Pore structure and adsorption performance of the activated carbons prepared from plum kernels

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Abstract

According to iodine number, amount of methylene blue adsorption, the BET specific surface area, and the yield, the conditions for preparing activated carbons as adsorbents from plum kernels were optimized. The activation temperature and time tested were in the ranges 750–900°C and 1–4 h, respectively. Adsorption isotherms of two commercial dyes and phenol from water on such activated carbons were measured at 30°C. It was shown that the optimal activation temperature and time depended on the molar mass of the solutes, and all equilibrium isotherms could be fitted by the Langmuir equation. The experimental results indicated that the prepared activated carbons were economically promising for adsorption removal of dyes and phenol, in contrast to other commercial adsorbents. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Activated carbons; Preparation; Plum kernels; Adsorption isotherms; Dyes; Phenol

1. Introduction

Liquid-phase adsorption process has been shown to be highly efficient for removal of suspended solids, colors, odors and organic pollutants from process or waste effluents. Activated carbon (powdered or granular) is the most widely used adsorbent because it

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has an excellent adsorption capability for organic compounds, but its use is usually limited due to its high cost [1–4]. This has lead many workers to search for cheaper substitutes like fly ash, silica gel, wool wastes, blast furnace sludge and clay materials (e.g. fuller's earth, diatomaceous earth, bentonite, kaolinite, montmorillonite, etc.). They have been already studied with varying success for the removal of color and metals [4,5]. Of these alternatives, agricultural and/or wood wastes such as bagasse pith, sawdust, maize cob, coconut husk fibers, rice bran, rice hull, nut shells, soybean and cotton seed hulls appear to be more economically attractive in certain countries because they are abundant [4,6].

In our laboratory a series of work is conducted to evaluate the possibility of the use of agricultural wastes for industrial pollution control. The aim of this paper was to determine optimal conditions for preparation of the activated carbons from plum kernels including the activation temperature and time according to iodine number, the BET specific surface area, amount of methylene blue adsorption and the yield. The performance for adsorption of two commercial dyes and phenol using such activated carbons from aqueous solutions were subsequently examined. These fundamental data are useful for further applications in the treatment of practical waste or process effluents.
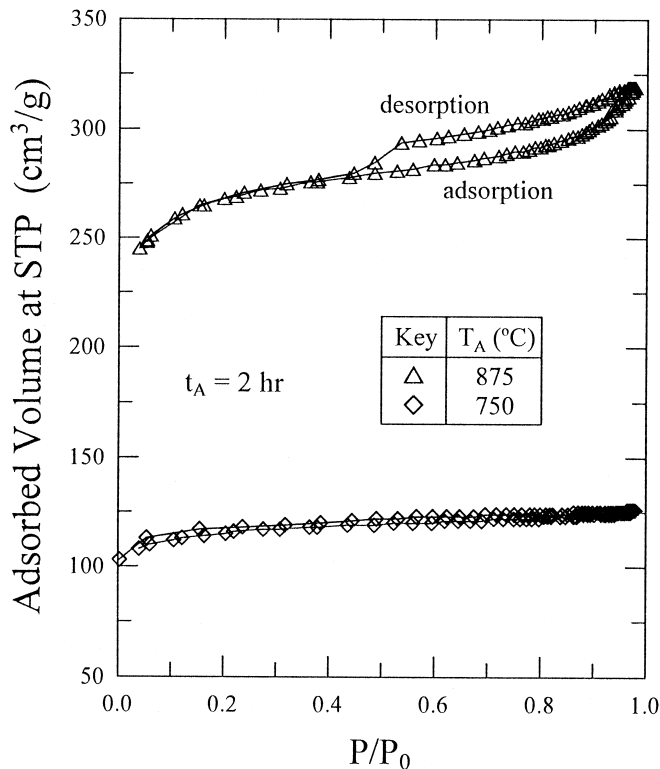

Fig. 1. Adsorption/desorption isotherms of N_2 at 77 K on the activated carbons prepared at different T_A.

2. Experimental

2.1. Preparation of activated carbons

Here, the dried plum kernels were placed in a sealed ceramic oven and were heated by a rate of 5°C/min to 450°C. In the meantime, the steams generated from deionized water (Millipore, Milli-Q) in the heated tube were poured into the oven by a rate of 5 cm^3/min for 2 h. Under oxygen-deficient conditions, the plum kernels were thermally decomposed to porous carbonaceous materials and some hydrocarbon compounds. This is the so-called carbonization process [7,8].

