

FINAL REPORT
U.S. Department of Energy

**"REMOVAL OF HEAVY METALS AND ORGANIC CONTAMINANTS FROM AQUEOUS
STREAMS BY NOVEL FILTRATION METHODS"**

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REMOVAL OF METAL AND ORGANIC CONTAMINANTS FROM WATER BY NOVEL FILTRATION METHODS

EXECUTIVE SUMMARY

The removal of hazardous waste, generated by the dismantling of nuclear weapons is a problem that requires urgent attention by the US Department of Energy. Low levels of radioactive contaminants combined with organic solvent residues have leaked from aging containers into the soil and underground water in the surrounding area. Due to the complexity of the problem it is evident that traditional adsorption methods are ineffective, since the adsorbent tends to saturate with the aqueous component. It has become apparent that a much more aggressive approach is required which involves the use of especially designed materials. We have investigated the potential of solids that combine high surface area/high pore volume and high electrical conductivity, a rare combination of properties found in a single material. In this program we examined the potential of newly developed materials for the trapping of organic solvents within specially engineered cavities without allowing the material to become saturated with water.

Catalytically grown carbon nanofibers are a set of novel structures that are produced by the decomposition of selected carbon-containing gases over metal particles. These materials consist of extremely small graphite platelets stacked in various orientations with respect to the fiber axis. Such an arrangement results in a unique structure that is composed of an infinite number of extremely short and narrow pores, suitable for the sequestering of small molecules. In addition, when the graphene layers are aligned parallel to the fiber axis, an unusual combination of high surface area and low electrical resistivity solids are attained. We have attempted to capitalize on this blend of properties by using such structures for the selective removal of organic contaminants from aqueous streams. Experimental results indicate that nanofibers possessing a structure in which the graphite platelets are aligned perpendicular to the fiber axis and possessing a high degree of structural perfection exhibit superior selective adsorption properties with respect to removal of alcohols from aqueous media over that

displayed by active carbon. Adsorption was enhanced when the carbon nanofibers were initially subjected to a treatment in 1M hydrochloric acid. In contrast, when this step was carried out in the presence of 1M nitric acid the beneficial properties of the nanofibers were effectively suppressed. An analogous series of experiments carried out with nanofibers possessing a structure in which the graphene layers were oriented at an angle with respect to the fiber axis did not result in the same degree of selective capture of the alcohols.

Furthermore, we have attempted to take advantage of the high electrical conductivity as well as the high availability of edges, we have used these materials for the removal of metal ions from solution. Preliminary results indicate that graphite nanofibers can in the presence or absence of an applied electric field capture metal ions from solution. In addition it has been found that certain types of nanofibers can absorb substantial amounts of water both in the vapor and liquid phase.

During this period collaboration with Prof. Carol Bessel, Villanova University was initiated. Two graduate students, Mr. Paul E. Anderson and Ms. Elizabeth Engel conducted research that will ultimately lead to Ph.D. degrees. Papers resulting from this work have been published in refereed journals and a number have submitted for publication. Two undergraduate students, Ms. Dalia Hildebrand and Ms. Andrea Crowe participated in the program as part of their Cooperative education experience. In this regard, it is significant that Ms. Hildebrand has elected to pursue Ph. D. in the area of environmental engineering.

Relevance, Impact and Technology Transfer

Using selected powdered metal catalysts it is possible to produce around 30 different types of CNF that have the potential for a variety of applications. These include: filtration devices, rubber reinforcement, fuel cells, hydrogen storage, conductive polymers, catalyst support media, lithium ion rechargeable batteries and electron emission source. Due to the renewed interest in the area of nano-technology, interactions are being initiated with several corporations in order to license some of the technology developed in this and other allied projects.

RESEARCH OBJECTIVES

Accumulation of waste generated by the disposal of nuclear weapons, particularly low level radioactive contaminants combined with organic residues, is becoming a problem of great concern. Due to the aging of the containers in which these residues were stored, a significant fraction of these pollutants have leaked and polluted soil and underground water in the surrounding area. A great deal of effort is being spent in the pursuit of methods for the safe recovery and disposal of this waste.

Activated carbons are the most universally used sorbents for the purification of water, since they exhibit a high adsorption capacity. This property is usually controlled by the physical -large surface area- rather than by the chemical nature of the solid. The dependence of the adsorption on the actual physical area can have negative consequences when dealing with solutions since the solid can indiscriminately adsorb both the adsorbate and the solvent and consequently reach saturation without selectively removing the desired contaminant. Due to the complexity of the problem it became apparent that traditional methods of adsorption are ineffective to deal with such a contamination issue. Recently, tailored carbons have been investigated with respect to their selective adsorption capacity with rather promising results. It has been found that fibrous activated carbons (FAC) exhibit superior adsorption properties than those of granular activated carbon [1-3].

