COMPARISON OF AQUEOUS PHASE INDICES FOR POWDERED ACTIVATED CARBON TO PORE SIZE DISTRIBUTION MEASURED VIA GAS ADSORPTION

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Abstract - The adsorptive capacity of powdered activated carbon (PAC) is related to the size of the target adsorbate compared with the quantity of pores with sufficient pore diameter into which the adsorbate may diffuse (i.e., the effective internal surface area). The adsorptive capacity of PACs are commonly characterized using aqueous-phase indices such as iodine (I_2), methylene blue (MB), *p*-nitrophenol (PNP), molasses, and tannin. PACs may also be characterized using gas adsorption with nitrogen to develop detailed pore size distribution information. This paper describes the characterization of the internal porous nature of 12 PACs used in water treatment using both aqueous- and gaseous-phase methods. The results showed that the internal surface areas of PACs tended to be ordered: wood>bituminous coal>lignite coal. The results showed that the bituminous and lignite carbons had a majority of their internal pores in the microporous range (<20Å) whereas wood-based carbons tended to have a much wider pore size distribution well into the mesoporous range. The results showed that the molasses and tannin numbers correlated well with the total pore volume of pores greater than about 11Å. The MB and I_2 numbers correlated well with total surface area if the micropores below 11Å also were included.

INTRODUCTION

Powdered activated carbon (PAC) is often used in water treatment plants to remove a wide variety of organic chemicals of varied molecular weights and sizes such as synthetic organic chemicals (SOCs), taste and odor compounds such as methylisoborneol (MIB) and geosmin, and natural organic matter such as humic acid and fulvic acid (Lee *et al.*, 1981). PACs are manufactured from source materials including bituminous coal, lignite coal, wood, coconut shells, peat, petroleum residue, bones, fruit seeds, and other sources (Greg and Sing, 1982). Due to the use of various source materials, and the common use of activation methods specific to each material, activated carbons may have different internal pore structures consisting of micropores (<20Å), mesopores (20-500Å), and macropores (>500 Å). Depending on the size of a target adsorbate molecule relative to the smallest pores, only a portion of a PAC's total surface area or pore volume may be available for adsorption.

PACs may be characterized experimentally using gas-phase and aqueous-phase methods. Gas-phase methods are particularly useful in characterizing the pore size distribution of a PAC as a function of surface area or pore volume because nitrogen molecules can move into very small pores, and are relatively inert with respect to interaction with the chemical functional groups on the surface of the carbon. More commonly used methods of PAC characterization, however, are the standardized adsorption tests with *p*-nitrophenol (PNP), iodine (I_2), methylene blue (MB), molasses, and tannin as sorbate surrogates (Hassler, 1951; Galbraith *et al.*, 1958; Kasaoka *et al.*, 1989b). There is a fundamental question, however, regarding what pore sizes are being characterized by each standardized aqueous index.

In this study, we examined 12 PACs commonly used in the water treatment industry using gas-phase and common aqueous-phase techniques. These data were then compared statistically to assess the correlations between each parameter. This information is useful for understanding the utility of commonly used indices, and may provide the basis for improving the specification and selection approach used by water utilities to choose a PAC for specific water treatment objective.

Gas Adsorption Characterization Methods

Gas adsorption is a standard method used to characterize the internal surface area and structure of porous materials. Different adsorbate gases that have been used to characterize adsorbents include nitrogen, carbon dioxide, krypton and argon (Gregg and Sing, 1982; Webb and Orr, 1997). Nitrogen is the most common adsorbate gas used to characterize surfaces because it is relatively inert and interacts with the adsorbent surface primarily through a mechanism of physical adsorption at liquid nitrogen temperatures (77 K).

The data from the gas adsorption measurements can be used to determine the surface area using the BET method, the mesopore volume using the BJH method, and the micropore volume using the HK method. The *density functional theory (DFT)* method is used to develop pore size distributions based on statistical thermodynamics and is one of the newer models used to analyze gas adsorption data (Ravikovitch *et al*., 1998). When a gas is introduced into a pore space, the gas molecules experience an attractive force (van der Waal's forces) by the adsorbent's surface, which results in a higher average density of gas near the surface during equilibrium. To calculate the pore size distribution, it is necessary to develop a model for pore filling which relates the pore width to the condensation pressure. Most theories related to isotherms tend to take a relatively macroscopic approach and may not be able to accurately predict the isotherms across their entire region. The DFT method takes a more microscopic approach and is based on statistical thermodynamics, taking the fluid-fluid and fluid-solid interactions into account as well as pore size, geometry and temperature.. Several researchers have used this model in their analyses for pore size distributions of microporous materials (Lastoskie *et al.*, 1993; Ravikovitch *et al*. 1998; Krupa and Cannon, 1996).

