

Conductance Measurement of Water-sorbed Activated Carbon

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RINGKASAN

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RINGKASAN

Kekonduksian sekeping karbon yang diaktifkan telah disukat semasa ia terendam dalam air pada lima suhu yang berlainan. Perubahan kekonduksian ini mengikut masa telah dianggapkan sebagai kesan pengionan kumpulan-kumpulan berfungsi pada dinding liang tatkala ia disebakki air. Jejari purata liang telah dianggarkan melalui persamaan-persamaan yang diterbitkan bagi mengaitkan perubahan ini dengan kadar pengaliran air ke dalam liang.

SUMMARY

The conductance of a piece of activated carbon has been measured while immersed under water at five different temperatures. The change in conductance with time has been attributed to the ionization of the functional groups on the walls of the pores as the latter were gradually filled. The average pore radius has been estimated by using the equations derived to relate the increase in the conductance to the rate of flow of water into the pores.

INTRODUCTION

A new technique for the preparation of activated carbon has been reported (Universiti Pertanian Malaysia, 1984). This new method may be used to produce fairly large pieces of activated carbon in contrast to the comparatively fine granules and powders prepared by current commercial processes. These large pieces are particularly valuable for determination of the physical properties of activated carbon. In this paper one such experiment is described.

Activated carbon is structurally different from graphite because of the presence of pores of various sizes. In the simplest way, activated carbon can be viewed as a cluster of graphite microcrystals separated by these pores. The diameters of the pores in the activated carbon which range from 2 nm to 1000 nm (Ponec *et al.*, 1974), are much larger than the interplaner spacing in graphite. Hence the pores act as barriers to the flow of electrons through the entire lattice of the microcrystals.

However the pores in activated carbon increase its surface area and make it an excellent adsorbant for many chemical species both in gaseous phase and in solution. In addition to the active centres due to unsaturation of the bonding orbitals of the carbon atoms at the surfaces and edges of the pores, it has been proposed that activated carbon also possesses almost all known organic functional groups lining up along the walls of the pores (Hassler, 1974). Some of these functional groups, such as carboxylic and phenolic, could dissociate to yield hydrogen ions in the presence of a solvent such as water. These ions could then act as charge carriers between the walls of the pores and, by doing so, would increase the conductance. The increase would continue as long as the sample is able to absorb more water until a maximum is reached when all the pores are completely filled.

The rate at which the conductance increases would then depend upon the rate at which the water was sorbed. Equations expressing the

rate of flow of water into a capillary have been given as

$$\frac{dh}{dt} = \frac{gr^2\rho}{8\eta} \left(\frac{h_f - h}{h} \right) \quad (1)$$

for a vertical capillary, and

$$\frac{d\ell}{dt} = \frac{\delta r}{4\eta} \frac{1}{\ell} \quad (2)$$

for a horizontal capillary (Bikerman, 1970). In these two equations, h and ℓ are the height and length of water column at time t ; ρ , δ and η are the density, surface tension and viscosity of water, respectively; g is the gravitational constant; r is the radius of the capillary and h_f is the final height of water.

Pores in the activated carbon can be likened to capillaries extending in all directions. If the rate of flow of water into the pores could also be described by (1) and (2), we could then relate the change in conductance to the gradual filling of the pores by water.

Whereas, for an ordinary conductor, the conductivity is proportional to the ratio of the cross-sectional area to the length, for the sorption conductor under study, the conductance is proportional to the product of the height of water column, h , and the cross-sectional area, A ; i.e.

$$(\sigma - \sigma_o) = khA \quad (3)$$

where σ is the conductance measured at time t , σ_o is the initial conductance and k is a proportionality constant. If the vertical flow of water in the capillary could be considered independent of the horizontal flow, differentiation of (3) would give

$$d\sigma = kh dA + kA dh \quad (4)$$

Equation (4) enables the contributions of the vertical and horizontal flow to the increase in the conductance of the sample to be considered separately.

