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Role of Microporosity of Activated Carbons on Their Adsorption Abilities for Phenols and Dyes

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Abstract. The amounts of adsorption of two commercial dyes, phenol, and 4-chlorophenol from water on activated carbons were measured at 30°C. The carbons were prepared from cane (bagasse) piths and were activated by steam. The activation temperature and time were in the ranges of 750–840°C and 2 h, respectively. It was shown that the isotherm data of all four solutes could be well fitted by the Langmuir equation under the conditions studied. The adsorption capacities of the solutes were correlated with the microporosity properties of the activated carbons including micropore volume and external surface area. Finally, the adsorption characteristics of the present carbons was compared with those prepared from various agricultural wastes.

Keywords: adsorption equilibrium, activated carbons, microporosity, dyes, phenols, cane piths

Introduction

It is well known that liquid-phase adsorption is one of the most efficient methods for the removal of colors, odors, and organic pollutants from process or waste effluents. In addition, activated carbons (granular or powdered) are the most widely used adsorbents because of their excellent adsorption ability for relatively low-molecular-weight organic matters. However, their use is usually limited due to its high cost (Bailey et al., 1999; El-Geundi, 1997; McKay et al., 1986; Nassar and El-Geundi, 1991). This led many workers to search for cheaper substitutes including fly ash, coal, silica gel, wool wastes, and clay materials (fuller's earth, diatomaceous earth, kaolinite, montmorillonite, etc.). They have been applied with varying success for removal of color and metals. Of these alternatives, many agricultural and wood wastes such as cane (bagasse) pith, sawdust, maize cob, fruit kernels, coconut husk fibers, and nut shells appear to be more economically attractive in certain countries such as Taiwan because they are abundant (El-Geundi, 1997; McKay et al., 1987).

In our laboratory a series of work is continuously conducted to evaluate the possibility of the use of agricultural wastes for industrial pollution control. The excellent ability and economic promising of the activated carbons prepared from bamboos, plum kernels, and corn cobs for adsorption of dyes and phenols from aqueous solutions have been recently

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presented (Wu et al., 1999a, 1999b, in press). The aim of this paper was to subsequently evaluate the application potential of cane pith wastes for this purpose. Furthermore, comparison of the adsorption abilities among using these activated carbons was made by correlating the micrioporosity properties of these adsorbents such as the micropore volume and external surface area (Sousa-Aguiar et al., 1998).

Experimental

Preparation of Activated Carbons

After drying at 110°C for 24 h, the cane piths 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 which were generated from deionized water (Millipore, Milli-Q) in a heated tube were poured into the oven by a rate of 5 cm^3/min for 2 h. The cane piths were thermally decomposed to porous carbonaceous materials and some hydrocarbons under oxygen-deficient environments. This is the so-called carbonization process. In the followed activation process, the oven was continuously heated by the same rate as above to different "fixed" temperatures (750, 790, 810, 840°C). Also, the steams were still poured at the same rate. The time taken for activation was 2 h. The resulting activated carbons were ground in a mill followed by washing and drying. They were sieved in the size range 0.25–0.42 mm for further use.

The iodine number of activated carbons at 30°C was measured based on the Standard Test Method, ASTM Designation D4607-86. The activated carbons (0.1 g) were placed in a dry 250-cm^3 Erlenmeyer flask equipped with a ground glass stopper, and were fully wetted with 10 cm^3 of 5 wt % HCl. Then, 100 cm^3 of 0.1 mol/dm^3 iodine solution were poured into the flask, and the contents were vigorously shaken for 30 s. After quickly filtration, 50 cm^3 of the solution was titrated with 0.01 mol/dm^3 sodium thiosulfate until the solution became pale yellow. Two milliliters of starch indicator solution (1 g/dm^3) was added and the titration was continued with sodium thiosulfate until the solution was colorless. The concentration of iodine in the solution was thus calculated from the total volume of sodium thiosulfate used considering volume dilution factor.

