

# The Specific Surfaces of Peat and Wood

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## Synopsis

The specific surface areas of various particle size ranges of wood and peat were determined. The methods employed are mercury porosimetry, nitrogen adsorption, and solution isotherms. The results indicate that dye solution isotherms offer an accurate means of surface area measurement, however, the values obtained are dependent on (a) the chemical nature of the solute and adsorbent and (b) the molecular dimensions of the solute. Nitrogen isotherms indicate specific surfaces of  $(21 \times 10^3)$ – $(27 \times 10^3)$   $\text{m}^2 \text{kg}^{-1}$  for wood depending on the particle size, while an area of  $26.5 \times 10^3$   $\text{m}^2 \text{kg}^{-1}$  was obtained for peat independent of particle size. Acid dye isotherms yield specific surfaces considerably lower than nitrogen isotherm values; for wood  $(7.3 \times 10^3)$ – $(9.6 \times 10^3)$   $\text{m}^2 \text{kg}^{-1}$  and for peat,  $(5.2 \times 10^3)$ – $(11.8 \times 10^3)$   $\text{m}^2 \text{kg}^{-1}$ . Basic dye studies, using wood, indicate surface areas similar in magnitude to those obtained from nitrogen isotherms. For peat, however, very large apparent surface areas are obtained ( $\sim 100 \times 10^3$   $\text{m}^2 \text{kg}^{-1}$ ) and are attributed to chemical interaction between dye molecules and adsorbent and stacking of dye molecules.

## INTRODUCTION

Adsorption is a physiochemical wastewater treatment process which is gaining prominence as a means of producing quality effluents which are low in concentrations of dissolved organics. Dissolved molecules are attracted to the surface of the adsorbent by physical-chemical processes. The important characteristics of an adsorbent must be expressed both in terms of adsorptive characteristics and physical properties. In order to design commercial treatment systems accurately, mass transfer coefficients are necessary, and these are generally stated in terms of the surface area of the adsorbent.

Activated carbon is the most widely used, and presently the most effective adsorbent for treatment of aqueous solutions<sup>1–8</sup> and the better grades of powdered carbons for decolorizing wastewaters are made from lignin and lignite.<sup>9</sup> The ability of silica<sup>10–13</sup> and alumina<sup>14–17</sup> in wastewater treatment processes have been extensively reviewed. Many studies<sup>18–22</sup> have been undertaken to measure the specific surfaces of activated carbons, silica, and alumina, and the mechanism of adsorption has been reported for gas- and liquid-phase adsorbates.

The adsorbents mentioned so far are quite expensive and a number of investigations have been undertaken to determine if any cheap commercially available materials hold promise for waste treatment and purification. The suitability of peat and wood as natural adsorbents was recognized some time ago. The use of peat as an adsorbent for wastewater treatment has received only limited study. The range of experiments using peat involve the purification of slaughterhouse wastewater,<sup>23,24</sup> the removal of phosphates and organics from wastewater,<sup>25</sup> and the removal of metal ions from effluents involving an ion exchange mechanism.<sup>26</sup> Peat has been ammoniated using a fluidized bed technique, yielding a "modified" peat with an enhanced cation exchange capacity<sup>27</sup> employed for the removal of heavy metal ions. A number of projects involving peat have been evolved re-

cently for treating spills<sup>28,29</sup> and for color removal from dyehouse effluents.<sup>30-32</sup> Spruce wood is found abundantly throughout the world, and the cost is only a fraction of the previous adsorbent materials. The treatment of textile mill wastes has been studied<sup>33,34</sup> for the removal of various dyes, and a number of investigations using chemically treated wood<sup>35-37</sup> have been successful for color removal.

The potential of peat and wood in waste treatment operations seems substantial; and to aid the design of commercial plant, a knowledge of the specific surfaces is necessary. Several methods of determining surface area and pore size distribution are available, e.g., high-pressure mercury porosimetry,<sup>38</sup> the use of nitrogen<sup>39</sup> and benzene<sup>40</sup> isotherms, and dye solution adsorption isotherm.<sup>18,21</sup> Solution isotherms have been found to give reliable results, providing the solute satisfies a number of requirements: (1) high polarity; (2) partly hydrophobic; (3) small molecular dimensions; (4) not surface active; (5) colored; (6) readily soluble. The influence of some of these conditions is commented on in the discussion section.