The Horizontal Flow

Consider a piece of activated carbon of rectangular shape having surface area ($h \times p$) cm^2 and thickness b cm completely immersed in water. If the conductance is measured across its height, h , as in Fig. 1, any change observed would only

correspond to the measure of water, ℓ penetrating into the sample through the pores normal to the hp surface. The change occurs because the cross-sectional area, A , of the water column in the sample also changes. The conductance is independent of the height since h remains constant. At any time t , the cross-sectional area could be given as

$$A = 2p\ell + \ell(b-2\ell)$$

for small b ,

$$A = 2p\ell \quad (5)$$

$$\text{and } dA = 2p d\ell \quad (6)$$

As h remains constant, equation (4) becomes

$$d\sigma = kh dA \quad (7)$$

Integration of (7) would yield

$$(\sigma - \sigma_o) = khA \quad (8)$$

$$\text{and } (\sigma_f - \sigma_o) = khA_f \quad (9)$$

where σ_f is the final conductance value when the whole cross-sectional area has been covered by water, A_f . Substituting (5), (6), (7) and (8) into (2) would give

$$(\sigma - \sigma_o)d\sigma = (kh)^2(p^2) \frac{\delta r}{\eta} dt \quad (10)$$

On integration, (10) would give (11)

$$(\sigma - \sigma_o)^2 = 2(kh)^2(p^2) \frac{\delta r}{\eta} t \quad (11)$$

To eliminate kh , we use (9). Then

$$\left(\frac{\sigma - \sigma_o}{\sigma_f - \sigma_o} \right)^2 = \frac{2p^2}{A_f^2} \frac{\delta r}{\eta} t \quad (12)$$

The Vertical Flow

The flow of water into a vertical capillary is governed by equation (1). If the conductor is dipped in water such that the whole of its bp surface is at all times in contact with water, any change in conductance would be due to the rise of the water column through the vertical pores. Equation (4) then becomes

$$d\sigma = kA dh \quad (13)$$

By integration, (13) becomes (14) and (15)

$$(\sigma - \sigma_o) = kAh \quad (14)$$

$$(\sigma_f - \sigma_o) = kAh_f \quad (15)$$

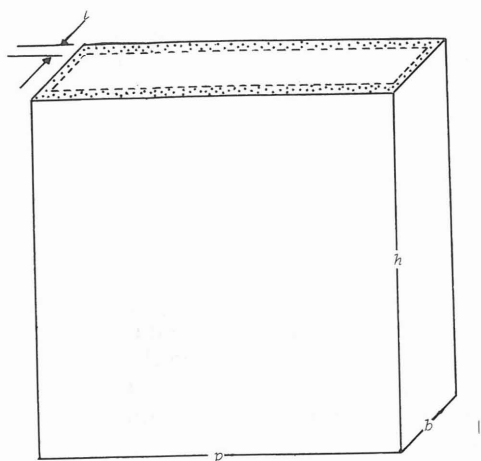


Fig. 1 Horizontal flow of water through capillaries into a rectangular slab of activated carbon.

Dotted area shows the surface covered at any time t . This area, A , is given as

$$A = 2(1 \times p) + 1(b - 2l)$$

which is approximated as $A \approx 2lp$.

where h_f is the final height of the column. Substituting (13) and (14) into (1) we would obtain

$$\frac{1}{kA} \frac{d\sigma}{dt} = \frac{gr^2\rho}{8\eta} \frac{(\sigma_f - \sigma)}{(\sigma - \sigma_o)} \quad (16)$$

and on integration

$$(\sigma_f - \sigma_o) \ln \left(\frac{\sigma_f - \sigma_o}{\sigma_f - \sigma} \right) - (\sigma - \sigma_o) = \frac{kA}{8\eta} \frac{gr^2\rho}{t} \quad (17)$$

Substituting kA from (15) and dividing through by $(\sigma_f - \sigma_o)$, (17) becomes (18)

$$\ln \left(\frac{\sigma_f - \sigma_o}{\sigma_f - \sigma} \right) - \left(\frac{\sigma - \sigma_o}{\sigma_f - \sigma_o} \right) = \frac{gr^2\rho}{8\eta h_f} t \quad (18)$$

Thus measurement of the conductance of the sample completely immersed in water would seem to lead to the possibility of evaluating the average pore radius, r , since all the other constants are known.