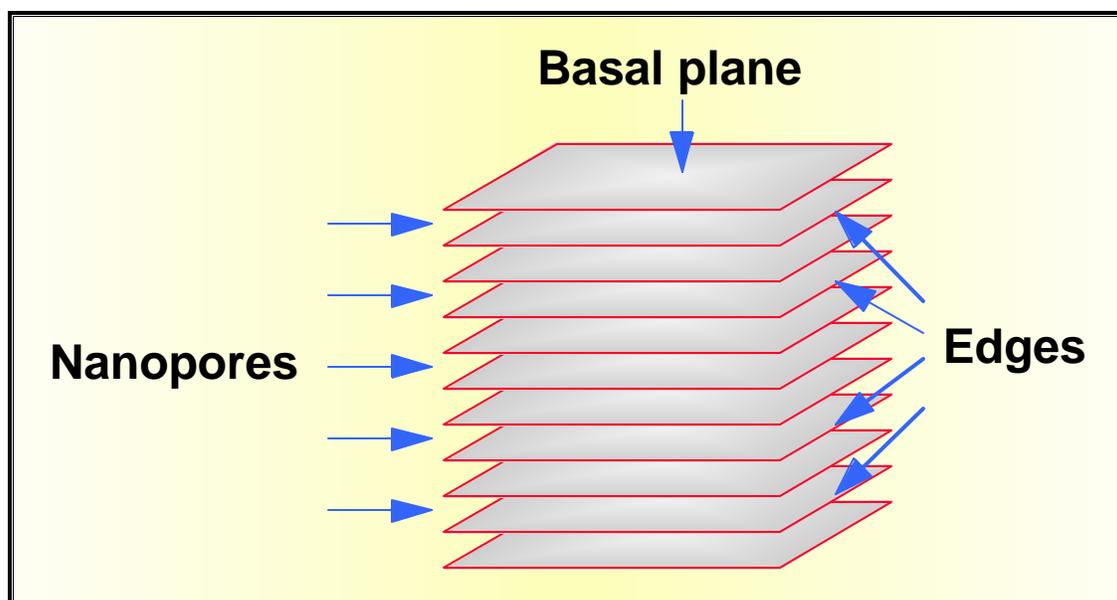


Figure 1. Schematic representation of a carbon nanofiber consisting of a multitude of small graphite layers separated at a distance of 0.35 nm. Adsorption of organic molecules occurs by diffusion into the nano- pores.

In this program we have used a unique approach that involves the use of a new engineered solid. Catalytically grown carbon nanofibers (CNF) are produced by the decomposition of selected carbon-containing gases over metal particles at temperatures ranging from 500 to 900°C. CNF vary from 5 to 100 μm in length and between 5 to 100 nm^2 in cross-sectional area [4-10]. These solids combine both a relatively high surface area and high electrical conductivity a rare combination of properties that we have utilized for the simultaneous removal of metals and organic contaminants from aqueous streams. CNF consist of nano-

sized graphite layers separated at a distance of 0.34 nm. Such an arrangement results in a unique structure consisting of an infinite number of extremely short and narrow pores, suitable for the sequestering of small molecules (Figure 1). Since there is no chemical bond between the platelets, the interlayer spacing can be expanded by the introduction of suitable groups that can further "open-up" the structure. Due to the very nature of graphite, the basal plane would favor the interaction with non-polar (organic) molecules, whereas the edges -to which functionality can be added- will preferentially interact with polar (water) groups. The hydrophilic edges allow for a good interaction with the solution without saturating the non-polar pores. Due to the abundance of pores CNF constitutes perhaps the most efficient selective adsorption medium.

The major objectives of this investigation were as follows:

- To establish the suitability of CNF for the selective removal of organic molecules from aqueous streams.
- To explore the effects of the structural characteristics (cross-sectional area and conformation) of CNF for this adsorption process.
- To identify the effect of the crystallinity of the CNF on their ability to selectively adsorb certain organic molecules.

