



Preparation of waste tea activated carbon using potassium acetate as an activating agent for adsorption of Acid Blue 25 dye

M. Auta, B.H. Hameed*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

ARTICLE INFO

Article history:

Received 6 February 2011

Received in revised form 8 April 2011

Accepted 8 April 2011

Keywords:

Waste tea

Activated carbon

Acid Blue 25

Adsorption isotherm

Kinetics

ABSTRACT

Waste tea activated carbon (WTAC) was prepared through chemical activation with a novel activating agent, potassium acetate and used for the sorption of Acid Blue 25 (AB25) dye. Batch adsorption studies were carried out with the consideration of factors such as initial dye concentration (50–350 mg/L), temperature (30, 40, 50 °C), contact time and initial pH (2–12). This was done to enable the determination of kinetics and isotherms behaviour. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherm models were tested and the adsorption of AB25 dye on WTAC was best fitted to Langmuir and the maximum monolayer of WTAC was 203.34 mg/g. Pseudo-second order kinetic model was found to adequately describe the adsorption process. The adsorbent, WTAC gave 97.88% adsorption of AB25 dye.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Dyeing technology is synonymous to man's existence and the usage of dye products is inevitable [1]. The major challenge with dyeing process is how dyes are indiscriminately released into the environment causing pollution to man and his environment due to their slow biodegradability [2–4]. The world has numbered over 100,000 commercial dyes and more than 700,000 metric tons produced annually with over 35,000–70,000 released in wastewaters [5,6]. Anionic dyes (direct, acid and reactive) are commonly used and represent 20–30% of commercial dyes; they usually have bright colours and are problematic since they have high hydrolyzing tendency and greater tinctorial value [7]. Attempts have been made to proffer solution to this anomaly via biological, chemical and physical methods with some level of success but they all possess certain degree of limitations that hinders their effectiveness and usability. Adsorption processes have been tested and found reliable in tackling this menace caused by dye pollution through various methods [8,9].

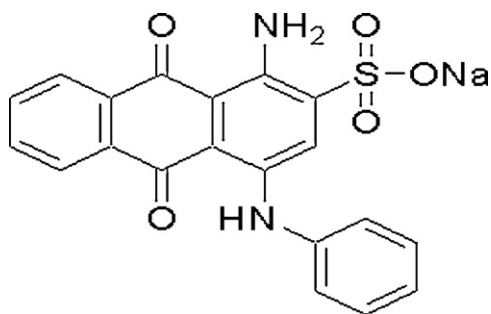
Commercial activated carbon is used mostly for adsorption processes but its expensive nature has equally motivated researchers to find substitutes [10]. Agricultural waste based activated carbon has shown very promising prospects as adsorbents for pollution control due to their natural abundance, renewability, cost effectiveness and eco-friendly [11–13]. Biomass material such as wood, coconut husk, coconut shell, rice husk, corncobs, bamboo, saw dust,

and so on are some of such substitutes that have been tested in this regard. The activated carbon obtained depends on the type of biomass or starting material and the preparation method [14,15].

Physical and chemical methods of activation are generally used for adsorbents preparation [16]. Carbonization in an inert atmosphere and subsequent activation of the carbonized carbon (char) in the presence of steam, air, and CO₂ is termed physical activation while, chemical activation involves treating the carbon materials with chemicals which are either in liquid or solid form before application of heat at inert atmospheres. All of these processes are aimed at developing the pores and increasing the surface area of the carbonaceous material thereby making it a better adsorbent. A number of chemicals have been used for activation, some of which includes: potassium hydroxide [17,18], sodium hydroxide [19,20], zinc chloride [14,21], phosphoric acid [22], potassium carbonate [18,23,24], sulphuric acid [13,19], hydrochloric acid [14], hydrogen peroxide [25], manganese oxide [26] and so on. The choice of chemical for activation determines the type of treatment method to be used with consideration to the nature of the precursor. Potassium hydroxide has proven to be a good activating agent going by its ability to develop large pore sizes and surface areas of biomass [20,27]. This therefore calls for more research to explore how best it can be used and in which form it can be impregnated into the precursors for activation.

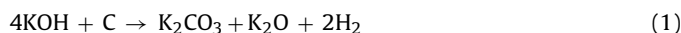
Potassium acetate is one of the compounds of potassium which when dissolved in water ionizes to provide potassium and acetate ions. Pure water ionizes depending on its temperature into equal amount of H₃O⁺ and OH⁻, so that their molarities are equal. At optimum conditions, the attraction of opposite charges (ions) in solution of both potassium acetate and water gives rise to forma-

* Corresponding author. Tel.: +60 45996422; fax: +60 45941013.
E-mail address: chbassim@eng.usm.my (B.H. Hameed).



Scheme 1. Chemical structure of Acid Blue 25.

tion of new compounds of which KOH is feasible because of metal ion hydrolysis [18]. Potassium hydroxide formed, now undergoes reaction with carbon material as follows [27]:



The intrinsic reaction is thus:



The reaction mechanism revealed that carbon materials are consumed at three stages ((3), (7) and (8)) and this consumption leads to subsequent development of pores [23,24].

This research is aimed at harnessing the potentials in waste-tea, which is usually discarded after usage in cafes and restaurants. Tea has been tagged the most popular drink in the world with its production slated for 3.15 million tonnes annually in 2003, and its waste or spent form has also been confirmed to be good adsorbent of pollutants [28]. In Malaysia and many part of the world, tea is one of the staple drinks or beverages consumed in the society. Therefore, a waste generated after the tea has served its purpose becomes a menace to the seller rather than a commodity. Evacuating this waste material for this study was like removing a plank from the eyes of the seller.

Although many researches have been carried out on development of activated carbon using different activating agents for adsorption processes, to the best of our knowledge, there has been none reported concerning usage of potassium acetate as an activating agent on any precursor and for the production of activated carbon from waste tea; and its usage for adsorption of acid blue 25 dye (AB25). Thus, this research introduces a new activating agent, potassium acetate that was used to develop activated carbon from waste tea (WTAC) for the adsorption of AB25 dye.

2. Materials and methods

2.1. Materials

The potassium acetate and AB25 used were supplied by Aldrich and Sigma Chemical, Malaysia and were used without any further purification. Acid Blue dye has an empirical formula of $\text{C}_{20}\text{H}_{13}\text{N}_2\text{NaO}_5\text{S}$, molecular weight of 416.38 g/mol, chemical index (CI) of 62055 and its chemical structure is shown in Scheme 1.

Waste tea was obtained from Universiti Sains Malaysia, Engineering Campus Cafeteria at Nibong Tebal, Malaysia, washed thoroughly with hot distilled water and dried before usage.