The BET surface area of the activated carbons (S_{BET}) was obtained from N_2 adsorption isotherms at 77 K with a sorptiometer (Porous Materials Inc., Model BET-202A). Based on these data, the manufacturer's software also provided the total pore volume (V_{pore}) by the BJH theory (Barrett et al., 1951), as well as the micropore volume (V_{micro}) and external surface area (S_{ext}) using the t-plot method (De Boer et al., 1966; Sing et al., 1985; Sing, 1989). The volume due to external surface (V_{ext}) and the surface area due to micropores (S_{micro}) were directly obtained from mass balance (Sousa-Aguiar et al., 1998). The point of zero charge of the activated carbons was obtained to be about 6.2 from zeta potential measurements (Malvern, UK, Model Zetasizer 3000).

Experimental Procedures

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 Co.). They were abbreviated as BR22 and AB25, respectively. The aqueous phase was prepared by dissolving the dyes or phenols (Merck) in deionized water without any pH adjustment. Under the concentration ranges studied, the initial solution pH was about 4.1 for BR22, 5.9 for AB25, 6.1 for phenol, and 6.6 for 4-chlorophenol.

In equilibrium experiments, an amount of activated carbons (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 d using a water bath controlled at 30°C. Preliminary tests showed that the adsorption studied was complete after 4 d. After filtration with glass fibers, the aqueous-phase concentrations of dyes and phenols were analyzed with a UV/visible spectrophotometer (Hitachi Model U-2000) at each proper wavelength. Each experiment was duplicated at least under identical conditions. The amount of adsorption at equilibrium q_e, in g/kg, was obtained by

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

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

Results and Discussion

Physical Properties of the Activated Carbons

The effect of activation temperature (T_A) on the yield and iodine number of activated carbons is shown in

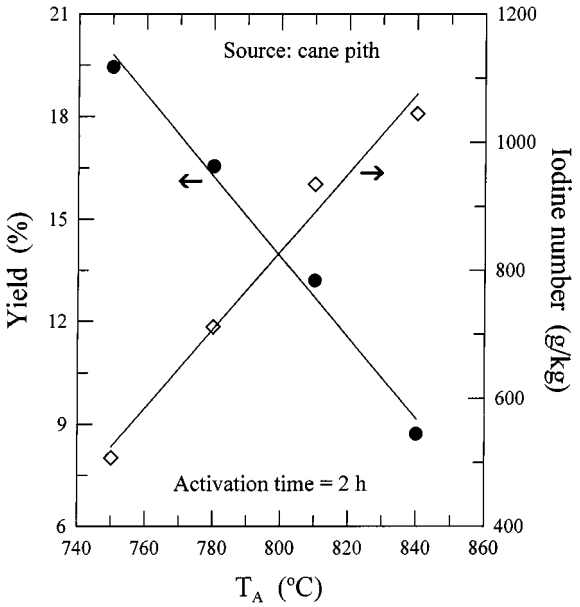

Figure 1. The yield and iodine number of the activated carbons prepared from cane piths at different T_A.

Fig. 1. Here, the yield is calculated on a dry basis. It is found that the yield decreases with increasing T_A under the conditions studied. This tendency has been reported for preparation of the activated carbons from several agricultural wastes such as bamboo, plum kernels, and corn cobs (Wu et al., 1999a, 1999b, in press) and other sources such as the used automotive tires (Ogasawara et al., 1987).

The iodine number is generally considered as a measure of adsorption ability of the adsorbents for low-MW solutes (Gergova et al., 1993). As shown in Fig. 1, the iodine number increases from 508 to 1045 g/kg when T_A changes from 750 to 840°C. They are basically comparable to those of commercially available activated carbons, e.g., 650 (ICI Hydrodarco 3000), 900 (Calgan Filtrasorb 300), 950 (Westvaco Nuchar WL), and 1000 g/kg (Witco 517). This demonstrates the prospective potential of the present products for adsorption of low-MW species.

