High adsorption capacity NaOH-activated carbon for dye removal from aqueous solution

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Abstract

In this study, the surface coverage ratio (S_c/S_p) and monolayer cover adsorption amount per unit surface area (q_{mon}/S_p) were employed to investigate the adsorption isotherm equilibrium of the adsorption of dyes (AB74, BB1 and MB) on NaOH-activated carbons (FWNa2, FWNa3 and FWNa4); the adsorption rate of the Elovich equation ($1/b$) and the ratio of 1 min adsorption amount of adsorbate to the monolayer cover amount of adsorbate (q_1/q_{mon}) were employed to investigate adsorption kinetics. The q_{mon}/S_p of NaOH-activated carbons was better than that of KOH-activated carbons prepared from the same raw material (fir wood). The S_c/S_p values of the adsorption of all adsorbates on adsorbent FWNa3 in this study were found to be higher than those in related literature. Parameters $1/b$ and q_1 of the adsorption of dyes on activated carbons in this study were higher than those on KOH-activated carbons; the q_1/q_{mon} value of FWNa3 was the highest. The pore structure and the TPD measurement of the surface oxide groups were employed to explain the superior adsorption performance of FWNa3. A high surface activated carbon (FWNa3) with excellent adsorption performance on dyes with relation to adsorption isotherm equilibrium and kinetics was obtained in this study. Several adsorption data processing methods were employed to describe the adsorption performance.
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Keywords: Activated carbon; NaOH activation; Adsorption; Dyes; Surface oxide groups

1. Introduction

Many dyes are used extensively in industrial products such as fabrics, food, carpet, rubber, paper, plastic and cosmetics [1]. Most commercial dyes are chemically stable and are difficult to be removed from wastewater [2]. At present, more than 10,000 dyes have been effectively commercialized [3]. They interfere with biodegradation, retard photodegradation [4] and inhibit the reaction of oxidizing agents [5]. These coloring compounds are aesthetically displeasing. Some dyes are also toxic and carcinogenic [6]. Thus, before letting effluents run into rivers, it is necessary to remove dyes from wastewater. Processes for lowering dye concentration in wastewater include chemical oxidation, biological treatment, coagulation and flocculation, precipitation, filtration, electrodialysis and membrane processing [7,8]. However, these processes are usually expensive and cannot treat all

dyes from wastewater [7]. However, the chemical and physical properties of activated carbon are stable and can be used in the adsorption of most dyes and they can also be reactivated for reuse [7]. But, ordinary commercial activated carbon is micropore high surface area activated carbon, highly efficient for adsorbing low molecular compounds but less efficient for adsorbing large molecular compounds [9]. Producing high capacity activated carbon for adsorbing large molecular compounds (such as dyes) has become an important issue in wastewater treatment.

Activated carbon has been prepared from fir wood with NaOH activation with a BET specific area (S_p) from 380 to 2406 m^2/g, a micropore ratio (V_{micro}/V_{pore}) of 0.33–0.84 and large variations in its physical properties. In this study, these activated carbons were used to study the adsorption on dyes and 4-CP in order to investigate the adsorption performance of activated carbons of different pore structures on larger molecules (dyes) and a smaller molecule (4-CP). Isotherm equilibrium adsorption was used to determine the adsorption amount and curve. Adsorption kinetics were employed to obtain the adsorption parameters and short time adsorption amount. A comparison between the

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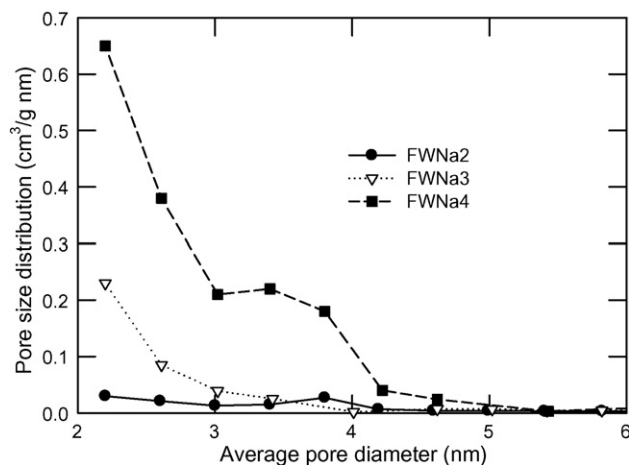*E-mail address:* trl@nuu.edu.tw (R.-L. Tseng).

Fig. 1. Pore size distribution of the activated carbons derived from fir wood by NaOH activation (carbons are FWNa2 (●), FWNa3 (▽) and FWNa4 (■), respectively).

results of this study and those of KOH-activated carbons of previous studies revealed a better adsorption performance of the NaOH-activated carbons. Comparisons of adsorption capacities in the literature and of this study revealed a superior adsorption performance of the NaOH-activated carbons. The TPD measurement of the surface oxide groups of the activated carbon was employed to determine the relationship between chemical properties and adsorption capacity and to provide activated carbon with improved performance.

2. Materials and methods

2.1. Preparation of carbon with NaOH activation

In this study, activated carbon was prepared using a two-step process [10]. Fir wood was dried at 110 °C for 24 h, placed in a sealed ceramic oven and heated at a rate of 5 °C/min from room temperature to 450 °C. At the same time, N_2 was poured into the oven at a rate of 3 dm^3/min for 1.5 h. This was the carbonization step. The char was then soaked in a concentrated NaOH solution. Then, it was oven-dried and activated. The activated products were cooled to room temperature and washed with deionized water. These samples were poured into a beaker containing 0.1 mol/dm^3 HCl (250 cm^3) and stirred for 1 h. Finally, they were washed with hot water until pH of the washing solution was ca. 6–7 [11]. From these three activated carbons with special characteristics, denoted as FWNa2, FWNa3 and FWNa4, were selected for adsorption investigation. Their pore size dis-

tribution and physical properties are listed in Fig. 1 and Table 1 for of further discussion. In Table 1, the three activated carbons have a negative zeta potential under operting conditions (pH 5.5) (Malvern, Zetasizer 3000). This negative zeta potential is usually attributed to the surface functional groups distributed on the PAC surface [12].

2.2. Temperature programmed desorption

Activated carbon was oven-dried at 130 °C overnight, weighed, and placed in a U shape reactor. The gas was introduced into the reactor at 30 cm^3/min. The thermal conductive detector (TCD) was set at 150 °C. After the instrument was stable, the temperature rising program was started; the temperature rose from room temperature to 800 °C in 50 min. An information collecting machine was used to read the data.

At lower temperatures (<550 °C) CO_2 was desorbed because of the presence of anhydrides, lactones, and carboxyl; the desorption of CO occurred at higher temperatures (above 500 °C) because of the presence of quinine, hydroxyl and carbonyl groups [13–15]. Thus, the distribution of oxygen-containing functional groups could be analyzed with the TPD results.