METHODS AND RESULTS

Unsupported Metal Catalyst Preparation. The bimetallic metal powders used in this investigation were prepared by the co-precipitation of the respective metal carbonates from metal nitrate solutions using ammonium bicarbonate according to the previously outlined procedure [11]. The precipitate was dried in an oven at 110°C overnight, after which it was calcined in air at 350°C for 4.0 hours to convert the carbonates to metal oxides. This step was followed by a reduction in 10% hydrogen/helium at 350°C for 20 hours. The reduced powders were cooled to room temperature in flowing helium and passivated in a 2% oxygen/helium mixture for 1.0 hour before removal from the reactor. The passivated catalysts were stored in sealed containers until required for use. Single metal catalyst powders were prepared by a similar protocol and in all cases reagent grade nitrates were obtained from Fisher Scientific. The compositions of the various catalysts were determined from X-ray diffraction analysis using a Scintag diffractometer and found to agree within experimental error, with the desired ratios. The gases used in this work, hydrogen (99.999%), helium (99.999%) and carbon monoxide (99.95%) were purchased from Med Tech Gases and used without further purification.

Table 1. Characteristics of the Support Media

Support	Surface Area N₂ BET m²/g	Geometric Properties	Electronic Properties
SiO ₂	255	-	Insulator
SP1-Graphite	6	~ 5% edge sites	Conductor in basal plane
Platelet GNF	120	~ 99% edge sites	Conductor (basal plane) and semiconductor (along edges)

Supported Metal Catalyst Preparation. Three different types of support media were selected for this investigation; Cab-o-Sil amorphous fumed silica, SP1 Graphite obtained from Alfa Aesar and demineralized platelet CNF. The physical properties of the various supports are presented in Table 1. Iron, cobalt and nickel were separately introduced onto each of the supports via incipient wetness impregnation in water or ethanol using the respective metal nitrates as precursor salts to produce a 5 wt. % metal loading. The impregnated materials were all dried overnight in air at 110°C, followed by calcination in air at 350°C for 4 hours and finally reduced in 10% H₂/He at 350°C for up to 36 hours. These treatments and the subsequent carbon nanofiber growth reactions were performed in a horizontal flow reactor system. All gas flow rates were regulated with MKS mass flow controllers.

Synthesis of CNF

The preparation of the CNF was carried out in a horizontal quartz tube (40 mm i.d. and 90 cm long) contained in a Lindberg tube furnace, at temperatures over the range 450 to 700°C. In a typical experiment 50 mg of the given catalyst powder was dispersed in a uniform manner along the base of a ceramic boat, which was subsequently placed at the center of the reactor tube. After reduction of the sample at 600°C for 2 hours, the system was flushed with helium and brought to the desired temperature before being treated in the desired C₂H₄/H₂ or CO/H₂ mixture for a period of 2.0 hours. The total amount of solid carbon formed in any given experiment was determined at the completion of the reaction by weight difference. The composition of the gas phase was measured at regular intervals by taking samples of the inlet and outlet streams, which were then analyzed by gas chromatography using a 30-m megabore (GS-Q) capillary column in a Varian 3400 GC unit. Carbon and hydrogen atom balances in combination with the relative concentrations of the respective components were applied to obtain the various product yields. In order to obtain reproducible carbon deposition data it was necessary to follow an identical protocol for each experiment.

Characterization of CNF

The structural details of the solid carbon product resulting from the interaction of the carbon containing gas/H₂ mixtures with the various powdered bimetallic catalysts were examined in a JEOL 2000 EX II transmission electron microscope that was fitted with a high resolution pole piece capable of providing a lattice resolution of 0.18 nm. For these experiments specimens were prepared by application of a drop of the ultrasonic dispersion of the carbon deposit in iso-butanol onto a holey carbon support grid. Temperature programmed oxidation

studies (TPO) of the various carbon deposits were carried out in a Cahn 2000 microbalance in the presence of a CO₂/Ar (1:1) mixture at a heating rate of 5°/min up to a maximum temperature of 1100°C. This approach has been shown to be a very useful method for assessing the graphitic nature of a given carbon deposit from a comparison the oxidation profile with those of two standard materials, amorphous carbon and single crystal graphite when treated under the same conditions [7]. In order to make such an evaluation meaningful it is essential to remove all metallic impurities from the carbon deposit before performing the oxidation step, otherwise distortions in the profile could occur due to catalytic processes. Therefore, before performing the TPO experiments, all carbon deposits were treated in 1N hydrochloric acid for a period of 7 days to remove the associated catalyst particles. Following this step the samples were washed in deionized water and dried in air at 110°C. Finally, BET surface area measurements of the deposits were carried out in a Coulter Omnisorp 100 CX unit by N₂ adsorption at -196°C.

