

Degradation in the Performance of Activated Carbon Filters and How to Overcome the Problem

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Abstract

The performance of activated carbon vapour filters against volatile hydrophobic chemicals is strongly dependent on the carbon water content, degrading rapidly as the relative humidity (RH) is increased. This observation highlights the importance of evaluating filters under environmental conditions appropriate to their use. In addition, exposure to humid air (>RH40%) results in further filter degradation due to "ageing." Ageing is the chemisorption of oxygen and/or water vapour by the carbon, which results in an increase in the hydrophilic character of the surface. Chemical modification of the carbon has been investigated as a method for improving the efficiency with which volatile hydrophobic chemicals are adsorbed from humid air, and as a way of producing carbon adsorbents which will be resistant to ageing effects. Chlorinated carbons adsorb volatile hydrophobic chemicals from humid air more efficiently than unmodified control carbons, and, more importantly, are resistant to ageing. The preparation and properties of chlorinated carbon are addressed.

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Introduction

It is widely recognised that the level of protection afforded by activated carbon filters used for respiratory protection depends upon the properties of the adsorbent and challenge vapour and the environmental conditions (e.g., Nelson and Harder 1974; Nelson, Correia, and Harder 1976). In many practical situations, the filter is required to remove volatile hydrophobic vapours from airstreams containing moisture. At equivalent partial pres-

sures, the adsorption of the organic vapour will be favoured. However, it is likely that water vapour will be present in much greater concentrations than the organic component, and that the filter will have been exposed to humid air for some time prior to use. In such circumstances, it is probable that filter performance will depend critically on the kinetics of water displacement from the carbon pore structure.

It is the objective of this article to illustrate the importance of preadsorbed water on filter performance, and to examine the factors limiting the efficiency with which the volatile hydrophobic chemical trichloronitromethane (chloropicrin, PS) is adsorbed from humid air. PS has been selected on the basis that it is often used for quality assurance testing of filters, or for carbon batch testing

(e.g., NATO 1967; Shali and Aharoni 1974; Specification TS50605 1985). The importance of the surface chemistry of the carbon on filter performance will be discussed, and it will be shown that chlorinated carbons overcome, at least in part, the limitations imposed on such filters by storage and use in humid air.

Experimental

Two activated carbons supplied by Chemviron have been used in this study, BPL, which is derived from coal, and SCII which is a coconut shell carbon. Both carbons were of a similar particle size (12 x 30 ASTM), and were stored dry in hermetically sealed containers prior to use. PS adsorption was measured after equilibrating 2 cm diameter filters of 1 cm or 2 cm bed depth with air of relative humidity (RH) 40 or 80% at 22°C. After equilibration, filters were challenged in air at the same RH and at a flow rate of 1.2 l min⁻¹ using a PS concentration of 5000 mg m⁻³. The influent and effluent PS concentrations, temperatures, and

dew points were monitored continuously during each determination. Water adsorption isotherms were measured in flowing air at 22°C, and nitrogen isotherms were measured at -196°C using a Carlo Erba Sorptomatic instrument. The apparatus and experimental methods used for the measurement of PS and water adsorption are described in detail elsewhere (Hall and Holmes 1989; Adams et al., 1988). Surface modified carbons were prepared either by exposure of the carbon to RH80% air, or by chlorination using carbonyl chloride (phosgene) or chlorine at 200°C followed by washing with water or methanol.

Results and Discussion

Figure 1 shows a water adsorption isotherm measured for BPL carbon at 22°C. The quantity of water adsorbed is dependent on the equilibration RH, but is independent of the temperature between at least 40°C and -3°C (Emmett 1948; Hall, Holmes, and Lawston 1991). Because the average RH in Europe is often high (60% or greater), activated carbon filters stored in contact with air can contain substantial quantities of adsorbed water at the time of the arrival of any hazardous vapours. In addition, dry filters will rapidly adsorb water vapour from a humid airstream. For example, at a breathing rate of 30 l min⁻¹, a typical respirator canister exposed to RH80% air for two hours can contain upwards of 25% w/w of adsorbed water. Equilibrium under these conditions is attained after approximately 16 hours.

In many situations, the filter will be required to remove volatile hydrophobic vapours, which may be present in low concentrations. Figure 2 shows the effect of the equilibration RH on the efficiency with which BPL carbon adsorbs PS vapour from an airstream. It is apparent that preadsorbed water can result in a major loss of filter performance (defined as the time at which

the effluent vapour concentration is 1% of the influent). For example, at RH80%, this loss equates to approximately 80% of the performance of the dry carbon.

Figure 3 shows the PS breakthrough curve, the effluent temperature and RH profiles, and the concentration of displaced water, for a sample of BPL carbon challenged in equilibrium with RH40% air (the effluent RH profile was calculated using the effluent air temperature and water vapour concentration). In this example, preadsorbed water has little effect on filter performance, the overall process of PS adsorption and water displacement is exothermic, and all of the preadsorbed water is displaced (Table 1). Similar measurements, but at RH80%, reveal that the behaviour of the system is substantially different (Figure 4). In this case, the PS breakthrough curve is distinctly biphasic, and the process of PS adsorption and water displacement is notably endothermic. Examination of the effluent RH profile suggests that the shape of the PS breakthrough curve is a consequence of the airstream reaching saturation. That is, PS adsorption is limited by the inability of the airstream to carry