2.3. Procedures for adsorption experiments

Four solutes, namely acid blue 74 (AB74), basic brown 1 (BB1), methylene blue (MB) and 4-chloropenol (4-CP) all from Merck Co. were used. Molecular weights were, respectively, 466.4, 419.4, 284.3 and 128.6 g/mol. Characteristics of dye molecules used in this study as well as in previous literature are listed in Table 2 for the comparisons in Section 3. The molecular structures of MB, BB1 and AB74 are shown in Fig. 2. For the aqueous phase, AB74, BB1, MB and 4-CP were dissolved in deionized water without pH adjustment. Of the ranges studied, the initial pH was about 6.6 for 500 g/m^3 AB74, 5.6 for 500 g/m^3 BB1, 6.6 for 200 g/m^3 MB and 6.4 for 128.6 g/m^3 4-CP.

In the adsorption equilibrium experiments, an amount of the carbon (0.1 g) and 0.1 dm^3 of an aqueous phase were placed in a 0.25 dm^3 flask and stirred for 5 days in a water bath (Haake Model K-F3) at 30 °C. Preliminary tests showed that adsorption was complete after 3 days. After filtration with glass fiber, the concentrations of solutes in the aqueous phase were determined with a Hitachi UV/visible spectrophotometer (U-2001) and the maximum wavelength for each adsorbates listed in Table 2. Each experiment was repeated at least three times under identical con-

Table 1
Physical properties of carbons derived from firwoods under NaOH activation conditions

Carbon	Activation	NaOH/char weight ratio	S_p^* (m^2/g)	V_{pore} (cm^3/g)	V_{micro}/V_{pore}	D_p^{**} (nm)	Y_p (%)	Zeta potential (MV) at pH 5.5
FWNa2	NaOH	2	380	0.28	0.54	3.0	56.7	−10.5
FWNa3	NaOH	3	1672	0.94	0.84	2.3	43.6	−6.25
FWNa4	NaOH	4	2406	1.32	0.33	2.2	29.4	−10.6

S_p^*, BET surface area; D_p^{**}, average pore diameter ($4V_{pore}/S_p$).

Table 2
Characteristics of dye and 4-CP molecules

Dyes	Molecular weight	Width (nm)	Depth (nm)	Thickness (nm)	A_m[a] (nm^2)	λ_{max} (nm)
MB[b]	284.3	1.43	0.61	0.4	0.244	663.5
BB1[c]	419.3	1.71	0.98	0.3	0.294	446.0
AB74[c]	466.4	1.55	0.64	0.4	0.620	609.8
4-CP[d]	128.6				0.482	279.0

[a] A_m of MB, BV3 and BB1 calculated by the depth × thickness, AB74 and AB80 calculated by the width × thickness.
[b] Pelekani and Snoeyink [28], MB does not include associated chloride ion.
[c] Tamai et al. [29].
[d] Caturla et al. [30].

ditions. The amount of adsorption at equilibrium, q_e (g/kg), was calculated by

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

where C_0 and C_e are the initial and equilibrium liquid concentrations (g/m^3), V the volume of the solution (m^3) and W is the weight of dried carbon used (kg).

The kinetic experiments were made in a Pyrex glass vessel of 100 mm (i.d.) by 130 mm (height), fitted with four glass baffles 10 mm wide. The aqueous solution (0.6 dm^3) was agitated at 500 rpm using a Cole-Parmer Servodyne agitator with a six-blade, flat-bladed impeller (12 mm high, 40 mm wide). A stirring speed higher than 500 rpm had little effect on adsorption. An amount of the carbon (0.6 g) was added to the vessel

(A) methylene blue

MB **(M.W.=284.3)**

(B) Basic Brown 1

BB1 **(M.W.=419.3)**

(C) Acid Blue 74

AB74 **(M.W. =466.4)**

Fig. 2. Molecular structures and CI number of dyes.

and the recording was started. The vessel was also immersed in a water bath controlled at 30 °C. At preset time intervals, aqueous samples (5 cm^3) were taken and the concentrations were also analyzed. The amount of adsorption at time t, q_t (g/kg), was similarly calculated by Eq. (1), where C_t is the liquid concentration at time t (g/m^3). The reproducibility of the measurements was within 4%.

3. Results and discussion

3.1. Equilibrium adsorption

Three dyes (AB74, BB1 and MB) and 4-CP were used as adsorbates and FWNa2, FWNa3 and FWNa4, activated carbons of different pore structures and chemical properties, were used as adsorbents for the isotherm equilibrium adsorption study. The results are shown in Fig. 3a–d and will be discussed later. A Langmuir isotherm equation was used for analysis. The equation is as follows:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L q_{mon}}\right) + \left(\frac{1}{q_{mon}}\right) C_e \quad (2)$$

where q_{mon} is the amount of adsorption (in g/kg) corresponding to complete monolayer coverage and K_L is the Langmuir constant. If C_e/q_e is on the Y-axis and C_e is on the X-axis, the slope ($1/q_{mon}$) and intercept ($1/K_L q_{mon}$) can be obtained from the least number of squares and correlation coefficient (r^2) and the separation factor (R_L) can also be obtained from the data. Table 3 lists the q_{mon}, K_L, r^2 and R_L values. The r^2 is between 0.990 and 1.000, implying a good equation fitting. Calculation values of curves in Fig. 3 were obtained from calculating the Langmuir parameters as listed in Table 3 revealing good agreement between calculated and experimental values.

Fig. 3a shows that the adsorption amount of AB74 increased with an increased specific surface area (S_p) value, q_{mon} values being, respectively, 73.5, 777 and 912 g/kg as shown in Table 3. Table 4 gives the adsorption of dyes from both earlier literature and this work. Both the S_p and q_{mon} values of FWNa4 in this study are the highest as shown in Table 4. It is interesting that the S_p value of FWNa3 is the sixth highest and the q_{mon} value the second highest.