Aqueous Indices

Another way to characterize the pore structure of activated carbon is the adsorption of molecule out of aqueous solution (Galbraith, et al., 1958, Chern and Huang, 1998, Kasaoka *et al,.* 1989a, Kasaoka *et al.,* 1989b, Krupa and Cannon, 1996, Linares-Solano *et al.*, 1984, Pelekani and Snoeyink, 2000, Pelekani and Snoeyink, 2001). These methods of characterization often use PNP, I_2, MB, molasses, and tannin. These methods are especially appropriate to characterize PACs because they specifically involve the aqueous-phase adsorption of sorbates from solution. The specific methods are described below.

EXPERIMENTAL

Materials

In this study, the adsorption of PNP, I_2, MB, molasses and tannin from their aqueous solutions on twelve different PACs was determined. The PACs were from source materials including bituminous coal, lignite coal and wood. Two different batches of Hydrodarco B were included in this research to study the variability of activated carbon as provided by the manufacturer. These replicate batches produced excellent reproducibility. The twelve activated carbons studied are shown in Table 1. Table 2 contains information about each liquid phase adsorbate. In the table the critical dimension (i.e., second largest dimension) are those reported in the literature (Linares-Solano et al., 1984) or calculated using the MacSpartan 3-D modeling software (Ver. 1.1, Wavefunction Inc., Irvine, CA, USA).

Table 1. Powdered activated carbons (PACs) examined in study.

Name of PAC	*Symbol*	Manufacturer	*Carbon source*	Reported I_2 Number (mg/g)	Reported Molasses Number	Reported Tannin Number (mg of PAC/L)
WPL Pulverized	WPL	Calgon[1]	Bituminous coal			
WPH Pulverized	WPH	Calgon[1]	Bituminous coal			
PWA Pulverized	PWA	Calgon[1]	Bituminous coal	900 min	210 min	
Colorsorb GP	COL	Calgon[1]	Wood	900 min	550	
Centaur Powder	CEN	Calgon[1]	Bituminous coal	800 min		
PAC 20 B	20B	NORIT[2]	Bituminous coal	900	200	360-400
HDW	HDW	NORIT[2]	Lignite coal	530		350
Hydrodarco B (Batchs 1091 and 135-10C)	HD-A	NORIT[2]	Lignite coal	560	450-650	200
Watercarb PAC	WAT	Acticarb[3]	Wood Bark	600		
Nuchar SA-20	N-SA	Westvaco[4]	Hard wood	900 min		225
Nuchar SA	N-20	Westvaco[4]	Hard wood	900 min		225

[1] Calgon Carbon Corp., Pittsburgh, PA
[2] NORIT Americas Inc., Atlanta, GA
[3] Acticarb, Inc., Dunnellon, FL
[4] Westvaco Chemical Division, Westvaco Corp., Covington, VA

Table 2. Data regarding the molecular weight and size for the adsorbates.

Compounds		M.W.	Dimensions	Critical Dimension (Å)	Average Critical Pore Dimension (Å) ††
Nitrogen		28	-	3†	-
p-Nitrophenol		139	7.6 x 5 x 1.9*	4.6†	8
Methylene Blue		320	16 x 8.4 x 4.7	8.4	15.2
Iodine		254	7 x 4.4 x 4.4	4.4	< 14.8
Tannic Acid		1701	26.8 x 24.8 x 13.2*	24.8	-
Molasses **		Mixture	-	-	-
Sucrose	35%	342	11.8 x 7.1 x 6.4*	7.1	-
Glucose	7 %	156	8.9 x 5.4 x 4.5*	5.4	-
Fructose	9 %	156	9.8 x 4.1 x 3.3*	4.1	-
Water	20 %	18	2.3 x 1.6 x 1.2*	1.6	-
Ash (K_2O, SiO_2, etc)	12 %	~64-94	Ex: SiO_2 4.3 x 2.6 x 2.6*	2.6	-

* The dimensions of molecule and the critical dimension calculated using MacSpartan
** The general composition molasses, which is a mixture of several compounds, is given.
† From (Linares-Solano et al, 1984)
†† From (Kasaoka et al, 1989b)

Gas Adsorption

In the nitrogen adsorption tests, the samples were analyzed using static volumetric technique for nitrogen adsorption with the Quantachrome Autosorb-1C gas sorption apparatus. In the method, PAC samples are dosed with nitrogen at 77K to attain pressure equilibrium points during adsorption and desorption cycles to generate isotherms. The adsorption isotherm data are analyzed by a variety of techniques.