2.2. Preparation of activated carbon

The tea waste was dried in an oven and sieved into a size range of 125–1000 μm . The impregnation ratio of the activating agent with precursor was maintained at 2:1 g/g. The mixture was left overnight at room temperature, and dried in the oven before loading into a tube furnace embedded in a tubular reactor. The reactor was heated for 80 min at 800 °C at a heating rate of 5 °C/min under purified nitrogen (99.99%) atmosphere and 100 cm^3/min flow rate. At this operating temperature or above based on preliminary studies, the potassium metal formed intercalates with carbon material. The sample was cooled to room temperature when the activation process was completed. It was washed with distilled water to obtain a pH in the range of 6.8–7; it was oven dried at 110 °C and finally packaged in an airtight container for further use.

2.3. Characterization of activated carbon

The techniques used to characterize the WTAC, include Brunauer Emmett Teller (BET), Fourier transform infrared spectroscopy (FTIR), Boehm titration and pH point of zero charge (pHzpc).

The surface area, total pore volume and average pore diameter of the samples were determined from the adsorption isotherms of nitrogen at 77 K by using micrometrics model, ASAP 2020, 700VA, made in U.S.A. volumetric analyzer. Mesopore volume was calculated by subtracting the total volume obtained at a relative pressure of 0.99 from the micropore volume obtained from t -plot.

The FT-IR analysis was done using a Thermo Scientific; model IS10 Nicolet and a KBr model 4350 L Carver Inc., made in U.S.A. The spectra of the WTAC before and after adsorption was in a range of 3735.83–588.02 cm^{-1} .

The traditional Boehm titration method [29] which has been standardized [30] was used as a chemical method to identify oxygen surface groups on the WTAC. This is based on the principle that oxygen groups on the carbon surface have different acidities which can be neutralized by bases of different strength. One gram of WTAC was added to 50 mL of 0.05 M of these solutions: sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium bicarbonate (NaHCO_3). The samples were shaken for 24 h and then filtered to separate the WTAC from solution, and 10 mL of each filtrate was pipetted from the bulk of the samples. To each filtrate of NaOH and NaHCO_3 , 20 mL of 0.05 M HCl was added to acidify the solution while 30 mL of 0.05 M HCl was added to aliquot of Na_2CO_3 (diprotic base) to ensure complete neutralization. The samples were titrated with 0.05 M each of NaOH and HCl for the determination of acidic and basic groups. The number of acidic sites of the WTAC was calculated under the assumption that NaOH neutralizes carboxylic, lactonic and phenolic groups, while Na_2CO_3 neutralizes carboxylic and lactonic groups and NaHCO_3 neutralizes carboxylic groups.

The zero surface charge of the WTAC characteristics was done by using the solid addition method [31]. Three initial concentrations of KNO_3 (0.1, 0.01, 0.001 mol/dm^3) of 40 mL each were measured into eighteen 100 mL conical flasks with glass stoppers and 0.1 g of WTAC added. The pHs of the prepared KNO_3 solutions were adjusted between 2 and 12 with either 0.1 M of KOH or 0.1 M H_2SO_4 . The samples were shaken for 40 h at 140 rpm. At the expiration of time, when equilibrium was established between the KNO_3 solution and the WTAC, the final pH readings were noted. The final pH values were plotted against the initial pH values of the solution and at the point where plateau like feature occurred on the plot, the corresponding pH reading was noted and taken as the pHzpc of

WTAC. This method is similar to Babic et al. [32] and Cerovic et al. [33].

2.4. Batch equilibrium studies

Batch equilibrium studies were conducted at different temperatures of 30, 40 and 50 °C in a set of Erlenmeyer flasks (250 mL) with different concentrations (50–350 mg/L) of AB25. WTAC of 0.20 g was measured into each of the flasks and the initial pH of the dye solution was maintained. Thereafter, the flasks were placed in a water bath shaker at a controlled temperature with constant speed of 140 rpm. After 6 h of agitation, equilibrium condition was attained and samples were taken, filtered to determine concentration of the dye left in the solution with the aid of UV-Vis spectrophotometer (Shimadzu UV/vis 1700, Japan) at maximum wavelength, $\lambda_{\text{max}} = 602 \text{ nm}$. The amount of the dye adsorbed at time t , at equilibrium q_e (mg/g) was calculated using

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (9)$$

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

The effect of initial pH on the adsorption of the AB25 by WTAC was carried out by adjusting the pH of the solution with 0.1 M HCl and 0.1 M NaOH solutions. The study was conducted in a set of 250 mL Erlenmeyer flasks charged with 200 mg/L and 0.20 g of the dye concentration and WTAC respectively. This was run at a temperature of 30 °C for 6 h.

2.5. Batch kinetic studies

Kinetics study, which involved temperature regulation, shaking rate, initial concentration and the neutral pH of the solution, were identical to those of the equilibrium tests. The aqueous samples were taken at pre-set time intervals and their concentrations were determined.

3. Results and discussion

3.1. Characterization of the activated carbon

The Brunauer Emmett Teller analysis of WTAC gave BET surface area of 820 m²/g, Langmuir surface area of 1224 m²/g, average pore diameter of 2.458 nm and a cumulative pore volume of 0.219 cm³/g. The relatively high surface area was attributed to the intercalation of potassium metal from intermediate reaction of KOH (formed through hydrolysis of potassium metal) with carbon [34].

The FT-IR spectra for the WTAC before and after adsorption are presented in Fig. 1. The spectra of the three samples (precursor, activated carbon before adsorption and after adsorption) revealed the presence of several peaks of functional groups. They all had a long stretch bandwidth around 3500–3200 cm⁻¹ signifying presence of O–H and N–H functional groups, although located at different bandwidths. The waste tea had its O–H band width from 3448.04 cm⁻¹ and above, 3421.65–3854.07 cm⁻¹ for WTAC before adsorption and WTAC after adsorption had its O–H/N–H band width from 3853.61–3415.01 cm⁻¹. This could be attributed to pyrolysis and some chemical reactions undergone by the carbon surface material. The precursor had C=O functional group peaks located on 1734.87 and 1654.34 cm⁻¹. Some C=C, benzene groups were located on 1508.25 and 1541.29 cm⁻¹. Some inorganic carbonates compounds in plane bend of C–O were found on 1458.11 cm⁻¹, band width 1375.14 cm⁻¹ had N–O stretch, 1034.20 cm⁻¹ and 588.02 cm⁻¹ band widths had some molecules containing sulfur/oxygen bonds (S=O) and sil-

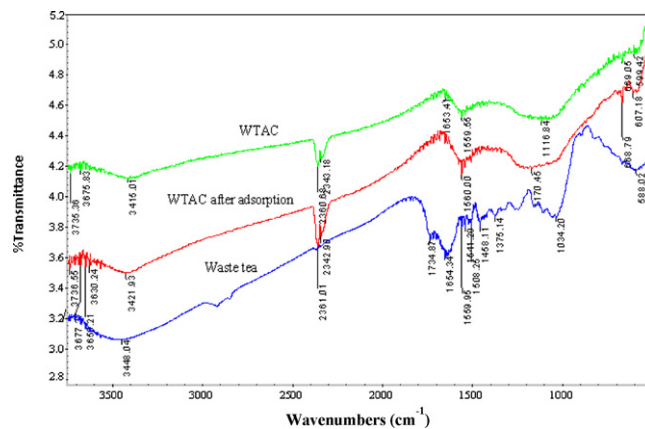


Fig. 1. FT-IR spectra for the waste tea (precursor), WTAC before and after adsorption.