The adsorption amounts on BB1 in Fig. 3b also increased with an increased S_p value. Table 5 lists the adsorption of basic dyes on activated carbons from earlier literature. As shown in Table 5, the q_{mon} values of FWNa4 and FWNa3 were, respec-
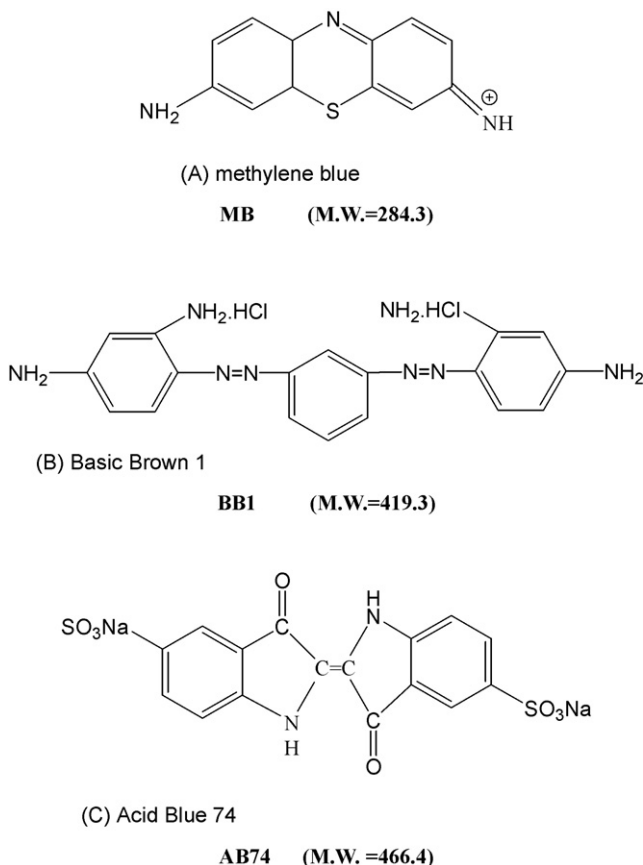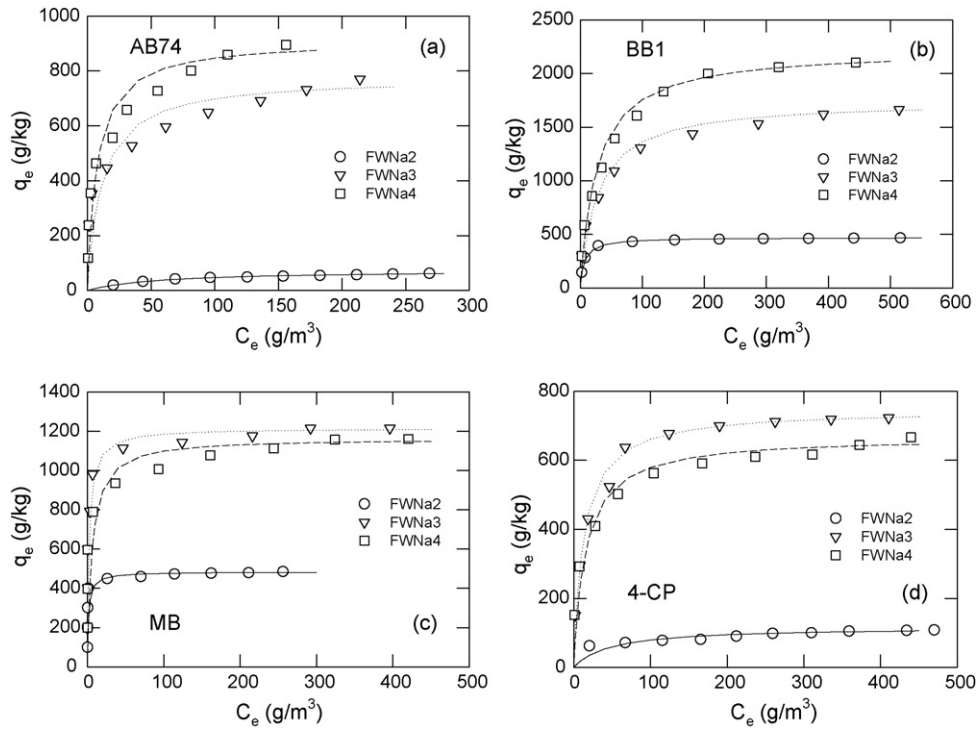
Fig. 3. Adsorption isotherms of: (a) AB74, (b) BB1, (c) MB and (d) 4-CP at 30 °C on the carbons of FWNa2 ($\bigcirc$), FWNa3 ($\triangledown$) and FWNa4 ($\square$), respectively. The curves were calculated with the Langmuir equation.

Table 3
Parameters of the Langmuir equation and capacities for the adsorption of dyes and 4-CP at 30 °C

Solute		Adsorbent		Langmuir			
	C^*_{max} (g/m^3)		W/V (kg/m^3)	q_{mon} (g/kg)	K_L (m^3/g)	r^2	R_L
AB74	300	FWNa2	0.5	73.5	0.018	0.996	0.085
	600	FWNa3	0.5	777	0.088	0.992	0.019
	600	FWNa4	0.5	912	0.131	0.993	0.013
BB1	750	FWNa2	0.5	472	0.148	1.000	0.005
	1500	FWNa3	0.5	1744	0.036	0.999	0.018
	1500	FWNa4	0.5	2226	0.038	0.998	0.017
MB	500	FWNa2	0.5	484	0.625	1.000	0.0016
	1000	FWNa3	0.5	1215	0.398	1.000	0.0025
	1000	FWNa4	0.5	1165	0.166	0.999	0.0060
4-CP	514	FWNa2	0.5	117	0.021	0.990	0.058
	771	FWNa3	0.5	732	0.077	1.000	0.017
	771	FWNa4	0.5	668	0.065	0.997	0.020

C^*_{max}, Maximum initiation concentration of adsorption system (g/m^3).

Table 4
Data of the parameters of the Langmuir equation and capacities of the adsorption of acid dyes

Adsorbate	Adsorbent	S_p (m^2/g)	q_{mon} (g/kg)	q_{mon}/S_p (mg/m^2)	S_c (m^2/g)	S_c/S_p	Reference
AB74	FWNa4	2406	912	0.38	730	0.30	This work
AB74	FWKC1030	2240	359	0.16	279	0.12	[21]
AB74	A-20	1990	513	0.26	411	0.21	[9]
AB74	FWKC1015	1718	294	0.17	228	0.13	[21]
AB74	3.0(KOH/char)	1687	460	0.27	368	0.22	[22]
AB74	FWNa3	1672	777	0.46	622	0.37	This work
AB80	CC-15	1433	384	0.27	225	0.16	[7]
AB74	C_u	683	230	0.34	184	0.27	[31]

Table 5
Data of the parameters of the Langmuir equation and capacities of the adsorption of basic dyes

Adsorbate	Adsorbent	S_p (m^2/g)	q_{mon} (g/kg)	q_{mon}/S_p (mg/m^2)	S_c (m^2/g)	S_c/S_p	Reference
BB1	Cob4030	2844	1669	0.59	705	0.25	[23]
BB1	FWNa4	2406	2226	0.93	940	0.39	This work
BB1	FWKC1030	2240	1476	0.66	623	0.28	[21]
BB1	A-20	1990	461	0.23	195	0.10	[9]
BV3	A-20	1990	818	0.41	593	0.30	[9]
BB1	FWKC1015	1718	1174	0.68	496	0.29	[21]
BB1	3.0(KOH/char)	1687	1058	0.63	447	0.26	[22]
BB1	FWNa3	1672	1744	1.04	737	0.44	This work
BB1	Cob1030	1625	1208	0.74	510	0.31	[23]

