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Design of New Materials for Environmental Control

James Economy* and Chris Mangun
Dept. of Materials Science, University of Illinois, Urbana, IL 61801 USA

SUMMARY: During the past several years we have pursued a program here at UIUC to tailor the pore size and surface chemistry of activated carbon fibers (ACFs) to greatly increase their efficiency and selectivity for removal of trace contaminants from the environment. In addition we have evolved new ways of preparing the ACFs to sharply reduce their cost (typically ~$100/lb) to be more competitive with activated carbon granules ($1-2/lb), but also to greatly improve the abrasion resistance of the fibers. This was accomplished by coating glass fibers with a phenolic resin and then activating the coating under a controlled atmosphere to produce a variety of tailored micropores. Using chemically tailored ACFs, we describe major improvements over current activated carbons for adsorption of environmental contaminants.

Introduction

One of the undesirable features of the modern day world is widespread contamination associated with the release of a large number of chemicals into the environment. In recent years there has been a tremendous amount of work done to quantify the harmful effect of these trace contaminants. Society's growing concern has led many governments to establish stricter standards for clean air and water, many of them in the ppb range. This necessitates the development of greatly improved methods for controlling the release of toxic contaminants and on designing new materials tailored to selectively remove a wide range of contaminants and permit for recovery and reuse. Industry has also recognized the potential economic benefit that can be achieved through the recycling of chemicals instead of disposal.

Therefore the objective of our research program was to develop activated carbon fibers (ACFs) with greatly enhanced properties to address the above problems. Our approach focused on: 1) to develop a more fundamental understanding of the mechanism of adsorption, 2) to learn how to tailor the pore size/surface chemistry to make the ACFs far more selective toward specific contaminants, and 3) to design ACFs which are much lower in cost and more abrasion resistant. To date, we have been highly successful in all three areas.

Historical Review

Commercially available activated carbon granules (GAC) have been the industry standard for many years as adsorbents to purify polluted waste streams. Primarily because of their low cost they have been determined to be the best available technology for removal of many contaminants. However, GAC suffers from a number of drawbacks including poor selectivity, slow kinetics, the need for expensive containment systems, less than 100% working capacity, and costly reactivation. Perhaps the most serious problem is the absence of a comprehensive

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understanding as to the effect of pore size and chemistry on the adsorption properties. Such knowledge would allow one to tailor activated carbons for control of specific contaminants.

To address some of these disadvantages, Economy[1-3] reported on the development of phenolic based activated carbon fibers (ACFs) which displayed significantly improved adsorption capacities over GACs. Today, these ACFs are commercially available from Nippon Kynol and are prepared by direct activation of a cross-linked phenolic fiber at 800-1000°C using a mixture of steam/CO_2. The ACFs offered a number of advantages over the GACs including improved contact efficiency with the media leading to greater rates of adsorption, much higher surface areas (up to 2500 m^2/g) and the potential for greatly simplified *in situ* regeneration through electrical resistance heating. Unfortunately the ACFs are very expensive (~$100/lb) and are not very durable during handling.

It was with this background that we undertook to establish a sound scientific foundation that would lead to a predictive capability for this poorly understood but important technology. In addition, by designing new kinds of low cost systems with far greater versatility it was our hope that we would further liberate this technology from the limitations imposed by the product forms of GAC.

Role of Pore Surface Chemistry

Currently GAC is prepared by an oxidative etching process which results in a pore surface containing several percent oxygen in the form of phenolic hydroxyls, carboxylic acids, and quinones. Hence the pore surface is slightly acidic which of course strongly influences the adsorption characteristics toward acidic or basic materials. In our program we have shown how to alter the pore surface chemistry to make it basic, more acidic, neutral or polar.[4,5] By this relatively simple approach we can dramatically increase adsorption efficiency and capacity. For example an ACF further oxidized from 3-5% oxygen to 25-30% oxygen content will have 30x the adsorption capacity for ammonia gas as demonstrated by breakthrough experiments (Figure 1). Note that the untreated ACF does not adsorb an appreciable amount of ammonia and thus the breakthrough time is fairly short. Following the oxidation treatment, the breakthrough time increases tremendously from 25 minutes up to 800. This improvement is due to the enhanced interaction of the ammonia molecule with the acidic functional groups that have been introduced onto the pore surface. Conversely, an ACF fiber activated in an atmosphere of ammonia gas will contain basic nitrogen groups (typically in the form of pyridine/aniline type units) which are effective for adsorption of acidic contaminants (Figure 2). The amount of HCl adsorbed scales with the quantity of basic nitrogen (as determined by elemental analysis), for example a basic ACF containing 10% N will adsorb up to 7x by weight of hydrogen chloride gas as compared to a slightly acidic ACF containing 3-5% oxygen. Surprisingly, this adsorption is completely reversible upon low temperature heating in a clean stream. Other dramatic increases in adsorption capacity over currently used systems have been demonstrated for SO_2, acetone, and trichloroethlyene.[5,6]