Liquid Phase Adsorption

The PNP capacity was determined for all the PAC samples using the procedure based on Hassler (1963), Linares-Solano *et al.* (1984), and Krupa and Cannon (1996). In this method, the PNP capacity is determined for a specific residual PNP concentration (100 mg/L) from isotherm data.

The iodine number was determined for all the PAC samples using the standard method (ASTM D4607-94, 1994) with five different masses of activated carbon instead of the three required by the standard method. The I_2 number is determined as the amount of I_2 adsorbed per mass of PAC at a residual I_2 concentration of 0.02 N from a log-log plot ($0.95<R^2<0.99$).

The MB number is the adsorptive capacity corresponding to the residual concentration of 100 mg/L of MB (Galbraith *et al.*, 1958; Linares-Solano *et al.*, 1984; Krupa and Cannon, 1996). A MB capacity was determined for all the PAC samples following two different methods. The first method involved developing an adsorption isotherm similar to the PNP method. The second method was developed by Hassler (1963) who proposed that a “single point” adsorption gives quantitative information for the MB adsorptive capacity of carbon as long as the amount of carbon added results in the removal of 60-99 percent of the initial dye. The method is reasonable since in the adsorption isotherm, there is a relatively flat region where the amount adsorbed is not a strong function of the final equilibrium concentration.

The molasses number was determined for all PACs following the standard procedure (EPA 625/1-71-002a, 1973). The molasses number is different from the other standard indices in that the decolorization capacity of a carbon is compared to that of a given standard carbon with “known” molasses number.

The tannin number was determined for all the PAC samples using the AWWA Standard for Powdered Activated Carbon (AWWA, 1996a). The tannin number is different from the other tests mentioned above in the fact that a higher tannin number value for a PAC signifies a lower tannin adsorptive capacity for the PAC. The tannin number denotes the concentration of PAC needed to achieve a certain amount of tannin removal. Thus a lower concentration of carbon with greater capacity is required to reach a desired final tannin concentration.

RESULTS AND DISCUSSION

For each PAC studied, two sets of gas adsorption data were generated. The first set, generated from atmospheric pressure nitrogen isotherms ($0.025<P/P_0<0.998$), was used to calculate BJH, BET, and DFT results. The second set, generated from low pressure nitrogen isotherms ($2(10^{-6}) <P/P_0<0.12$), was used to calculate the HK results.

The BET results show that there are significant differences ($\alpha=0.05$) between the BET surface areas for wood-, bituminous-coal-, and lignite-coal-based PACs (excluding WAT) which were 1615(±39), 902(±255), and 449(±104) m^2/g, respectively. Sorial *et al.* (1993) also noted that the lignite carbons had much lower BET surface areas than either bituminous carbon or wood-based carbons. Sorial *et al.* (1993) did not, however, observe significantly greater BET surface areas for wood-based versus bituminous-coal-based carbon.

The density functional theory (DFT) results (as used in this study) characterize the surface area for pores between 4 and 59Å (thus including both micro- and meso-porous ranges). The results correlate relatively well with the BET surface area results (r=0.88), and indicate that the average DFT surface areas were ordered: wood>bituminous carbon>lignite carbon.

Micropore analyses

The HK volumes represent the microporous nature of activated carbons. Comparison of the total pore volume (mesopores plus micropores) with the HK pore volume indicates the relative amount of micropores. It was found that 43-44 percent of the pore volume is as micropores for the wood- and lignite-coal carbons. Based on HK pore volume for the bituminous-coal carbon, however, the micropores account for 75 percent of the combined mesopore and micropore pore volume.

Aqueous indices

Activated carbon capacities for small molecules are frequently characterized by use of the PNP, I_2 and MB methods, while capacities for large molecules are often characterized by the molasses and tannin methods (AWWA, 1996b). For the PNP sorption, it was found that bituminous carbon and wood-base carbon had significantly greater capacities than lignite carbons (α=0.05). For the I_2 number results, bituminous carbon and wood-based carbons also had significantly greater capacities than for lignite coal. The WAT bark-based carbon had a similar I_2 number to the lignite coal carbon. The PNP and I_2 results agree with the gas adsorption results in that the bituminous and wood-based carbons tend to have much greater microporous structure than the lignite carbons.