The pores of adsorbents are classified into three groups, micropores (pore size <2 nm), mesopores (2–50 nm), and macropores (>50 nm). In addition, micropores often account for over 95% of the total surface area of common activated carbons (El-Geundi, 1997). The pore properties of the present activated carbons including S_{BET}, S_{ext}, S_{micro}, V_{pore}, V_{micro}, V_{ext}, and average pore diameter are listed in Table 1. Increasing T_A leads to an increase in S_{BET}, S_{ext}, V_{pore}, and V_{micro}, but a decrease in the fractions of micropores to the total surface area (S_{micro}/S_{BET}) and pore volume (V_{micro}/V_{pore}, not shown). This proves that the increment of micropores is less than that of meso-/macropores with increasing T_A. It is noticed that a value of (S_{micro}/S_{BET}) within 87–95% can justify the validity of the present results.

On the other hand, the value of S_{BET} for the activated carbons prepared from cane pith (445 to 607 m^2/g) is smaller compared to those of the commercial ones. For example, it is 300–600 (ICI Hydrodarco 3000), 950–1050 (Calgan Filtrasorb 300), 1000 (Westvaco Nuchar WL), and 1050 m^2/g (Witco 517). This is likely due to the loose structure of cane pith fibers. It was actually found that the activated carbons prepared from straw and tires have a S_{BET} of 596 and 346 m^2/g, respectively (Streat et al., 1995). Furthermore, Gergova et al. (1993) prepared the activated carbons from apricot stones, grape seeds, and cherry stones, and obtained a S_{BET} of 1175, 487, and 836 m^2/g, respectively.

Table 1. Physical properties of the activated carbons prepared from various agricultural wastes at different activation temperatures[a].

Source	T_A (°C)	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{ext} (m^2/g)	S_{micro}/S_{BET} (%)	V_{pore} (cm^3/g)	V_{micro} (cm^3/g)	V_{ext} (cm^3/g)	Average pore diameter (nm)
Cane pith	750	445.8	403.9	41.9	90.6	0.287	0.223	0.064	2.57
	780	544.6	489.1	55.5	89.8	0.342	0.263	0.079	2.62
	810	593.1	526.1	67.0	88.7	0.401	0.303	0.098	2.70
	840	606.8	527.1	84.5	86.9	0.445	0.306	0.139	2.94
Plum kernel	750	353.6	333.6	20.0	94.4	0.194	0.168	0.026	2.20
	875	824.8	751.1	73.7	91.1	0.493	0.376	0.117	2.39
Corn cob	830	537.7	477.6	60.1	88.8	0.348	0.262	0.086	2.59
	890	943.3	819.5	123.8	86.9	0.592	0.392	0.200	2.51

[a]Activation time for the carbons is 2 h.

Adsorption Isotherms of Phenols and Dyes

Figures 2 and 3 typically show the adsorption isotherms of phenol and dye BR22 at 30°C on the activated carbons prepared at different T_A. Evidently, the amount of adsorption increases with increasing T_A. Adsorption isotherm is basically important to describe how solutes interact with adsorbents, and is critical in optimizing the use of adsorbents. The correlation of isotherm data by either theoretical or empirical equations is thus desired to practical operation. According to the data shown in Figs. 2 and 3, it is expected that the common two-parameter Langmuir equation can be applied.

$$C_e/q_e = (1/Kq_{mon}) + (1/q_{mon})C_e \qquad (2)$$

where K is the Langmuir constant. q_{mon} commonly refers to the amount of adsorption corresponding to monolayer coverage. In the case of microporous solids, q_{mon} can include some molecules adsorbed inside micropores; thus it is preferred to define as adsorption capacity or surface phase capacity.

A linearized plot of (C_e/q_e) vs. C_e would give K and q_{mon}. The parameters obtained for adsorption of

