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Analysis of the Pore Structure of Activated Carbons Produced from Paper Mill Sludge Using Small Angle Neutron Scattering Data

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DISCLAIMER

ANALYSIS OF THE PORE STRUCTURE OF ACTIVATED CARBONS PRODUCED FROM PAPER MILL SLUDGE USING SMALL ANGLE NEUTRON SCATTERING DATA

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ABSTRACT

A novel, cost-effective, and environmentally benign process was developed to produce highly efficient carbon-based adsorbents (CBAs) from paper mill sludge. The production process required chemical activation of sludge using zinc chloride and pyrolysis at 750°C in N_2 gas. The produced CBAs were characterized according to their surface area and pore size distribution using N_2-BET adsorption isotherm data. Further characterization of the surface and pore structure was conducted using a unified exponential/power law approach applied to small angle neutron scattering (SANS) data. The structural features analyzed by SANS revealed the dependence of porosity with zinc chloride concentration. The presence of inaccessible pores was also determined by contrast-match experiments.

KEYWORDS: SANS, carbon-based adsorbents, paper mill sludge, porosity.

INTRODUCTION

A series of novel carbon-based adsorbents (CBAs) are produced from paper mill sludge. The significant feature of the produced sludge-based activated carbon, that makes it a unique and particularly economical adsorbent/catalyst/catalyst support, is that waste materials are used for its production. Although the produced CBAs can be extensively used as adsorbents, catalysts and catalyst supports in a variety of industrial and environmental applications (i.e., purification processes, recovery of chemical products, and removal of organic and metals), their adsorption capability and catalytic activity are largely controlled by their surface characteristics [1,2]. For example, carbons used for the adsorption of gases and vapors should include pores with effective radii considerably smaller than 16-20 Å [2], while activated carbons with developed transitional porosity in the range of 20-500 Å have been shown to be significant adsorbents for removal of coloring impurities from liquid phase systems [3]. The existing relationship between the surface properties of activated carbon and its effectiveness as adsorbent or catalyst, emphasize the importance of developing methodologies by which activated carbons with specified surface properties could be produced.

Analysis of the surface physical properties of the produced carbons initially included determination of the total surface area, extent of microporosity, and characterization of the pore size distribution using nitrogen adsorption isotherms data [2, 3, 4]. While the results of the surface analysis have shown that activation methodology used to produce novel CBAs has a significant impact on the surface structure and performance of the produced carbons, these data were not sufficient to draw definite conclusions about the extent of correlation between the carbon's microporous structure and the employed activation methodology. Therefore, SANS data was used to supplement existing analysis and provide valuable information about the microscopic structures of the produced carbons such as; produced pore distribution, pore width, pore radii, characteristic lengths, and voids. The information provided by SANS therefore was used to: a) calculate fractal dimension, carbon radii, and cutoff length of the carbon clusters, b) identify the role of porosity given the complexity of the system, c) identify the distribution of the pores and the distribution of the pores that are not available to adsorption, and d) identify the characteristics of the pores (if they are closed or can be filled by liquid).

This information was fundamental for characterization of the pores and evaluation of the extent of availability of the pores to the adsorbates in the gas and/or liquid phase environments. The employed method of analysis for SANS data used an unified power law exponential model similar to one proposed by Beaucage et al. [5, 6].

EXPERIMENTAL

Raw sludge was first dried in an oven at 110°C for 24 hours, then crushed mechanically using a paint-mixing machine. Crushing provided smaller particles with increased surface area and also enabled more efficient chemical activation of the raw material. Samples were sieved after mechanical crushing to obtain particle sizes smaller than 600 μm. This particle size range was found to be the most suitable for the chemical activation process that was performed using six different $ZnCl_2$ to dried sludge mass ratios of 0.75 (M90), 1 (M92), 1.5 (M93), 2 (M94), and 2.5 (M91). To ensure a complete reaction between $ZnCl_2$ and sludge particles, sludge was mixed with zinc chloride at 85°C for 7 hours. After chemical activation, samples were dried at 110°C for 24-36 hours. The time required for drying varied depending on the amount of zinc chloride used for the activation process (i.e., higher impregnation ratios required longer drying time). After drying, the sludge was crushed again into a fine powder. Chemically activated samples were exposed to light and humidity for about 22 hours to enhance development of the pore structure during pyrolysis [7].

Pyrolysis of the chemically activated and L&H-treated sludge was carried out in an inert environment (70ml/min flow of nitrogen gas) at 800°C for two hours. Upon completion of the pyrolysis, the sample was removed from the reactor and crushed using a mortal and a pestle. Pyrolysis was followed by rinsing using 500 ml of 1.2 M HCl, and 500 mL of distilled water to remove excess zinc chloride and residual inorganic matter. Upon drying, samples were transferred to 20-mL vials for storage prior to conducting the physical activation process. During the physical activation, samples were heated for two hours at 800 °C in a mixture of 75% of CO and 25% of CO_2. Upon completion of the physical activation, the produced carbons were characterized according to their surface properties.