MB capacities determined using the isotherm methods versus the Hassler method correlated very well (r=0.992). Thus, these data provide justification for the use of the much-quicker and easier Hassler method versus the isotherm method. While the average MB values were ordered wood>bituminous coal>lignite coal, the differences were not significant (α=0.05).

The molasses and tannin number results showed that wood-based carbons (excluding bark) exhibit a greater capacity for these compounds than bituminous or lignite carbons. This result is consistent with the fact that the wood-based carbons tend to have greater mesoporous nature than coal-based carbons.

DFT Analysis

The DFT surface area is computed for pores from 4 to 59Å, that is, on the order of the size of smaller molecules. The DFT surface area correlations with molasses and tannin are weaker than correlations with smaller molecule indices (PNP, I_2, and MB) even though the DFT characterizes the lower range of the mesopore sizes. The correlation coefficient with DFT is weaker for the larger molecules because the DFT does not account for pores greater than 59 Å. It should be noted that the DFT method can be expanded to much larger pore diameters than it was applied in this study.

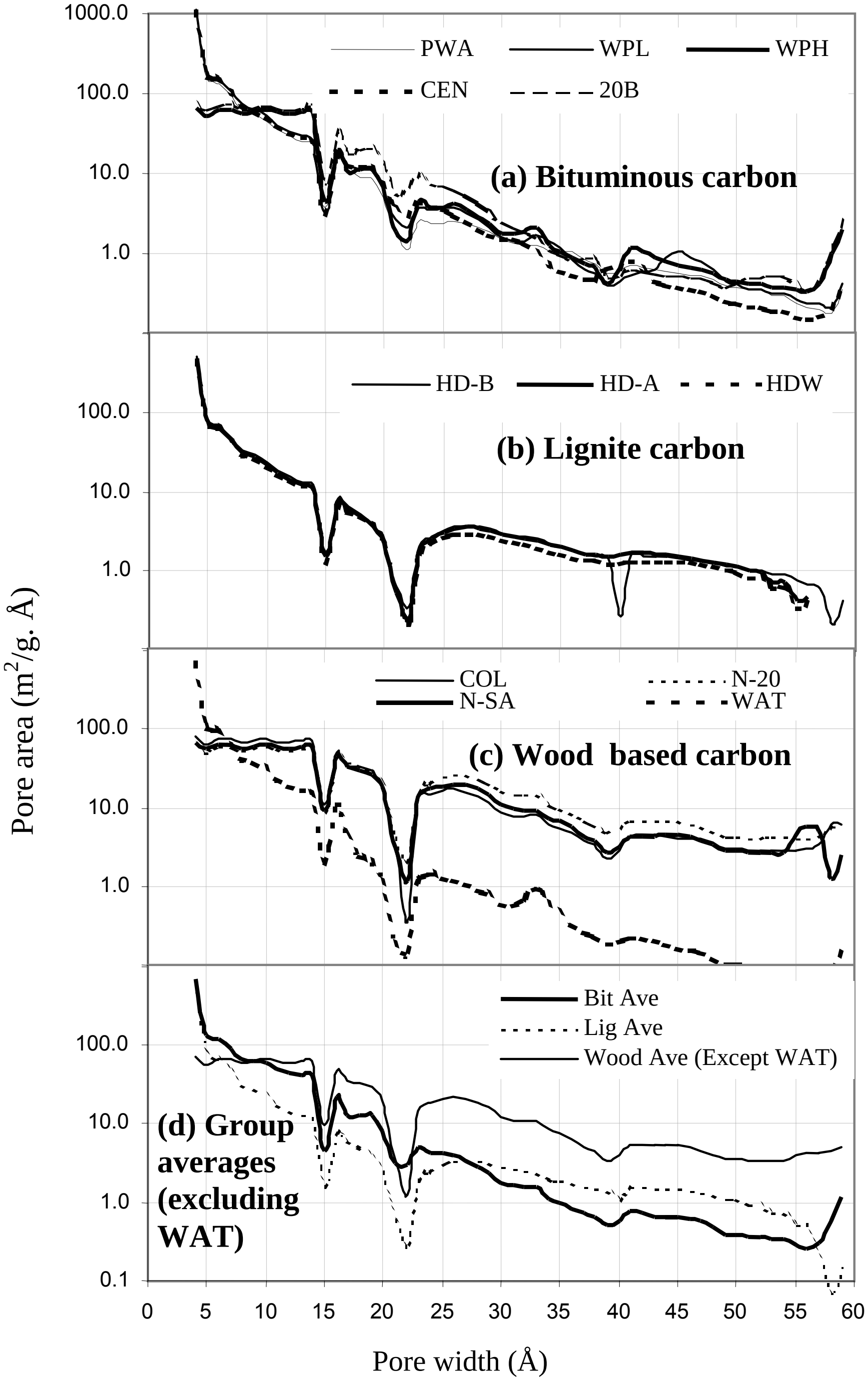

Figure 1. DFT pore size distribution based on surface area for 12 PACs grouped by: (a) bituminous carbon, (b) lignite carbon, (c) wood-based carbon, and (d) group average values

The pore size distributions based on surface areas were determined for the 12 PACs using the DFT method (Figure 1). The cumulative surface area was calculated from these data and plotted in Figure 2. These data show an interesting anomaly with very few pores being indicated at both 15 and 22Å. Similar anomalies have also been noted by other researchers studying six GACs (Krupa and Cannon, 1996). Because it is unlikely that there are no or few pores at these two distinct diameters, it has been suggested that the anomalies are a function of the DFT model itself. Krupa and Cannon (1996) suggested that the cause may be related to: 1)difficulties of the model transitioning from 1 to 2 molecular layers, 2) the model presumption of a single adsorption energy, or 3) both.