Table 1

Boehm titration for determination of oxygen surface groups on WTAC.

Carboxylic	Lactonic	Phenolic	Acid	Basic	Total
0.341	0.022	1.211	1.574	2.558	4.132

ica Si–O–Si bend respectively. The WTAC before adsorption had peaks between 2360.68–2343.18 cm⁻¹ signifying C–H stretching position <3000 cm⁻¹ for saturated CH₃, CH₂ and CH, functional groups such as C=O, C–O and C=C were located between 1653.41 and 1559.95 cm⁻¹ band width and some inorganic sulfates and silica Si–O–Si asymmetric stretch were found on wave number range of 1116.84–599.42 cm⁻¹. The WTAC after adsorption had its C–H position slightly shifted to 2360.87–2343.14 cm⁻¹. Some C=O and C=C groups were found between 1685.42 and 1654.43 cm⁻¹ wave numbers, the presence of some amines and nitro functional groups were located on peak numbers 1560.01 cm⁻¹ (NH₂ scission), and 1541.30 cm⁻¹ (NO₂ asymmetric stretch), 1170.24 cm⁻¹ (saturated secondary amine C–N stretch) respectively which were attributed to the AB25 adsorbed on the WTAC. On the whole, band intensities were decreased after the adsorption of dye molecule on WTAC which support the adsorption of dye molecules on the pores of WTAC. Peaks on 1458.17 cm⁻¹, 668.77–607.57 cm⁻¹, and 458.87 cm⁻¹ signified presence of carbonates C–O, sulfates S–O bends, silica Si–O–Si bends respectively. The observed spectra showed that WTAC produced consists of several surface functional groups which contributed positively to its colour removal efficiency.

The result for experimental determination of pH_{Zpc} from various KNO₃ concentrations used (figure not shown) was 7.2 ± 1.

The result of the Boehm titration further confirmed the nature of the WTAC surface produced which enhanced the adsorption of the AB25 from the solution. The titration result is presented in Table 1.

3.2. Effect of solution pH

The solution pH is an important parameter in adsorption processes especially in the evaluation of adsorption capacity. Fig. 2 shows the effect of initial pH of solution on the adsorption of AB25 by WTAC. An investigation of the effect of pH on adsorption of the dye was carried out at pH range of 2–12 for 6 h. The climax of adsorption was attained at lowest pH 2 and the least removal was obtained at pH 12. At lower pH, more hydrogen ions (protons) were in the solution making the surface of the adsorbent more positive thereby promoting electrostatic attraction activities between the negatively charged SO₃⁻ anion of the dye and the adsorbent. More so, between pH 7 and 11, optimum adsorption occurred due to interaction of amines groups of AB25 with carboxyl groups of WTAC

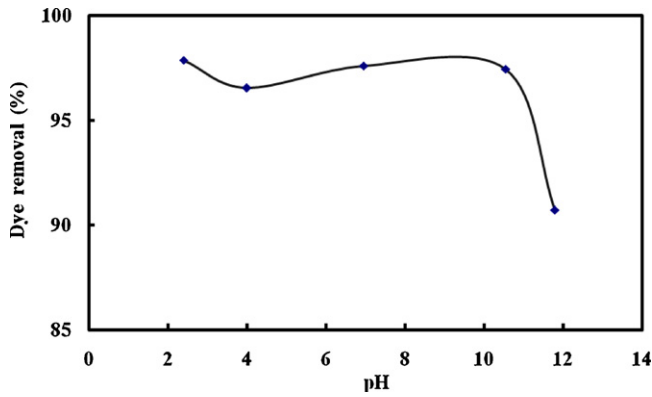


Fig. 2. Effect of pH on AB25 adsorption by WTAC ($C_0 = 100$ mg/L, $V = 200$ ml, $W = 0.20$ g, shaking speed: 140 rpm, temperature = 30 °C).

[35]. The pHzpc 7.2 result revealed that the free H^+ and OH^- in the solution couple with and $Si-O-Si$, NH_2^+ and NH^+ , and numerous $N-H/O-H$ functional groups on WTAC promoted free electrostatic attraction which lead to adsorption of the dye. At both acidic and basic mediums, a remarkable adsorption of the dye was obtained, this was due to the presence of both amino and silica groups on AB25 a characteristic behaviour of amphoteric substances.

However, beyond pH 11 (>pH 11), a slight decrease in dye uptake occurred due to numerous and keen competition between OH^- and COO^- in binding with the $-N^+$ of WTAC. Between pH 2 and 4, electrostatic repulsion of similar charges (anionic and cationic) in the solution occurred leading to reduction in adsorption; similar trend has been reported [36].

3.3. Effect of initial dye concentration

Concentration variation, which is synonymous to change in driving force in all reactions, was studied by varying the initial concentrations of the dye solution for adsorption by WTAC to a range of 50–350 mg/L. It was observed that the changes in the adsorption uptake (46–199 mg/g) was directly proportional to increase in concentration of the initial dye solution but equilibrium of adsorption was achieved faster at lower concentration than at higher concentrations. The equilibrium adsorption percentages of 50–150 mg/L was between 97.53 and 98.20% while at higher concentrations of 250 and 350 mg/L, the adsorption percentages were 82.66 and 57.72% respectively. This is because more molecules of the adsorbate were in solution competing for the available binding sites of the adsorbent at higher concentrations than at lower concentrations which further translated to higher adsorption [3,4]. Equilibrium position was achieved at lower concentrations (50–100 mg/L) in 50 min at higher temperature of 50 °C (figure not shown), while at lower temperature of 30 °C it took 120–360 min for adsorption of the dye solution to attain equilibrium. Nevertheless, the total equilibrium position was measured after 6 h in order to accommodate all concentrations involved. The effect of initial concentration on AB25 adsorption on WTAC and the equilibrium adsorption percentage removal at various concentrations, at 30 °C are shown in Figs. 3 and 4 respectively.