In the following activation process, the oven was continuously heated by the same rate as above to different ''fixed'' temperatures (750°C, 850°C, 875°C, 900°C). More-over, the steams were still poured at the same rate. The time elapsed for activation changed from 1 to 4 h. The resulting activated carbons were ground in a mill followed by washing and drying. They were sieved in the size range 250–420 μm for further processing.
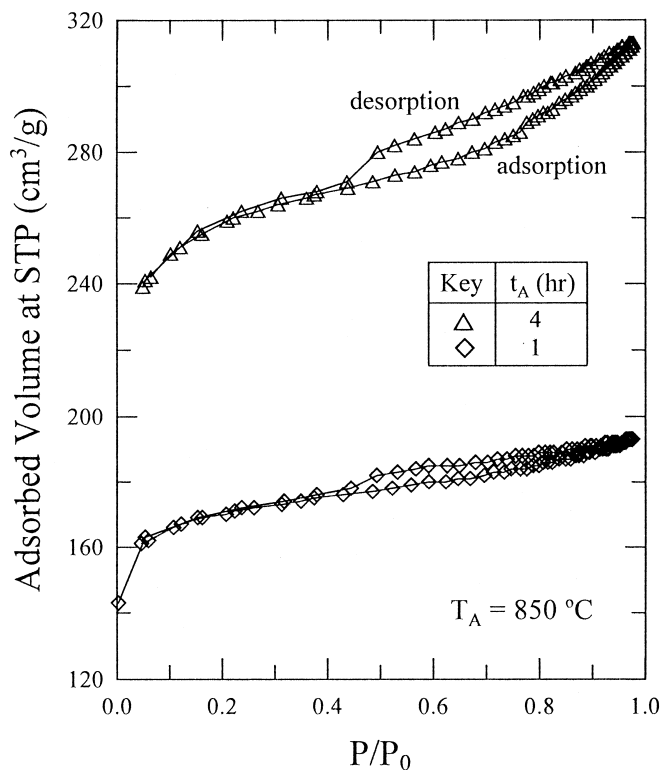

Fig. 2. Adsorption/desorption isotherms of N_2 at 77 K on the activated carbons prepared at different t_A.

2.2. Measurements of physical properties of activated carbons

Some physical properties of the activated carbons were measured including the iodine number, the BET specific surface area, amount of methylene blue adsorption and the yield. The adsorption performance of activated carbons for low-molar-mass species is generally indicated by the iodine number [9], which was determined at 30°C based on the Standard Test Method (ASTM Designation: D4607-86). On the other hand, the amount of methylene blue adsorption is often regarded as a measure of its performance for high-molar-mass species [9]. In this work, an amount of the activated carbons (0.1 g) and 0.1 dm^3 of aqueous solution containing 500 g/m^3 methylene blue were placed in a 0.25-dm^3 glass-stoppered flask and stirred at 130 rpm for 5 days using a bath (Firstek Model B603, Taiwan). The temperature was controlled at 30°C. After settling, the concentration of methylene blue was analyzed with a Hitachi UV/visible spectro-photometer (Model U2000) at 664 nm.

The BET specific surface area was determined from N$_2$ adsorption isotherms with a sorptiometer (Porous Materials, Model BET-202A). Also, the yield was calculated as the ratio of the weight of final activated carbons to that of initial raw materials.
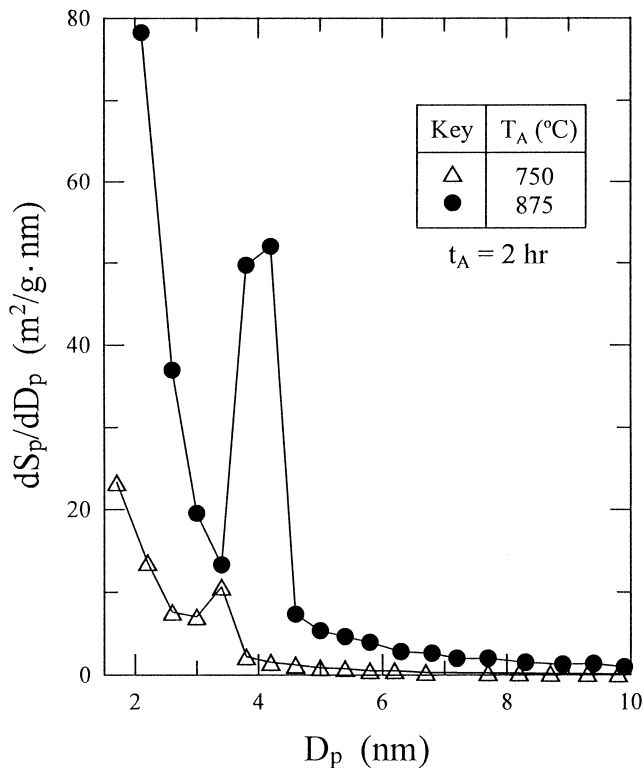

Fig. 3. Pore size distribution of the activated carbons prepared at different T_A.

2.3. Adsorption experiments for dyes and phenol

The commercial-grade basic dye Astrazon Red F3BL (C.I. No. 11055, Basic Red 22) and the acid dye Telon Blue ANL with chemical nature of anthraquinone (C.I. No. 62055, Acid Blue 25) were used as received (Bayer). They were abbreviated as BR 22 and AB 25, respectively. The aqueous phase was prepared by dissolving the dyes or phenol (Merck) in deionized water to the required concentrations.