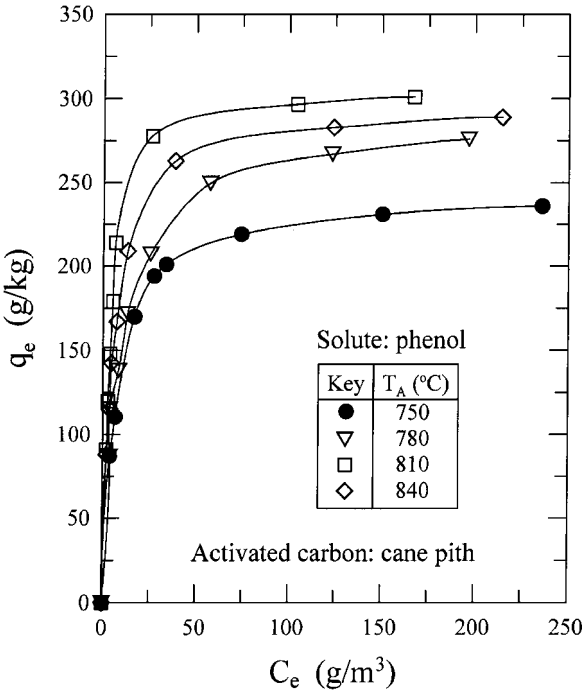

Figure 2. Adsorption isotherms of phenol at 30°C on the activated carbons prepared from cane piths at different T_A.

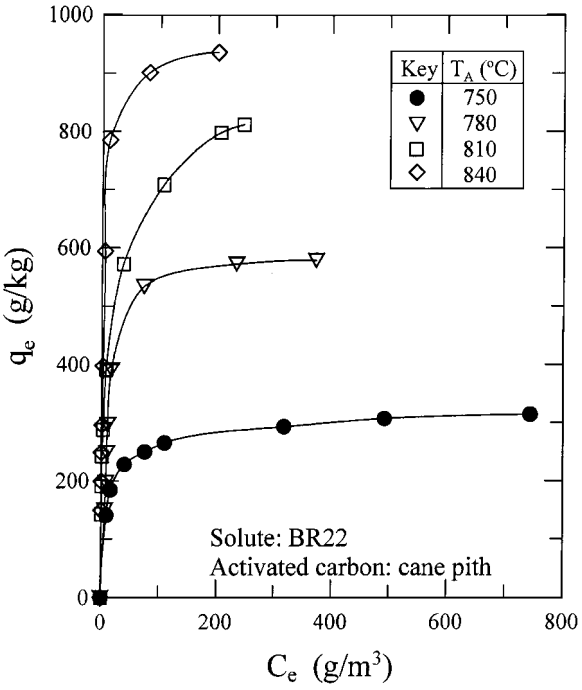

Figure 3. Adsorption isotherms of dye BR22 at 30°C on the activated carbons prepared from cane piths at different T_A.

solutes are listed in Table 2. The fit is quite good under the concentration ranges studied (correlation coefficient, $r^2 > 0.987$). It is seen that the adsorption capacity (q_{mon}) of dyes BR22 and AB25 increases with increasing T_A. At $T_A = 840$°C, the values of q_{mon} for BR22 and AB25 are 942 and 674 g/kg, respectively, which are larger than those obtained earlier in similar solute-adsorbent systems (Al-Duri and McKay, 1988; Juang et al., 1996; McKay, 1982; McKay and Al-Duri, 1988; Teng and Hsieh, 1999). However, phenol and 4-chlorophenol has a maximum q_{mon} against T_A. The unfavorable adsorption of both phenols on the activated carbons prepared at sufficiently high T_A will be discussed in the next section. Figures 4–6 show the superior ability of the present activated carbons to those prepared from other sources (Wu et al., 1999a, 1999b, in press). A much lower activation temperature for preparation of the carbons is required to achieve equivalent performance.

Effect of Microporosity of Activated Carbons on Adsorption Ability

From Tables 1 and 2, it appears that the adsorption capacity per unit BET surface area (q_{mon}/S_{BET}) for both

Table 2. Parameters of the Langmuir equation for adsorption of solutes at 30°C on the activated carbons prepared from cane pith[a].

	Phenol			4-Chlorophenol			BR22			AB25		
T_A (°C)	q_{mon}	K	r^2	q_{mon}	K	r^2	q_{mon}	K	r^2	q_{mon}	K	r^2
750	231.8	0.053	0.997	233.3	0.081	0.996	270.3	0.860	0.998	273.0	0.025	0.999
780	263.1	0.164	0.999	290.0	0.023	0.987	611.7	0.222	0.997	325.5	0.024	0.997
810	300.8	0.128	0.997	400.7	0.081	0.997	894.2	0.037	0.996	450.9	0.338	0.999
840	286.1	0.073	0.998	397.6	0.012	0.994	941.7	0.511	0.999	673.6	0.894	0.999

[a]Unit: q_{mon} (g/kg) and K (m^3/g).