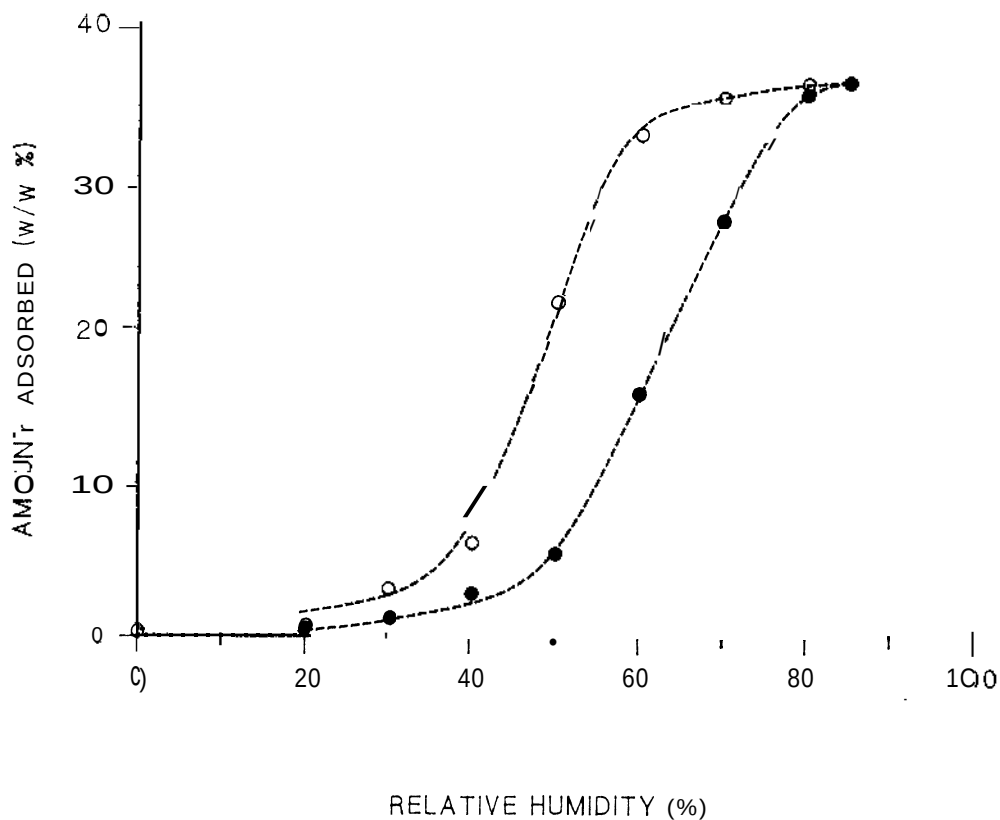


Figure 1. Water adsorption-desorption isotherm for BPL activated carbon measured at 22°C. Open symbols denote desorption.

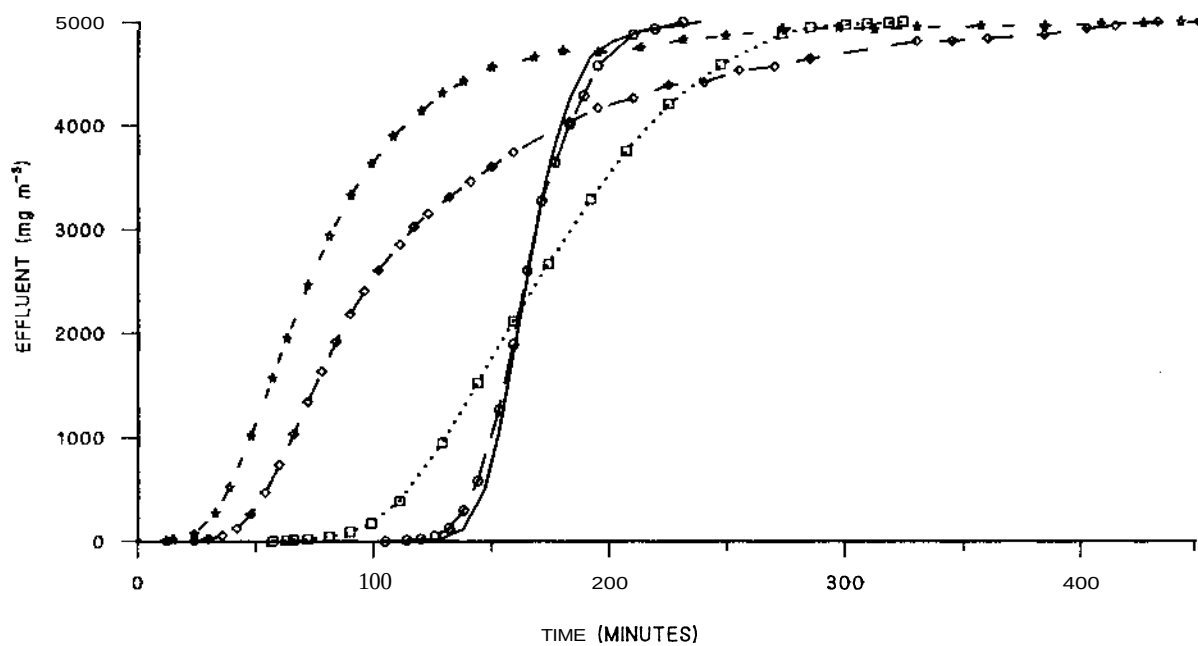


Figure 2. Chloropicrin breakthrough curves measured at RH<2% (·), RH40% (○), RH65% (□), RH80% (○) and RH95% (★) at 22°C for 1 cm beds of BPL activated carbon.