In equilibrium experiments, an amount of activated carbon (0.1 g) and 0.1 dm^3 of an aqueous phase were placed in a 0.25-dm^3 glass-stoppered flask and stirred for 5 days by using a bath controlled at 30°C. Preliminary experiments showed that the adsorption studied was complete after 4 days. After filtration with glass fibers, the aqueous-phase concentrations of dyes and phenol were spectrophotometrically analyzed at each proper wavelength. Each experiment was duplicated at least under identical conditions. The amount of solutes adsorbed q_e, expressed in mol/kg or g/kg, was obtained by

$$q_e = (C_0 - C_e)V/W$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations (mol/m^3 or g/m^3), V is the volume of the solution (m^3), and W is the weight of dry activated carbons used (kg).
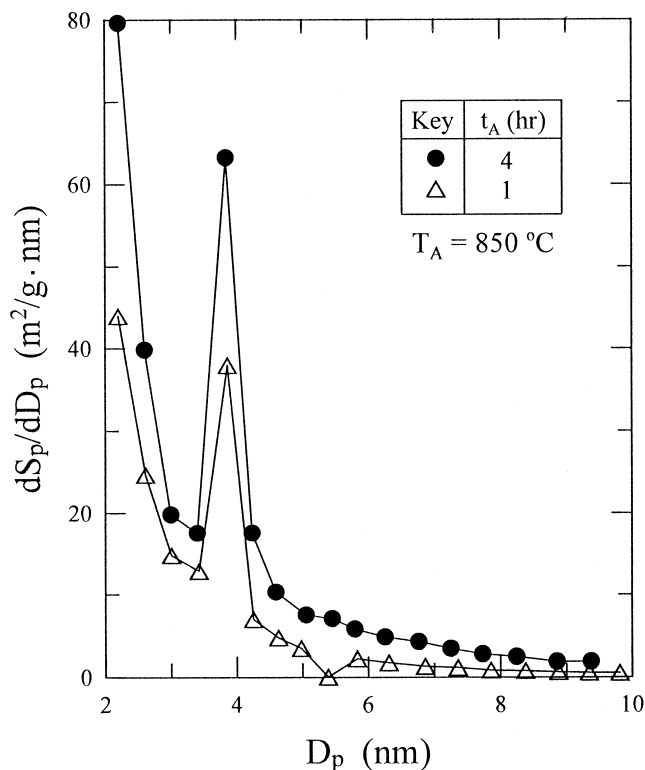

Fig. 4. Pore size distribution of the activated carbons prepared at different t_A.

3. Results and discussion

3.1. Pore structures of the prepared activated carbons

Basically, the structure of activated carbons contains pores classified into three groups, micropores (pore size < 2 nm), mesopores (2–50 nm) and macropores (> 50 nm). Also, micropores usually account for over 95% of the total surface area of common activated carbons [4]. Figs. 1 and 2 show the isotherms of adsorption/desorption of N_2 at 77 K on the activated carbons prepared at different activation temperatures (T_A) and activation times (t_A). The hysteresis phenomena exist due to the presence of ink-bottle type of pores [10]. According to the Kelvin equation, such ink-bottle pores have a large pore diameter because hysteresis occurs at high relative pressures (P/P_0). In addition, the larger amount of adsorption and the wider hysteresis loop at higher T_A and t_A mean that there are the more porous spaces and the more the amount of ink-bottle pores.

Figs. 3 and 4 show the corresponding pore size distributions, where D_p and S_p are the pore diameter and particle specific area, respectively. It is clearly found that there
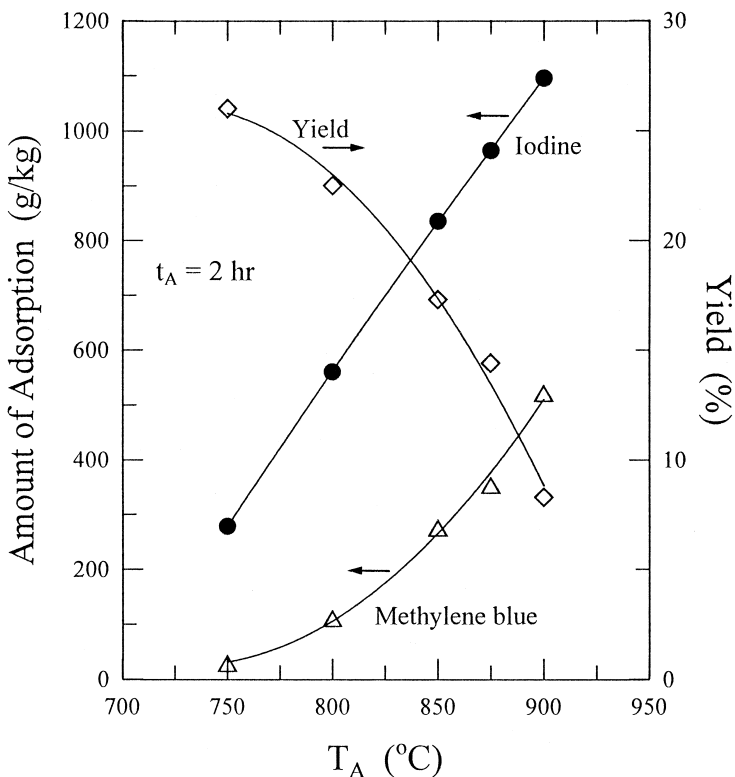

Fig. 5. The iodine number, amount of methylene blue adsorption and the yield on the activated carbons prepared at different T_A.

are two peaks, 0–3 and 3.5–4.5 nm, regardless of the activation times (Fig. 4). They are mostly located in the range of micropores/mesopores. Similar results are obtained at different T_A (Fig. 3), however, the distribution is slightly wider at higher T_A. It is hence expected that increasing T_A, rather than t_A, increases the amount of mesopores more efficiently.