A number of methods for surface area determination are discussed with reference to wood and peat since very little information is available in the literature regarding such data. A value for the specific surface of peat using iodine adsorption has been quoted<sup>24</sup> as  $220 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ , but these workers failed to obtain any successful gas isotherm measurements. The aim of the present paper is to compare the surface areas obtained from a number of techniques and comment on the merits of the various methods.

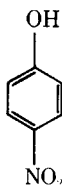
## EXPERIMENTAL

### Adsorbents

The wood shavings were of the spruce wood type, and no form of pretreatment was applied except for sieving into various particle size ranges. The peat moss was dried for 30 min at 80°C prior to sieving and allowed to equilibrate in the air.

### Solutes

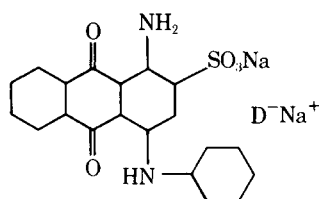
*p*-Nitrophenol was recrystallized from water.



(a) *p*-nitrophenol

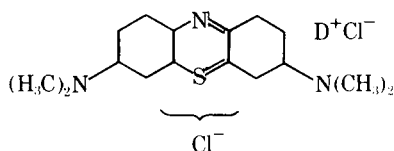
The acid dye Telon Blue was prepared by extraction from the commercial salt.<sup>41</sup> Extractions were carried out using ethanol-water mixtures (50:50, v/v) and dried at 105°C until consecutive apparent molar extinction coefficients were achieved, and it was assumed that all inorganic salts had been removed. The calculated compositions for C<sub>20</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub>SNa is C = 57.69%, N = 6.73%, and H

= 3.12%; the composition found by analysis is C = 57.45%, N = 6.70%, and H = 3.30%.



anionic dye — Telon Blue (CI 62,055)

Methylene Blue was pure analar material supplied by B. D. H. The calculated composition for  $C_{16}H_{18}N_3SCl \cdot 3H_2O$  is C = 51.47%, N = 11.24%, and H = 6.43%; the composition found by analysis is C = 51.50%, N = 11.18%, and H = 6.49%.



cationic dye — Methylene Blue B (CI 52,015)

### Analysis

*p*-Nitrophenol was determined using an Optica spectrophotometer at 400 nm after being buffered with a drop of sodium hydroxide.

Telon Blue was determined by the spectrophotometer at 600 nm and Methylene Blue, at 585 nm.

All experiments were undertaken at  $20 \pm 2^\circ\text{C}$ , and contact time tests were carried out to establish the time required to reach equilibrium, at the concentration ranges under investigation. The isotherms were then measured at times in excess of the equilibrium contact times. The specific surfaces of the adsorbents were determined by applying the data to the Langmuir and Freundlich equations and considering coverage factors and orientations of the dye molecules on the adsorbent surfaces.

### DISCUSSION

A number of methods of determining the surface area of wood and peat are considered. The effective surface area has been calculated assuming the particles to be spherical, i.e., surface area =  $4\pi r^2$ , where  $r$  = particle radius. The results for peat and wood are given in Tables I and II, respectively.

### Mercury Porosimetry

High-pressure mercury porosimetry may be used to estimate the pore size distribution, pore volume, and surface area. The total pore volume,  $\Sigma V_p$ , is obtained from the following equation and given in Table III:

$$\Sigma V_p = \frac{\pi r^2 H^1}{W} \text{ cm}^3 \text{ g}^{-1} \quad (1)$$

TABLE I  
Surface Areas of Peat by Various Techniques

Particle size, microns	Surface area, m <sup>2</sup> /g				
	Sphere (×10 <sup>3</sup> )	Mercury porosimeter	Methylene Blue	Telon Blue	Nitrogen adsorption
150-250	24.8	2.62	122.2	11.8	27.3
250-355	16.4	2.52	113.6	8.7	26.6
355-500	11.6	2.47	104.0	7.8	26.6
500-710	8.2	2.40	88.9	6.7	26.5
710-1000	5.8	2.33	77.5	5.2	26.5

TABLE II  
Surface Areas of Wood by Various Techniques

Particle size, microns	Surface area, m <sup>2</sup> /g				
	Sphere (×10 <sup>3</sup> )	Mercury porosimeter	Methylene Blue	Telon Blue	Nitrogen adsorption
150-250	25.4	1.39	24.9	9.6	28.7
250-355	16.8	1.37	24.4	8.8	25.2
355-500	11.9	1.36	23.4	7.8	22.3
500-710	8.4	1.34	22.5	7.6	22.0
710-1000	5.9	1.32	22.0	7.3	19.0

TABLE III  
Pore Volume Using the Mercury Porosimeter

Particle size, microns	Pore volume, (m <sup>3</sup> /g) × 10 <sup>6</sup>	
	Peat	Wood
150-250	1.25	1.03
250-355	1.02	0.90
355-500	0.84	0.81
500-710	0.71	0.65
710-1000	0.60	0.53

where  $r$  = dilatometer radius (cm),  $H^1$  = compression in dilatometer limb (cm Hg), and  $W$  = sample weight (g).