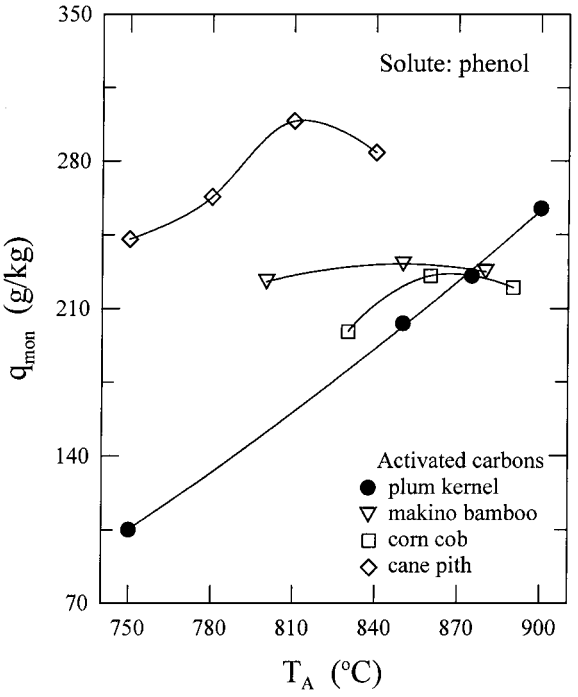

Figure 4. Adsorption capacity (q_{mon}) of phenol at 30°C on the activated carbons prepared from various agricultural wastes at different T_A.

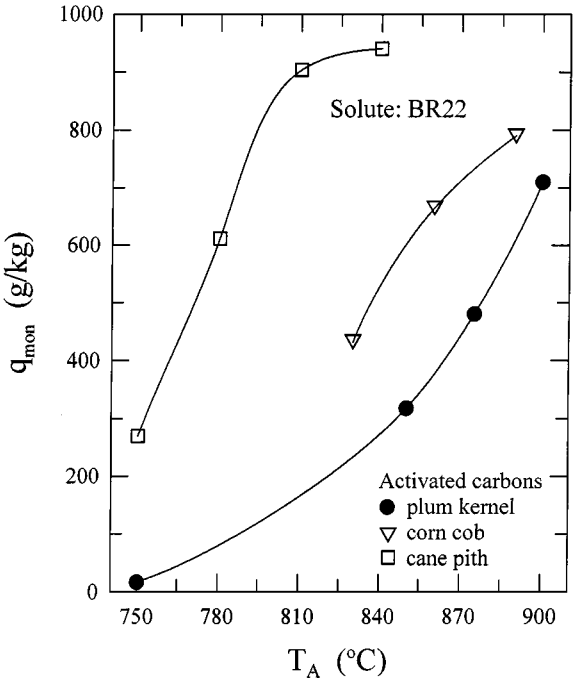

Figure 5. Adsorption capacity (q_{mon}) of dye BR22 at 30°C on the activated carbons prepared from various agricultural wastes at different T_A.

phenols increases first and then decreases with increasing T_A; however, it always increases for both dyes under the T_A ranges studied. In addition, the T_A trend of iodine number is the same as the dyes. As indicated above, S_{BET} of the carbons increases with increasing T_A and the increment of micropores is less than that of meso-/macropores. Moreover, S_{ext} and V_{micro} were obtained here from N_2 isotherm data by the t-plot, which is done by plotting the adsorbed N_2 volume against the statistic thickness of the adsorbed N_2 layer. This method assumes that micropore adsorption is a primary phenomenon, and that above a given relative pressure the micropores are filled completely and only adsorption on the external surfaces affects the isotherm. In this regard, the different phenomena for both phenols from other solutes are dominantly due to their small MW and partly to the interactions between phenols and the functional groups on the carbon surfaces.