3.2. Physical properties of the prepared activated carbons

Figs. 5 and 6 show the effects of T_A and t_A on iodine number, amount of methylene blue adsorption and the yield of the activated carbons. It is evident that under the ranges tested the yield decreases with increasing T_A and t_A. Ogasawara et al. [7] prepared the activated carbons by thermal decomposition of the used automotive tires but found that the yield first decreases gradually and then sharply by increasing T_A from 700°C to 830°C. Such discrepancies are likely due to the more ordered fibers in plum kernels than those in automotive tires, giving a narrower pore size distribution in plum kernels. This facilitates removal of hydrocarbon and other oxidation species at lower T_A and t_A [8].
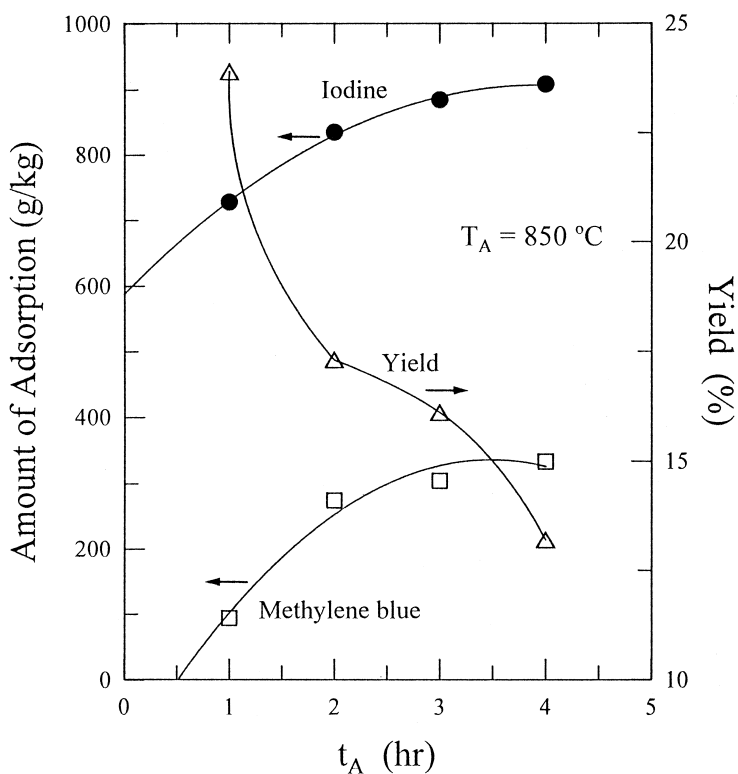
Fig. 6. The iodine number, amount of methylene blue adsorption and the yield on the activated carbons prepared at different t_A.

Also, the iodine number increases from 278 to 1095 g/kg when T_A increases from 750°C to 900°C, and increases from 728 to 909 g/kg when t_A increases from 1 to 4 h. They are comparable to those of commercially available activated carbons (600–1000 g/kg); for example, 650 (ICI Hydrodarco 3000), 900 (Calgan Filtrasorb 300), 950 (Westvaco Nuchar WL) and 1000 g/kg (Witco 517). In addition, the iodine numbers of the activated carbons prepared from apricot stones, grape seed, and cherry stones were 894, 607 and 907 g/kg, respectively [9]. The present results imply the prospective potential for practical applications.

The amount of methylene blue adsorption obtained at an initial dye concentration of 500 g/m^3 increases from 28.3 to 521 g/kg with increasing T_A from 750°C to 900°C, and increases from 94.1 to 334 g/kg when t_A increases from 1 to 4 h. In contrast to those of 285, 192 and 185 g/kg for the activated carbons prepared from apricot stones, grape seeds and cherry stones, respectively [9], the present products are more promising.

