Removal of Metal and Organic Contaminants from Aqueous Solutions by Novel Filtration Methods

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Background

- **Activated carbons: the most universally used sorbents for the purification of water, since they exhibit a high adsorption capacity.**
- **This parameter is usually determined by the physical - large surface area - rather than by the chemical nature of the solid.**
- **Recently it has been found that fibrous activated carbons (FAC) exhibit superior adsorption properties than those of granular activated carbon - Delanghe et al. Water Supply (1996) 14 177.**

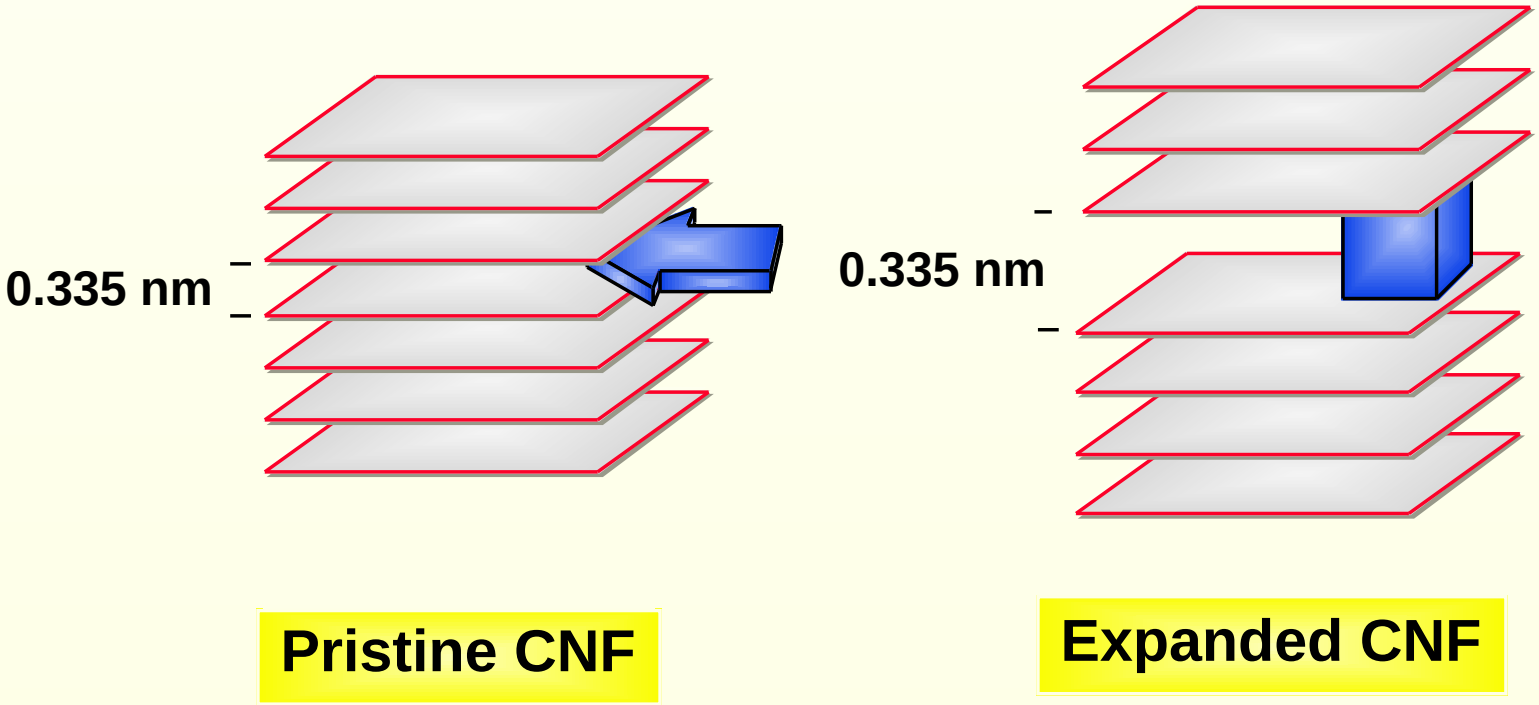
Adsorption in Carbon Nanofibers

- CNF consist of nano-sized graphite platelets 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.
- 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.

Objectives

- 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.

