

ADSORPTION OF HERBICIDES USING ACTIVATED CARBONS

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INTRODUCTION

This paper describes the results of research in which novel activated carbons have been examined for their efficacy in water treatment and, specifically, for the adsorption of a common herbicide and wood preservative, sodium pentachlorophenolate. To place this work in context, the introduction will discuss first some of the considerations of using activated carbons for water treatment, and then certain aspects of the authors' research that has led to this particular topic.

Activated Carbons for Water Treatment

One of the largest uses of activated carbons lies in the treatment of domestic and industrial water supplies. Activated carbons in various physical forms, have been used for more than 50 years to treat public water supplies for the removal of organic compounds that adversely affect taste, odor, and toxicity. Powdered activated carbons are used on a once-through basis, while granular activated carbons (GAC) possessing high surface areas, coupled with high attrition resistance, are used in packed bed applications.

Rising concern about the quality of drinking water supplies as well as the increased awareness of pollution from industrial waste waters have led to a significant growth in the activated carbon market. Demand for ion exchange resins and activated carbons for water treatment reached 200 million lb in 1992 and is expected to grow 4.6% per year to 251 million lb by 1997, mainly due to increased demand for activated carbons. The corresponding market value for these materials reached \$271 million in 1992 and it is expected to rise to \$376 million by 1997¹. A small but ever-increasing market for activated carbons is also developing in the area of household water filtration systems for improving the quality of drinking water.

The surfaces of most commercial activated carbons are hydrophobic, which means that they are very effective for the adsorption of non-polar organic molecules. Activated carbons are less effective for the removal of polar compounds, and still less useful for the adsorption of ionic species (e.g. metals). For this reason, household treatment systems use activated carbon in multi-component filters that may also include materials such as ion-exchange resins. The high cost of ion-exchange media excludes their use in large-scale water treatment processes, where activated carbon is the preferred choice. However, there is a need to develop activated carbons that can be comparably effective for the adsorption of a wide range of pollutants.

Granular activated carbons have gradually replaced powdered activated carbons in water treatment and are now used on a much larger scale than ever before. In 1986 the Amendments to the Safe Drinking Water Act specified adsorption with GAC as the benchmark technology for organic chemical removal². Alternative technologies must be at least as effective in controlling synthetic organic chemicals. Municipal water plants traditionally incorporate fixed beds of GAC as part of the filtration system, the carbon bed acting as a physical filter, as well as an adsorbent. The high attrition resistance of GAC is important to water treatment applications in that it allows for the carbons to be backwashed, pumped, excavated and recycled through regeneration units without suffering excessive material loss due to mechanical abrasion³. Although granular carbons are generally more expensive than powdered carbons, they have been found to be more cost-effective when their overall usage rate is high. Pressure drop, containment, and other considerations make powdered carbons impractical for use in adsorber beds.

Activated carbon fibers have recently started to attract interest as adsorbents for a number of applications, including water treatment⁴. Among other factors, the narrow fiber diameters (typically 10 to 30 microns) allow rapid rates of adsorption and desorption - a characteristic that also applies to fine particle powdered carbons. However, cost has so far presented one of the major obstacles to wide-scale development (over \$20/Kg for carbonized fibers, i.e. before activation). In addition, to surmount problems in handling and utilization, it will be necessary to incorporate the fibers into some type of structure.

Current Research

Over the past few years, research at this Center has been involved with investigations of the synthesis of activated carbons by different methods and from a range of precursor materials⁵⁻¹⁰. The general objectives are to develop a basic understanding of the mechanisms leading to the formation of an extensive pore structure, and ultimately to be able to produce activated carbons with controlled porosity and surface chemistry, as well as other properties. These investigations have included: the formation of activated carbon particles and extrudates by the phosphoric acid activation of hardwoods and blends of hardwood with other materials^{5,6}; activated carbon particles by the KOH activation of bituminous coals⁷; activated carbon extrudates by the KOH activation of lignite and oxidized bituminous coal⁸; activated carbon fibers from isotropic pitch precursors⁹;

and the development of rigid, monolithic activated carbon composites¹⁰.