Table 6
Data of the parameters of the Langmuir equation and capacities of the adsorption of MB

Adsorbent	S_p (m^2/g)	q_{mon} (g/kg)	q_{mon}/S_p (mg/m^2)	S_c (m^2/g)	S_c/S_p	Reference
Cob4030	2844	847	0.30	438	0.15	[23]
FWNa4	2406	1165	0.48	602	0.25	This work
FWKC1030	2240	580	0.26	300	0.13	[21]
CZ8	2191	426	0.19	220	0.10	[32]
FWKC1015	1718	458	0.27	237	0.14	[21]
3.0(KOH/char)	1687	772	0.46	399	0.24	[22]
FWNa3	1672	1215	0.73	628	0.38	This work
Cob1030	1625	421	0.26	218	0.13	[23]
Apricot stones	1175	285	0.24	147	0.13	[33]
t_A-7	1131	590	0.52	305	0.27	[34]
Pistachio(KOH)	1096	522	0.48	270	0.25	[11]
PKSAC	1088	333	0.31	172	0.16	[35]
GAC F400	1069	920	0.86	476	0.45	[36]
t_A-4.0	902	556	0.62	287	0.32	[37]
OZN-50	646	224	0.35	116	0.18	[38]
AC	629	28	0.04	14	0.02	[39]

tively, 2226 and 1744 g/kg, the first and second highest; the q_{mon} value of Cob4030 was 1669 g/kg, the third highest, but its S_p was 2884 m^2/g, the highest.

As shown in Fig. 3c, the adsorption amount of MB on FWNa3 was the highest. In Table 3, the q_{mon} values of FWNa2, FWNa3 and FWNa4 are, respectively, 484, 1215 and 1165 g/kg. Table 6 lists the adsorption of MB on activated carbons from earlier literature. There are many reports on the adsorption of MB, only the highest ones were selected for comparison in Table 6. The S_p of FWNa3 working this study is the seventh highest, but its q_{mon} value is the highest.

As shown in Fig. 3d, the adsorption amount of 4-CP on FWNa3 was the highest. Table 7 gives the adsorption of chlorophenol on activated carbons from earlier literature. The q_{mon} value of Cob4030 is 863 g/kg, the highest. Those of FWNa3 and FWNa4 are, respectively, the second and fourth highest.

Table 7
Data of the parameters of the Langmuir equation and capacities of the adsorption of chlorophenol

| Adsorbent	S_p (m^2/g)	q_{mon} (g/kg)	q_{mon}/S_p (mg/m^2)	S_c (m^2/g)	S_c/S_p	Reference
Cob4030	2844	863	0.30	1968	0.61	[23]
FWNa4	2406	668	0.28	1524	0.63	This work
FWKC1030	2240	417	0.19	951	0.43	[21]
FWKC1015	1718	364	0.21	830	0.48	[21]
3.0(KOH/char)	1687	706	0.42	1610	0.95	[22]
FWNa3	1672	732	0.44	1670	1.00	This work
Cob1030	1625	436	0.27	994	0.69	[23]
AP-44	1303	120	0.09	274	0.21	[40]
NC60	1200	233	0.19	531	0.44	[41]
t_A-7	1131	441	0.39	1006	0.89	[36]
CP-10	1114	234	0.21	534	0.48	[42]
Pistachio(KOH)	1096	407	0.37	928	0.37	[11]
CF$_2$	1000	406	0.41	926	0.93	[43]
AP-10	828	206	0.25	470	0.57	[42]
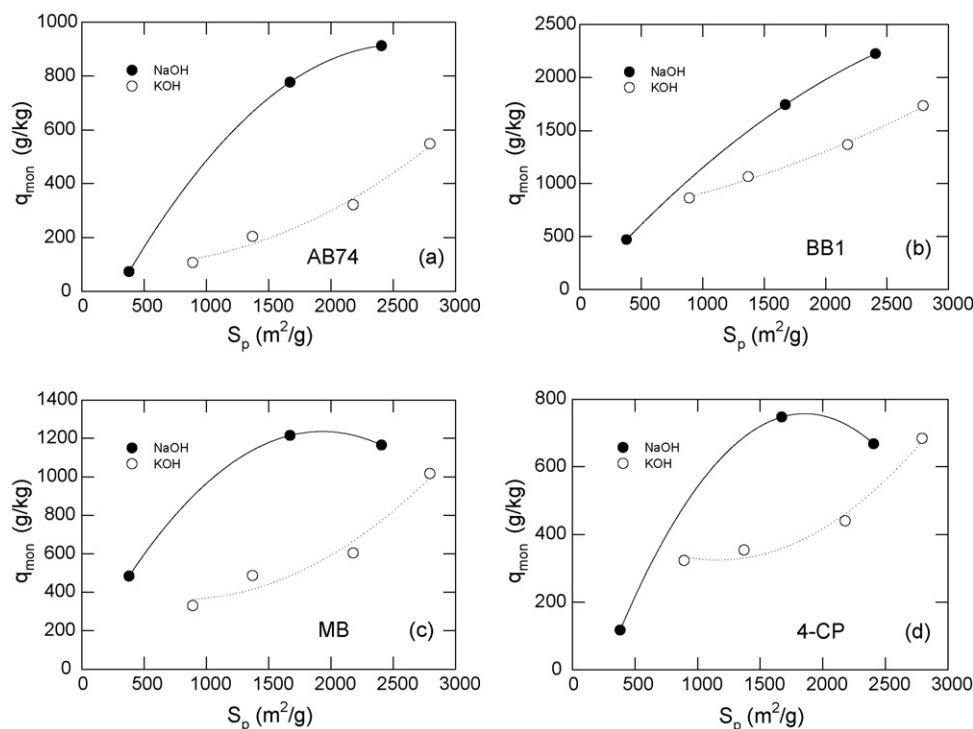
Fig. 4. Plots of q_{mon} of: (a) AB74, (b) BB1, (c) MB and (d) 4-CP at 30 °C against BET surface area of NaOH- and KOH-activated carbons.

Thus, the molecular weights of AB74 and BB1 used in this study were, respectively, 466 and 419 g/mol and the q_{mon} increased with increased S_p. The average pore size of the activated carbon studied was larger than 2.2 nm, much larger than the thickness (<0.4 nm) of dyes in Table 2. Indications were that when the ratio of pore size to molecular size was larger than 5, the solid hindrance problem of adsorption was not significant [16]. The molecular weights of MB and 4-CP were, respectively, 284 and 128.6 g/mol and the q_{mon} value of FWNa3 was the highest. Though the S_p value of FWNa4 was 1.44 times that of FWNa3, the V_{micro}/V_{pore} values of FWNa4 and FWNa3 were, respectively, 0.33 and 0.84. Furthermore, the fact that the micropores of FWNa4 were smaller was disadvantageous to the adsorption on the capillary condensation of solute in the pores [16]. Micropores are an important factor for adsorption of small molecules (benzene and toluene) [17].