For the SANS measurements the carbons were ground to a powder prior to loading in the sample containers. SANS of dry powders of carbons in Suprasil cells (pathlength = 1 mm) were measured at the time-of-flight SANS instrument, SAD at the Intense Pulsed Neutron Source at Argonne National Laboratory [8]. SAD uses neutrons from a solid CH_4 moderator at 24 K with a wavelength of 0.5 to 14 Å, binned into 67 wavelength channels with 5 % wavelength spread in each channel. The scattered neutrons are detected by a 20 x 20 cm^2 ^3He area detector with 64 x 64 spatial channels. This instrument provides data in a q range of 0.005-0.35 $Å^{-1}$ in a single measurement. For contrast-variation SANS study, carbons were measured as slurries in toluene (0, 25, 50, 75 and 100 % d-toluene) in 1mm pathlength Suprasil cells. For the slurries, the powders were slowly evacuated to avoid air bubble formation prior to adding the solvent. The scattering from an empty cell was used for background correction for the powder samples, and the corresponding solvent of appropriate volume not occupied by the carbon was used as the background for the samples soaked in the solvent. All other routine corrections [9] were carried out prior to the analysis.

RESULTS AND DISCUSSION

The results of the 2-layer unified fit [5,6] indicate that at the lowest Q scale behavior for all of the carbon samples in air is that of surface-fractal interfaces of large objects with the exception of the M90 sample, where the behavior is that of a smooth interface (figure 1 and table 1). The high–Q power-law behavior of the M91, M93, and M94 samples is similar and consistent with a mass-fractal dimension of about 2.5.

The M90 sample at high Q shows a 1.33 mass fractal dimension with a very large range of applicability (120 Rg is too large for satisfactory accuracy) while the high Q behavior of the M92 sample appears to be rodlike. The visibility of these features is enhanced by subtracting the low-Q power law from the data and fitting the residuals with Teixeira and cylinder

models as appropriate (see figure 2 and table 2). Beaucage and coworkers [10] have observed similar behavior in silica systems.

The same approach was used in the M91 in toluene series (figure 3 and table 3). The low-Q power law of the M91 sample in 100% D-toluene was that of a mass fractal while all of the other samples had surface-fractal power-laws. Similarly, while the other four samples were well described by the Teixeira mass fractal model at high Q, the sample in 100% D-toluene is far better modeled as an essentially hollow spherical shell. An interpretation of this phenomenon can be seen as follows: the mass fractals seeing in this sample are ornamenting a smooth surface of a carbon with a scattering length density in bulk very similar to that of D-toluene. Since the D-toluene is a relatively large molecule, it is unable to penetrate the dendrites of the mass fractals. However, in a dendritic mass fractal structure, like those produced by diffusion limited aggregation, the core is more dense than the periphery, with a density approaching the bulk density. Thus, when the scattering length density of the surrounding medium is less than the scattering length density of the mass-fractals, only the mass fractal behavior is seen, but when it approaches that of the core, only the scattering from the void-shell between the solvent and the core is observed. Therefore, what we are seeing in the 100% D-toluene sample is a mass fractal composed of the polydisperse void-shells rather than the surface fractal due to the ornamentation of the mass-fractal aggregates of carbon clusters as seen in air.

CONCLUSIONS

The result of SANS analysis showed that the microstructure of the CBAs produced from paper mill sludge varies according to the method of activation. As shown in figures and tables 1 to 3, the Guinier parameter I_o at high Q values increases with increasing the amount of zinc chloride used for the production of carbons. With exponential parameter being constant, the length scale increases with the addition of zinc chloride at low Q, however, its value decreases for the same carbons at high Q values. The estimated fractal dimension and cutoff length presented a positive correlation with the amount of activating agent used for the production of the carbons. The Teixeira mass fractal presented suitable fit for M90, M91, M93, and M94 carbons. Data obtained for M92, however, fitted to the fractal model assuming a cylindrical form factor. The results of the SANS analysis for slurry of carbons in Toluene (at 0 to 75%) supported the results of shape analysis conducted for powder study and supported Teixeira mass fractal fit for M91 sample.

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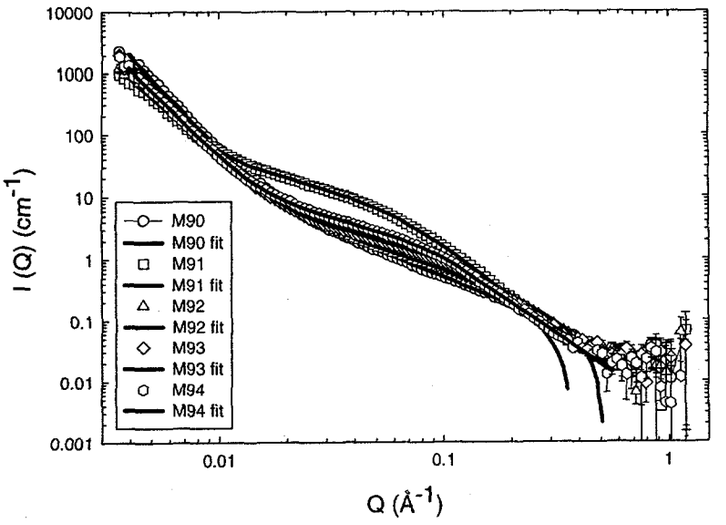

Figure 1: SANS plot of CBAs activated with different ratios of $ZnCl_2$ to sludge. M90: 0.75/1, M91: 2.5/1, M92: 1/1, M93: 1.5/1, M94: 2/1.