The present work is related primarily to activated carbon composites. These are strong, highly permeable materials that can be produced in almost any size or shape, and are particularly suitable for applications where it is desirable to achieve high rates of throughput with minimum pressure drop. Moreover, the use of an immobilized bed can eliminate the attrition that would occur with a granular bed. Emanating from this work, we have found that it is possible to alter the pore structure of the activated carbon, and to introduce heteroatoms, such as nitrogen, into the structure by altering the method of synthesis. These attributes are germane to water treatment applications in two respects. First, the effectiveness of activated carbons in any particular application is dependent upon the pore size distribution: generally, for water treatment, a proportion of wider pores is desirable, both to facilitate diffusion of the adsorbate through the liquid phase, and to be able to accommodate large adsorbate molecules, such as color bodies and humic acids. Second, as already noted, activated carbons are typically hydrophobic. A number of studies has shown that the deliberate introduction of surface species, such as oxygen-containing groups, can enhance the ability to remove contaminants such as polar compounds and metals¹¹⁻¹³. However, the necessary treatments can be expensive, and it is difficult to control the type and distribution of the surface groups. By the introduction of heteroatoms directly during the synthesis process, it should be possible to provide specific surface functionalities that are uniformly distributed over the adsorbent surface, and that may enhance the adsorptive capacities for non-polar species. In the research described here, we have conducted preliminary experiments to assess the potential of different formulations of activated carbon composites for the removal of a representative polar contaminant of groundwaters.

EXPERIMENTAL

In their original form, activated carbon composite materials have been prepared in collaboration with the Oak Ridge National Laboratory^{10,14}. These composites are made from water slurries containing chopped carbonized pitch based fibers (~ 15 - 20 μm diameter \times ~ 0.35 mm length, supplied by Ashland Carbon Fibers Division, Ashland Inc.) and a phenolic resin. The slurry is vacuum molded into tubular or plate configuration, followed by drying, curing and carbonization to 650°C. The composite is activated in steam or CO₂ at temperatures from 800-900°C to introduce porosity. The method of preparation of the other composites that have been prepared for this work is proprietary and will not be described here.

Some properties of the activated carbon composites are presented in Table 1, together with data for a commercial granular activated carbon that was used for comparison. Composite J was prepared by the method described above. It can be seen that these adsorbents possess quite different pore structures. The BET surface areas range from 660 to 1940 m²g⁻¹, and have very different pore size distributions: some are predominantly microporous (pores < 2 nm diameter) and some have very high mesopore volumes (pores 2 - 50 nm diameter). The commercial water treatment carbon has a BET surface area at the low end of this range, but possesses an appreciable mesopore volume.

To measure the adsorptive capacities of the activated carbon composites for sodium pentachlorophenolate (PCP), 1.3 cm diameter plugs were cut from 1.5 cm blocks of activated monolith using a hole-saw. Three such plugs were lain end to end to form a column of total length 4.5 cm and volume 6 cm³. The column was then sealed into a water-tight assembly using heat-shrink tubing (Markel Corporation, polyolefin tubing), by heating to approximately 180°C using a heat gun. The ends of the column were fitted with plastic barbed connections enabling Tygon tubing to be attached.

Comparable columns of granular activated carbon were prepared by sealing 2.0 g samples of carbon into polyolefin tubing, using the same technique, to create a column of volume 8 cm³ and length 6 cm. Plugs of quartz wool were fitted at the column ends to contain the bed. A peristaltic pump, Pulsafeeder - Mec-o-matic VSP-20, located downstream of the column continuously drew a 40 ppm solution of sodium pentachlorophenolate (NaC₅Cl₅O) from a reservoir and through the column. The concentration of PCP in the column effluent stream was monitored via a UV-Vis spectrophotometer (Varian, Series 634) fitted with a 10 mm path length flow-through quartz cell, at a wavelength of 317.5 nm. Column breakthrough was determined as the point where the ratio of effluent to inlet PCP (C/Co) was equal to 0.3. The flow rate of PCP solution through each of the columns was held constant at 1 ml.min⁻¹.

RESULTS AND DISCUSSION

At the time of writing, adsorption data for PCP are available for the composite J and the commercial carbon. A plot of C/Co is shown as a function of the number of column volumes of PCP solution that have been processed in Figure 1. The breakthrough time for composite J was found to be almost 1400 column volumes, whereas it was closer to 150 column volumes for the granular carbon - a factor of about nine. It should also be noted that both columns continued to adsorb PCP after breakthrough and never reached saturation.