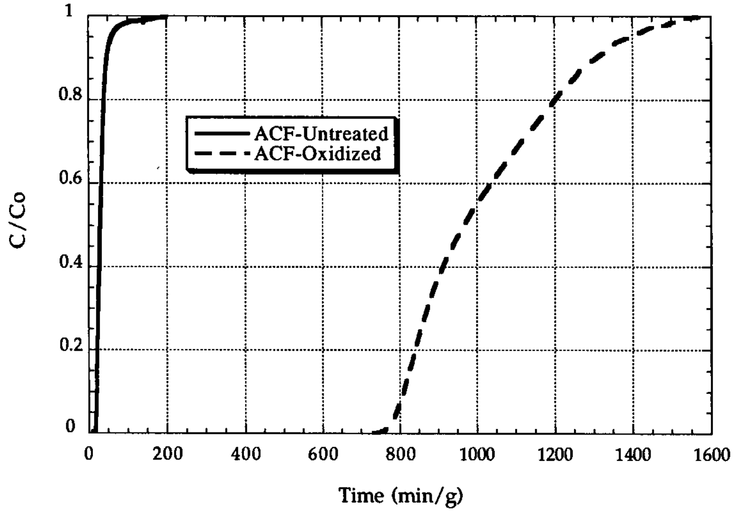

Fig. 1: Normalized breakthrough curves for ammonia (Co=970 ppmv) on ACFs

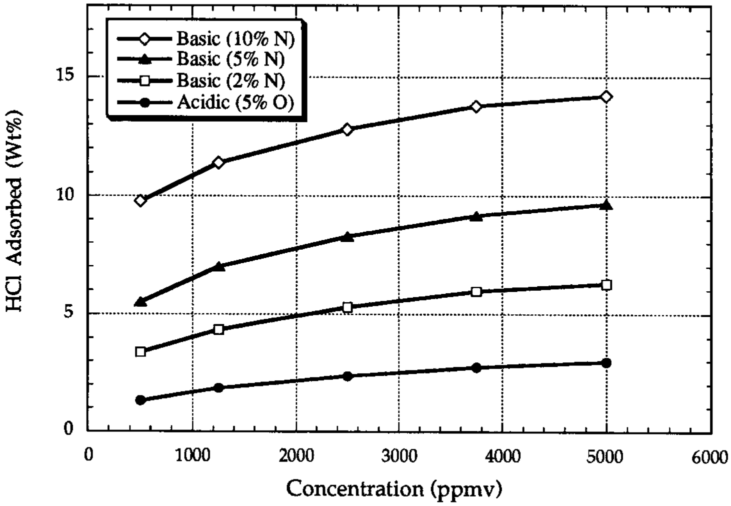

Fig. 2: Adsorption isotherms of HCl on ammonia treated ACFs

Role of Pore Size and Shape

As part of our program we also undertook to characterize the nature of the pore size and shape of activated carbons. Initially we used a variety of molecular probes ranging from large dye molecules down to small organics such as butane, benzene, iso-butane and cyclohexane.⁷⁾ Considerable insights were obtained from these indirect studies; however, we needed a more direct approach for accessing the porous structure. It should be noted that the prevailing view up to several years ago was that the pores in activated carbons were slit shaped. We found that we could successfully image the pores in the ACFs using scanning tunneling microscopy (STM) techniques.8,9) Over one thousand scans were prepared from a wide range of ACFs permitting us to conclusively define the pore size/shape and the pore size distributions. Thus, the fiber surface is composed of large mesopores while the bulk of fiber contains a homogeneous dispersion of micropores which are ellipsoidally shaped. We have been able to establish a direct correlation between pore size and conditions for activation, thus permitting preparation of ACFs with controlled pore dimensions down in the range of 5-7 angstroms (molecular sieves) and up to dimensions of 20-28 angstroms.