Moreover, the BET surface area increases from 353 to 1162 m^2/g when T_A increases from 750°C to 900°C, and increases from 497 to 783 m^2/g when t_A increases from 1 to 4 h. In practice, the surface areas of the activated carbons prepared from the used automotive tires exponentially increased from 87 to 960 m^2/g when T_A raised from
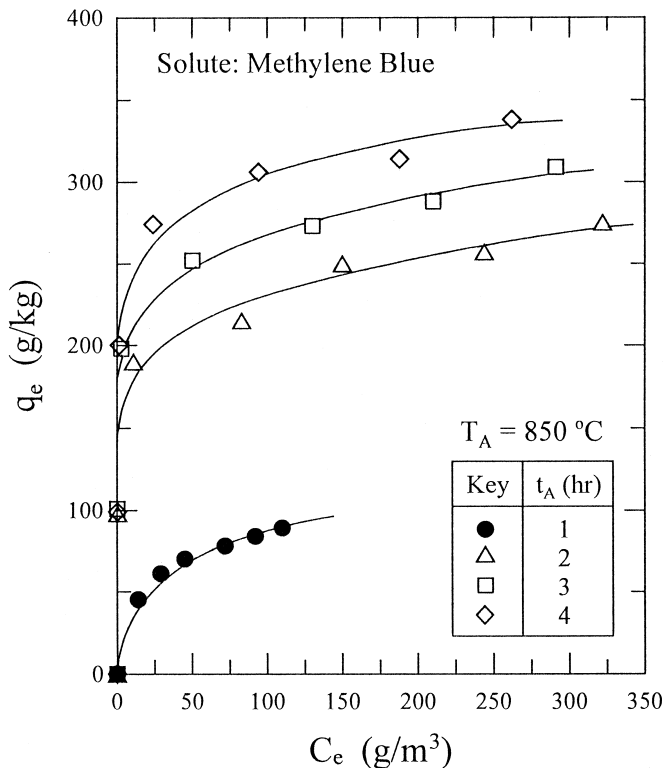

Fig. 7. Adsorption isotherms of methylene blue at 30°C on the activated carbons prepared at different t_A.

700°C to 830°C [7]. The much larger surface area obtained at higher T_A is likely due to the easier formation of porous spaces [8]. The present surface areas are comparable to those of commercial ones; for example, 300–600 (ICI Hydrodarco 3000), 950–1050 (Calgan Filtrasorb 300), 1000 (Westvaco Nuchar WL) and 1050 m^2/g (Witco 517). It was reported that the activated carbons prepared from apricot stones, grape seeds and cherry stones have a surface area of 1175, 487 and 836 m^2/g, respectively [9]. Furthermore, Streat et al. [11] prepared the activated carbons from straw and tires and obtained a surface area of 596 and 346 m^2/g, respectively.

As shown in Figs. 5 and 6, the iodine number, surface area and amount of methylene blue adsorption increase by a factor of 3.94, 3.29 and 18.4, respectively with increasing T_A from 750°C to 900°C, and by a factor of 1.25, 1.58 and 3.55, respectively by increasing t_A from 1 to 4 h. This likely indicates that the amount of three types of pores increases when T_A and t_A increase, and that the increase in mesopores or macropores is more significant.

In fact, Gergova et al. [9] found that the iodine number, surface area and amount of methylene blue adsorption reach a maximum as the carbonaceous adsorbents prepared
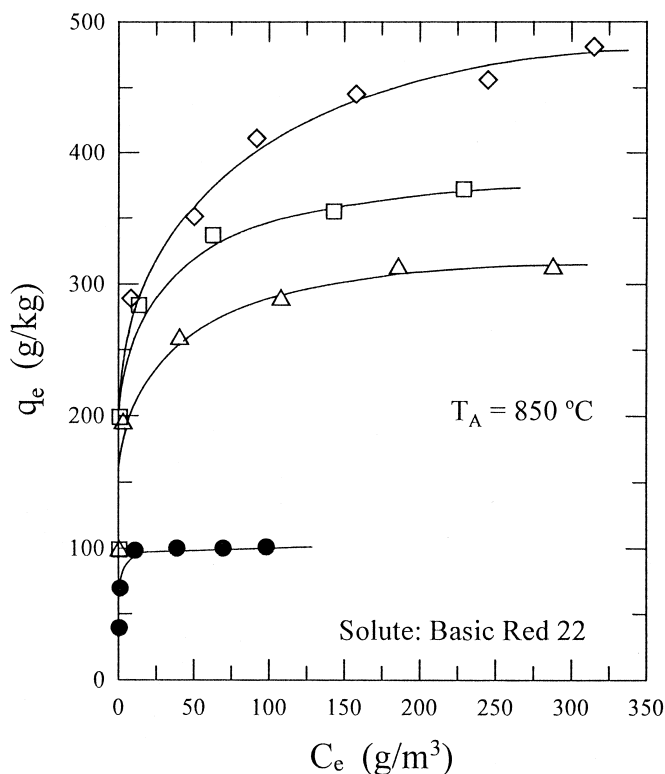

Fig. 8. Adsorption isotherms of the dye BR 22 at 30°C on the activated carbons prepared at different t_A. The meaning of the symbols is identical to that in Fig. 7.

from apricot stones were activated for 2 h at 700°C. The drop in adsorption performance of the activated carbons is likely due to the formation of a larger amount of mesopores and/or macropores. Cleveland et al. [12] used fullerene wastes to prepare carbonaceous adsorbents and also found that the iodine number increases by increasing t_A up to 1 h. However, increasing t_A from 1 to 2 h the difference of iodine number is undetectable but the molasses decolorizing index increases. That is, the favorable adsorption of high molar mass species at a longer t_A is more apparent, in contrast to the present products.