The surface area may be calculated using incremental evaluation of the pore size distribution, and the results for peat and wood are shown in Tables I and II. It should be noted that the method assumes the pore are cylindrical. An additional limitation is the area of the mercury molecule, 90 Å<sup>2</sup>, and thus mercury will not penetrate much of the microporous structure of the particles. This limitation is verified by the low surface areas obtained using mercury porosimetry. The specific surface for wood is constant for different particle size ranges, while for peat a slight decrease in area is observed with increasing particle size, indicating that the mercury is unable to diffuse to the center of the larger particles.

### Nitrogen Isotherms

Surface area determinations were carried out by low-temperature ( $-196^{\circ}\text{C}$ ) nitrogen adsorption after the method of Brunauer, Emmett, and Teller.<sup>42</sup> The adsorbent particles were degassed for 4 hr at  $110^{\circ}\text{C}$  before nitrogen was observed. The BET equation was used in the form

$$\frac{P}{V_E(P_0 - P)} = \frac{1}{V_M B} + \frac{(B - 1)P}{V_M B P_0} \quad (2)$$

where  $V_E$  is the volume of gas adsorbed at equilibrium pressure ( $\text{cm}^3$ ),  $P_0$  is the saturation vapour pressure of adsorbate (mm Hg),  $V_M$  is the volume of gas contained in the monolayer ( $\text{cm}^3$ ), and  $B$  is a constant related to the heats of adsorption and liquefaction of the gas.

Hence, from a plot of  $P/[V_E(P_0 - P)]$  against  $P/P_0$ , a line of slope  $(B - 1)/V_M B$  and intercept  $1/V_M B$  was obtained. The values of  $V_M$  were determined for the various size ranges and the specific surface area (S.S.A.) was calculated from the equation

$$\text{S.S.A.} = \frac{V_M N A}{V_g} \quad (3)$$

where  $A = 16.2 \text{ \AA}^2$ , the cross-sectional area of the nitrogen molecule;  $N =$  the Avogadro number,  $6.019 \times 10^{23}$  molecules/mole; and  $V_g = 22.4$  l, the molar gas volume. The specific surfaces calculated by this method are listed in Tables I and II and give a larger surface area for physical adsorption than the mercury porosimetry method due to (1) the smaller size of adsorbent molecule enabling it to diffuse into smaller pores and (2) the high-temperature degassing which would remove moisture from adsorbed sites. The trend of decreasing surface area with increasing particle size is apparent with wood and indicates the high microporosity of wood particles. The peat surface areas give a more consistently fixed value.

The areas obtained by gas adsorption are more than a factor of 10 greater than the areas obtained by mercury porosimetry in all instances, and there must be a large number of pores with openings in the range of 14 to  $90 \text{ \AA}^2$ . The two studies so far have been performed on dried samples and therefore are comparable in this sense. The remaining experiments are methods using solution isotherms, and therefore since both adsorbents swell in water it will make a comparison of methods difficult. This swelling phenomenon, while normally making the external surface area larger, may lead to a blocking of internal pores due to the expansion of fibers inside the bulk particle making intraparticle diffusion difficult.

### Acid Dye Isotherms

Several successful methods of determining surface area have been evolved using *p*-nitrophenol. However, there was a slight reaction between the dye and both adsorbents, which resulted in a discoloration (dark yellow) of the solution. The yellow discoloration was probably due to humic and fulvic acids which masked the extent of adsorption of *p*-nitrophenol, yielding "apparent" surface areas from 5 to  $50 \text{ m}^2 \text{ g}^{-1}$ . Attempts to extract the acids with sodium hydroxide and sodium sulfite failed to yield any consistent data. Consequently, a second

acidic dye was used, namely, Telon Blue, and the adsorption system was successful. The specific surface area (S.S.A.) may be calculated from the following formula for any dye adsorption system:

$$\text{S.S.A.} = \frac{x_M N A F}{M C} \quad (4)$$

where  $x_M$  = monolayer coverage, (g dye/g adsorbent),  $M$  = molecular weight of pure dye,  $A$  = surface area per molecule ( $\text{m}^2$ ),  $F$  = fraction pure dye in commercial dyestuff salt, and  $C$  = coverage factor.<sup>21</sup> The coverage factor is defined as the theoretical area of the dye molecule orientated flat, divided by the apparent area when adsorbed.