Activated carbon was prepared from the same raw material (fir wood) by KOH activation [11]. Fig. 4a–d shows that the adsorption capacity of NaOH-activated carbon was higher than that of KOH-activated carbon at the same surface area. Compared with KOH-activated carbon, NaOH-activated carbon produces less pollution, is needed in lower dosages and is more economic [10]. This study has proven the advantage of higher adsorption capacity of the NaOH-activated carbon.

3.2. Surface coverage

From the above discussion, it is clear that adsorption of the dyes and 4-CP on high surface area activated carbon is not necessarily related to specific adsorption capacity. This means that other factors are also important in the adsorption of larger molecules. Following is a comparison of the surface coverage principle.

An adsorbate forms monolayer coverage on the surface of activated carbon. Based on the covered mass (q_{mon}) obtained from the Langmuir equation and the projected area of an adsorbate molecule, the adsorbate coverage per unit gram of activated carbon (S_c, m²/g) can be obtained using the following equation [18]:

$$S_c = 6.023 \times 10^{23} \times A_m \times \frac{q_{mon}}{M_w \times 1000} \qquad (3)$$

where A_m is the projected area of a molecule (defined in Table 2). In addition, the surface coverage (S_c/S_p) is defined as the ratio of S_c to BET surface area of the activated carbon. The calculated results are listed in Tables 4–7.

Tables 4–6 show surface coverage (S_c/S_p) for the adsorption of dyes (AB74, BB1 and MB). The surface coverage values of FWNa3 are higher than the highest reported in the literature. Table 7 shows that the surface coverage for the adsorption of 4-CP on FWNa3 is 1.59 times that on FWNa4. The surface coverage reported in the literature is only as high as 0.95 [18] and that on FWNa3 in this study was 1.0, meaning that the BET surface area of FWNa3 was used more sufficiently. The values of adsorption of higher molecular dyes (from 284 to 466 g/mol) on activated carbons are far less than 1, meaning that much of the BET surface area is not used.

However, not all adsorbates (dyes) in engineering practice have clear molecular structures and A_m. For convenience in practical applications, another column of mass coverage (q_{mon}/S_p) was added in Tables 4–7 of this paper for reference. In previous studies it was found that the q_{mon}/S_p values of KOH-
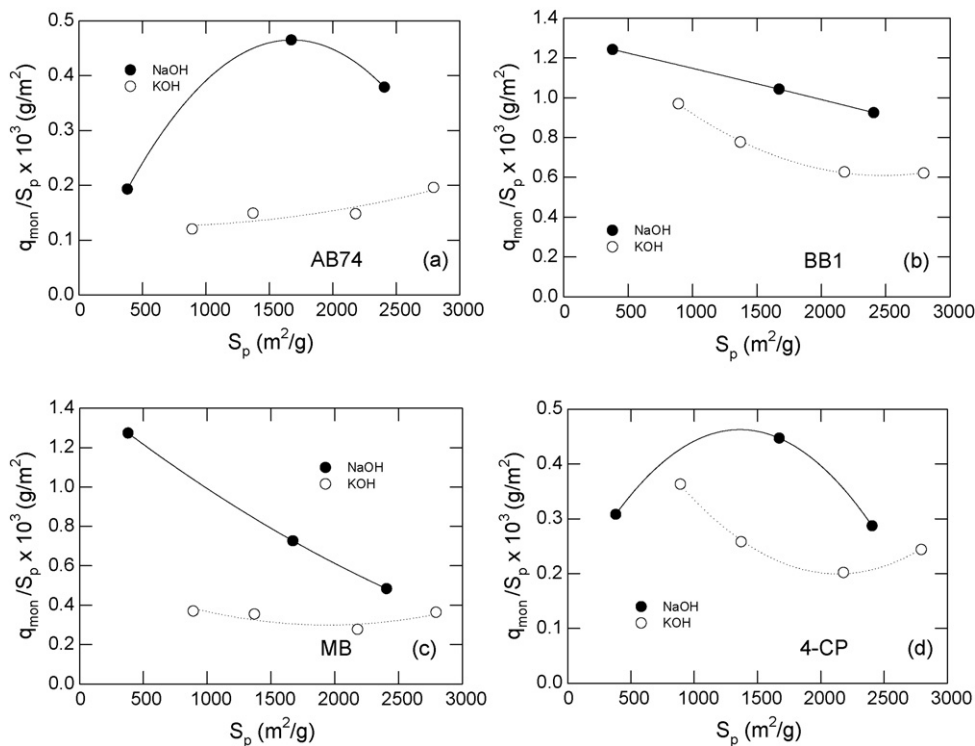
Fig. 5. Plots of q_{mon}/S_p of: (a) AB74, (b) BB1, (c) MB and (d) at 30 °C against BET surface area of NaOH- and KOH-activated carbons.

activated carbons with various chemical activation agent doses were similar [19,20]. The reason is that their pore characteristic (V_{micro}/V_{pore}) are similar, thus, their adsorption capacities per unit surface area are similar [10]. However, this is not the case with the NaOH-activated carbons in this study, because the V_{micro}/V_{pore} values of NaOH-activated carbons at various doses are from 0.33 to 0.84 a large variation. Fig. 5a–d are plots of q_{mon}/S_p against S_p for adsorption capacity comparison between NaOH- and KOH-activated carbons. As shown in Fig. 5a–d, the q_{mon}/S_p values of KOH-activated carbons were less varied while those of NaOH-activated carbons were highly varied. Overall, the NaOH-activated carbons displayed a higher adsorption capacitiy. Adsorption of AB74 and 4-CP on FWNa3 were the best as shown in Fig. 5a and d. Though the q_{mon}/S_p values of adsorption of BB1 and MB on FWNa2 were the highest, the S_p and q_{mon} value of FWNa2 were too low. Thus, FWNa3 in this study performed the best in terms of adsorption performance (S_c/S_p or q_{mon}/S_p) on high surface area activated carbon.

3.3. Separation factor

Adsorption capacity can be determined from the isotherm equilibrium adsorption data and the adsorption equipment can be designed according to the shape of the adsorption equilibrium curve. A usually dimensionless parameter, the separation factor, derived from the Langmuir adsorption equilibrium curve was used to determine the type of isotherm adsorption. Separation factor (R_L) is defined as:

$$R_L = \frac{1}{1 + (K_L C_i)} \quad (4)$$

If R_L is between 0 and 1, the adsorption process is favourable. The R_L of adsorption of AB74, BB1, MB and 4-CP on FWNa3 in this study are, respectively, 0.019, 0.018, 0.0025 and 0.017 as shown in Table 3. The lower the R_L value, the more irreversible the adsorption process [18]. In the engineering practice, it means that if FWNa3 is used in a series batch adsorption operation, only a few operation steps are needed to obtain high removal levels; or if FWNa3 is used in a column adsorption operation, sharp straight breakthrough curves will appear, meaning that the adsorbent is being used sufficiently.