At first sight, the difference in the performance of these carbons is surprising, since they are of comparable surface area (see Table 1), and the commercial product has a much greater total pore volume (0.76 vs 0.39 cc/g) and, therefore, expected adsorption capacity. It is possible that part of

the difference may be attributable to the way in which the two columns are formed. As the activated composite is a monolith, the composition of the column is uniform over its cross section and length, and all of the solution has to pass through the interior of the composite before emerging: the monolithic form effectively ensures that the fluid feed is distributed uniformly through the column. With any granular bed, inefficiencies in packing can lead to channeling, allowing some of the feed to experience shorter contact times than the average that is calculated over the whole column: this phenomenon is more likely to occur in shallow packed beds.

At the same time, it is interesting to find that, at a similar overall space velocity (the volume feed rate per weight of carbon is 33.3 h⁻¹ for the composite and 30.0 h⁻¹ for the granular carbon), the column of composite is much more effective in adsorbing PCP. This observation indicates that the rate of adsorption is faster over the composite than the granules, which is consistent with other observations. The narrow diameter of the fibers (15 - 20 μm) essentially minimizes mass transfer limitations, and allows much faster rates of adsorption (and desorption) than is possible over large granules, as illustrated by an example obtained by a TGA study of the gas phase adsorption of NO, Figure 2. The rate of NO uptake is found to be higher by as much as three orders of magnitude for an activated carbon fiber composite than for 2 mm granules. Only when the granules are reduced to a size comparable to that of the fiber diameter, do the rates correspond. Thus, powdered carbons could be used with comparable effectiveness if the practical difficulties of containment, and the penalty of the pressure drop over a column of fine particles could be surmounted.

A second factor is that the composites have a very open architecture (approximately 90% is free volume), which means that the contacting fluid enjoys free access to the adsorbent surfaces. Essentially, the composite can be viewed metaphorically as a situation in which the granules have been "peeled open" to allow the adsorbent to readily access all of inner adsorbent surface, which can otherwise only be approached by diffusion through an extensive pore network.

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Table I: Properties of activated carbon adsorbents

Sample	BET surface area (m ² /g)	Pore volume (cc/g)		Bulk Density (g/cc)
		micro	meso	
A	870	0.42	0.03	-
E	1140	0.43	0.87	-
F	1940	0.76	0.73	-
I	1930	0.61	1.10	-
J	790	0.38	0.01	0.30
Granular carbon*	660	0.29	0.47	0.25

* commercial water-treatment carbon, 1-2 mm granules

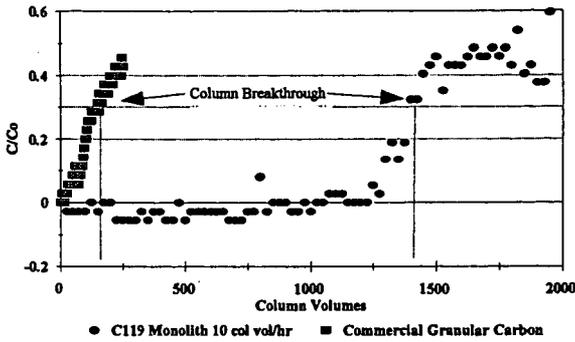


Fig. 1. Adsorption of Na-PCP by Carbon Columns

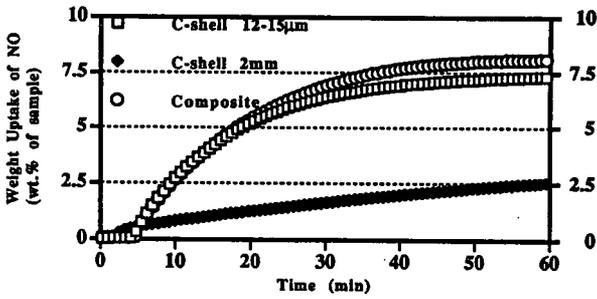


Figure 2: Adsorption rate of NO on activated carbon composite compared with a commercial granular activated carbon at two average particle sizes; 2mm, and finely ground to 14µm. (c-shell= coconut shell)