Transmission Electron Microscopy (TEM)

CNF from Unsupported Metal Powders. TEM examination of the carbonaceous solids produced from the metal catalyzed decomposition of C₂H₄/H₂ mixtures over Cu:Ni and CO/H₂ over Fe indicated that they consisted exclusively of nanofibers, with no indication of any other forms of carbon being present. Two types of structures were generated with these systems: herring-bone type where the graphene sheets are aligned at an angle with respect to the nanofiber axis from the bimetallic system, whereas the latter system yielded a "platelet" type of nanofiber in which the graphite platelets are aligned perpendicular to the nanofiber axis. Close examination of the structures indicated that under the conditions used in the experiment, the nanofibers generated from the interaction of C₂H₄/H₂ with Cu:Ni catalysts possessed significantly more structural imperfections than those synthesized from the decomposition of CO/H₂ over Fe powders. In both cases, however, the width of an individual nanofiber corresponded to that of the cross-sectional area of the catalyst particle. It should be noted that although the initial powders consisted of granules that were ~1 μm in size, these entities fragmented during the reaction to produce much smaller particles. In the unsupported systems, however, it is very difficult to exercise control over the catalyst particle size and this aspect results in a wide size distribution of carbon nanofibers. Figures 2a-2b are transmission electron micrographs of nanofibers that were produced from the interaction of carbon monoxide/hydrogen mixtures at 600°C over metal catalyst powders. By measurement of the width of over 500 nanofibers it was possible to determine that the average cross-section of the structures was ~ 100 nm.

The structural perfection of carbon nanofibers has been related to the ability of the metal catalysts to interact with the basal plane of graphite [7]. Under such conditions, metal particles undergo rearrangement so as to generate faces in which the interstices are perfectly matched with the atomic arrangement of the carbon atoms in single crystal graphite and as a consequence, the deposited material will possess a high degree of crystalline perfection. This rearrangement occurs when Fe particles are allowed to interact with CO/H₂ at 600°C. At lower synthesis temperatures it has been found that the structure of the nanofibers is less ordered. It was interesting to find that when Fe powders were reacted with C₂H₄/H₂ mixtures, very little solid carbon was obtained, an observation that is consistent with previous work reported in the literature [9].

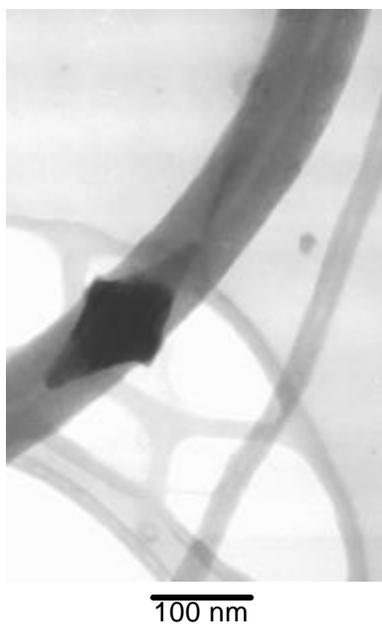


Figure 2a. Transmission electron micrograph of carbon nanofibers produced by the catalyzed decomposition of ethylene/hydrogen over a nickel containing catalyst. The diamond shaped black body is the metal catalyst particle

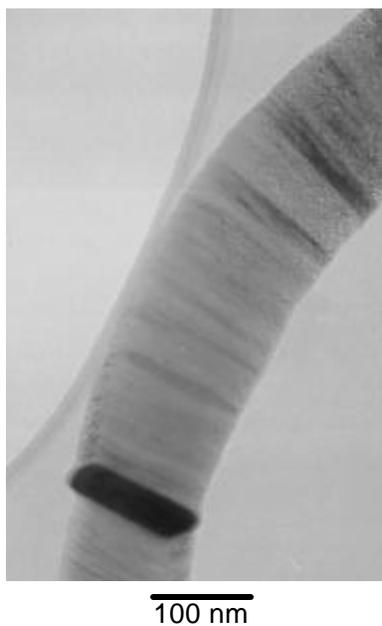


Figure 2b. Transmission electron micrograph of carbon nanofibers produced by the catalyzed decomposition of carbon monoxide/hydrogen mixtures over an iron based catalyst. The black body in the center is the metal particle responsible for their growth.