MATERIALS AND METHODS

A piece of activated carbon was prepared by heating a piece of coconut shell in vacuum as described elsewhere (Universiti Pertanian Malaysia, 1984). It was cut into a conductor of definite shape and dimensions as shown in Fig. 2a. The surfaces and edges were ground with sand paper and a fine grinding stone. The conductor was then boiled in distilled water for 2 days and in 0.1M HCl for an additional 2 days, washed with distilled water in a Soxhlet apparatus for 4 days and left to dry in air. The conductor was then attached with epoxy resin (Araldite) to a length of glass tubing at one end and a B7 ground glass cone at the other, Fig. 2b. When the glue had set, the whole assembly was dried at 110°C overnight, heated at 70°C for three hours in vacuum, and stored in a desiccator.

For the conductance measurements, the conductor assembly was joined to a J-tube through the ground joint, Fig. 2b. A few drops of mercury were then placed in each arm. Connections to an Autobalance Universal Bridge B642 were made through platinum wires. The conductor was placed in a dry test tube and equilibrated at the experimental temperature in a waterbath. The conductance of the dry conductor was measured before each experiment. When constant readings were obtained, some distilled water at that temperature was poured slowly into the test tube until the whole piece of carbon was submerged. After the initial conductance, σ_o was noted, the conductance, σ , was followed throughout the experiment until the final conductance, σ_f , was obtained (after 4 days).

After each experiment, the conductor assembly was dried in vacuum and kept in a desiccator as described above.

RESULTS

When the activated carbon was immersed in water, its conductance increased with time until a constant value of σ_f was reached as it became completely soaked. The results obtained at five different temperatures are given in Fig. 3. The increase in conductance showed a short inductive period followed by an accelerated one before slowing down again as σ_f was approached. The total time taken for the sample to reach its final conductance value became shorter as the temperature was raised.

Analyses of the results have been made using equations (12) and (18) for two different stages of each experiment. Plots obtained using equation

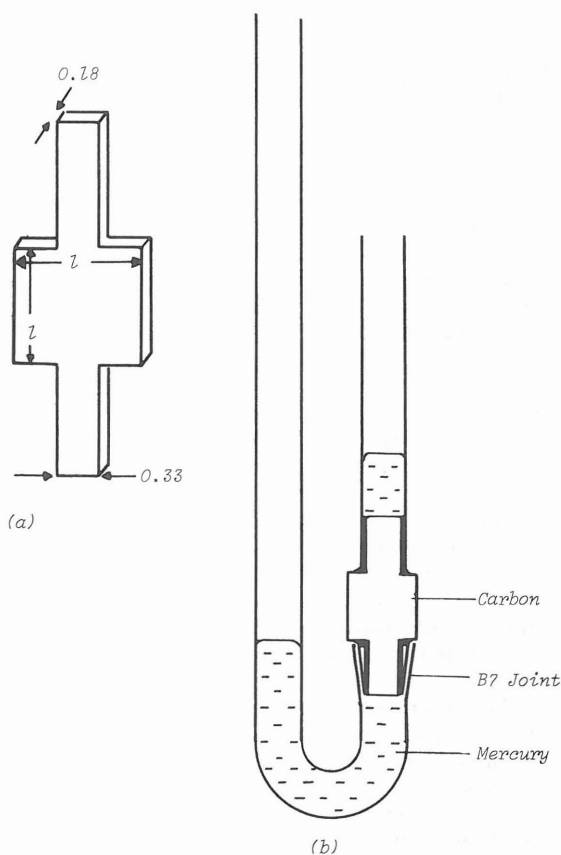


Fig. 2 Conductor assembly

- (a) carbon conductor with dimensions given in cm. The length of each tip is 1 cm.
- (b) carbon conductor attached to glass and a J-tube through B7 glass joint. The tips were covered with mercury for proper contact.