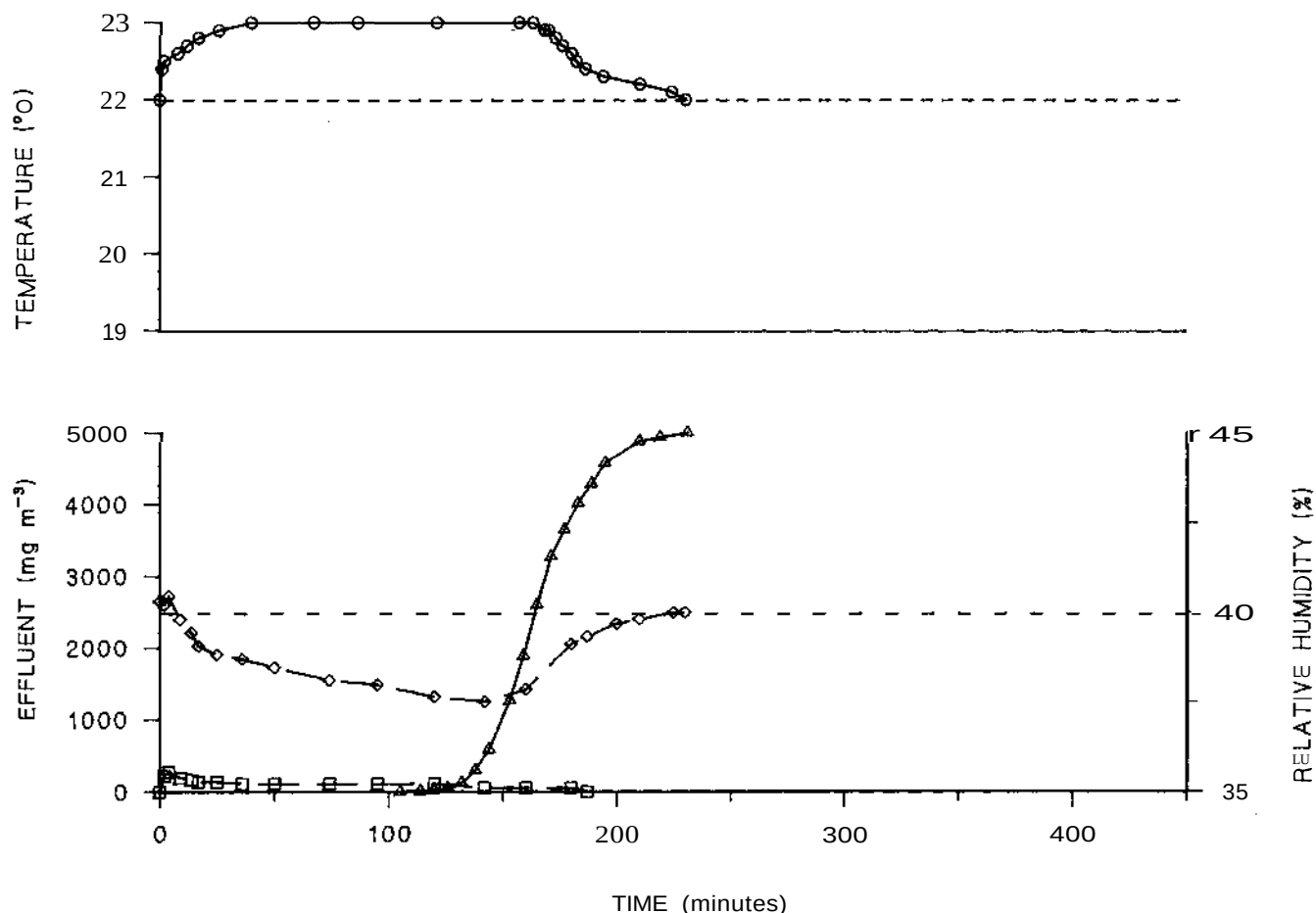


Figure 3. PS breakthrough (A), water displacement ($\square$), effluent RH (O), and effluent temperature (O) curves for a 1 cm bed of control bpl carbon pre-equilibrated and challenged at RH40% and 22°C.

away displaced water: as a result, the micropores are occluded, and the capacity of the filter for PS decreases markedly (the breakthrough curve steepens). As the effluent RH begins to decrease, the PS adsorption rate increases, and the slope of the breakthrough curve decreases. It is notable that at the end of the experiment, a significant quantity of preadsorbed water remains on the filter bed (Table 1) (Hall and Holmes 1989). These observations illustrate that the process of PS adsorption is dependent on the carbon water content. They also identify the principle limitation on filter performance at high RH and highlight the importance of evaluating filters under conditions appropriate to their use. Comparison of the breakthrough profiles at Figure 2 suggests that controlling the RH of the air at or below 40% maximises filter performance.

In addition to the immediate effect of preadsorbed water on filter performance, it is known that contact with high humidity air results in a change in the surface chemistry of the carbon (e.g., Billinge and Evans 1984). This is due to the chemisorption of water and/or oxygen by the carbon, which results in an increase in the hydrophilic character of the surface. This effect, which is commonly referred to as ageing, has a major impact upon the adsorptive properties of activated carbon (Collins et al., 1980; Adams et al., 1988; Hall and Holmes 1989). Figure 5 shows water adsorption isotherms for control BPL carbon, and BPL carbon which had been exposed to RH80% air at 22°C for 860 days. The enhancement in hydrophilic character results in an increase in the quantity of water vapour adsorbed at low values of the RH (below ca. 60%), and the displacement of

Table 1. The amounts of PS adsorbed and water displaced by 1 cm bed depth, 2 cm diameter filters containing control and aged (860 days, **RH80%**, 22°C) BPL carbon, and tested at different relative humidities.