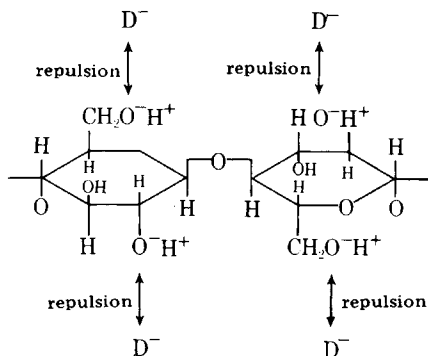
When values of  $\log C$  obtained from tests with many dyes and substrates were plotted against  $\log$  weight of the color ion of the respective dyes, a linear relationship was established<sup>43</sup>:

$$\log_{10} C = 1.2 \times 10^{-7} W^{2.93} \quad (5)$$

where  $W$  = the weight of color ion of the dye, which for Telon Blue is 393. From eq. (5) the coverage factor is 2.8, and assuming the dye molecules are adsorbed flatwise the molecular area is  $143 \text{ \AA}^2$ . Equation (3) was used to determine the specific surfaces of wood and peat, and the results are given in Tables I and II.

A series of contact time experiments were performed to establish the time required to reach saturation for Telon Blue. A constant initial dye concentration of 100 ppm was selected as being typical of dyehouse effluent concentrations, and the particle size range of peat was varied. Equilibrium was reached after approximately 2 hr for wood and 4 hr for peat. Consequently, wood isotherms were allowed 4 hr to equilibrate and peat isotherms, 8 hr. The adsorption isotherms for the acid dye on wood and peat are shown in Figures 1 and 2, respectively.

The surface areas obtained using acid dye isotherms are significantly lower than those derived from nitrogen adsorption studies. The structure of wood is cellulose based, and the surface of cellulose in contact with water is negatively charged.<sup>44</sup> The approach of an acidic dye molecule to cellulose is shown in the following scheme:



The low surface areas are probably due to Coulombic repulsion between the dye anion and the negatively charged cellulose. A further feature is noted by comparing the ratio of the monolayer coverages of nitrogen and Telon Blue on

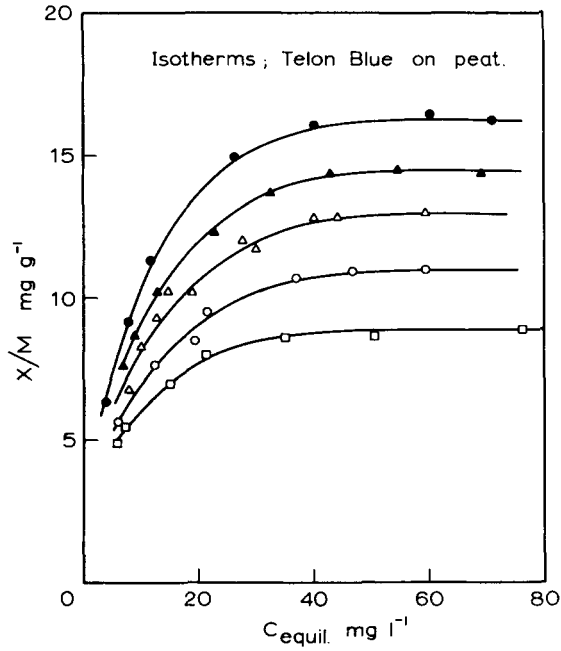


Fig. 1. Adsorption of Telon Blue on peat. Pore size: (●) 150–250  $\mu$ ; (▲) 250–355  $\mu$ ; (△) 355–500  $\mu$ ; (○) 500–710  $\mu$ ; (□) 710–1000  $\mu$ .