According to the average pore size of 2.63 nm (Figs. 3 and 4) and surface area, the present products are economically promising because the average pore size and surface area of the activated carbons widely used for water treatment are within 1.7–2.9 nm and 650–1200 m^2/g, respectively [4].

3.3. Adsorption isotherms of dyes and phenol

Figs. 7–10 show the adsorption isotherms of methylene blue, BR 22, AB 25 and phenol at 30°C on the activated carbons prepared at different t_A. Results for adsorption on the activated carbons prepared at different T_A are also obtained (not shown).
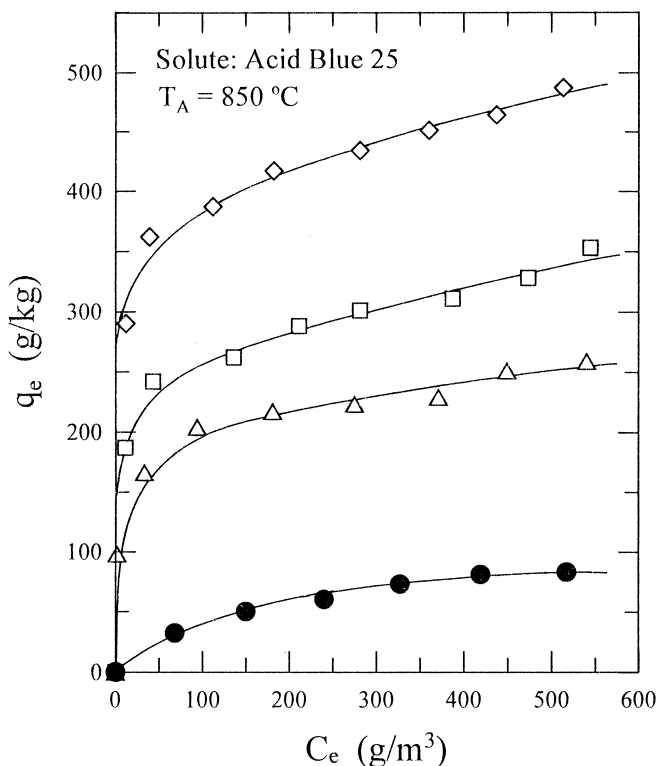

Fig. 9. Adsorption isotherms of the dye AB 25 at 30°C on the activated carbons prepared at different t_A. The meaning of the symbols is identical to that in Fig. 7.
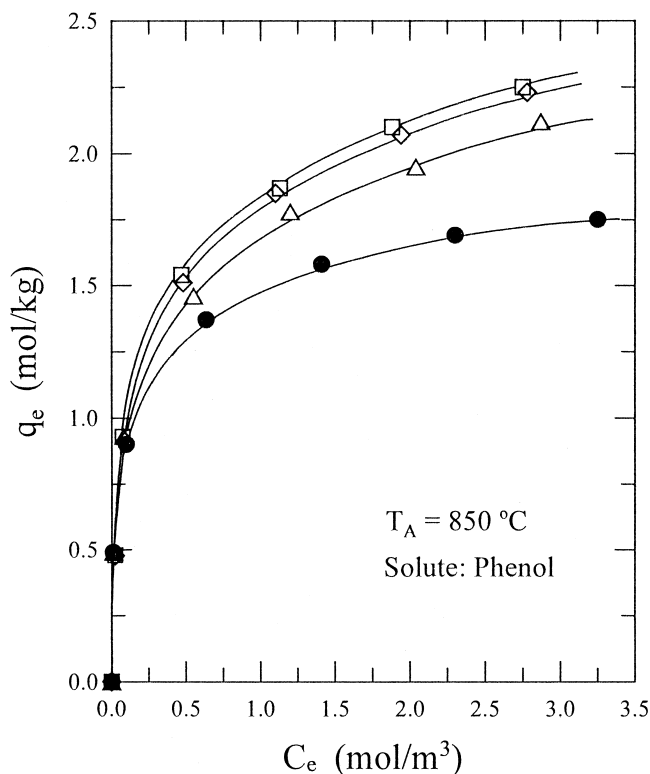
Fig. 10. Adsorption isotherms of phenol at 30°C on the activated carbons prepared at different t_A. The meaning of the symbols is identical to that in Fig. 7.

Basically, adsorption isotherm is important to describe how solutes interact with adsorbents and is critical in optimizing the use of adsorbents. Correlation of isotherm data by theoretical or empirical equations is thus desired to practical operation. Based on the data shown in Figs. 7–10, the conventional two-parameter Langmuir equation can be applied.

$$C_e/q_e = (1/Kq_{mon}) + (1/q_{mon})C_e$$

where K is the Langmuir constant and q_{mon} is the amount of adsorption corresponding to monolayer coverage. The values of K and q_{mon} can be determined from linearized plots of (C_e/q_e) vs. C_e. Parameters obtained are listed in Table 1. The fit is quite good for all solutes under the concentration ranges studied (correlation coefficient, $r > 0.982$).