Sample	Carbon Weight (dry) (g)	Test RH (%)	PS Adsorbed (mg g^{-1})	Water Desorbed (mg g^{-1})	Carbon Water Content (mg g^{-1})	
					Initial	Final
Control	1.755	80	438	219	352	133
Aged	1.746	80	372	225	354	128
Control	1.758	65	593	203	206	3
Aged	1.754	65	447	262	294	32
Control	1.743	40	584	19	22	3
Aged	1.726	40	546	64	62	2
Control	1.742	<2	583			
Aged	1.734	<2	544			

the pore filling region of the isotherm to lower values of the RH. This behaviour is a consequence of the increased number of polar adsorption centres, which act as a focus for the adsorption of water vapour. It is notable that these effects are not dependent on the carbon source, as the isotherms for SCII control and aged carbons shown at Figure 6 illustrate (the aged SCII carbon was prepared by exposure of control carbon to **RH80%** air at 45°C for 45 days). Figure 7 demonstrates the dramatic reduction in PS adsorption efficiency (defined as the time at which the effluent vapour concentration is 1% of the influent) that results from exposing BPL carbon to **RH80%** air at 22°C. The measurements were made using 2 cm bed depth filters, after first equilibrating the carbon with **RH80%** air. Under dry test conditions (**RH**<2%), no significant change in filter performance was observed. This suggests that the polar functional groups introduced during ageing do not directly influence PS adsorption, rather that they reduce the ease with which preadsorbed water is displaced by PS because of strong hydrogen bond-

ing interactions. It is notable that this effect cannot be due to differences in the initial carbon water content, because at **RH80%**, this is not dependent upon the extent of ageing. It was noted above that filter performance can be maximised by controlling the RH of the air to **RH40%** or below. This approach offers a further advantage, in that carbons are found not to age significantly in air of low RH (40% or below).

It is apparent that the combined effects of uncontrolled storage and use of activated carbons in humid air can result in a major degradation in filter performance. However, because the carbon surface is shown to be chemically reactive, it is apparent that manipulation of the surface chemistry of the carbon may offer some advantages. For example, it may be possible to prepare adsorbents of enhanced hydrophobic character which will be resistant to ageing. Thus, activated carbons have been chemically modified in order to demonstrate the range of effects that may be brought about.