3.4. Effect of temperature

The effect of temperature on the equilibrium of adsorption of AB25 on WTAC was carried out at various temperatures of 30, 40 and 50 °C. The result of this effect is given in Fig. 5. Increasing the temperature of the adsorption process translated to decrease in adsorption capacity. This could be due to the fact that the process was more exothermic in nature.

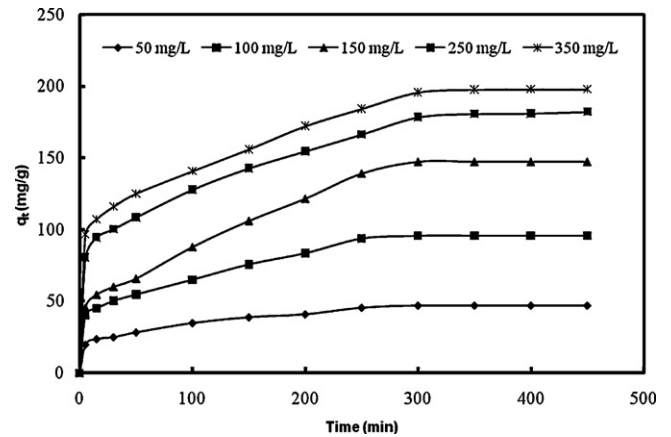


Fig. 3. Effect of initial concentration on the adsorption of AB25 on WTAC (temperature = 30 °C, rpm = 140, $V = 200$ ml, $W = 0.20$ g, pH 7).

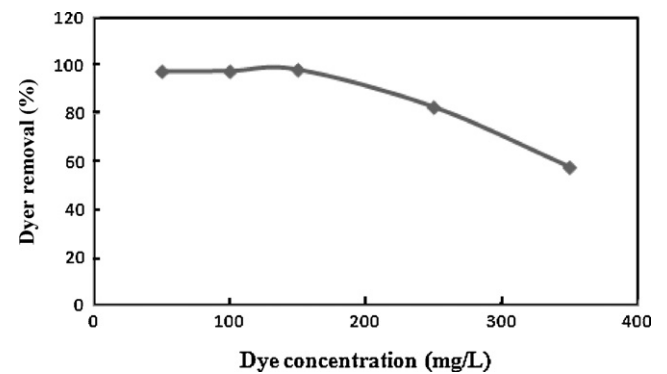


Fig. 4. Effect of initial concentration on the equilibrium adsorption removal of AB25 on WTAC (temperature = 30 °C, rpm = 140, $V = 200$ ml, $W = 0.20$ g, pH 7).

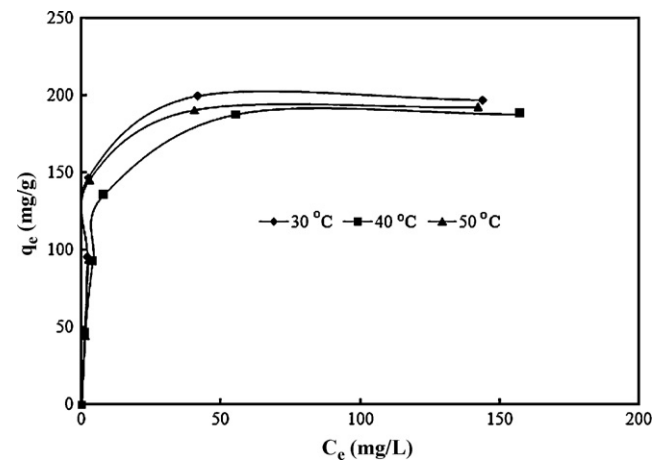


Fig. 5. Effect of temperature on the adsorption of AB25 on WTAC ($W = 0.20$ g, $V = 200$ ml, rpm 140, pH 7).

3.5. Adsorption isotherm

3.5.1. Langmuir isotherm

The non-linear form of the Langmuir isotherm model [37] is given as:

$$q_e = \frac{q_m C_e b}{(1 + b C_e)} \quad (10)$$

where C_e is the equilibrium concentration of the AB25 adsorbed mg/L, q_e is the amount of AB25 adsorbed mg/g, q_m and b (Lang-

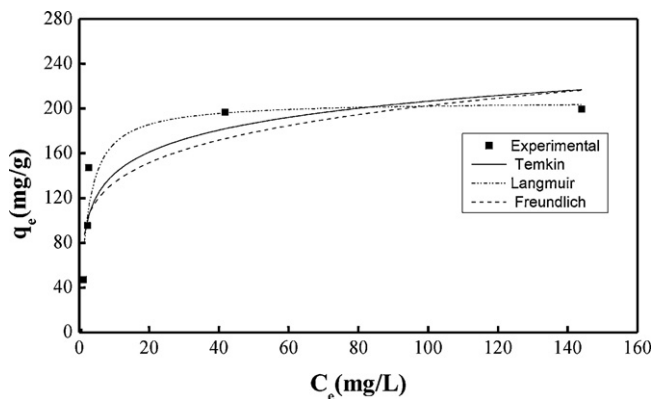


Fig. 6. Langmuir Freundlich and Temkin non-linear isotherms for adsorption of AB25 on WTAC at temperature 30 °C.

Table 2
Langmuir Freundlich, Temkin and Dubinin–Radushkevich isotherm model parameters for the adsorption of AB25 onto WTAC.

Temperature (°C)	q_m (mg/g)	b (L/mg)	R^2	
Langmuir isotherm				
30	203.34	0.422	0.999	
40	200.81	0.189	1.000	
50	180.23	0.291	0.999	
Temperature (°C)	K_F	$1/n$	R^2	
Freundlich isotherm				
30	88.26	0.180	0.786	
40	69.07	0.223	0.832	
50	84.29	0.184	0.630	
Temperature (°C)	k_T (L/mg)	B	R^2	
Temkin isotherm				
30	10.218	28.020	0.907	
40	4.880	31.018	0.894	
50	11.981	28.163	0.910	
Temperature (°C)	q_m (mol/g)	β (mol ² /J ²) 10 ⁷	E (kJ/mol)	R^2
Dubinin–Radushkevich (D–R) isotherm				
30	198	6	0.913	0.960
40	160	7	0.845	0.868
50	192	8	1.118	0.986

muir constants), the monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively.

A plot of q_e against C_e (Fig. 6) gave a fitted curve, and the Langmuir constants were generated from the plot of sorption data (Table 2). The results of essential characteristics of Langmuir isotherm expressed in dimensionless separation factor R_L , calculated for all concentrations at various temperatures investigated revealed that the entire adsorption processes were favourable since their values were in the range of $0 < R_L < 1$. The R_L equation [38] is given by:

$$R_L = \frac{1}{(1 + bC_0)} \quad (11)$$

where b is the Langmuir constant, and C_0 the highest dye concentration mg/L.