CNF from Supported Metal Particles. The removal of impurities from aqueous media is generally carried out by an adsorption process in which the solution is passed over a bed containing the adsorbent. In order for the system to become commercially viable it is necessary for the removal process to be completed within a very short period of time. In the present

system, adsorption of impurities is expected to occur via migration of the organic molecule from the aqueous solution to the inner regions of the nanofibers. This process involves a number of steps, one of which is diffusion of the adsorbate through the very narrow pores existing between two graphene layers. We believe that the uptake can be accelerated if a reduction in the path length traversed by the adsorbed molecule can be realized. Such a modification would result in a substantial enhancement in the efficiency of the process and should be achievable by utilizing a catalytic protocol that results in the growth of very narrow carbon nanofibers. Materials produced from the decomposition of carbon-containing gases over metal powders have a wide size distribution. This is due to inability to control the initial size of individual catalyst particles in the powders. On the other hand, the use of a supported catalyst system allows one to generate a fine dispersion of metal particles, which subsequently results in the production of nanofibers possessing narrow widths.

In this investigation we have demonstrated that major modifications in the growth characteristics of carbon nanofibers can be achieved when metals such as iron, cobalt and nickel are used in a supported form to catalyze the decomposition of ethylene at 600°C. Moreover, there were significant differences in the performance of these metals depending upon the nature of the metal-support interaction. In this respect one of the most intriguing aspects to emerge was the finding that while powdered iron samples did not generate carbon nanofibers from ethylene/hydrogen mixtures, when the metal was dispersed on either silica, graphite or carbon nanofiber supports, the growth of these structures proceeded in a very facile manner.

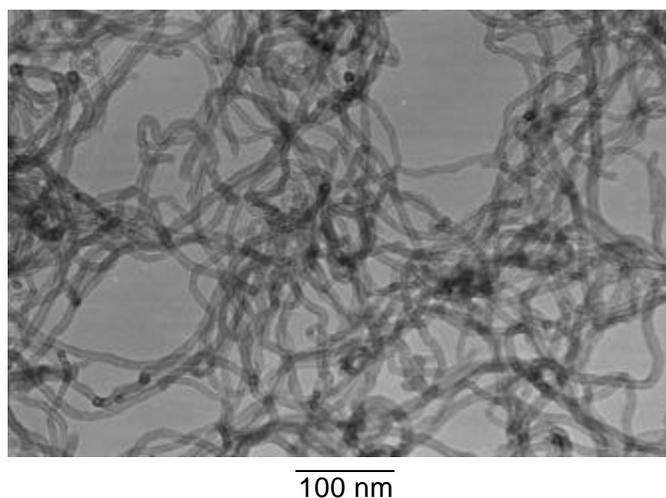


Figure 3. Transmission electron micrograph of carbon nanofibers produced by the catalyzed decomposition of carbon monoxide/hydrogen mixtures over a silica supported iron based catalyst.

High resolution transmission electron microscopy studies of the solid carbon deposit formed in these reactions revealed that, as with the unsupported systems, nanofibers were the exclusive product of the reaction. The most striking feature, however, was the finding that the cross-sectional area of the nanofibers was substantially smaller than those encountered when such structures were generated from powdered catalysts under otherwise identical conditions and this contrast is evident in the electron micrograph Figure 3. It can be seen that the average width of individual fibers is about 10 - 15 nm, nearly an order of magnitude smaller than those found in unsupported systems. Examination of the detailed structural characteristics of the nanofibers grown from the various supported metals indicated that the material produced from iron catalysts exhibited the highest degree of crystalline perfection. In all cases, the nanofibers

derived from iron adopted a structure in which the graphite platelets were aligned in a direction parallel to the fiber axis. Close inspection showed that these nanofibers were not rounded, but instead acquired a faceted outline, where the wall thicknesses varied from a single to multiple graphite sheets. It was fascinating to find that this nanofiber geometry was maintained even when such "secondary" structures were generated from iron particles supported on "parent" carbon nanofibers where the graphite sheets were aligned in a direction perpendicular to the fiber axis.

X-ray Diffraction Measurements

X-ray diffraction patterns of the two types of pristine nanofibers produced from unsupported metal catalysts showed that the "platelet" type of structure was highly graphitic in nature with a d -spacing very close to that of single crystal graphite, 0.335 nm, an indication of their high crystallinity, Table 2. The average stack height, L_c , was determined from the broadening of the principal graphite peak (the 002 reflection) and was found to be 17.5 nm. On the other hand, the "herring-bone" material, contained more imperfections as evidenced by the wider d -spacing distribution, (0.347 nm) and a small L_c of 5.4 nm. Inspection of these data indicates that, as expected, the more disordered "herring-bone" structures have a relatively short stack height. It is interesting to find that in the "platelet" nanofibers, a significant expansion in the lattice spacing to 0.344 nm was observed following adsorption of butanol into this material, which suggests that the organic molecule "slides" between two graphene layers indicating that following adsorption between the layers, the structure undergoes expansion.