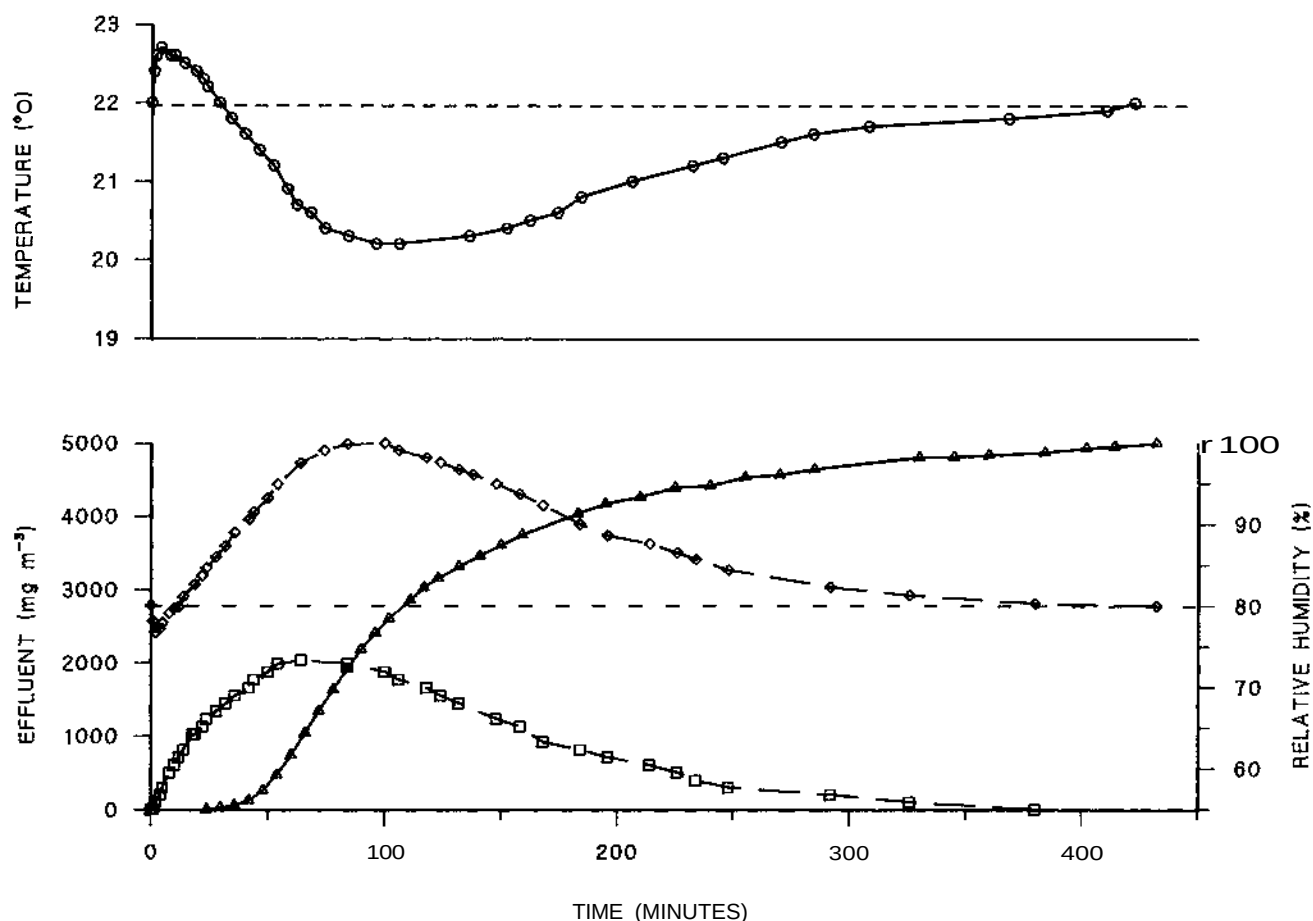


Figure 4. PS breakthrough (A), water displacement (□), effluent RH (O), and effluent temperature (O) curves for a 1 cm bed of control bpl carbon pre-equilibrated and challenged at RH80% and 22°C.

Carbons of enhanced hydrophilic character have been prepared by treatment with dinitrogen tetroxide (NO_2). The intention of this approach was to prepare "aged" carbon more rapidly, and to use these carbons as substrates for further chemical transformations. Examination of the adsorptive properties of the oxidised carbons indicated that they were similar to materials aged by exposure to humid air (Hall and Holmes 1990).

Because of the limitations on filter performance in humid air described above, further research was undertaken in order to identify modification techniques that would enable carbons of improved hydrophobic character to be prepared, which would also be resistant to ageing effects. Direct fluorination was studied, as fluorinated surfaces are generally chemically inert and hydrophobic. However, the modified adsorbents were found to be reactive, and unstable in humid air (Hall and Holmes 1991). On the basis of these observations, indirect fluorination was investi-

gated. Thus, carbons modified with difluoroethene were found to be more hydrophobic than control material, and to adsorb PS from humid air more efficiently (Hall and Holmes 1990). However, the modified adsorbents aged in humid air, although at a reduced rate compared to control carbon. Of the approaches studied to date, chlorination has proven to be most successful (Hall and Holmes 1991). The properties of chlorinated carbon are discussed below.

Chlorinated carbons were prepared, containing, after washing with methanol or water, ca. 5–7% by weight of chlorine (by gravimetric and elemental analysis). This quantity of chemisorbed chlorine did not result in any major change to the carbon pore structure, as the nitrogen isotherms at Figure 8 demonstrate. In each case, the data have been compared on the basis of equal carbon weights, on the assumption that modification does not result in significant carbon gasification (gas analysis for any reaction products supported the

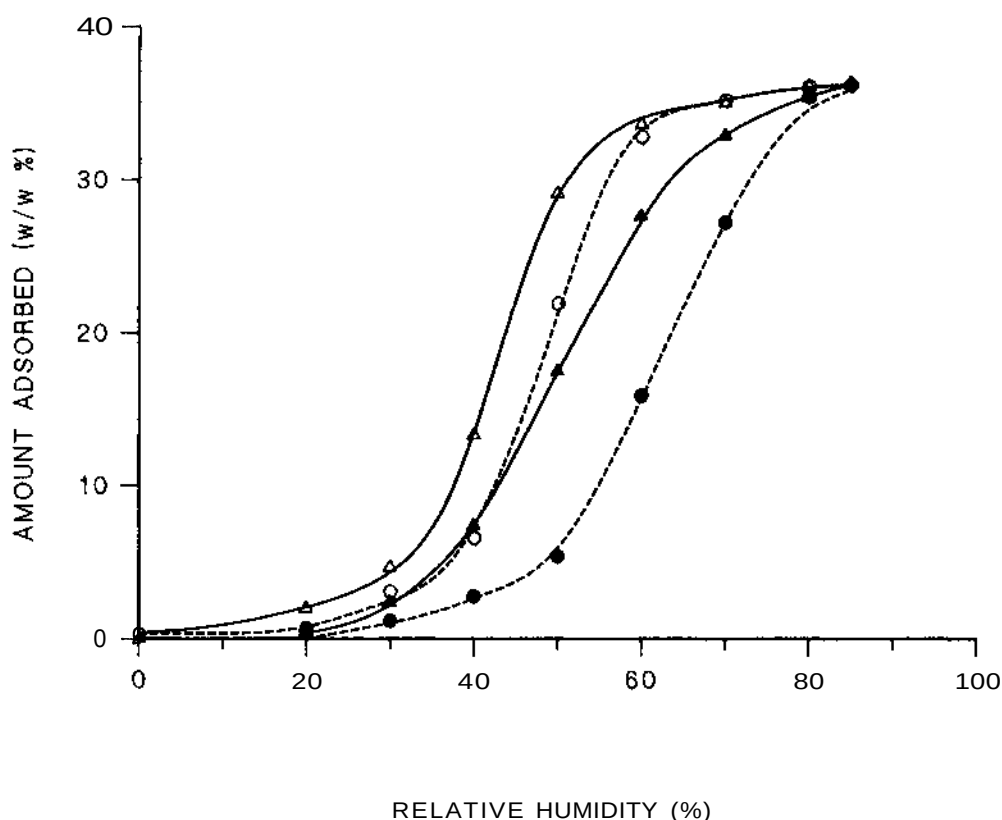


Figure 5. Water adsorption-desorption isotherms for control BPL carbon (O), and BPL carbon aged at RH80% and 22°C for 860 days (A). Open symbols denote desorption.