3.5.2. Freundlich isotherm

The non-linear form of the Freundlich model is given [39] as:

$$q_e = K_F C_e^{1/n} \quad (12)$$

where q_e is the amount adsorbed at equilibrium, mg/g; C_e is the equilibrium concentration of the adsorbate, mg/L; K_F and n are the

Freundlich equilibrium coefficients. The value of n gives information on favourability of adsorption process and K_F is the adsorption capacity of the adsorbate.

A plot of q_e against C_e (Fig. 6) gave poor curves indicating that the adsorption process did not follow the model. The values of the Freundlich equilibrium coefficients K_F and n were generated from the plot of sorption data. The parameter $1/n$ is a measure of adsorption intensity or surface heterogeneity with values between 0 and 1 becoming more heterogeneous as the value gets closer to zero. The graphs of the Langmuir and Freundlich isotherms and their parameters obtained are presented in Fig. 6 and Table 2 respectively.

3.5.3. Temkin isotherm

Temkin and Pyzhev [40] considered the effect of the adsorbate interaction on adsorption and proposed the model known as Temkin isotherm, which can be expressed as:

$$q_e = B \ln(k_T C_e) \quad (13)$$

where k_T is the equilibrium binding constant corresponding to the maximum binding energy, B is related to the heat of adsorption, q_e is the experimental adsorption capacity (mg/g), C_e is the concentration of the AB25 adsorbed at equilibrium position (mg/L);

$$B = \frac{RT}{b_T} \quad (14)$$

where $1/b_T$ indicates the adsorption potential of the adsorbent; R is the universal gas constant (8.314 J/kmol); and T is the temperature in Kelvin (K).

A plot of q_e against C_e at various temperatures of operation gave good curves (Fig. 6). The interaction of adsorbate proposed by Temkin leads to linear decrease in heat of adsorption of molecules layer as adsorbate coverage progresses. It also talks about the uniform distribution of binding energies to certain level, which may be dependent strongly on the density and distribution of functional groups of both the dye and the adsorbent surface.

3.5.4. Dubinin–Radushkevich (D–R) isotherm

The Dubinin–Radushkevich model [41] is used to estimate the characteristic porosity and the apparent free energy of adsorption. It helps to determine the nature of adsorption processes whether physical or chemical. The D–R sorption is more general than the Langmuir isotherm, as its derivation is not based on ideal assumptions such as equipotent of the sorption sites, absence of steric hindrances between sorbed and incoming particles and surface homogeneity on microscopic level.

The non-linear presentation of the D–R isotherm equation is as follows:

$$q_e = q_m \exp(-\beta \varepsilon^2) \quad (15)$$

where q_e is the amount of dye molecules adsorbed on per unit weight of adsorbent (mol/L), q_m is the maximum adsorption capacity mol/g; β is the activity coefficient related to adsorption mean free energy mol²/J²; and ε is the Polanyi potential given by

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (16)$$

A plot of q_e against ε^2 gave non-linear graphs (figure not shown). The adsorption mean free energy, E (kJ/mol) is given as:

$$E = \frac{1}{(2\beta)^{0.5}} \quad (17)$$

The mean free energy (E) of adsorption specifies the adsorption mechanism whether its physical or chemical. Physical adsorption process occurs if the value of $E < 8$ kJ/mol while $8 < E < 16$ kJ/mol describes chemical (ion-exchange) adsorption mechanism [41].

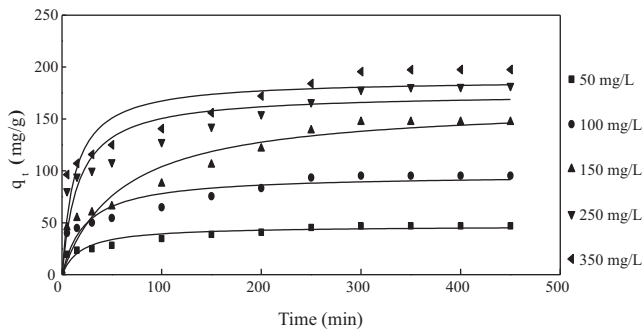


Fig. 7. Pseudo-second-order non-linear method for adsorption of AB25 on WTAC at 30 °C.

The parameters obtained for non-linear plots the Temkin and Dubinin–Radushkevich models are presented in Table 2.

The values of the parameters as presented in Table 2 clearly showed that Langmuir model described more of the adsorption process of AB25 on WTAC due to the high R^2 values; this is similar to results obtained on basic dye adsorption by oil palm fiber activated carbon [42]. According to Langmuir model, the adsorption process followed a homogeneous and monolayer mechanism and the maximum monolayer adsorption capacity was 203.34 mg/g. The more general form of Langmuir model, Dubinin–Radushkevich model, further supported the monolayer mechanism which was physical in nature as the values of mean free energy E , were less than 8 kJ/mol. Physical adsorption has also been reported for systems of Rhodamine B on scrap tires [43].

A lot of researches have been done on adsorption of acid based dyes from wastewater, comparisons of this research result with some results of similar works done in the past are tabulated in Table 3. The new activating agent potassium acetate, developed very well the surface area of the waste tea (820 m²/g) and exposed its numerous functional groups as revealed by the FTIR analysis; this gave the new adsorbent WTAC, good adsorption of AB25 that is comparable to other works on adsorption of acid dyes from other adsorbents.

3.6. Adsorption kinetic models

3.6.1. Pseudo-first-order model

The non-linear form of pseudo-first-order equation [52] is given as:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (18)$$

where q_e and q_t are the amount of AB25 adsorbed (mg/g) at equilibrium and at time t (h) respectively; k_1 is the rate constant of adsorption (h^{-1}). Plots of q_t against t , at various temperatures studied were plotted (figure not shown) and their parameters generated are presented in Table 4.

3.6.2. Pseudo-second-order model

The pseudo-second-order adsorption model [53] can be calculated using the equation:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (19)$$

where k_2 (g/mgh) is the rate constant of second order adsorption. Plots of q_t versus t at various temperatures studied gave very good curves as shown in Fig. 7. Table 4 has results of parameters generated from the plots of pseudo-second-order kinetic model for the adsorption of AB25 on WTAC.