If the adsorption of phenol (MW = 94, molecular volume = 0.162 nm^3) and 4-chloro-phenol (MW = 128.5, molecular volume = 0.178 nm^3) is assumed to proceed only within the micropores of the adsorbents

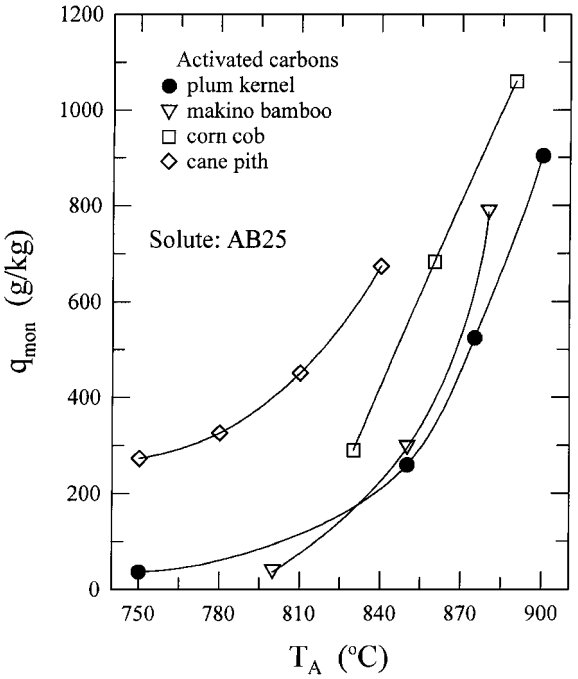

Figure 6. Adsorption capacity (q_{mon}) of dye AB25 at 30°C on the activated carbons prepared from various agricultural wastes at different T_A.

(i.e., pore filling), q_{mon}/V_{micro} should remain constant. Similarly, if the adsorption of BR22 and AB25 (MW = 449, molecular volume = 0.69 nm^3) proceeds only at the external surfaces, q_{mon}/S_{ext} also remain constant. Figures 7 and 8 show the results. It is evident that q_{mon}/S_{ext} for AB25 increases with S_{ext} (i.e., T_A), as in the case of q_{mon}/S_{BET}. On the other hand, q_{mon}/V_{micro} for phenol always decreases with V_{micro} (i.e., T_A), indicating that the adsorption of phenols is not completely restricted to occur within the micropores. However, the decrease in q_{mon} for phenols at high T_A obviously means that the adsorption mostly occur within the micropores of the adsorbents. Considering the two factors of the yield and adsorption capacity (Wu et al., 1999b), it was actually found that the activated carbons prepared from plum kernels at $T_A = 900$°C are preferred to high-MW solutes (>300), and the ones prepared at $T_A = 850$°C are more suitable to low-MW solutes (<120).

Under the ranges studied, the solution pH changes from 6.1 to 8.14 for phenol and 6.6 to 7.7 for 4-chlorophenol before and after adsorption. This means that they exist mostly as undissociated forms in water

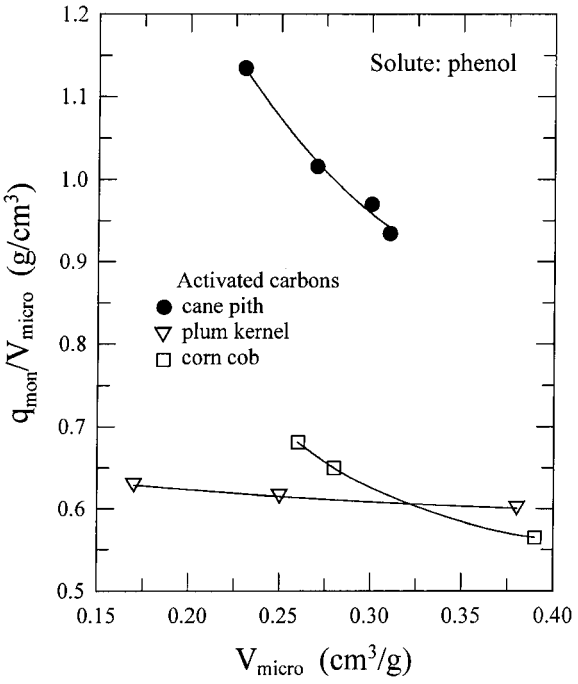

Figure 7. Adsorption capacity per unit micropore volume (q_{mon}/V_{micro}) of phenol at 30°C on the activated carbons prepared from various agricultural wastes.