(12) are given in Fig. 4. Except for slight deviation at 28°C, the results obtained seem to fit a straight line up to 70% of the total sorption fraction, $\frac{\sigma - \sigma_o}{\sigma_f - \sigma_o}$.

The slopes of these lines have been estimated and are given in Table 1 together with the values of r calculated using equation (12).

Plots obtained using equation (18) are also given for the various temperatures, Fig. 5. The data seem to fall on two straight lines intersecting at sorption fraction of about 70%. Since the lower fraction has been accounted for by equation (12), the upper line has been associated with the flow of water into the vertical pores. The slopes of these lines at all five temperatures are given in Table 2 together with the calculated values of r using equation (18).

DISCUSSION

On a molecular scale, the external surface of the carbon piece would still be very rough with many large depressions and crevices despite the care taken during the grinding. The initial slow increase in the conductance during the inductive period could have been due to the gradual filling of these crevices with water. As the walls of these crevices came into contact with water, the functional groups either ionized or reacted with water to give hydrogen ions which could act as charge carriers in the solution within the crevices. Since the ratios of the surface area of these crevices to their volume and to the total surface area including those of the pores are small, the number of functional groups involved in this step must be small also. Therefore, the initial increase in the conductance would be small.

TABLE 1
Pore radius obtained using equation (12)

Temperature °C	Slope $10^{-6} s^{-1}$	Surface Tension* dyne cm^{-1}	Viscosity* $10^{-2} g cm^{-1} s^{-1}$	Radius pm
0	5.975	75.6	1.787	22.9
28	14.64	71.5	0.8327	27.6
36	20.19	70.25	0.7052	32.8
56	44.00	67.00	0.4961	52.8
78	85.58	62.90	0.3638	80.2

*CRC Handbook of Chemistry & Physics, 1970-1971.

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 TABLE 2
 Pore radius obtained using equation (18)

Temperature °C	Slope $10^{-5} s^{-1}$	Density* $g\ cm^{-3}$	Viscosity* $10^{-2} g\ cm^{-1} s^{-1}$	Radius nm
0	0.9449	0.9998	1.787	643
28	2.042	0.9962	0.8327	646
36	2.445	0.9937	0.7052	652
56	5.487	0.9852	0.4961	822
78	10.02	0.9730	0.3638	957

*CRS Handbook of Chemistry & Physics, 1970-1971.

The openings of the internal pores are probably sited in the walls of crevices. Once the crevices were filled, the water would start to flow into the pores. Since the proportion of the total surface area due to the pores is large, the number of functional groups involved must be large also. Their ionization would enhance the conductance of the sample tremendously. This is probably the factor responsible for the accelerated period noted in *Fig. 3*. When these pores were filled, the water would start flowing into the smaller, "closed-end" ones. The flow would be slower and perhaps complete filling might never be achieved because of air trapped in these pores, thus restricting the conductance to a certain value. At higher temperatures, more of these "close-end" pores would be filled in a shorter time. The greater mobility of the ions and the increased dissociation constants of the functional groups at higher temperatures would result in a higher final conductance obtained in a shorter time. This is shown very clearly in *Fig. 3*.