The results of the two kinetic models tested showed that both pseudo-second and pseudo-first-order models described well the

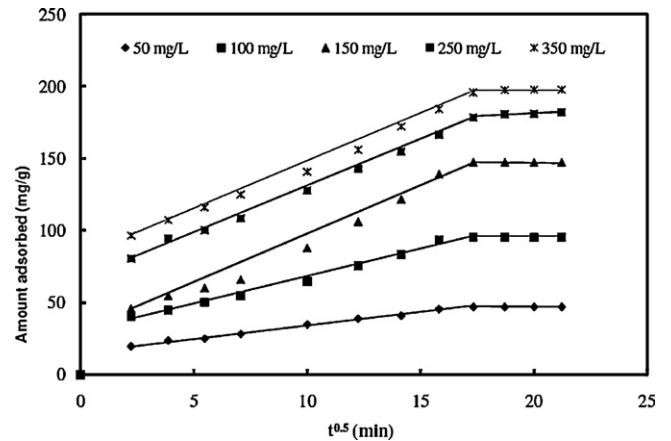


Fig. 8. Intra-particle diffusion plots under different initial AB25 concentrations (temperature = 30 °C, rpm = 140, V = 200 ml, W = 0.20 g, pH 7).

adsorption process but, pseudo-second-order model gave the best adsorption of AB25 on WTAC as can be seen from the small value of the model's rate adsorption constant when compared with the adsorption constant values for first order. Similarly, the calculated adsorption capacity values for second-order model were equally closer to the experimental adsorption capacity values than those of the pseudo-first-order adsorption capacity. Going by the values of correlation coefficient R^2 , for the two models, it might have been difficult to conclude and select the best model for the adsorption process since the values were higher interchangeably from one model to the other; couple with the fact that results of correlation coefficient is not a sufficient criteria for selection of an adsorption kinetic model [54]. However, the correlation coefficient R^2 values were more tending towards unity for the pseudo-second-order model than for first order model; and the calculation of pseudo-first-order model parameters gave higher values of standard errors SE, than those of second-order model which further showed non-preference for first order model fit for description of the adsorption process.

3.6.3. Intra-particle diffusion model

Adsorption mechanism of the adsorption of AB25 on WTAC was investigated. This was done by testing the possibility of intra-particle diffusion as rate limiting step using intra-particle diffusion model, which can be represented by an equation [55] as:

$$q_t = k_{ip} t^{0.5} + C \quad (20)$$

where k_{ip} (mg/g min^{1/2}) is the intra-particle diffusion rate constant and C gives idea on the boundary thickness. A plot of q_t against $t^{0.5}$ at various initial AB25 concentrations gave two phases of linear plots. The steep sides of the plots indicated boundary layer diffusion and intra-particle diffusion of AB25 molecules was represented by the most linear portion. Adsorption of the dye was more gradual when intra-particle diffusion was the rate controlling step. The values of the slope obtained from the boundary layer diffusion plots represented by k_{ib} , were much higher than k_{ip} , intra-particle diffusion plots (table not shown). This indicated that intra-particle diffusion greatly controlled the adsorption rate; although boundary layer diffusion or initial external mass transfer also contributed since the slope will be linear but will not pass through the origin [56]. The intra-particle diffusion plot is shown in Fig. 8.

3.7. Thermodynamics of adsorption

In a typical adsorption study, a very important decision has to be made on whether the reaction is spontaneous or not; with the

Table 3
Comparison of monolayer adsorption of Acid dyes onto various adsorbents.

Adsorbents	Dyes	Maximum monolayer adsorption capacities (mg/g)	Reference
WTAC	Acid blue 25	203.34	This work
Soy meal hull	Acid blue 92	114.94	[44]
Soy meal hull	Acid red 14	109.89	[44]
Baggase pith	Acid blue 25	17.5 ± 0.5	[45]
Baggase pith	Acid red 114	20.0 ± 0.5	[45]
Activated palm ash	Acid green 25	123.4	[46]
(HDEDMABr) modified <i>P. coccinea</i>	Acid red 44	105.0	[47]
Azolla filiculoides	Acid Red 88	109.0	[48]
Azolla filiculoides	Acid Green 3	133.5	[48]
Azolla filiculoides	Acid Orange 7	109.6	[48]
Mesoporous granular pine-cone derived activated carbon	Acid Black 1	452.9	[49]
Mesoporous granular pine-cone derived activated carbon	Acid Blue 113	298.4	[49]
Sawdust carbon	Acid Yellow 36	183.8	[50]
Rice husk carbon	Acid Yellow 36	86.90	[50]
PEI-modified <i>Penicillium chrysogenum</i> biomass	Acid orange 8	352	[51]
PEI-modified <i>Penicillium chrysogenum</i> biomass	Acid blue 45	196	[51]
Pristine <i>P. chrysogenum</i> biomass	Acid orange 8	33	[51]
Pristine <i>P. chrysogenum</i> biomass	Acid blue 45	18	[51]

Table 4
Kinetic parameters of pseudo-first and pseudo-second order models for the adsorption of AB25 on WTAC at 30 °C.

Dye conc. (mg/L)	q_e , exp (mg/g)	Pseudo-first order parameters				Pseudo-second order parameters			
		k_1 (h ⁻¹)	q_e , cal	R^2	Standard error, SE	k_2 , 10 ³	q_e , cal	R^2	Standard error, SE
50	46.992	0.034	42.98	0.947	2.439	1.2	46.46	0.987	0.899
100	95.423	0.031	85.97	0.817	5.793	0.5	93.31	0.967	0.848
150	147.138	0.011	144.61	0.776	11.868	0.1	168.85	0.890	0.885
250	196.608	0.041	158.42	0.878	10.279	0.4	169.32	0.960	0.848
350	199.326	0.046	174.09	0.943	11.960	0.4	186.08	0.981	0.827

Table 5
Thermodynamic parameters at various temperatures studied.

Gibbs free energy ΔG (kJ/mol)			Enthalpy ΔH (kJ/mol)	Entropy ΔS (J/Kmol)
30 °C	40 °C	50 °C		
26.72	26.97	27.68	5.7699	10.3459

aid of thermodynamic parameters such as change in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS), the thermodynamic behaviour of the adsorption reaction towards spontaneity can be evaluated. The parameters were calculated using the equation:

$$\Delta G = -RT \ln K_0 \quad (21)$$

where R is the universal gas constant (8.314 J/Kmol); T is the absolute temperature (K); K_0 is the distribution coefficient.

The thermodynamic parameters such as change in Gibbs free energy ΔG , entropy ΔS and enthalpy ΔH ; were evaluated using Van't Hoff equation which is given as:

$$\ln K_0 = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (22)$$

A plot of $\ln K_0$ against $1/T$ gives a graph (figure not shown) where we can obtain ΔS from the intercept and ΔH from the slope.