3.4. Adsorption kinetics

To theoretically analyze the adsorption of dyes on activated carbon many hypotheses and complicated mathematics are needed. In practical applications there is often insufficient basic data. The Elovich equation, frequently used in gas phase adsorption, has been employed recently by researchers in aqueous solution adsorption and a good description to adsorption system with a fast rate was found [19–21]. The derivation of the Elovich equation is detailed in the literature [21–23] and described as follows:

$$q_t = \left(\frac{1}{b}\right) \ln(ab) + \left(\frac{1}{b}\right) \ln t \quad (5)$$

When $t = 1$ min, $q_t = q_1$ and

$$q_1 = \left(\frac{1}{b}\right) \ln(ab) \quad (6)$$

Table 8
The Elovich equation parameters and standard deviations of adsorption of dyes and 4-CP at 30 °C

Solute	Carbon	$1/b$ (g/kg)	q_1 (g/kg)	t_0 (10^{-3} h)	r^2	Δq (%)	C_o^* (g/m³)
AB74	FWNa2	5.32	21.2	0.31	0.993	1.3	150
	FWNa3	86.5	113.7	4.48	0.999	1.0	300
	FWNa4	99.8	113.8	5.33	0.997	1.1	300
MB	FWNa2	39.9	33.3	7.23	0.996	3.2	250
	FWNa3	105.4	260.9	1.40	0.991	2.4	500
	FWNa4	125.3	299.1	1.53	0.993	2.1	500
4-CP	FWNa2	15.7	71.4	0.18	0.992	1.3	257
	FWNa3	49.2	376	0.008	0.996	0.7	385.5
	FWNa4	37.9	369	0.001	0.997	0.5	385.5

C_o^*, Initiation concentration (g/m³).

Eq. (6) can be rewritten as

$$q_t = q_1 + \left(\frac{1}{b}\right) \ln t. \tag{7}$$

q_1 is employed for showing the adsorption capacity of activated carbon in a short time and $1/b$ for the capability of mass transfer and adsorption of adsorbate in the interior of particle pores, which is meaningful important for engineering application.

The Elovich equation was used for adsorption kinetics analysis. Results are listed in Table 8. All of the standard deviations, Δq, were less than 3.2%, which means that the Elovich equation was suitable. When Eq. (6) is employed, the basic hypothesis $t \gg t_0$ ($t_0 = 1/ab$) should be met. The values from the Elovich equation analysis are listed in Table 8, showing that the basic requirements of employing the Elovich equation were met [24].

Fig. 6a–c shows the adsorption performance of batch contact time of AB74, MB and 4-CP on the activated carbons; curves from the fitted Elovich equation were in good agreement with experimental data. Adsorption capacities of FWNa3 and FWNa4 were much higher than that of FWNa2; elevated S_p values of activated carbons in this study still maintained good mass transfer ability. Usually high surface area activated carbons are microporous making their adsorption ability on larger molecular adsorbates much lower. However, the adsorption of dyes and 4-CP on the high surface area activated carbons FWNa3 and FWNa4 was highly effective. The adsorption curves of FWNa3 and FWNa4 rose abruptly in short contact time and then gradually approached a plateau, indicating the adsorption of a large amount of adsorption sites in a short time. Activated carbons of this kind could be of use in many practical applications.

Fig. 7 shows the plots of $1/b$ of the Elovich equation versus S_p. Solid points in Fig. 7 stand for the adsorption of the NaOH-activated carbons. The $1/b$ values of two dyes increased with an increased S_p value. The $1/b$ value of the adsorption of 4-CP on FWNa3 is the highest. Empty points stand for the adsorption of KOH-activated carbons. The $1/b$ values of the adsorption of two dyes on KOH-activated carbons were less than those on the NaOH-activated carbons, revealing the better mass transfer characteristics of NaOH-activated carbons in the adsorption of dyes.

Table 9 lists the values of Elovich equation parameters for the adsorption of 4-CP and dyes on the corncob [16] and fir wood activated carbons. Value of $1/b$ and q_1 in Table 9 of the adsorption of dyes AB74 and MB on FWNa3 and FWNa4 are higher than those of CobNa30 and CobNa40 reported in the literatures, showing the superior adsorption kinetics of the activated carbons in this study.

3.5. Adsorption capacity in 1 min

Activated carbon of high surface area and high pore volume is possible because of the improved technology in activated carbon preparation. Short time contact adsorption also becomes significant. Though some reports have described it using the multilinearity intraparticle diffusion model [25–27], the time duration of each step is not the same making it difficult to compare. So far, no easy simple adsorption kinetics model can completely describe this phenomenon. This paper has tried to describe it with the adsorption value of the beginning 1 min contact time ($q_1 = (1/b) \ln(ab)$) derived from the Elovich equation. Fig. 8 shows plots of q_1 of Elovich equation versus S_p. Solid

Table 9
The Elovich equation parameters for the adsorption of 4-CP and dyes on the corncob and fir wood activated carbon