Table I: Results of the 2-layer unified fit [5,6] for the samples shown in figure 1.

	Low Q data				High Q data			
Sample	Guinier I_0	Guinier Rg (Å)	Length Scale (Å)	Exp.	Guinier I_0	Guinier Rg (Å)	Length Scale (Å)	Exp.
M90	Fixed	Fixed	37.96	4.02	16.04	121	15.74	1.34
M91	Fixed	Fixed	37.26	3.52	25.35	54.3	8.43	2.62
M92	Fixed	Fixed	33.56	3.46	4.11	55.3	12.58	1.16
M93	Fixed	Fixed	35.21	3.59	3.95	34.0	9.82	2.34
M94	Fixed	Fixed	37.22	3.70	6.73	40.5	9.70	2.49

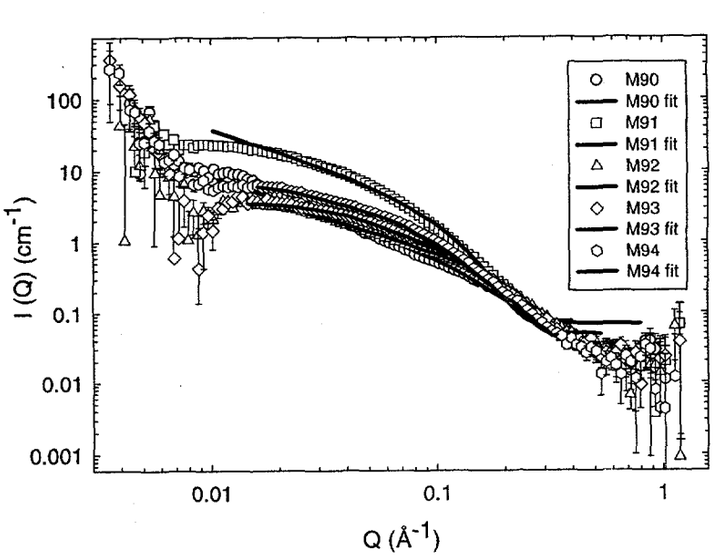

Figure 2: Resulting SANS plots after subtraction of the low Q power law from the plots of figure 1.

Table II: Results of the Teixeira sphere mass fractal fit to the samples shown in figure 2.

Sample	Scale factor	Sphere radius (Å)	Fractal dimension	Cutoff Length (Å)
M90	0.0353	2.15	1.37	NA
M91	0.0280	2.62	2.50	23.4
M92*	NA	NA	NA	NA
M93	0.0228	2.18	2.18	15.6
M94	0.00941	2.36	2.36	17.2

* Fitted to cylindrical form factor; scale factor = 4.42; r = 7.84 Å; L = 179.6 Å.

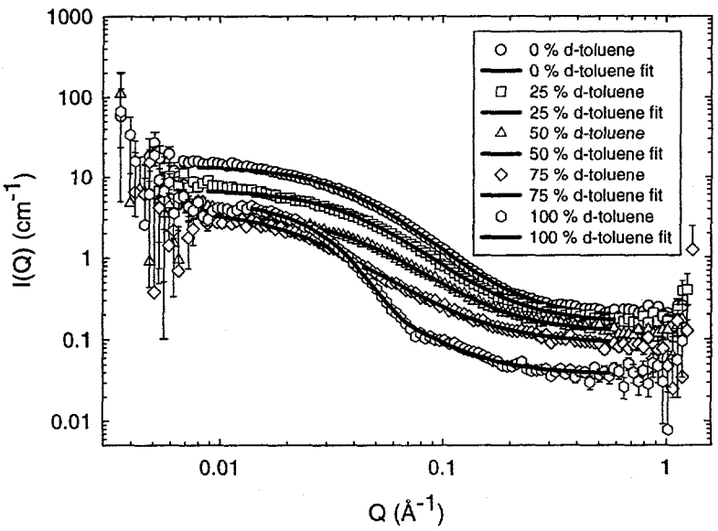

Figure 3: SANS plots of sample M90 in different percentages of d-toluene.

Table III: Results of the Teixeira sphere mass fractal fit to the samples shown in figure 3.

Sample M91 in	Scale factor	Sphere radius (Å)	Fractal dimension	Cutoff Length (Å)
0 % d-toluene	0.0217	2.61	2.42	23.6
25 % d-toluene	0.0144	2.57	2.35	22.6
50 % d-toluene	0.00894	2.56	2.26	23.1
75 % d-toluene	0.00533	2.60	2.03	46.5
100 % d-toluene*	NA	NA	NA	NA

* Fitted to polydisperse core spherical shell; scale factor = 5.15; core radius = 36.2 Å; thickness = 5.324 Å.