The thermodynamic parameters obtained at various temperatures investigated for 50 mg/L dye concentration are presented in Table 5. The negative values obtained for change of Gibbs free energy (ΔG), showed that the adsorption of AB25 on WTAC was spontaneous in nature. This was further confirmed by the negative values of enthalpy (ΔH) obtained at all temperatures signifying the adsorption process was exothermic, physical in nature and involves weak forces. Also, it is spontaneous depicting the general pattern of exothermic reactions. Similar results were reported for adsorption of Reactive blue 19 and some reactive dyes (RY-145, RR-194 and RB-B) on modified bentonite and Sorel's cement respectively [57,58].

The positive value of entropy (ΔS) at all temperatures under study revealed that excitement or randomness increased at the interface (solid–liquid) during the adsorption AB25 dye on WTAC and also showed affinity between the adsorbent and adsorbate [58,59].

4. Conclusion

This study confirmed that the new activating agent potassium acetate is good for chemical activation of carbon material and also showed that, waste tea can be utilized for production of WTAC which is a good potential adsorbent for the adsorption of AB25. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models were tested for the adsorption of AB25 onto WTAC, but Langmuir model distinctively stood out as the best model representing the adsorption process. The prepared adsorbent exhibited high adsorption capacity of 203.34 mg/g and the BET surface area was 820 m²/g. The two kinetic models tested, Lagergren and Svenska for pseudo-first-order and pseudo-second order both relatively represented well the kinetics of AB25 on WTAC but pseudo-second order model gave the best.

Acknowledgements

The authors acknowledge the financial support provided by Universiti Sains Malaysia under the Research University (RU) Scheme (Project No. 1001/PJKIMIA/814072).

References

- [1] M.A. Rauf, S.S. Ashraf, Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution, Chem. Eng. J. 151 (2009) 10–18.
- [2] C. Shen, Y. Wen, X. Kang, W. Liu, H₂O₂-induced surface modification: a facile; effective and environmentally friendly pretreatment of chitosan for dyes removal, Chem. Eng. J. 166 (2011) 474–482.