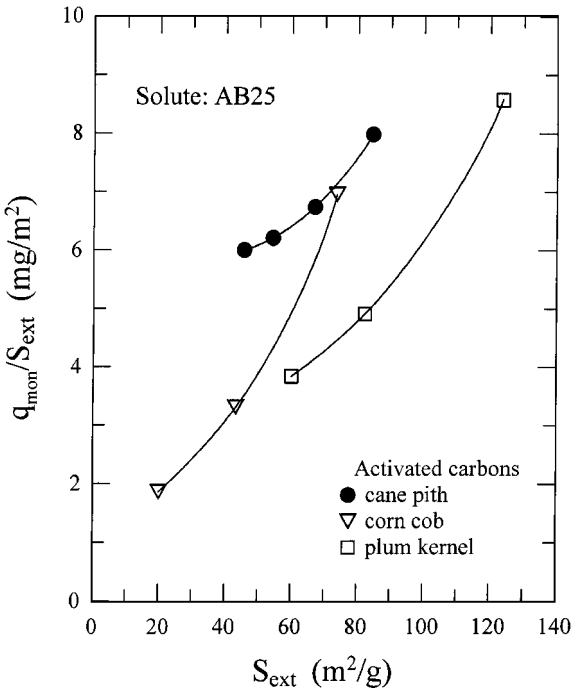

Figure 8. Adsorption capacity per unit external surface area (q_{mon}/S_{ext}) of dye AB25 at 30°C on the activated carbons prepared from various agricultural wastes.

during adsorption because phenol and 4-chlorophenol have a pK_a of 9.92 and 9.43, respectively (Grant and King, 1990). The electrostatic repulsive interaction between phenols and the carbon would be insignificant although the present activated carbon has a point of zero charge of near 6.2. The chemisorption (Langmuir) nature likely due to hydrogen-binding between the hydroxyl groups of phenols and the functional groups on carbon surfaces such as carboxylic can explain the contribution of external surfaces (Figueiredo et al., 1999).

Conclusions

Physical properties of the steam-activated carbons prepared from cane piths have been evaluated. The amounts of adsorption of dyes BR22, AB25, phenol, and 4-chlorophenol on such activated carbons were also measured at 30°C. Increasing activation temperature (T_A) led to an increase in BET surface area (S_{BET}), external surface area (S_{ext}), total pore volume (V_{pore}), and micropore volume (V_{micro}). The increment of micropores was less than that of meso-/macropores with increasing T_A. All isotherm data were well fitted by the Langmuir equation under the ranges studied (Table 2). A much lower T_A was required for the present carbons to achieve equivalent performance, compared to those prepared from other sources.

The unfavorable adsorption of phenols on the carbons prepared at sufficiently high T_A was dominantly due to their small MW and partly to the interactions between phenols and the functional groups on carbon surfaces. However, the trends of (q_{mon}/V_{micro}) for phenols against T_A indicated that the adsorption mostly, rather than completely, occurred within the micropores of the adsorbents. The chemisorption (Langmuir) nature possibly due to hydrogen-binding between the hydroxy groups of phenols and the functional groups such as carboxylic on the carbon surfaces could explain the contribution of external surfaces.

Nomenclature

C_0	initial solute concentration in the aqueous phase (g/m^3)
C_e	equilibrium solute concentration in the aqueous phase (g/m^3)
K	Langmuir parameter defined in Eq. (2) (m^3/g)
q_e	amount of adsorption at equilibrium (g/kg)
q_{mon}	adsorption capacity (g/kg)
r^2	correlation coefficient
S_{BET}	BET specific surface area of the adsorbent (m^2/g)
S_{ext}	external surface area of the adsorbent (m^2/g)
S_{micro}	surface area of adsorbent due to micropores (m^2/g)
T_A	activation temperature for preparation of activated carbons (°C)
V	volume of the solution (m^3)
V_{ext}	macro- and mesopore volume of the adsorbent (cm^3/g)
V_{micro}	micropore volume of the adsorbent (cm^3/g)
V_{pore}	total pore volume of the adsorbent (cm^3/g)
W	amount of dry adsorbent used (kg)

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