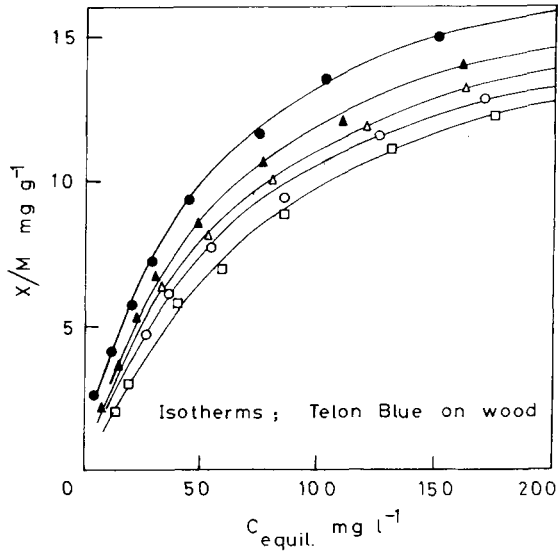


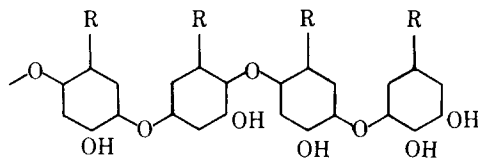
Fig. 2. Adsorption of Telon Blue on wood. Pore size: (●) 150–250  $\mu$ ; (▲) 250–355  $\mu$ ; (△) 355–500  $\mu$ ; (○) 500–710  $\mu$ ; (□) 710–1000  $\mu$ .

each adsorbent and the ratios are listed in Table IV. The average ratio of nitrogen to Telon Blue is 2.9 on wood and 3.5 for peat. The differences are mainly due to chemical composition, since peat will have a substantially greater negative potential well across the surface than wood due to phenolic hydroxylic groups and carboxylic acid groups, resulting in a strong repulsion of approaching anions.

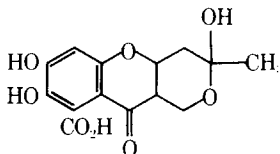
TABLE IV  
Relative Monolayer Coverages of Nitrogen: Dye on Peat and Wood

Particle size, microns	Relative monolayer coverages			
	N <sub>2</sub> :Telon Blue	N <sub>2</sub> :Methylene Blue	N <sub>2</sub> :Telon Blue	N <sub>2</sub> :Methylene Blue
150-250	2.3	0.22	3.0	1.1
250-355	3.0	0.23	2.9	1.0
355-500	3.4	0.26	2.9	0.95
500-710	4.0	0.30	2.9	0.98
710-1000	5.1	0.34	2.6	0.86

The main chemical constituents of peat are humic and fulvic acids. A general formula for each constituent is given below, illustrating the high concentration of anionic groups:

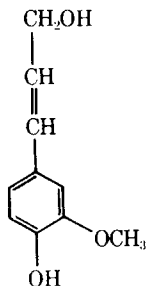


humic acid<sup>45</sup>



fulvic acid<sup>46</sup>

Another species present in considerable quantities in both wood and peat is lignin. For spruce wood the composition is likely to comprise up to 50% cellulose and 30%–35% lignin.<sup>47</sup> The lignins in spruce wood are mainly derived from coniferyl alcohol and have the following general formula:



The hydroxylic groups in lignin do not possess the same degree of activity as the phenolic and carboxylic groups in the humic and fulvic acids<sup>48</sup> present in peat, but nevertheless they will exert a considerable repulsive force on approaching anions.

The effect of isotherm shape has also been considered<sup>49</sup> with a view to predicting if an adsorption system is "favorable" or "unfavorable." The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter  $R$  which is defined by the following relationship:



$$R = \frac{1}{1 + aC_0} \quad (6)$$

The parameter indicates the isotherm shape accordingly:

$R$ Value	Type of isotherm
$R > 1$	unfavorable
$R = 1$	linear
$0 < R < 1$	favorable
$R = 0$	irreversible

The constant  $a$  is the constant from the Langmuir isotherm when expressed in the following way:

$$\frac{X}{M} = \frac{abC_e}{1 + aC_e} \quad (7)$$

where  $C_e$  is the experimental concentration of dye in the solution at equilibrium.

The values of  $R$  are given in Table V, and the results show that Telon Blue adsorption is favorable on both wood and peat, although complete monolayer coverage is not achieved.