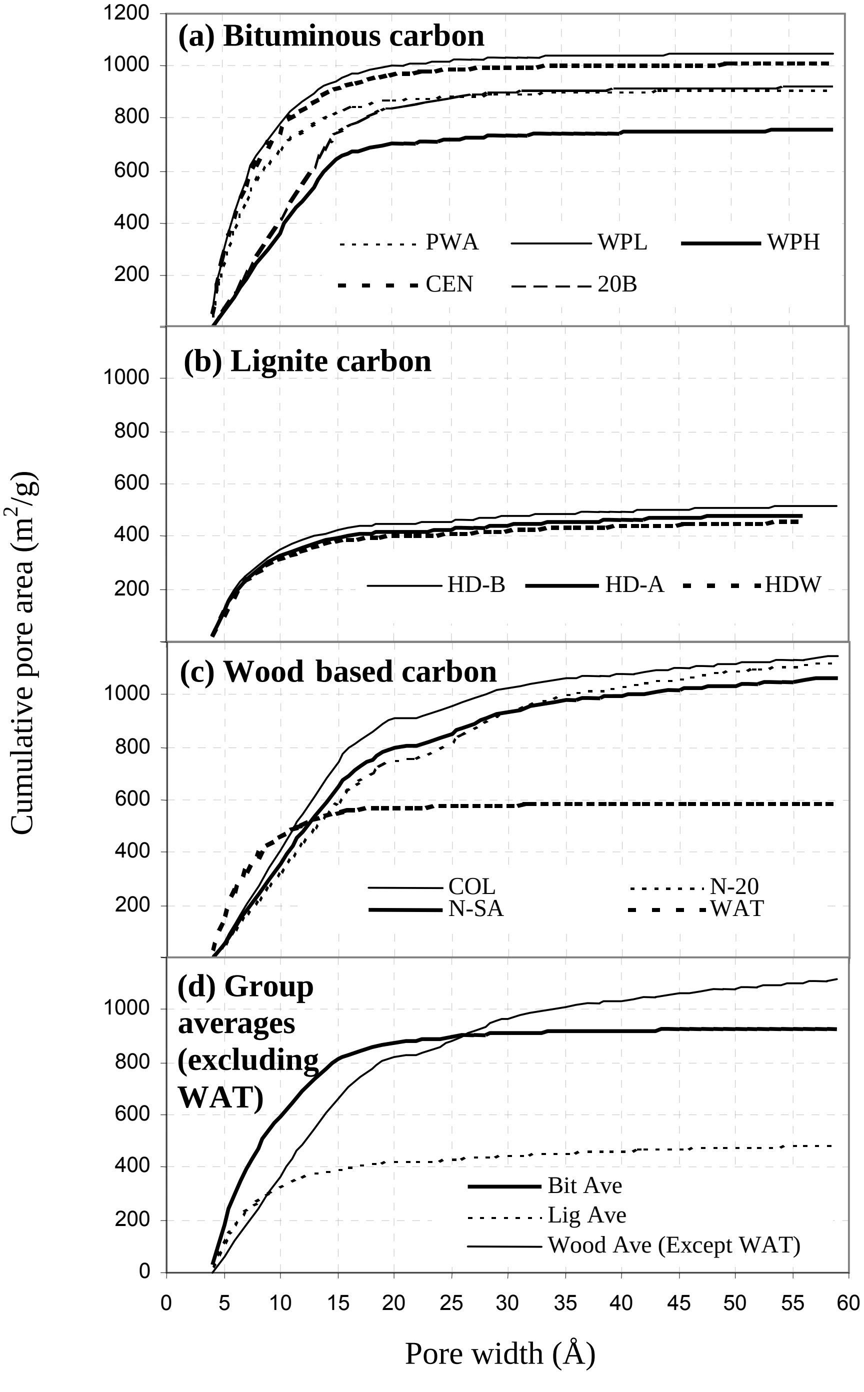

Figure 2. Cumulative DFT pore size distribution based on surface area for 12 PACs groups by: (a) bituminous carbon, (b) lignite carbon, (c) wood-based carbon, and (d) group average values.

These data show that each bituminous carbon has very similar pore size distributions except below 15Å where CEN and WPL had significantly greater pore surface area below 7 Å than PWA, 20B and WPH (Figure 1). Each of the lignite and each of the wood-based carbons (with the exception of WAT) also have very similar pore size distributions.

Based on DFT model data, bituminous and lignite carbons have a majority of their porous structure (> 95%) in the microporous range. The wood-based carbon (excluding bark), however, have a much broader range of pore sizes contributing to the cumulative pore surface area (Figure 2). Overall, these data show that the average cumulative pore area ranged from 750-1050, 450-510, and 1050-1150 m^2/g for bituminous, lignite, and wood-based carbons (excluding bark), respectively. The cumulative pore area for WAT was 590 m^2/g. These results are consistent with work by Salame and Bandosz (2000) who stated that coal-based carbons (as well as petroleum pitch and coconut shell carbons) tend to be highly microporous in nature, and that wood-based carbons tend to be mesoporous in nature.