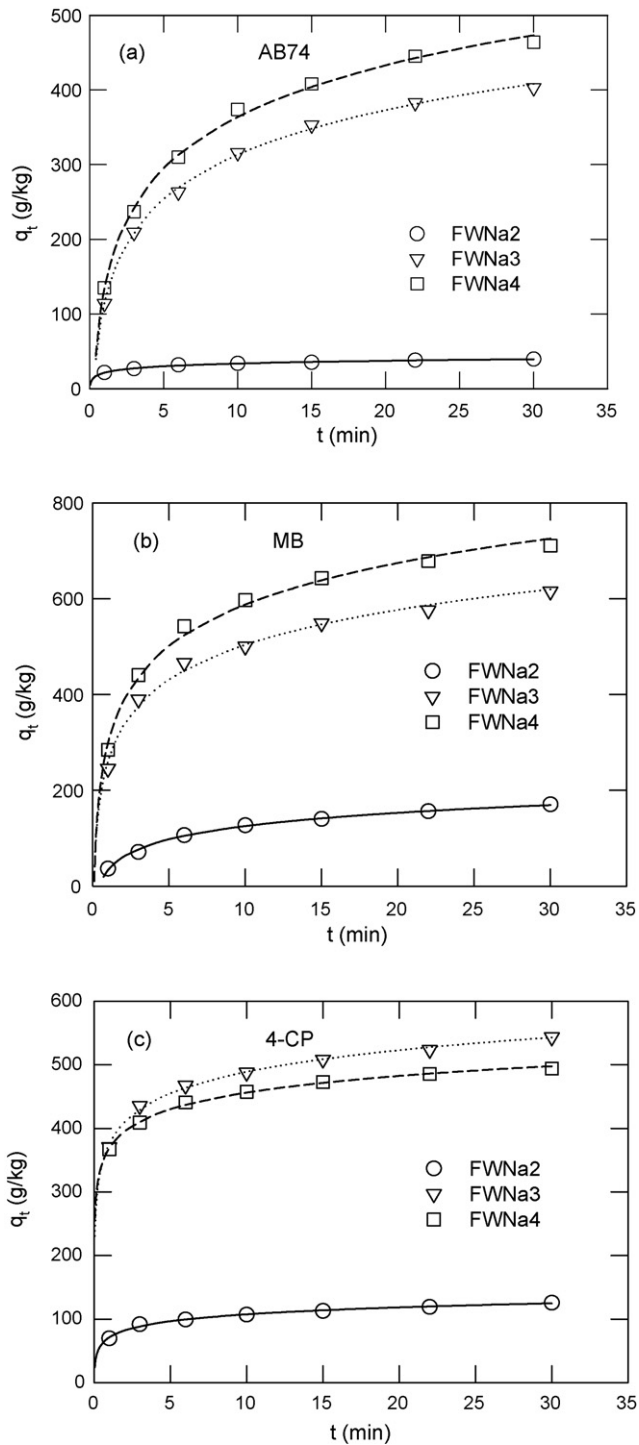| Carbon	NaOH/char	S_p (m²/g)	4-CP		AB74		MB	
			$1/b$ (g/kg)	q_1 (g/kg)	$1/b$ (g/kg)	q_1 (g/kg)	$1/b$ (g/kg)	q_1 (g/kg)
CobNa20	2	1352	97.1	138	34.5	13.1	58.9	31.0
CobNa30	3	2318	100	190	51.5	26.6	85.0	61.7
CobNa40	4	2475	98.0	218	57.8	36.4	93.3	81.9
FWNa2	2	380	15.7	71.4	5.32	21.2	39.9	33.3
FWNa3	3	1672	49.2	376	86.5	113.7	105.4	260.9
FWNa4	4	2406	37.9	369	99.8	113.8	125.3	299.1

Fig. 6. Adsorption kinetics of: (a) AB74, (b) MB and (c) 4-CP at 30 °C on carbons of FWNa2 (◯), FWNa3 (▽) and FWNa4 (☐), respectively. The curves were calculated with the Elovich equation.
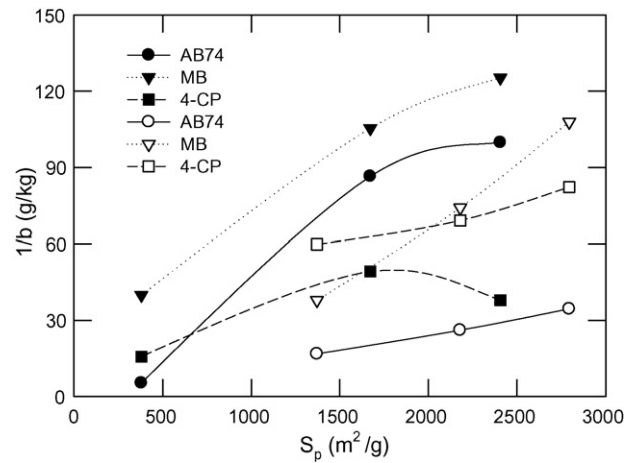

Fig. 7. Plots of $1/b$ of Elovich equation against BET surface area of NaOH-activated carbons (solid points) and KOH-activated carbons (empty points) (adsorbates are AB74 (◯, ●), MB (▽, ▼) and 4-CP (☐, ■), respectively).
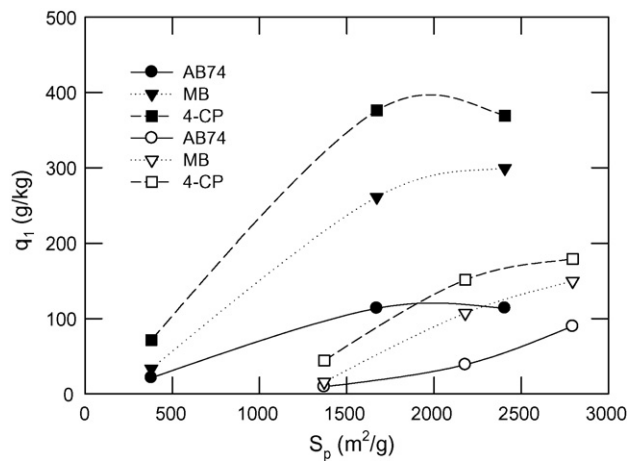

Fig. 8. Plots of q_1 of Elovich equation against BET surface area of NaOH-activated carbons (solid point) and KOH-activated carbons (empty point) (adsorbates are AB74 (◯, ●), MB (▽, ▼) and 4-CP (☐, ■), respectively).
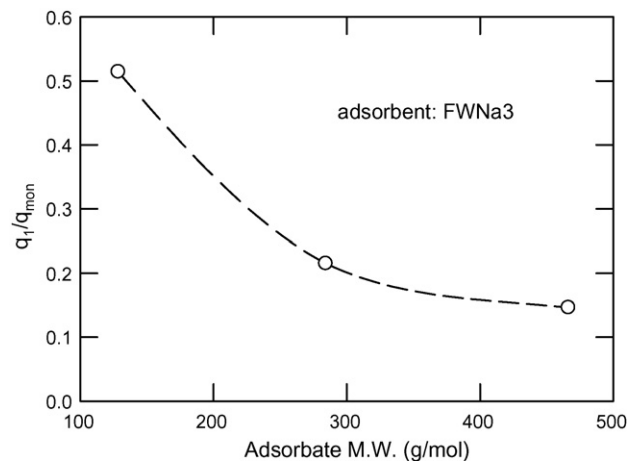

Fig. 9. Plots of q_1/q_{mon} against BET surface area of NaOH-activated carbons (solid point) and KOH-activated carbons (empty point) (adsorbates are AB74 (◯, ●), MB (▽, ▼) and 4-CP (☐, ■), respectively).

points stand for adsorption on NaOH-activated carbons. The q_1 value increased with increased S_p for adsorption of MB. The q_1 values of adsorption of 4-CP and AB74 on FWNa3 were the highest. Empty points stand for adsorption on KOH-activated carbons. The q_1 values of three kinds of adsorbates were much lower than those on NaOH-activated carbons at the same S_p value, indicating the stronger short time adsorption ability of

NaOH-activated carbons. Short time adsorption ability of an absorbent surface can be expressed as 1 min adsorption amount per unit surface area of activated carbon.