### Basic Dye Isotherms

A series of isotherms were determined using Methylene Blue, and the plots are shown in Figures 3 and 4 for the different particle size ranges of wood and peat, respectively. The data were found to conform to the Langmuir<sup>50</sup> and Freundlich<sup>51</sup> equations over certain ranges of the adsorption process. The Freundlich constants  $K_F$  and  $n$  and the Langmuir constants  $Q_0$  and  $b$  are given in Tables VI and VII. The Langmuir constant  $Q_0$  corresponds to monolayer coverage for Methylene Blue, which has a coverage factor  $C = 1.95$  and a molecular area of  $120 \text{ \AA}^2$ , assuming the dye molecule adsorbs flat onto the surface.<sup>43</sup> The molecular weight of the dye was calculated to be 794, and the weight of the colored ion has been found by analysis<sup>43</sup> to be 284. The surface areas determined using Methylene Blue are significantly greater than those measured from Telon Blue isotherms for both wood and peat.

The specific surfaces of wood using Methylene Blue isotherms are very similar to the values obtained using nitrogen and the B.E.T. isotherms. The results are mainly independent of particle size, indicating that the porous nature of wood does not inhibit the diffusion of dye molecules into its internal pores any more than it does for nitrogen molecules for the larger wood particles. The short contact times (approximately 1 hr) required to reach equilibrium indicate the

TABLE V  
Equilibrium Parameter  $R_L$  for the Adsorption of Acid and Blue Dyes Onto Wood and Peat

Particle size, microns	Peat		Wood	
	Basic Blue	Acid Blue	Basic Blue	Acid Blue
	$69 C_0 =$ 200 mg/dm <sup>3</sup> $R_L$	$25 C_0 =$ 100 mg/dm <sup>3</sup> $R_L$	$69 C_0 =$ 200 mg/dm <sup>3</sup> $R_L$	$25 C_0 =$ 100 mg/dm <sup>3</sup> $R_L$
150-250	0.062	0.55	0.065	0.29
250-355	0.058	0.45	0.063	0.29
355-500	0.056	0.38	0.061	0.28
500-710	0.044	0.33	0.057	0.30
710-1000	0.083	0.29	0.054	0.29

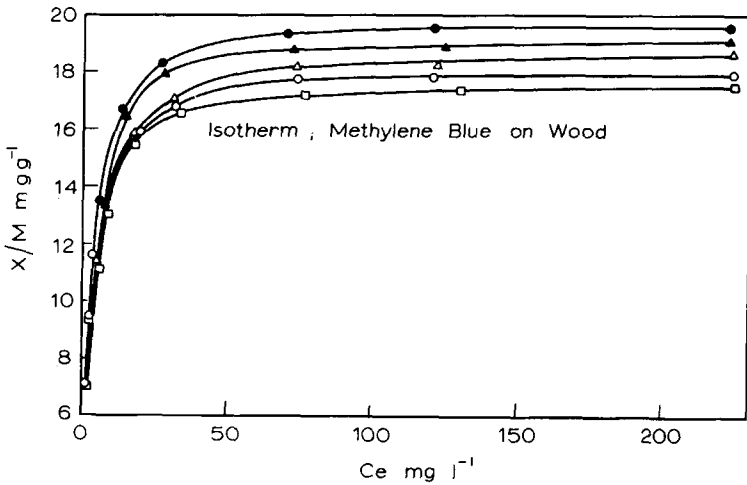


Fig. 3. Adsorption of Methylene Blue on wood. Pore size: (●) 150–250  $\mu$ ; (▲) 250–355  $\mu$ ; (△) 355–500  $\mu$ ; (○) 500–710  $\mu$ ; (□) 710–1000  $\mu$ .