Table 2 Structural characteristics of pristine and acid treated "Platelet" and "Herring-bone" CNF materials obtained from X-ray Diffraction Studies.

Type of CNF*	Treatment	Mean d -spacing (nm)	Stack Height, L_c (nm)
P-CNF	Pristine	0.335	17.5
P-CNF	HNO ₃	0.336	12.8
P-CNF	HCl	0.338	13.8
P-CNF	H ₂ SO ₄	0.340	15.6
H-CNF	Pristine	0.347	5.4
H-CNF	HNO ₃	0.346	4.7
H-CNF	HCl	0.347	4.6
H-CNF	H ₂ SO ₄	0.349	5.6

Surface Area Determinations.

The Brunauer, Emmett and Teller (BET) method was used to determine surface area of the various carbons at -196°C in N₂ [12]. The results presented in Table 3 indicate that the surface area of the "platelet CNF" was 119 m².g⁻¹, whereas that of the "herring-bone" form was 161 m².g⁻¹. In contrast, the active carbon sample exhibited a significantly higher value of 750 m².g⁻¹. Subsequent treatment of both types of CNF materials in 1M hydrochloric acid resulted in

a slight decrease of the respective surface areas. On the other hand, when this process was conducted in 1M nitric acid the surface areas of both nanofiber samples decreased by almost a factor of two. Loss of active sites as a result of nitric acid treatment may be due to the formation of oxygenated species that undergo cross-linking at the edge regions of the graphite sheets. Immersion of the nanofibers in 2M sulfuric acid appeared to cause an increase in the interlayer spacing of both materials and in contrast to the nitric acid treatment did not exert a deleterious effect with respect to loss of active sites. It was interesting to find that no equivalent changes were apparent when the active carbon sample was subjected to the same series of acid treatments.

Table 3. Surface Areas of Various Carbon Materials

Material	BET N ₂ Surface Area (m ² /g)	Micropore* (%) Surface Area
Norit Carbon	646.1	81.85
P-CNF (pristine)	119.1	6.9
P-CNF (HCl treated)	112.92	46.4
P-CNF (HNO ₃ treated)	60.48	66.8
P-CNF (H ₂ SO ₄ treated)	82.16	40.0
H-CNF (pristine)	161.3	25.6
H-CNF (HCl treated)	257.3	66.7
H-CNF (HNO ₃ treated)	161.7	77.45
H-CNF (H ₂ SO ₄ treated)	187.7	60.2

*P-CNF: Platelet Carbon Nanofiber

*H-CNF: Herringbone Carbon Nanofiber

Adsorption of Organic Molecules on "Platelet" CNF.

In this series of experiments, the adsorption of ethanol on active carbon and "platelet" CNF was examined. The results (Table 4) show that the ability of the nanofibers to adsorb the alcohol far exceeds that of active carbon. After a period of about 60 hours the uptake of ethanol on active carbon was only 6%, but was 38% on the nanofibers. Although active carbon has a much larger surface area, it is apparent that with this material adsorption of the organic from an aqueous solution is non-selective in nature; i.e. pores in active carbon are quickly saturated with water thus preventing the alcohol from being adsorbed into these regions. On the other hand, due to the chemical character of CNF, which consists entirely of graphite platelets, we believe that it is possible for relatively narrow molecules to "slide" between the layers where they interact with the basal plane regions of the material. Indeed, although ethanol has some polarity, the molecule is known to be capable of wetting graphite due to such interactions. In contrast, water molecules are expected to have negligible affinity for the basal plane of graphite, and so do not gain access to the inner structure as illustrated in Figure 4.