Three main factors in adsorption process are: (1) physical and chemical properties of adsorbents, (2) physical and chemical properties of adsorbates and (3) conditions of solutions. In Fig. 9, factors 1 and 3 were fixed to investigate the relationship between dimensionless q_1/q_{mon} and adsorbate. And the physical meaning of dimensionless q_1/q_{mon} is instant ratio of solid phase concentration to highest phase concentration starting adsorption capability can be judged from q_1/q_{mon} value of various adsorbate, and based on which the feasibility of engineering application can readily be judged, and in theory, behavior of adsorbate instant (1 min) coverage on porous material can also be understood. FTIR analysis will be considered in later studies.

The ratio of a 1 min adsorption amount of adsorbate to a monolayer cover amount of adsorbate is the ratio (q_1/q_{mon}) of effective adsorption sites of adsorbent that can be covered with adsorbate in short time (1 min), a meaningful parameter. Fig. 9 shows that the q_1/q_{mon} value decreased with the increased molecular weight of the adsorbate for adsorbent FWNa3. Their relationship can be expressed in the following equation:

$$\ln\left(\frac{q_1}{q_{mon}}\right) = 4.169 - 1.005 \ln(M.W.) \tag{8}$$

where M.W. is the molecular weight of the adsorbate and the correlation coefficient r^2 is 0.993. If the slope of Eq. (8) is −1(or very nearly −1), then q_1/q_{mon} is inversely proportional to the molecular weight of the adsorbate. If the Elovich equation is employed to process 1 min adsorption ratio with several groups of data and these are then compared the adsorption performance expressed by outer surface and marcropores of the activated carbon will be found. It is expected that the q_1/q_{mon} value will be an important new indicator of activated carbon adsorption.

3.6. Surface oxide groups on activated carbon

It has been reported that the surface oxide groups desorbed from activated carbon by pyrolysis increase the adsorption
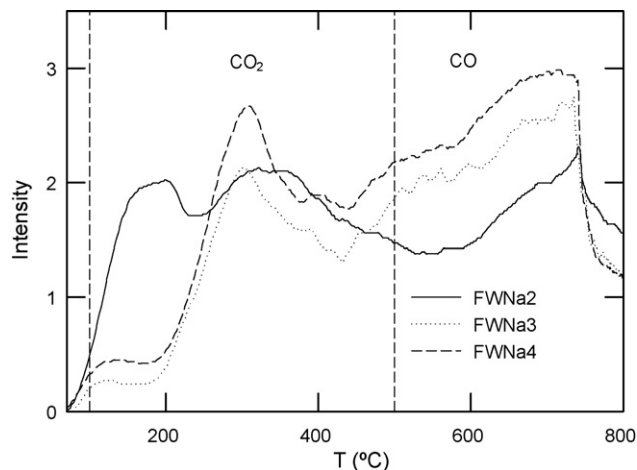

Fig. 10. Evolution profiles of CO_2 and CO by temperature programmed desorption (carbons are FWNa2 (—), FWNa3 (...) and FWNa4 (- -), respectively).

Table 10
Evolution profiles of CO_2 and CO by temperature programmed desorption

Carbon	CO_2 (100–500 °C) (intensity °C)	CO (500–800 °C) (intensity °C)
FWNa2	710	508
FWNa3	481	634
FWNa4	606	709

capacity by 18–36%, proving that surface oxide groups also affect adsorption [16]. In this study, temperature programmed desorption (TPD) was used to measure the surface oxide groups on activated carbon. Fig. 10 shows evolution profiles of CO_2 and CO on FWNa2, FWNa3 and FWNa4. Desorption intensities at both temperature ranges of 100–500 and 500–800 °C were quantitatively calculated and are listed in Table 10. The results are as follows:

1. With higher temperatures (above 500 °C), the desorption of CO was, in descending order, FWNa4 > FWNa3 > FWNa2, implying that the more abundant surface oxide groups (quinine, hydroxyl and carbonyl groups) were present in activated carbons that had been activated with more quantity activation agent (NaOH).
2. With lower temperatures (<550 °C), the desorption of CO_2 was, FWNa4 > FWNa3 and at temperatures < 200 °C, the curve of FWNa2 was quite different from the other two. This is because for FWNa2 the NaOH activation ran parallel with the same time concurrent with pyrolysis whereas for FWNa3 and FWNa4 it was only NaOH activation [10].
3. FWNa3 and FWNa4 were prepared by the same activation process with different doses of the chemical activation agent. However, in the whole TPD temperature range, the desorption of either CO or CO_2 was FWNa4 > FWNa3, meaning that larger amounts of surface oxide groups were retained in the activated carbon activated with larger doses of the activation agent (NaOH).

It has been proven by using TPD measurement that there are smaller amounts of surface oxide groups in FWNa3. Adsorption experiments have also proven that adsorption of dyes on FWNa3 was higher than that on other activated carbons, the result being in agreement with that of the literature [17]. This is one of the reasons why FWNa3 has better adsorption ability on dyes.

4. Conclusions

Three kinds of activated carbons (FWNa2, FWNa3 and FWNa4) of different characteristics were prepared by means of NaOH chemical activation. Adsorption equilibrium data were better fitted with the Langmuir isotherm equation. (a) The q_{mon} value: the adsorption amounts of AB74 and BB1 on FWNa4 were the highest and those of MB and 4-CP on FWNa3 were the highest; (b) the surface coverage (S_c/S_p) value: the adsorption of AB74, BB1 and MB on FWNa3 were higher than all the highest values reported on in literature and were, respectively, 1.37, 1.43 and 1.19 times of those; (c) the q_{mon}/S_p value: q_{mon}/S_p values

varied in large amount for NaOH-activated carbons and were higher than those of KOH-activated carbons; (d) the separation factor: favourable level of FWNa3 was very high, i.e. suitable for application.

Adsorption kinetics data were well fitted with the Elovich equation. (a) The parameter of adsorption rate ($1/b$): $1/b$ of the adsorption of dyes (AB74 and MB) and 4-CP were higher on NaOH-activated carbons than on KOH-activated carbons, revealing lower mass transfer resistance in NaOH-activated carbons; (b) the ratio of 1 min covered effective adsorption sites of adsorbent (q_1/q_{mon}) of FWNa3 were the highest, indicating a high adsorption amount of FWNa3 in a short time.

TPD measurement of surface oxide groups on activated carbon revealed that surface oxide groups on FWNa3 was the lowest, which is in agreement with the reports in literature about the relationship between surface oxide groups and the adsorption capacity of activated carbon. It was found in this study that FWNa3 performed the best for the adsorption of dyes based on adsorption isotherm equilibrium and kinetics. Several methods of adsorption data processing and interpretation are suggested for determining the potential for adsorbent applications.

Acknowledgment

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