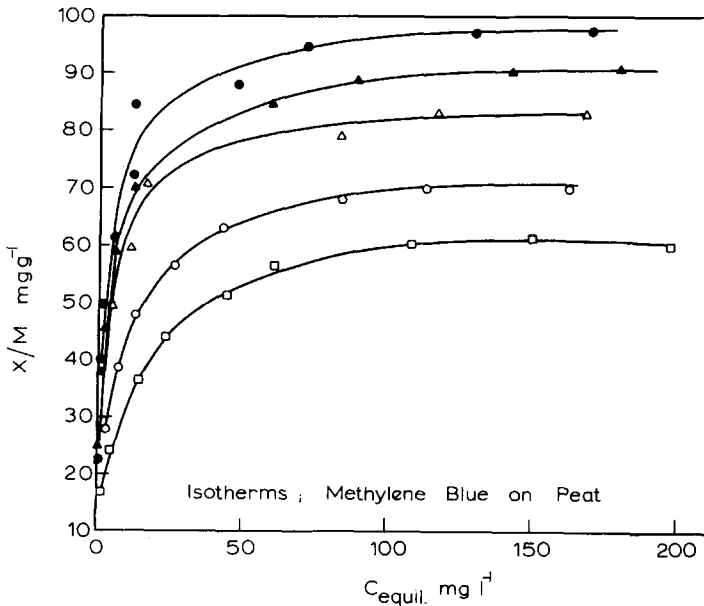


Fig. 4. Adsorption of Methylene Blue on peat. Pore size: (●) 150–250  $\mu$ ; (▲) 250–355  $\mu$ ; (△) 355–500  $\mu$ ; (○) 500–710  $\mu$ ; (□) 710–1000  $\mu$ .

affinity of anionic groups in the cellulose for the dye cations. The ratios of the monolayer coverages for nitrogen to Methylene Blue in Table IV indicate values close to unity for wood, showing that the cations adsorb flatwise onto the surface in a monolayer.

Very high monolayer ratios were obtained for peat due to strong cationic exchange between the dye ions and the acidic hydrogens in the carboxylic and phenolic hydroxyl groups. The strong bonds formed enabled multilayer adsorption to occur, but the different surface areas in Table I show a strong dependence on particle size. Therefore, although the monolayer ratios vary between 3 and 4, the number of layers adsorbed on the peat particle is uncertain.

TABLE VI  
Langmuir and Freundlich Parameters for Adsorption of Methylene Blue on Peat

Particle size, microns	Langmuir constants		Freundlich constants	
	$b$ , l/mg	$Q_0$ , mg/g	$n$ , g/l	$K_F$ , mg/g
150-250	0.34	96.1	9.3	54.9
250-355	0.34	89.3	7.2	47.5
355-500	0.32	81.8	6.9	41.2
500-710	0.18	69.9	4.2	25.3
710-1000	0.14	60.8	3.5	17.3

TABLE VII  
Langmuir and Freundlich Parameters for Adsorption of Methylene Blue on Wood

Particle size, microns	Langmuir constants		Freundlich constants	
	$b$ , l/mg	$Q_0$ , mg/g	$n$ , g/l	$K_F$ , mg/g
150-250	0.44	19.6	2.3	6.5
250-355	0.42	19.2	2.3	6.3
355-500	0.41	18.4	2.4	6.0
500-710	0.41	17.7	2.4	5.8
710-1000	0.41	17.3	2.5	5.7

The  $R$  values were determined for peat and wood and are listed in Table V, showing that Methylene Blue adsorption is "very favorable" on both materials.

Basic dye adsorption is predominantly a chemisorption process involving exchange sorption reactions with the hydroxylic groups in humic acid, fulvic acid, lignin, and cellulose; consequently, short contact times are required. Acid dye adsorption is probably a physical process with coulombic repulsion of the dye anions occurring, requiring longer contact times to reach equilibrium.

## SUMMARY

The specific surface areas of wood and peat were determined using a number of techniques. Under the experimental conditions employed, *p*-nitrophenol isotherms were unsuccessful. Mercury porosimeter measurements yielded low surface areas compared with nitrogen adsorption on the dry adsorbents, due to the immobility of mercury and the large area of the mercury molecule. Telon Blue solution isotherms yielded the surface areas available for physical adsorption which were lower than the nitrogen values, due to repulsion between the dye anions and the negatively charged cellulose and also due to the larger dye ion. Methylene Blue yielded the areas available for chemisorption, and the results suggested that a considerable amount of exchange adsorption was occurring.

The surface areas using nitrogen were the largest "physical" areas for adsorption since the nitrogen molecule was the smallest of the adsorbent molecular areas, thus enabling deeper penetration into the wood and peat micropores.

The adsorption mechanism involves adsorption across the boundary layer to the external sites, followed by intraparticle diffusion to the internal pores. In many cases the adsorption capacity increases with a decrease in particle size. This suggests that some of the surface area associated with pores inside the particle is being at least partially occluded due to the pore size distribution and that the effective adsorption regime is confined to the external surface and a narrow layer just below the surface.

## CONCLUSIONS

Solution isotherms offer an excellent means of determining specific surface areas of cellulosic materials with three limitations, namely: (a) the structure and chemical constitution of the adsorbent, (b) the chemical nature of the solute molecule, and (c) the molecular size of the solute ion.

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