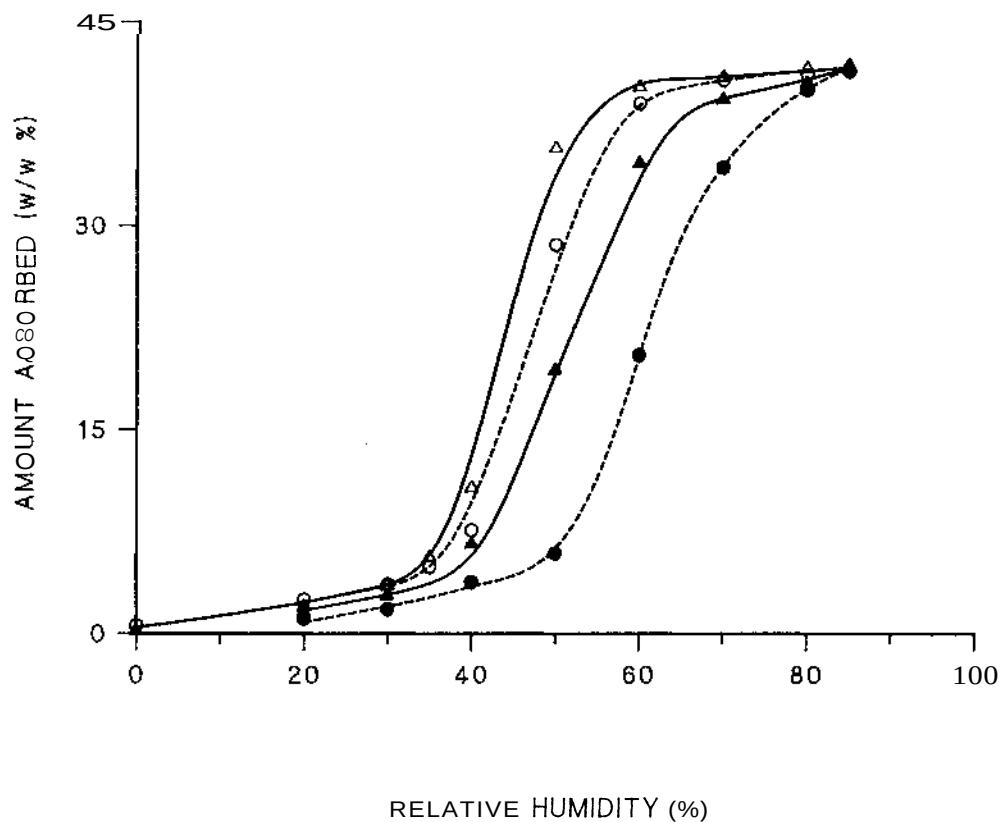


Figure 6. Water adsorption-desorption isotherms for control SCII carbon (O), and SCn carbon aged at RH80% and 45°C for 45 days (A). Open symbols denote desorption.

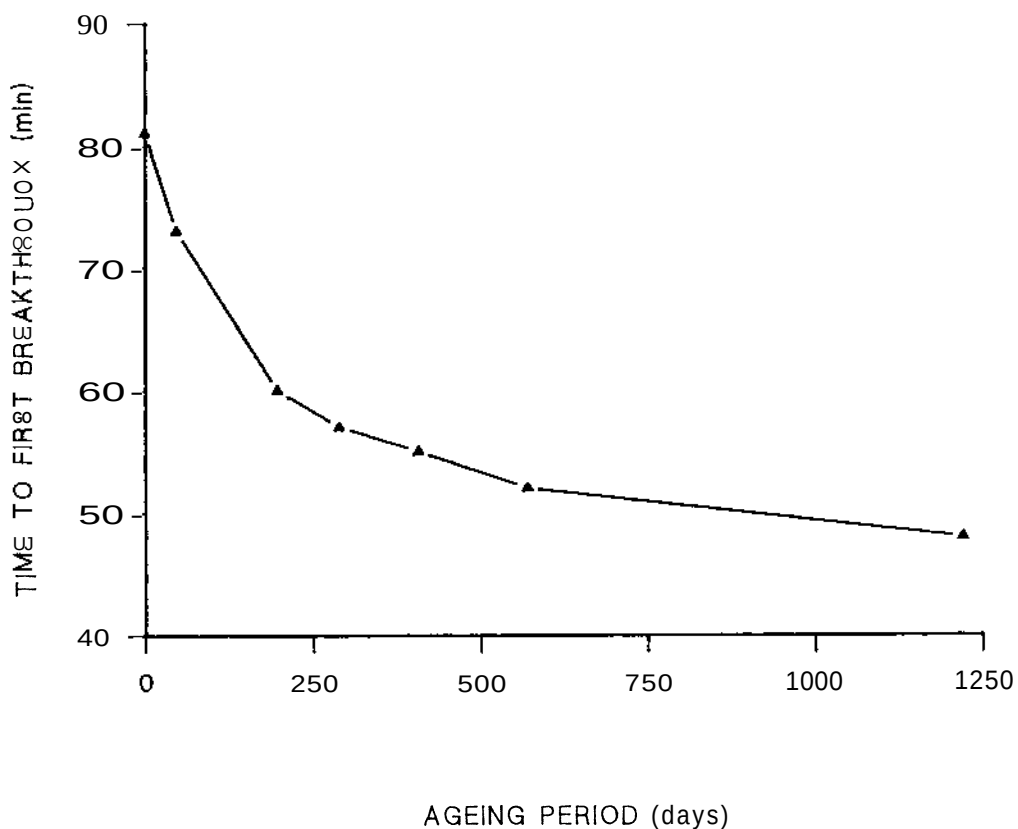


Figure 7. The breakthrough of chloropicrin vapour at RH80% and 22°C through 2 cm bed filters containing BPL carbon as a function of the ageing period in days at RH80% and 22°C.

