting a graph of $\ln k_c$ versus $1/T$ (figure not shown) the values ΔH° and ΔS° can be estimated from the slopes and intercepts. Table 6 shows the negative values of ΔG° and positive ΔH° obtained indicated that the AG25 dye adsorption process is a spontaneous and an endothermic. The positive value of ΔS° suggests increased randomness at the solid/solution interface occur in the internal structure of the adsorption of AG25 dye onto activated palm ash. Similar result removal of acid blue 62 anionic dye by sepiolite at 25, 35, 45 and 55 °C. The results obtain that the enthalpy change (ΔH) the adsorption process of acid blue 62 on sepiolite adsorbent was endothermic [17]. Also result of adsorption of acid red 57 and acid blue 294 onto acid-activated bentonite. The positive values of E_a, and ΔH° indicate the presence of

Table 6
Thermodynamic parameters of acid green 25 dye adsorption on activated palm ash

Temperature (°C)	Thermodynamic parameters			
	ΔG° (kJ/mol)	Activation energy, E (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
30	−0.90	33.09	26.64	77.99
40	−1.59			
50	−0.05			

Table 7
Comparison of adsorption capacities of various adsorbents for acid dyes

Dyes	Adsorbents	$q_{\max}$ (mg/g)	Reference
Acid green 25	Activated palm ash	123.40	This study
Acid red 114	Egyptian bagasse pith	20.00	[29]
Acid blue 25		17.50	
Acid violet	Orange peel	19.88	[30]
Acid blue 25	Egyptian bagasse pith	14.40	[31]
Acid violet	Coir pith	7.34	[32]
Acid blue 25	Wood sawdust	5.99	[33]

an energy barrier in the adsorption process and endothermic process [28].

6. Evaluation of activated palm ash as adsorbent

Table 7 shows the comparison of the maximum monolayer adsorption capacities of various adsorbents for dyes. The value of $q_{\max}$ in this study (123.40 mg/g) is larger than those in most of previous studies. This suggests that acid green 25 could be readily adsorbed by activated palm ash used in this work. Furthermore, the agriculture waste residue, palm ash, used in this work could be easily obtained in Malaysia with low cost and simply activated for application. The high performance of activated palm ash compared to other adsorbents could be due to the chemical composition of the adsorbent mentioned in Section 2.1. The results showed that activated palm ash is effective for AG25 dye and can be used to substitute the use of commercial activated carbon.

7. Conclusions

The results of this study indicate that palm ash can be successfully used for the adsorption of acid green 25 dye from aqueous solutions. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 123.4, 156.3 and 181.8 mg/g at 30, 40, and 50 °C, respectively. The R_L values showed that palm ash was favorable for the adsorption of AG25 dye. Freundlich isotherm best-fit the equilibrium data for adsorption of AG25 dye. Three simplified kinetic models, pseudo-first-order, pseudo-second-order, and intra-particle diffusion were tested to investigate the adsorption mechanism. The pseudo-second-order kinetic model fits very well with the dynamical adsorption behavior of AG25 dye. The activation energy of adsorption can be evaluated with the pseudo-second-order rate constants. The value of E_a confirms the nature of physisorption of AG25 dye onto activated palm ash. The negative values of ΔG° and positive ΔH° obtained indicated that the AG25 dye adsorption process is a spontaneous and an endothermic.

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References

[1] D. Inthorn, S. Singhtho, P. Thiravetyan, E. Khan, Decolorization of basic, direct and reactive dyes by pre-treated narrow-leaved cattail (*Typha angustifolia* Linn.), Bioresour. Technol. 94 (2004) 299–306.

[2] K.K.H. Choy, G. McKay, J.F. Porter, Sorption of acid dyes from effluents using activated carbon, Resour. Conserv. Recycl. 27 (1999) 57–71.

[3] I.D. Mall, V.C. Srivastava, N.K. Agarwal, Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash—kinetic study and equilibrium isotherm analyses, Dyes Pigments 69 (2006) 210–223.

[4] A.A. Attia, W.E. Rashwan, S.A. Khedr, Capacity of activated carbon in the removal of acid dyes subsequent to its thermal treatment, Dyes Pigments 69 (2006) 128–136.

[5] A. Dabrowski, Adsorption—from theory to practice, Adv. Colloid Interf. Sci. 93 (2001) 135–224.

[6] S.J. Allen, G. Mckay, J.F. Porter, Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems, J. Colloid Interf. Sci. 280 (2004) 322–333.

[7] S. Chakraborty, S. De, S. DasGupta, J.K. Basu, Adsorption study for the removal of basic dye: experimental and modeling, Chemosphere 58 (2005) 1079–1086.