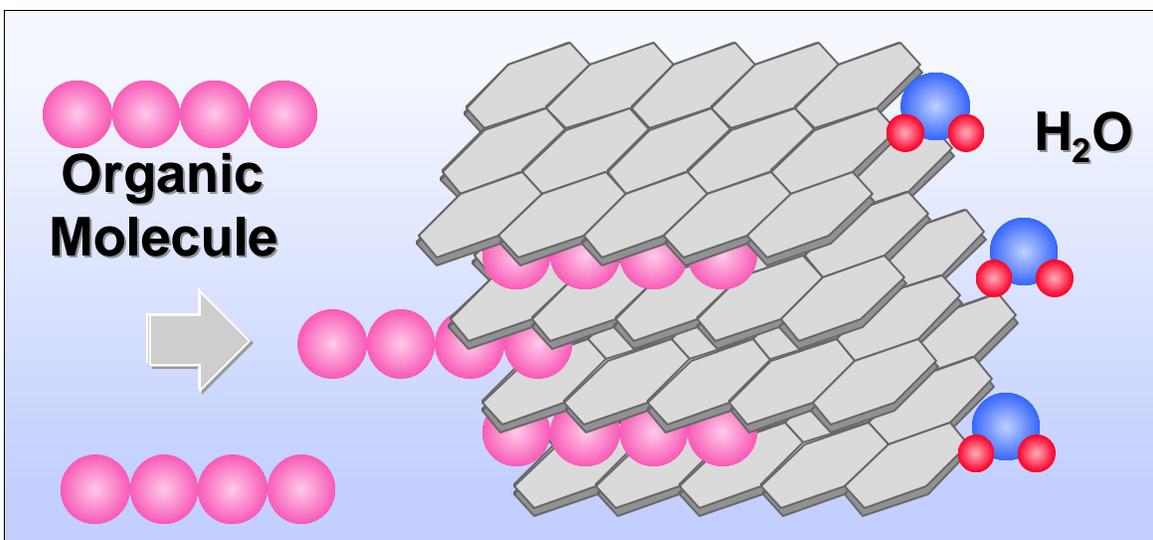


Figure 4. Schematic representation of the proposed adsorption mechanism of organic molecules by GNF. The polar water molecule preferentially adsorbs at the more polar edges of CNF. The organic molecule slides between the non-polar layers.

Table 4. Adsorption of organic compounds from aqueous solution on various carbon materials after 60 minutes of interaction.

Material	% Adsorbed		
	Ethanol	Butanol	Pentanol
Active Carbon	21.0	22.9	10.9
H-CNF (Pristine)	14.3	15.5	9.0
H-CNF (HCl treated)	0.5	14.8	6.0
H-CNF (HNO ₃ treated)	0.9	8.5	7.4
H-CNF(H ₂ SO ₄ treated)	0.0	17.0	6.0
P-CNF (HCl treated)	32.0	75.0	-
P-CNF (HNO ₃ treated)	2.0	0.0	-

Adsorption of Organic Molecules on "Herring-Bone" CNF.

When "herringbone" type nanofibers were used for the same set of adsorption experiments, the results were somewhat disappointing as evidenced by the finding that the performance of these materials was very similar to that exhibited by activated carbon (Table 4). We believe that due to the lower degree of crystalline character exhibited by these materials, abundant oxygenated groups are present at the edge regions, which in turn, will directly affect the adsorption properties of the material. These results demonstrate that while the molecular structure of the adsorbate is an important feature, the degree of crystalline perfection of the solid carbon must also be taken

into consideration when designing a material for selective adsorption. A combination of these two factors would therefore provide the best adsorption performance in novel filtration devices.

RELEVANCE, IMPACT AND TECHNOLOGY TRANSFER

The implementation of new and effective methods for clean up of hazardous waste constitutes an extremely urgent task to be accomplished within the next few years. We have selected to use carbon nanofibers as an adsorbent material because it is possible to manipulate the structure and consequently alter the properties of the solid so as to fit a particular application. It is a fact now generally accepted that solids having nano-sized dimensions possess properties that are not encountered in bulk materials. Since the materials that were selected for this research program are relatively inexpensive to make and in most cases easy to regenerate, they constitute an environmentally friendly option.

The results of this initial program have demonstrated the feasibility of removing small quantities of certain organic compounds from aqueous streams. Clearly, if the concepts developed in this study can be extended to cover other more complex molecules then it would be appropriate to conduct tests in the field. The development of carbon nanostructures having certain properties required the mounting of a fundamental research program in order to understand the kinetics mechanism of formation, and this work led to the development of CNF possessing truly outstanding properties. Some of the materials that were synthesized during this program have been found to have potential for a number of applications. These include:

- *Lithium ion rechargeable batteries:* CNF can be easily intercalated by Li⁺ ions. During this process, species are trapped between the graphene layers. Preliminary experiments indicate that the performance of such solids is superior to that of Li⁺/graphite samples, both in charging and discharging cycles.
- *Catalysts for Fuel Cells:* CNF supported platinum particles exhibit an outstanding performance as electrodes for fuel cells. The behavior of 5 wt. % Pt/CNF is comparable to that of a 30 wt. % Pt/Vulcan carbon catalyst. Furthermore, high catalytic activity of Pt/CNF can be achieved at temperatures well below 80°C.