For all solutes except phenol, q_{mon} increases with increasing T_A and/or t_A. At $T_A = 900°C$ and $t_A = 2$ h, q_{mon} for BR 22 and AB 25 is 710.1 and 904.4 g/kg, respectively. They are superior to those obtained previously in similar adsorbate–adsorbent systems [13–16]. However, at $T_A = 850°C$, q_{mon} for phenol adsorption has a maximum at $t_A = 3$ h although the difference of q_{mon} between the cases of $t_A = 3$ and 4

Table 1
Parameters in the Langmuir equation for adsorption of solutes at 30°C on the activated carbons prepared at different conditions

T_A (°C)	t_A (h)	Solute	K (m^3/g)	q_{mon} (g/kg)	r (−)	q_{mon}/area (mg/m^2)	R_L (−)
750	2	methylene blue	0.016	28.3	0.997	0.080	5.9×10^{-2}
850	1		0.062	94.1	0.982	0.189	1.6×10^{-2}
	2		0.101	274.5	0.997	0.400	9.8×10^{-3}
	3		0.161	305.0	0.998	0.426	6.2×10^{-3}
	4		0.253	333.7	0.999	0.433	3.9×10^{-3}
875	2		0.274	352.6	0.999	0.366	3.6×10^{-3}
900	2		0.314	520.6	0.994	0.448	3.2×10^{-3}
750	2	BR 22	0.049	17.1	0.993	0.049	2.0×10^{-2}
850	1		0.147	101.5	0.999	0.204	6.7×10^{-3}
	2		0.212	318.1	0.999	0.464	4.7×10^{-3}
	3		0.307	371.9	0.999	0.528	3.2×10^{-3}
	4		0.406	493.9	0.999	0.631	2.4×10^{-3}
875	2		0.165	480.3	0.999	0.498	6.0×10^{-3}
900	2		0.180	710.1	0.999	0.611	5.5×10^{-3}
750	2	AB 25	0.004	37.1	0.984	0.105	2.0×10^{-1}
850	1		0.005	114.2	0.995	0.230	1.7×10^{-1}
	2		0.022	259.2	0.996	0.378	4.3×10^{-2}
	3		0.034	352.5	0.995	0.501	2.8×10^{-2}
	4		0.044	486.8	0.997	0.622	2.2×10^{-2}
875	2		0.134	524.0	0.997	0.544	7.4×10^{-3}
900	2		0.166	904.4	0.999	0.778	6.0×10^{-3}
750	2	phenol	0.091	105.8	0.998	0.300	2.3×10^{-2}
850	1		0.094	167.4	0.999	0.337	2.2×10^{-2}
	2		0.067	203.0	0.996	0.306	3.1×10^{-2}
	3		0.065	218.1	0.997	0.296	3.2×10^{-2}
	4		0.061	216.9	0.998	0.277	3.4×10^{-2}
875	2		0.065	226.2	0.999	0.235	3.2×10^{-2}
900	2		0.070	257.4	0.996	0.222	2.9×10^{-2}

h are not so apparent as the case of dye adsorption. As will be discussed in Section 3.4, the amount of micropores, mesopores and macropores inside the activated carbons increases when t_A increases, but the extent of increment in mesopores and/or macropores is more significant. This explains the unfavorable adsorption of phenol on the activated carbons prepared at a sufficiently long t_A because phenol is a smaller molecule than the dyes.

It should be noted that the amount of adsorption per unit surface area (i.e. q_{mon}/area) increases with increasing T_A and/or t_A only for the two dyes BR 22 and AB 25 (Table 1). In the case of phenol adsorption, on the other hand, this quantity appears to decrease with increasing T_A and/or t_A. However, there are no certain trends for adsorption of methylene blue. Satisfactory evidence or explanation cannot be given at this stage. Pore structures of the adsorbents and the molar mass (and/or the molecular configuration) of the solutes may play an important role.
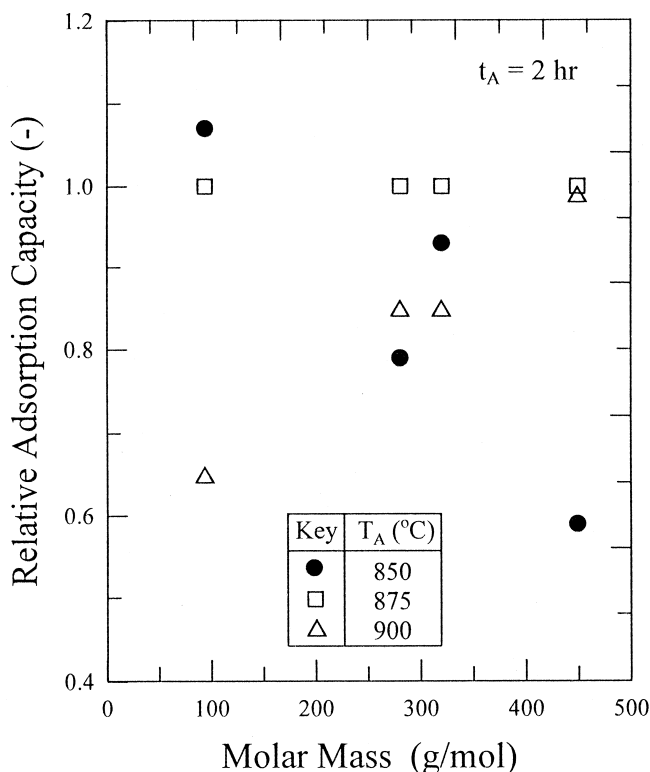
Fig. 11. Relationship between the molar mass of the solutes and effective q_{mon} on the activated carbons prepared at different T_A relative to 875°C.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L, defined as [17,18]

$$R_L = 1/(1 + KC_0)$$

where C_0 is the highest initial solute concentration. The R_L value implies the adsorption to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). According to the values of R_L obtained (Table 1), the present adsorption systems all reveal favorable.