The pore size distribution determined from the gas adsorption data can be used to further elucidate the relationship between pore structure and standard aqueous indices. The pore size distributions were used to calculate the total pore area for a given range of pore diameters for each carbon (i.e., between the given pore diameter and 59Å) which was then correlated with the five aqueous indices. The correlation coefficients for this analysis were plotted versus pore diameter (Figure 3) for each of the twelve carbons. In the case of the tannin number, the inverse of the tannin number was used in the correlations. The data shows that the larger molecule indices (molasses and tannin) correlated better than the smaller molecules (PNP, I_2, and MB) everywhere except when the extremely small pore diameters were included (i.e., <9Å for I_2 and MB, and <6Å for PNP).

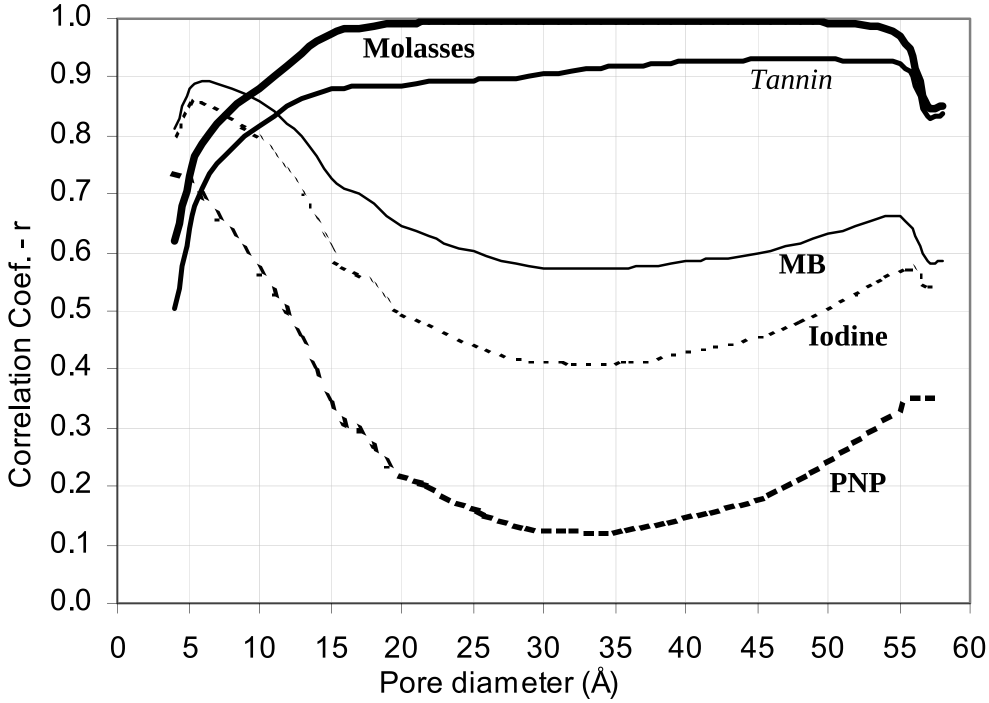

Figure 3. Correlation coefficient between the standard indices and the total pore surface area greater than the pore diameter plotted on the x- axis and <59 Å.