During the course of this investigation it was found that over 40 different types of CNF can be produced, all having different properties depending upon their synthesis conditions. It was also found that the respective pristine structures can easily be manipulated so as to introduce functional groups (acids: COOH; keto: CHO; hydroxyl: OH) that can further alter the properties of these solids. Various companies in the US have expressed interest to produce the material in large scale and we are currently having discussions on this subject with W. R. Grace & Co. and Engelhard.

During the course of this project several postdoctoral fellows and graduate students have participated in various aspects of the research and some of these students have now taken up positions with US companies. In addition, many of the graduate students have had the opportunity to interact with personnel at other Universities, including MIT and have presented papers at International meetings. Below are listed the personnel who have been involved in the research program:

- Post-doctoral Fellows
Colin Park
Christopher Toles

- Graduate Students
Paul E. Anderson (Ph. D. candidate)
Elizabeth Engel (Ph. D. candidate)
Rajesh Satyamurthi (Ph. D. candidate)
Waseff Khatib (M.S. graduate)
- Undergraduate Students
Andrea Crowe (Chemistry major)
Dalia Hildebrand (Chemical engineering graduate)

PUBLICATIONS RESULTING FROM THIS AWARD (All publications were or will be refereed)

- P. E. Anderson and N. M. Rodriguez, "Synthesis of Graphite Nanofibers from the Decomposition of CO/H₂ over Silica Supported Iron-Nickel Particles", J. Mat. Res. 14, 2912 (1999).
- P. E. Anderson and N. M. Rodriguez, "Synthesis of Graphite Nanofibers Over Transition Metal Catalysts Supported on Various Substrates", Chem. of Materials, 12, 823 (2000).
- C. Park, E. Engel, A. Crowe, T. R. Gilbert and N. M. Rodriguez, "Removal of Organic Molecules from Aqueous Solutions using Graphite Nanofibers", Langmuir, accepted for publication.
- P. E. Anderson, E. Engel, A. Crowe, C. Park and N. M. Rodriguez "Carbon Nanofibers for Environmental Applications", Proceedings of the WM2000 Conference, Tucson, AZ.
- P. E. Anderson and N. M. Rodriguez, "Effect of the Support on the Synthesis of Carbon Nanofibers", Mat Res. Soc. Symp. Proc. (2000) in press.
- R. Satyamurthi, P. E. Anderson and N. M. Rodriguez, "Synthesis of CNF from the decomposition of CO over Iron-Cu Catalysts", submitted to J. Phys. Chem.
- P. E. Anderson, S. W. Jong, M. S. Kim and N. M. Rodriguez, "Characterization Studies of CNF Grown from the Interaction of Supported Transition Metal Particles with Acetylene" submitted to J. Phys. Chem.

INTERACTIONS

This work was the result of a collaboration with Prof. Terry Baker who was responsible for the design of catalysts and the synthesis and characterization of carbon nanostructures possessing various properties. His extensive experience in catalysis was crucial for the development of these unique conformations.

TRANSITIONS

This project has served as the basis for the development of a number of advanced materials, some of them having unexpected properties. Due to the potential for applications in a variety of energy related areas, Catalytic Materials Ltd., a small company based in Pennsylvania has decided to undertake the further development of these materials. In addition, proprietary

discussions are being conducted with various large corporation in the US who have expressed interest in the large scale synthesis of CNF.

PATENTS

None

FUTURE WORK

The discovery and development of a variety of catalytically grown carbon nanofibers offers the opportunity for numerous applications. Taking advantage of the unique properties of these materials we plan:

- (a) To investigate the effect of the structural characteristics of carbon nanofibers on the selective adsorption of various organic molecules from aqueous streams.
- (b) To ascertain the impact of changing the chemical functionality of the edge sites of the carbon nanofibers on the selective removal of organic molecules from water.
- (c) To exploit the potential of carbon nanofiber supported metal particles to function as electro-catalysts for the reduction of organic liquids.
- (d) To capitalize on the electrosorption characteristics of carbon nanofibers for the demineralization of aqueous streams via ion exchange reactions.
- (e) To design a multiple bed separation system for the sequential removal of organic and metallic contaminants from water.

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