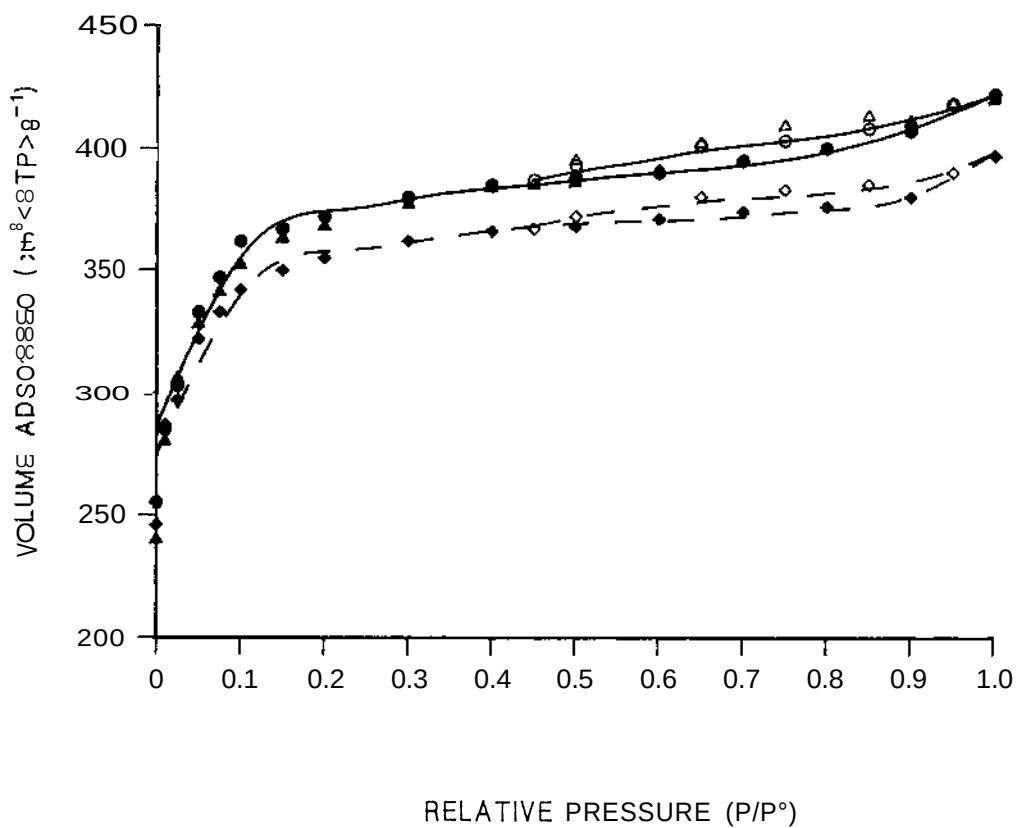


Figure 8. Nitrogen isotherms for control (O), and chlorinated and methanol treated (4), and chlorinated and water treated (A), SCn carbons. Open symbols denote desorption.

view that carbon gasification was not important). Comparison of the water adsorption isotherms for control and chlorinated SCII carbon (Figure 9) indicate that the chlorinated carbon is relatively hydrophobic. This results in an improvement in filter performance against PS vapour at high RH (Table 2). The improvement presumably reflects an increase in the ease with which preadsorbed water is displaced from the surface of the modified carbon by PS. Alternatively, the improvement may be because chlorinated carbons adsorb less water at RH80%. Of more significance is the fact that chlorinated carbons are resistant to ageing. That is, the water adsorption properties of the carbon do not change as a result of exposing the carbon to RH80% air at 45°C for 45 days (Figure 10). The water isotherms at Figure 6, for a sample of control SCII carbon, and SCII carbon aged under the same conditions and for the same time as the chlorinated carbon, illustrate the major changes which normally result from such exposure. It is also notable that the PS performance

obtained for the chlorinated carbon remains unchanged, whereas that for the aged control carbon is substantially lower. These observations suggest that **chlorination effectively masks** the active sites at the surface which normally react with oxygen **and/or** water vapour. Therefore, chlorinated carbons are found to adsorb volatile hydrophobic chemicals from humid air more efficiently than control carbons, and are also resistant to carbon ageing effects.

Although it is apparent that surface chemical aspects can have a major impact upon the adsorptive properties of carbon filters, at high RH, the principal limitation remains that of the transport and vapourisation of preadsorbed water from the bed. This limitation will only be overcome by modifying pore shape, because carbons produced using present technology possess a pore structure which is of a shape and size distribution favourable for water sorption (Carrott et al., 1991).