- [3] M.A. Ahmad, R. Alrozi, Optimization of preparation conditions for mangosteen peel-based activated carbons for the removal of Remazol Brilliant Blue R using response surface methodology, *Chem. Eng. J.* 165 (2010) 883–890.
- [4] P. Baskaralingam, M. Pulikesi, V. Ramamurthi, S. Sivanesan, Modified hectorites and adsorption studies of a reactive dye—technical note, *Appl. Clay Sci.* 37 (2007) 207–214.
- [5] Ö. Tunc, H. Tanaci, Z. Aksu, Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye, *J. Hazard. Mater.* 163 (2009) 187–198.
- [6] N. Dafale, S. Wate, S. Meshram, T. Nandy, Kinetic study approach of remazol black-B use for the development of two-stage anoxic-oxic reactor for decolorization/biodegradation of azo dyes by activated bacterial consortium, *J. Hazard. Mater.* 159 (2008) 319–328.
- [7] Y.S. Al-Degs, M.I. El-Barghouthi, A.H. El-Sheikh, G.M. Walker, Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon, *Dyes Pigment* 77 (2008) 16–23.
- [8] V.K. Konaganti, R. Kota, S. Patil, G. Madras, Adsorption of anionic dyes on chitosan grafted poly(alkyl methacrylates), *J. Chem. Eng.* 158 (2010) 393–401.
- [9] N.K. Amin, Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: adsorption equilibrium and kinetics, *J. Hazard. Mater.* 165 (2009) 52–62.
- [10] S.W. Won, H. Kim, S. Choi, B. Chung, K. Kim, Y. Yun, Performance, kinetics and equilibrium in biosorption of anionic dye Reactive Black 5 by the waste biomass of *Corynebacterium glutamicum* as a low-cost biosorbent, *Chem. Eng. J.* 121 (2006) 37–43.
- [11] F. Batzias, D. Sidiras, E. Schroederb, C. Weber, Simulation of dye adsorption on hydrolyzed wheat straw in batch and fixed-bed systems, *Chem. Eng. J.* 148 (2009) 459–472.
- [12] M. Ahmedna, W.E. Marshall, R.M. Rao, Production of granular activated carbons from selected agricultural by-products and evaluation of their physical, chemical and adsorption properties, *Bioresour. Technol.* 71 (2000) 113–123.
- [13] C. Duran, D. Ozdes, A. Gundogdu, M. Imamoglu, H.B. Senturk, Tea-industry waste activated carbon, as a novel adsorbent, for separation, preconcentration and speciation of chromium, *Anal. Chim. Acta* 688 (2011) 75–83.
- [14] H. Dolas, O. Sahin, C. Saka, H. Demir, A new method on producing high surface area activated carbon: the effect of salt on the surface area and the pore size distribution of activated carbon prepared from pistachio shell, *Chem. Eng. J.* 166 (2011) 191–197.
- [15] D. Prahas, Y. Kartika, N. Indraswati, S. Ismadji, Activated carbon from jackfruit peel waste by H_3PO_4 chemical activation: pore structure and surface chemistry characterization, *Chem. Eng. J.* 140 (2008) 32–42.
- [16] E.N. El Qada, S.J. Allen, G.M. Walker, Adsorption of basic dyes from aqueous solution onto activated carbons, *Chem. Eng. J.* 135 (2008) 174–184.
- [17] R. Tseng, S. Tseng, Pore structure and adsorption performance of the KOH-activated carbons prepared from corncob, *J. Colloid Interf. Sci.* 287 (2005) 428–437.
- [18] H. Deng, G. Li, H. Yang, J. Tang, J. Tang, Preparation of activated carbons from cotton stalk by microwave assisted KOH and K_2CO_3 activation, *Chem. Eng. J.* 163 (2010) 373–381.
- [19] Z. Aksu, A.B. Akın, Comparison of Remazol Black B biosorptive properties of live and treated activated sludge, *Chem. Eng. J.* 165 (2010) 184–193.
- [20] Y. Guo, S. Yang, K. Yu, J. Zhao, Z. Wang, H. Xu, The preparation and mechanism studies of rice husk based porous carbon, *Mater. Chem. Phys.* 74 (2002) 320–323.
- [21] K. Mohanty, D. Das, M.N. Biswas, Adsorption of phenol from aqueous solutions using activated carbons prepared from *Tectona grandis* sawdust by $ZnCl_2$ activation, *Chem. Eng. J.* 115 (2005) 121–131.
- [22] E. Yagmur, M. Ozmak, Z. Aktas, A novel method for production of activated carbon from waste tea by chemical activation with microwave energy, *Fuel* 87 (2008) 3278–3285.
- [23] D. Adinata, W.M.A. Wan Daud, M.K. Aroua, Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3 , *Bioresour. J.* 98 (2007) 145–149.
- [24] J. Hayashi, T. Horikawa, I. Takeda, K. Muroyama, F.N. Ani, Preparing activated carbon from various nutshells by chemical activation with K_2CO_3 , *Carbon* 40 (2002) 2381–2386.
- [25] N. Zhao, N. Wei, J. Li, Z. Qiao, J. Cui, F. He, Surface properties of chemically modified activated carbons for adsorption rate of Cr (VI), *Chem. Eng. J.* 115 (2005) 133–138.
- [26] M. Ahmaruzzaman, S.L. Gayatri, Activated tea waste as a potential low-cost adsorbent for the removal of *p*-nitrophenol from wastewater, *J. Chem. Eng. Data* 55 (2010) 4614–4623.
- [27] B. Viswanathan, P.I. Neel, T.K. Varadarajan, Methods of activation and specific applications of carbon materials, National centre for catalysis research Chennai 600, 36 (2009) 1–160.
- [28] A. Bhatnagar, M. Sillanpää, Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review, *Chem. Eng. J.* 157 (2010) 277–296.
- [29] H.P. Boehm, Chemical identification of surface groups, *Adv. Catal.* 16 (1966) 179–274.
- [30] A.M. Oickle, S.L. Goertzen, K.R. Hopper, Y.O. Abdalla, H.A. Andreas, Standardization of the Boehm titration. Part II. Method of agitation, effect of filtering and dilute titrant, *Carbon* 48 (2010) 3313–3322.
- [31] H. Deng, L. Yang, G. Tao, J. Dai, Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation—Application in methylene blue adsorption from aqueous solution, *J. Hazard. Mater.* 166 (2009) 1514–1521.
- [32] B.M. Babic, S.K. Milonjic, M.J. Polovina, B.V. Kaludierovic, Point of zero charge and intrinsic equilibrium constants of activated carbon cloth, *Carbon* 37 (1999) 477–481.
- [33] L.S. Cerovic, S.K. Milonjic, M.B. Todorovic, M.I. Trtanj, Y.S. Pogozhev, Y. Blagoveschenskii, E.A. Levashov, Point of zero charge of different carbides, *Colloids Surf. A: Physicochem. Eng. Aspects* 297 (2007) 1–6.
- [34] G.G. Stavropoulos, A.A. Zabaniotou, Production and characterization of activated carbons from olive-seed waste residue, *Micropor. Mesopor. Mater.* 82 (2005) 79–85.
- [35] P. Baskaralingam, M. Pulikesi, V. Ramamurthi, S. Sivanesan, Equilibrium studies for the adsorption of Acid dye onto modified hectorite, *J. Hazard. Mater.* 136 (2006) 989–992.
- [36] K. Badii, F.D. Ardjani, M.A. Saberi, N.Y. Limaee, S.Z. Shifaei, Adsorption of acid blue 25 on diatomite in aqueous solutions, *Indian J. Chem. Technol.* 17 (2010) 7–16.
- [37] I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [38] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore and solid diffusion kinetics in fixed adsorption under constant pattern conditions, *Ind. Eng. Chem. Fundam.* 5 (1966) 212–223.
- [39] H.M.F. Freundlich, Over the adsorption in solution, *J. Phys. Chem.* 57 (1906) 385–470.
- [40] M.J. Temkin, V. Pyzhev, Recent modifications to Langmuir isotherms, *Acta Physicochem. USSR* 12 (1940) 217–225.
- [41] M.M. Dubinin, L.V. Radushkevich, *Proc. Acad. Sci. U.S.S.R. Phys. Chem. Sect.* 55 (1947) 331–333.
- [42] I.A.W. Tan, B.H. Hameed, A.L. Ahmad, Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon, *Chem. Eng. J.* 127 (2007) 111–119.
- [43] L. Li, S. Liu, T. Zhu, Application of activated carbon derived from scrap tires for adsorption of Rhodamine B, *J. Environ. Sci.* 22 (2010) 1273–1280.
- [44] M. Arami, N.Y. Limaee, N.M. Mahmoodi, N.S. Tabrizi, Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull, *J. Hazard. Mater.* 35 (2006) 171–179.
- [45] 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.
- [46] B.H. Hameed, A.A. Ahmad, N. Aziz, Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash, *Chem. Eng. J.* 133 (2007) 195–203.
- [47] T. Akar, S. Celik, S.T. Akar, Biosorption performance of surface modified biomass obtained from *Pyraecanthes coccinea* for the decolorization of dye-contaminated solutions, *Chem. Eng. J.* 160 (2010) 466–472.
- [48] T.V.N. Padmesh, K. Vijayaraghavan, G. Sekaran, M. Velan, Batch and column studies on biosorption of acid dyes on fresh water macro alga *Azolla filiculoides*, *J. Hazard. Mater.* 125 (2005) 121–129.
- [49] M. Hadi, M.R. Samarghandi, G. McKay, Equilibrium two-parameter isotherms of acid dyes sorption by activated carbons: study of residual errors, *Chem. Eng. J.* 160 (2010) 408–416.
- [50] 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 Pigment* 56 (2003) 239–249.
- [51] B. Low, Y. Ting, S. Deng, Surface modification of *Penicillium chrysogenum* mycelium for enhanced anionic dye removal, *Chem. Eng. J.* 141 (2008) 9–17.
- [52] S. Lagergren, B.K. Svenska, On the theory of so-called adsorption of dissolved substances, *The Royal Swedish Academy of Sciences Document, Band* 24 (1898) 1–13.
- [53] Y.S. Ho, S. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [54] S. Azizian, B. Yahyaee, Adsorption of 18-crown-6 from aqueous solution on granular activated carbon: a kinetic modeling study, *J. Colloid Interface Sci.* 299 (2006) 112–115.
- [55] W.J. Weber Jr., J.C. Morris, *J. Sanitary Eng. Div. Proceed. Am. Soc. Civil. Eng.* 89 (1963) 31–60.
- [56] A. Gil, F.C.C. Assis, S. Albeniz, S.A. Korili, Removal of dyes from wastewaters by adsorption on pillared clays, *Chem. Eng. J.* (2011), doi:10.1016/j.cej.2011.01.078.
- [57] A. Ozcan, C. Omeroglu, Y. Erdogan, A.S. Ozcan, Modification of bentonite with a cationic surfactant: an adsorption study of textile dye Reactive Blue 19, *J. Hazard. Mater.* 140 (2007) 173–179.
- [58] S.S.M. Hassan, N.S. Awwad, H.A. Aboterika, Removal of synthetic reactive dyes from textile wastewater by Sorel's cement, *J. Hazard. Mater.* 162 (2009) 994–999.
- [59] S. Hong, C. Wen, J. He, F. Gan, Y. Ho, Adsorption thermodynamics of Methylene Blue onto bentonite, *J. Hazard. Mater.* 167 (2009) 630–633.