The correlation coefficients for molasses and tannin decreased as smaller pore diameters were included in the cumulative surface area summation. The reason for these observations is because the larger tannin molecule and the absorbing impurity in molasses cannot readily diffuse into these smaller pores.

Overall, the results of this study show that the commonly used I_2 and MB numbers are fairly good predictors of the volume of micropores plus mesopores within a PAC. Similarly, the molasses correlated well with the volume of mesopores within a PAC (with the tannin number correlating less well). Thus, it is proposed that the molasses-to-iodine ratio (MIR) (MIR = (molasses #) / (iodine #)) is a useful parameter for characterizing the pore size distribution of a PAC using aqueous indices. In Figure 4, MIR is plotted from each PAC versus BET-N_2 surface area (top) and versus the iodine number (bottom). It may be seen that PACs from each carbon source (bituminous coal, lignite coal, and wood (excluding bark)) are tightly grouped with respect to their overall surface area and their MIR. A small MIR (e.g. <0.5) corresponds to a more microporous carbon such as the bituminous carbons examined in this study (Figure 4). A larger MIR (e.g. >0.7) corresponds to a wider pore size distribution including significant mesoporous nature such as with the wood-based carbons in this study (excluding bark). The MIR may be a useful parameter for characterizing the pore size distribution of PACs to assist in the proper selection of a PAC for a specific application. (Alternatively, the inverse tannin-to-iodine ratio (ITIR) (ITIR = 1/ (tannin #)$\cdot$(iodine #)) may also provide similar information. Additional common PACs for which iodine and molasses or tannin number were also plotted in Figure 4 with designated source material. These data show clear grouping and/or trends based on source material. For example, bituminous coal has a consistent MIR on nominally 0.2 (indicating strong microporous nature) and a range iodine numbers (indicative of total surface area). Lignite carbons, however, have a fairly uniform iodine number (corresponding to total surface area) and range of MIR showing some variability in the degree of mesoporous character. The wood-based carbons tended to have a high iodine number (i.e., total surface areas) with a fairly mesoporous nature (high MIR).

While different raw materials are used to make PAC, the choice of source material in large measure dictates the producer's activation method. The progression of carbon reduction in nature under high temperature and pressure is (in order): wood, peat, lignite coal, bituminous coal, anthracite, graphite, and diamond. Thus, lignite coal contains greater volatile organics (and ash) than bituminous coal. Lignite coal may, therefore, be directly activated at high temperature (i.e., establishment of extensive micro- and mesopores). Bituminous coal, on the other hand, is generally processed via a reagglomeration process involving crushing, mixing with a volatile (i.e., coat tar pitch), heat/pressure treated into briquettes, crushed, and finally activated at high temperatures. Wood-based carbons are usually treated one of two ways: 1) steam activation, or 2) phosphoric acid treatment to dissolve cellulosic structure followed by high temperature activation (e.g. 500°C). The results of this study have demonstrated that the type of source material, and the associated activation method, results in an activated carbon with a distinct total pore volume and pore-size-distribution.

Finally, the chemical character of the carbon surface is affected by many parameters including source material, activation time, temperature, cooling rate and environment, and other parameters (Karanfil and Kilduff, 1999; Karanfil *et al.*, 1999). The surface properties (e.g., degree of oxidation) can have a profound effect on both the adsorption of both target contaminants as well as the aqueous indices themselves. Thus, jar testing still plays an important role in selection and optimization of the use of PAC in water treatment applications.