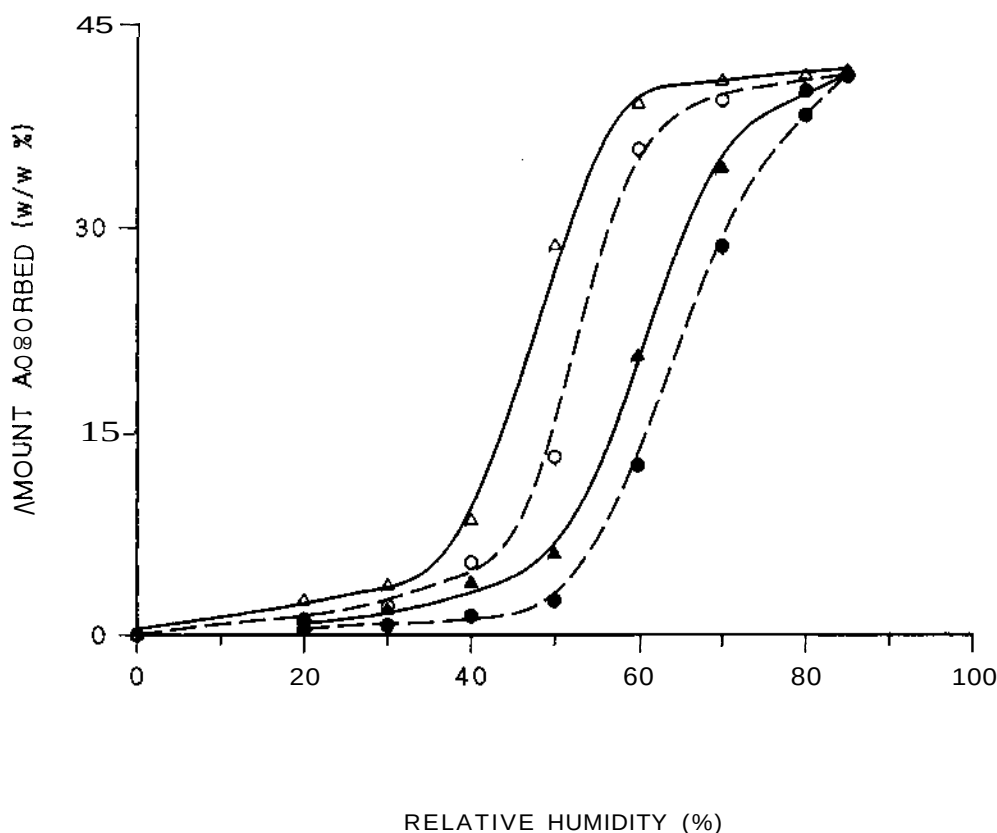
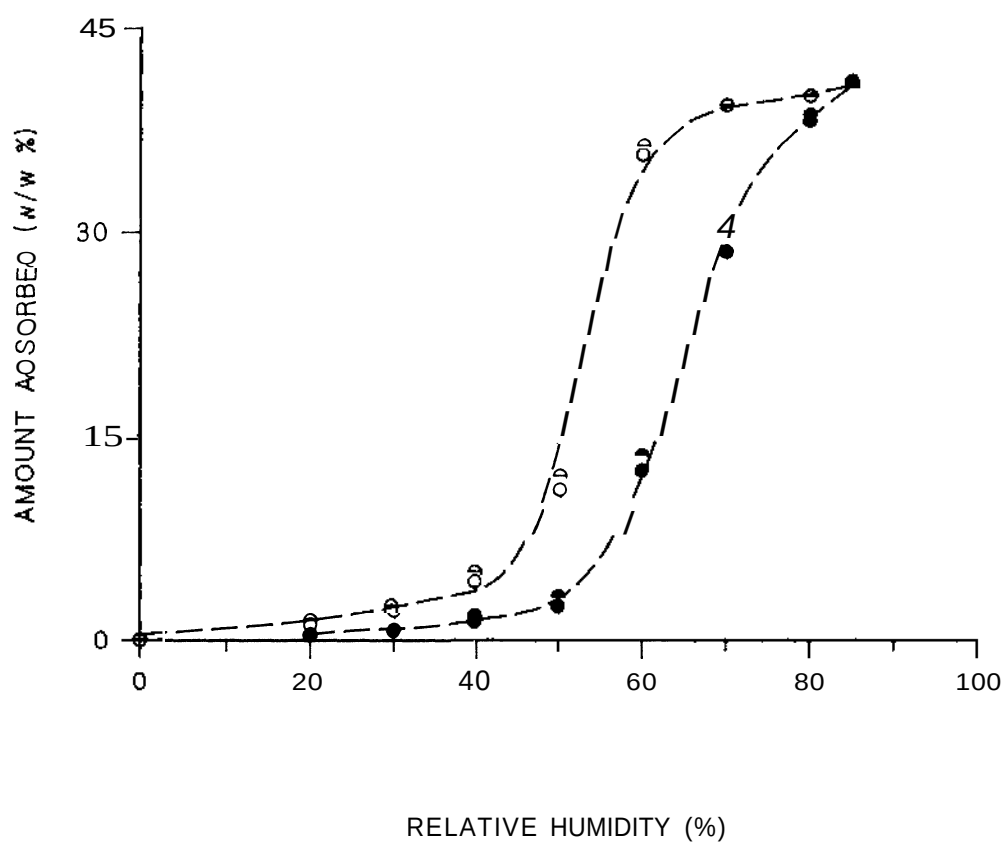


Figure 9. Water adsorption-desorption isotherms for samples of control (A) and chlorinated (O) SCII carbons. Open symbols denote desorption.

Table 2. Chloropicrin adsorption for 2 cm bed depth, 2 cm diameter filters containing SCII carbon.

Sample	Time to 1% PS Breakthrough (min)
Control	96
Aged	65
Chlorinated	110
Chlorinated—Aged	110

**Figure 10. Water adsorption-desorption isotherms for samples of chlorinated (O), and chlorinated and aged (RH80%, 45°C, 45 days) (a) SCII carbons. Open symbols denote desorption.**

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