We have also elucidated the mechanism of pore formation showing that the first step of heating and charring of the phenolic fiber creates a microporosity of ~ 600 m^2/g just from the evolution of volatiles. In the second step, etchants such as steam, CO_2, air or ammonia act to produce a mesoporous region to a depth of about 10nm. The microporous structure in the core remains relatively uniform in diameter but increases in size with increasing time of activation.

Design of Advanced Fiber Assemblies

To address the problems of fiber brittleness of the ACF as well as their very high cost, completely new approaches were explored. Initially we looked at directly activating the phenolic fiber in air which resulted in a 2x increase in carbon yield and a modest improvement in fiber durability. A major breakthrough was achieved when it was realized that we could coat glass fibers with a phenolic resin and then activate the coating using the various techniques described earlier.10) Since glass fabrics can be purchased at prices of 35-50¢/lb (non-woven) to $1.50/lb (fabrics) and the phenolic resins are available for 60-70¢/lb it is clear that the potential exists for designing a new kind of ACF which is cost competitive to GAC.

What we found was that this concept worked extremely well e.g. in the case of glass fabric substrates we were limited to coatings of 30% by weight to minimize fiber bridging while with the non-wovens we could coat up to 70% by weight while still retaining good mechanical integrity. One unexpected benefit was that the abrasion resistance (Taber abrader) was improved at least 20x over the ACFs. Clearly the carbon coating was acting to protect the glass fiber surface against damage. Better abrasion resistance means lower attrition losses during handling and the potential for greatly increased utility as protective garments. Of significance is the fact that the kinetics of adsorption and desorption of these new fibers are 5x faster than the GACs and 25% better than current ACFs (as shown in Figure 3). This is because the diffusion path length of several microns is shorter than in the ACFs which is much shorter than in the GACs.

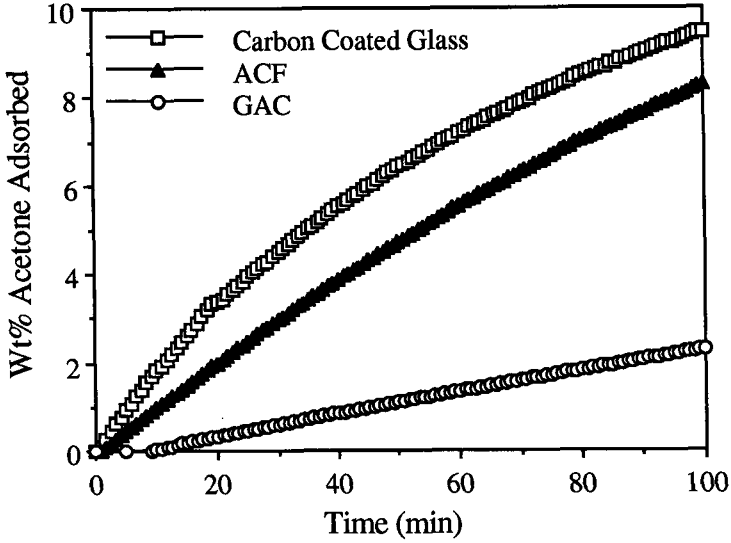

Fig. 3: Comparison of rates of adsorption for activated carbons (1000 ppmv acetone)

Conclusions

For the first time, we have been able to access the microporous structure of the ACFs using scanning tunneling microscopy. This work has led to the first detailed mechanism on the origin of the microporosity, as well as a capability to control the pore size from molecular sieve dimensions up to 20-25 angstroms. Techniques to control the chemical nature of the micropore surface from basic to highly acidic and polar to non-polar have also been developed. With this new knowledge a capability now exists to design systems tailored to remove trace contaminants in the ppb range. Equally as important we have also devised a new low cost approach for preparing the ACFs.

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