[8] M.N. Amiruddin, Malaysian palm oil research institute of Malaysia (PORIM), Kuala Lumpur, 1998, p. 1.

[9] A.S.M.A. Awal, M.W. Hussin, The effectiveness of palm oil fuel ash in preventing expansion due to alkali-silica reaction, Cement Concrete Compos. 19 (1997) 367–372.

[10] A.A. Ahmad, B.H. Hameed, N. Aziz, Adsorption of direct dye on palm ash: Kinetic and equilibrium modeling, J. Hazard. Mater. 141 (2007) 70–76.

[11] W.T. Tsai, C.Y. Chang, C.H. Ing, C.F. Chang, Adsorption of acid dyes from aqueous solution on activated bleaching earth, J. Colloid Interf. Sci. 275 (2004) 72–78.

[12] A. Ozcan, A.S. Ozcan, Adsorption of Acid Red 57 from aqueous solutions onto surfactant-modified sepiolite, J. Hazard. Mater. 125 (2005) 252–259.

[13] P.K. Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36, Dyes Pigments 56 (2003) 239–249.

[14] M. Alkan, M. Dogan, Adsorption kinetics of Victoria blue onto perlite, Fresen. Environ. Bull. 12 (2003) 418–425.

[15] H.M. Asfour, O.A. Fadali, M.M. Nassar, M.S. El-Geundi, Equilibrium studies on adsorption of basic dyes on hardwood, J. Chem. Technol. Biotechnol. 35 (1985) 21–27.

[16] Z. Bouberka, S. Kacha, M. Kameche, S. Elmaleh, Z. Derriche, Sorption study of an acid dye from an aqueous solution using modified clays, J. Hazard. Mater. 119 (2005) 117–124.

[17] M. Alkan, S. Çelikçapa, O. Demirbaş, M. Dogan, Removal of reactive blue 221 and acid blue 62 anionic dyes from aqueous solutions by sepiolite, Dyes Pigments 65 (2005) 251–259.

[18] I. Langmuir, Adsorption of gases on plain surfaces of glass mica platinum, J. Am. Chem. Soc. 40 (1918) 136–403.

[19] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore and solid diffusion kinetics in fixed-bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fundam. 5 (1966) 212–223.

[20] H.M.F. Freundlich, Uber die adsorption in losungen, J. Phys. Chem. 57 (1906) 385–470.

[21] C. Namasivayam, R. Jeyakumar, R.T. Yamuna, Day removal from wastewater by adsorption on 'waste' Fe(III)/Cr(III) hydroxide, Waste Manage. 14 (1994) 643–648.

[22] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe, K. Sven. Vetenskapsakad. Handl. 24 (1898) 1–39.

[23] G. McKay, Y.S. Ho, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[24] A.S. Ozcan, B. Erdem, A. Ozcan, Adsorption of Acid Blue 193 from aqueous solutions onto BTMA-bentonite, Colloids Surf. A: Physicochem. Eng. Aspect 266 (2005) 73–81.

[25] W.J. Weber, J.C. Morriss, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civil Eng. 89 (1963) 31–60.

[26] S. Wang, H. Li, L. Xu, Application of zeolite MCM-22 for basic dye removal from wastewater, J. Colloid Interf. Sci. 295 (2006) 71–78.

[27] H. Nollet, M. Roels, P. Lutgen, P. Van Der Meeren, W. Verstraete, Removal of PCBs from wastewater using fly ash, Chemosphere 53 (2003) 655–665.

[28] A.S. Ozcan, A. Ozcan, Adsorption of acid dyes from aqueous solutions onto acid-activated bentonite, J. Colloid Interf. Sci. 276 (2004) 39–46.

[29] B. Chen, C.W. Hui, G. McKay, Film-pore diffusion modeling and contact time optimization for the adsorption of dyestuffs on pith, Chem. Eng. J. 84 (2001) 77–94.

[30] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of Acid violet 17 (acid dye) from aqueous solutions, Waste Manage. 21 (2001) 105–110.

[31] Y.S. Ho, G. McKay, Sorption of dyes and copper ions onto biosorbents, Process Biochem. 38 (2003) 1047–1061.

[32] C. Namasivayam, M.D. Kumar, K. Selvi, R.A. Begum, T. Vanathi, R.T. Yamuna, ‘Waste’ coir pith—a potential biomass for the treatment of dyeing wastewaters, Biomass Bioenergy 21 (2001) 477–483.

[33] Y.S. Ho, G. McKay, Kinetic models for the sorption of dye from aqueous solution by wood, Trans. IChemE B 76 (1998) 183–191.