Since the middle portion of the conductor was completely covered by water, the flow of water into the internal cavities could have taken place from any direction. Though a vertical flow through the lower bp surface would be fast, the area in contact with water was quite small because most of it was covered with glue. Thus, the horizontal flow from both sides of the ph and bp surfaces, (*Fig. 1*), is more important. The measurements of the conductor, (*Fig. 2*), give $p = 1\ cm$ and $A_f = 0.18\ cm^2$. Therefore, for the purpose of calculation of the radius of the pore through which the horizontal flow had taken place, equation (12) could be written as

$$\left(\frac{\sigma - \sigma_o}{\sigma_f - \sigma_o} \right)^2 = \frac{\delta_f}{1.62\eta} 10^2 t \quad (19)$$

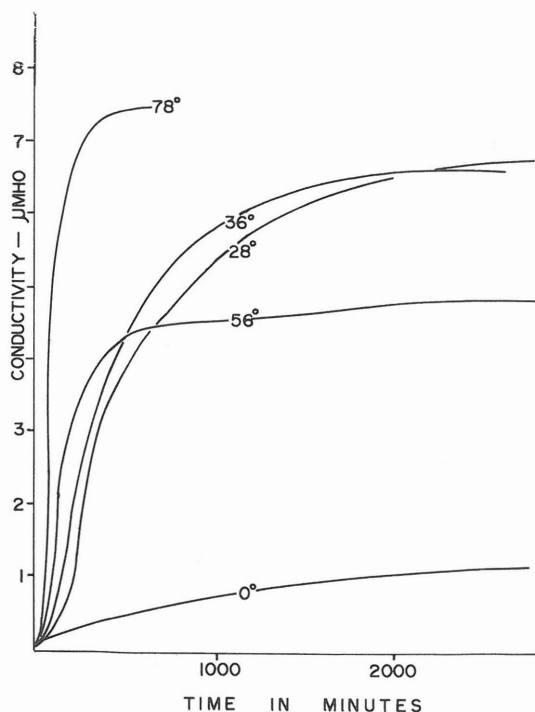


Fig. 3 The conductivity of activated carbon immersed in water at various temperatures indicated in °C.

Although about 70% of the sorption-fraction has been treated according to equation (12) in *Fig. 4*, it is also possible that the system can be treated using a combined mechanism including vertical flow. The assumptions already used still retain their validity since the two mechanisms are quite similar in the early part of the experiment when $(\sigma - \sigma_o)$ is very small, as evident

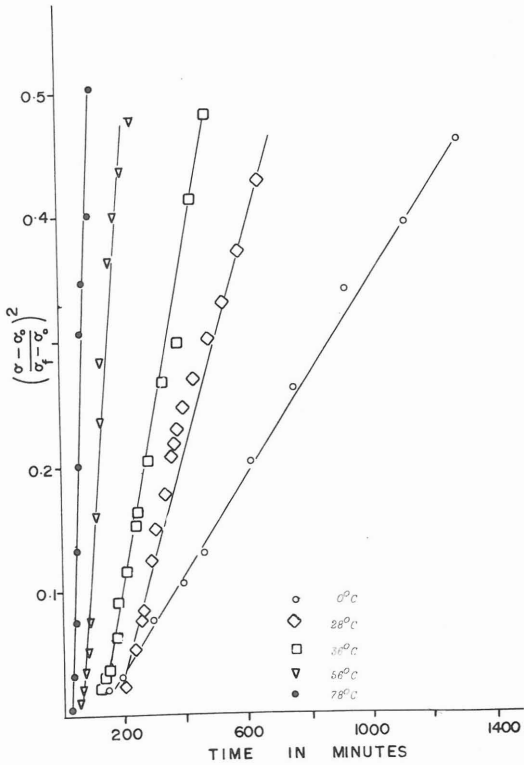


Fig. 4 The plot of $\left(\frac{\sigma - \sigma_0}{\sigma_f - \sigma_0}\right)^2$ against time, t .

below. Equation (18) could be transformed to (20).

$$-\ln \frac{\sigma_f - \sigma}{\sigma_f - \sigma_0} - \frac{\sigma - \sigma_0}{\sigma_f - \sigma_0} = \frac{gr^2\rho}{8\eta h_f} t \quad (20)$$

Consider the logarithm term on the left.