3.4. Optimal preparation conditions for adsorption applications

Owing to different T_A and t_A trends of the yield from the iodine number, surface area and amount of methylene blue adsorption (Figs. 5 and 6), there may be an optimal T_A or t_A from the viewpoint of practical use. The "effective" q_{mon} is defined as the product of q_{mon} and the yield. Fig. 11 shows effective q_{mon} of various solutes, in terms of the molar mass of the solutes, on the activated carbons prepared at other activation temperatures
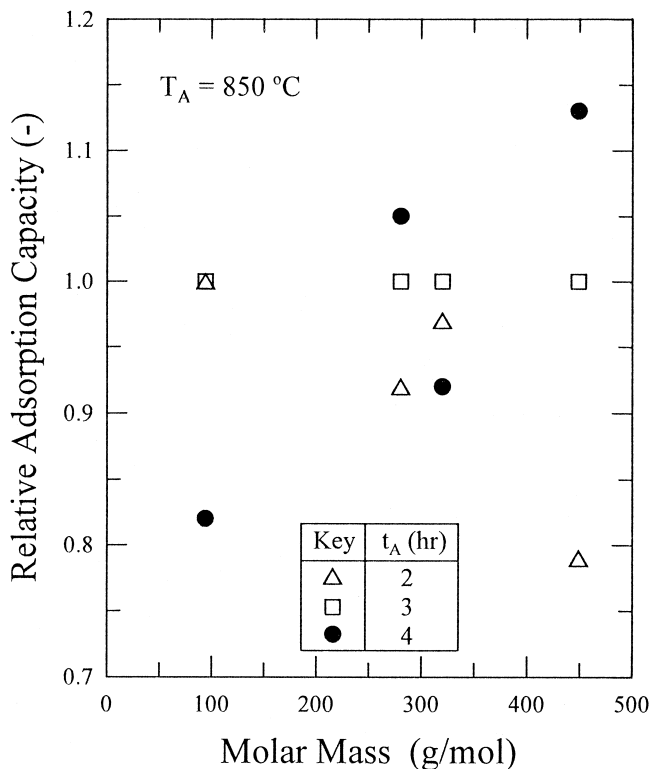
Fig. 12. Relationship between the molar mass of the solutes and effective q_{mon} on the activated carbons prepared at different t_A relative to 3 h.

relative to those at 875°C, and Fig. 12 shows similar results at other activation times relative to those at 3 h.

Under the conditions studied, it is found that the activated carbons prepared at $T_A = 900$°C and $t_A = 4$ h are preferred to adsorb high-molar-mass solutes (> 300 g/mol). Also, the activated carbons prepared at $T_A = 850$°C and $t_A = 2$ h are more suitable to adsorb low-molar-mass solutes (< 120 g/mol). This confirms the fact that an increase in T_A and t_A facilitates formation of mesopores and/or macropores inside the particles. This allows to prepare suitable activated carbons from plum kernels for various purposes.

4. Conclusions

Pore structures and optimal preparation conditions of the activated carbons from plum kernels were evaluated. Furthermore, the adsorption isotherms of methylene blue, two commercial dyes (BR 22, AB 25), and phenol on such activated carbons were measured at 30°C. The following results are obtained.

(1) The hysteresis phenomena exist due to the presence of ink-bottle type of pores. There is a more porous space and a larger amount of ink-bottle pores at a higher activation temperature (T_A) and longer activation time (t_A). Two groups of pores with diameters of 0–3 and 3.5–4.5 nm exist, which mostly locate in the range of micropores and mesopores.

(2) Unlike the yield, the iodine number, the amount of methylene blue adsorption and surface area all increase with increasing T_A and t_A. The results of pore size and surface area show that the activated carbons prepared in this work are economically promising, compared to commercially available products used for liquid-phase adsorption.

(3) All isotherm data are well fitted by the Langmuir equation under the ranges studied, and the present adsorption systems all reveal favorable. For all solutes except phenol, q_{mon} increases by increasing T_A and/or t_A (Table 1). The unfavorable phenol adsorption on the activated carbons prepared at sufficiently long t_A is likely due to the formation of large amount of mesopores or macropores.

(4) The activated carbons prepared at higher T_A and t_A are preferred to adsorb high-molar-mass solutes (> 300 g/mol), and those at lower T_A and t_A are more suitable to adsorb low-molar-mass solutes (< 120 g/mol). This allows us to prepare suitable activated carbons from plum kernels for various purposes.

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