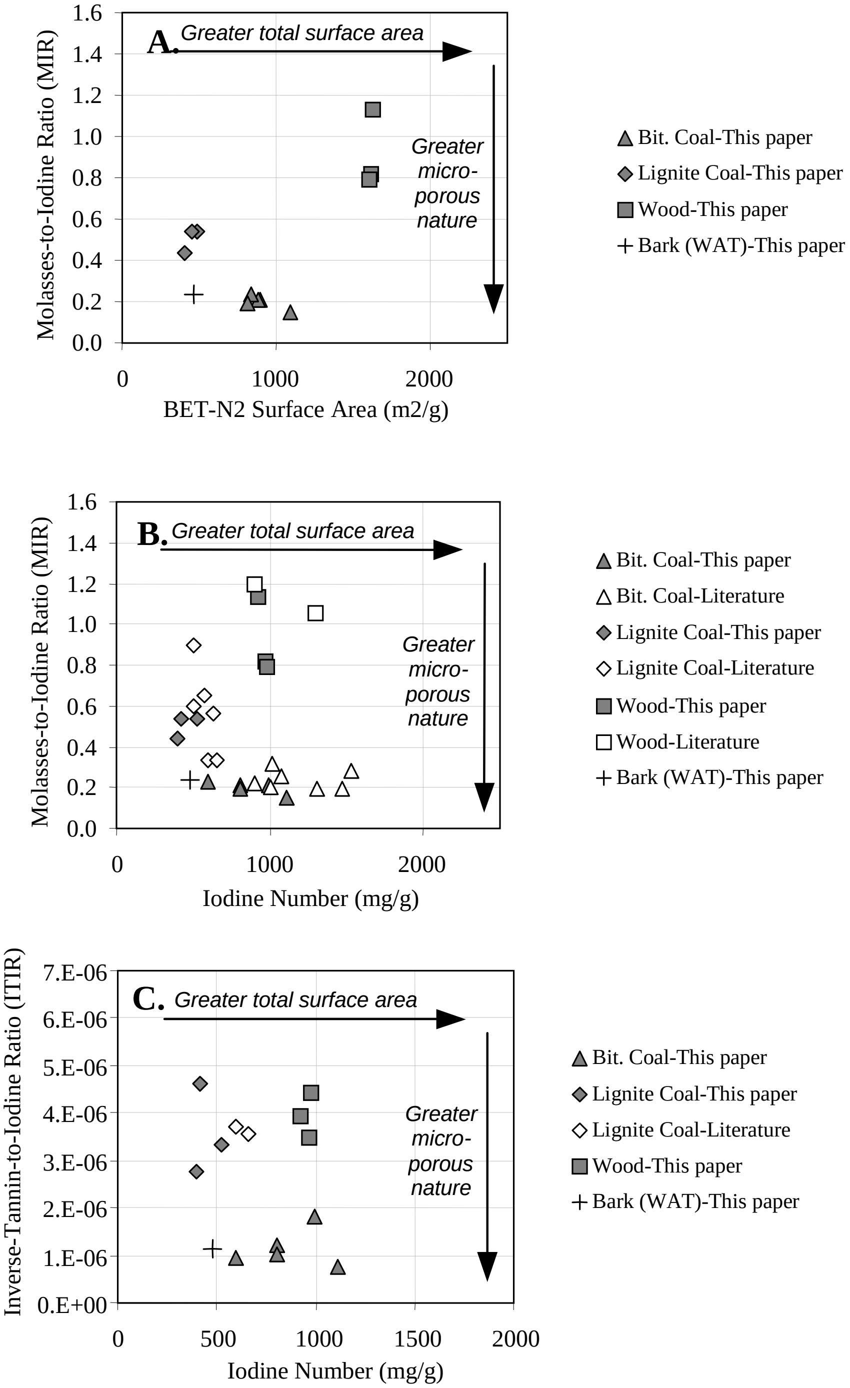

Figure 4. For 12 study PACs and additional PACs from literature references, the Molasses-to-Iodine Ratio (MIR) is plotted versus BET-N_2 Surface area (A (top)) and versus Iodine number (B (middle)). In the bottom plot (C), the Inverse-Tannin-to-Iodine Ratio (ITIR) is plotted versus iodine number.

CONCLUSIONS

To enhance the effectiveness of PAC application in water treatment plants, the intraporous nature of a PAC should be considered in the selection process. This study has shown that:

o I_2 and MB numbers are effective at characterizing total pore volume (and surface areas) of PACs

o Molasses and tannin numbers are effective at characterizing mesopore volume (and surface areas) of PACs

o The source material of a PAC may have a significant effect on its resulting porous nature

o The MIR is a useful means of characterizing the pore size distribution of PACs using aqueous indices.

Ongoing research is examining the implications of these results, and the relationship to surface function groups, for specific synthetic and natural organic chemicals in distilled and in natural water matrices.

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