$$\begin{aligned} \ln \frac{\sigma_f - \sigma}{\sigma_f - \sigma_0} &= \ln \frac{\sigma_f - \sigma_0 - \sigma + \sigma_0}{\sigma_f - \sigma_0} \\ &= \ln (1 - x) \end{aligned}$$

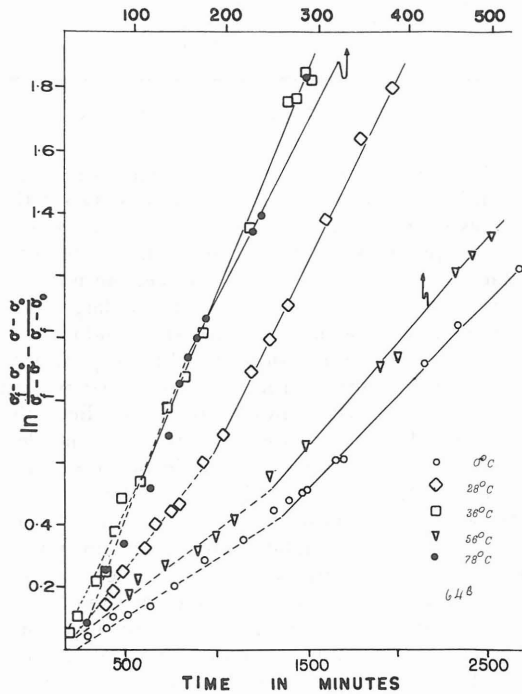


Fig. 5 The plot of $\ln \frac{\sigma_f - \sigma}{\sigma_f - \sigma_0} - \frac{\sigma - \sigma_0}{\sigma_f - \sigma_0}$ against time, t .

where $x = \frac{\sigma - \sigma_0}{\sigma_f - \sigma_0}$ and x would always be smaller

than one. The term could then be expanded into a series (Forbes and Smyth, (1963).

$$\ln (1 - x) = -x - \frac{1}{2}x^2 - \frac{1}{3}x^3 \dots\dots\dots$$

Therefore (20) becomes

$$\frac{1}{2} \left(\frac{\sigma - \sigma_0}{\sigma_f - \sigma_0} \right)^2 + \frac{1}{3} \left(\frac{\sigma - \sigma_0}{\sigma_f - \sigma_0} \right)^3 \dots\dots = \frac{gr^2\rho}{8\eta h_f} t$$

for small $(\sigma - \sigma_o)$ the cubic term can be neglected and we would obtain (21)

$$\frac{1}{2} \left(\frac{\sigma - \sigma_p}{\sigma_f - \sigma_o} \right)^2 = \frac{gr^2\rho}{8\eta h_f} t \quad (21)$$

Equation (21) which relates the increase in conductance to the vertical flow of water in the conductor is similar to (12). If the first part of the increase in the conductance was due to a combined mechanism, the slope would be the sum of the individual slopes in proportion; *i. e.*

$$\text{slope} = c \frac{gr^2\rho}{8\eta h} + d \frac{2p^2\gamma r}{A_f^2\eta}$$

where $(c + d) = 1$. Because r is small, the term containing r^2 is small, implying that the mechanism is predominated by the contribution from the horizontal flow as suggested.

Estimation of the radius of the pore using the slopes obtained is acceptable. The value of r calculated as shown in Table 7 falls within the mesopore classification (Ponec, 1974). The variation with temperature could have been due in part to thermal expansion of the conductor. However, a more likely explanation would be that the variation is due to the filling of the pores through condensation of vapour which would be expected to be more significant at higher temperatures. Such condensation would make the

pores seem larger because less time would be required for completion of the process.

The values of r given in Table 6 are much too small. Several factors may have contributed to this. The major factor could possibly be the assumption that equation (2) is applicable to carbon capillaries. Carbon is hydrophobic (Bikerman, 1970) whereas glass is not. Hydrophobicity would slow down the flow of water in the horizontal capillaries and make them seem smaller. To accomodate this, perhaps a correction is necessary in equation (12). This is left as a subject for future investigation.

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