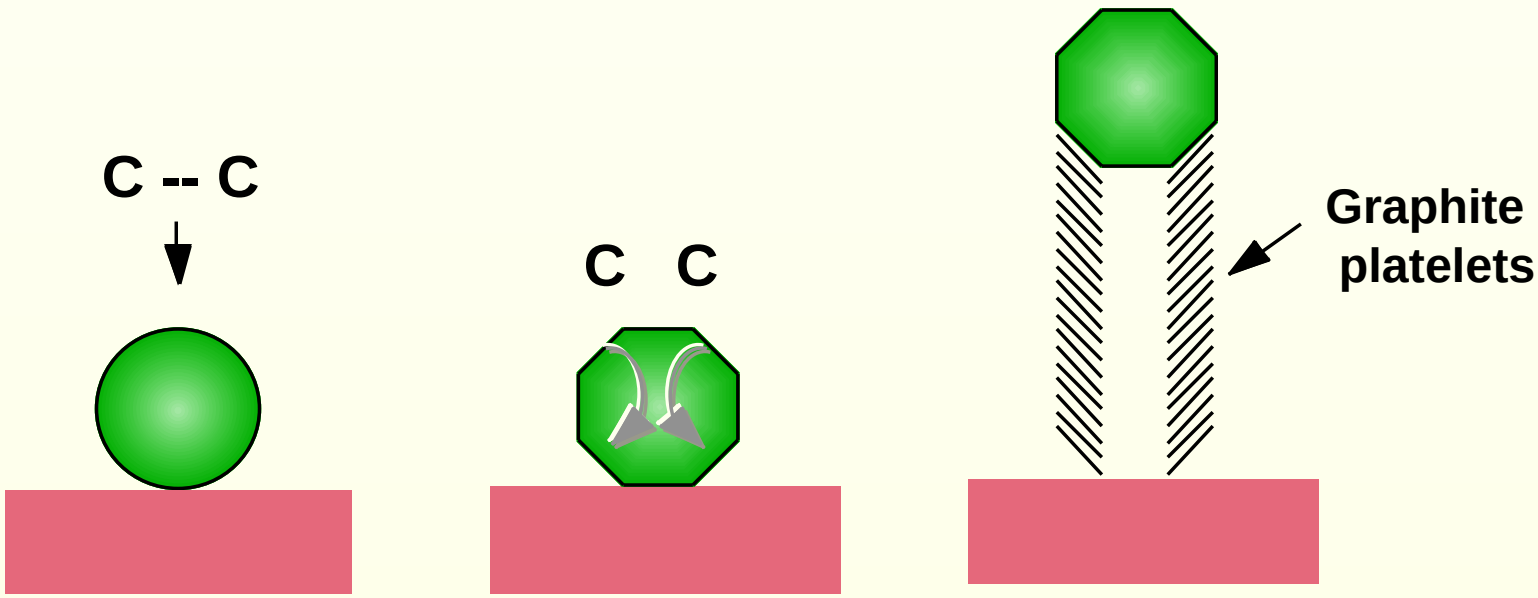
Adsorption Mechanism



Carbon Nanofibers (CNF)

- CNF are produced by the decomposition of hydrocarbons/CO over small metal particles at temperatures ranging from 500 to 900°C.
- The structure and crystalline perfection of the CNF is dictated by the nature of the catalyst particle, the temperature and the reactant gas composition.
- The width of the CNF is controlled by the size of the catalyst particle responsible for the growth .

Carbon Nanofiber Growth



Initial
Metal Particle

Reconstructed
Metal Particle

Metal Particle -
Carbon Nanofiber

Control of Nanofiber Width

Unsupported Metal Particles

- **Metal powders (~ 1μm in size) undergo fragmentation to produce nanofibers with a wide cross-sectional area distribution, typically 20 to 200 nm.**

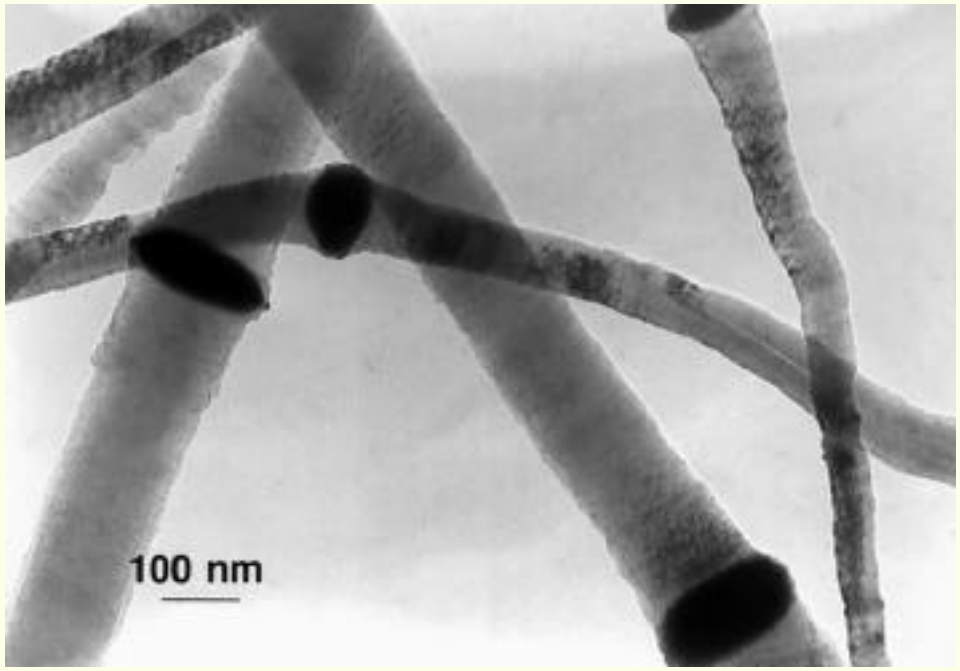
Supported Metal Particles

- **Particles dispersed on suitable supports maintain their initial small size and produce nanofibers of comparable widths ~ 5 to 20 nm.**

Transmission Electron Microscopy

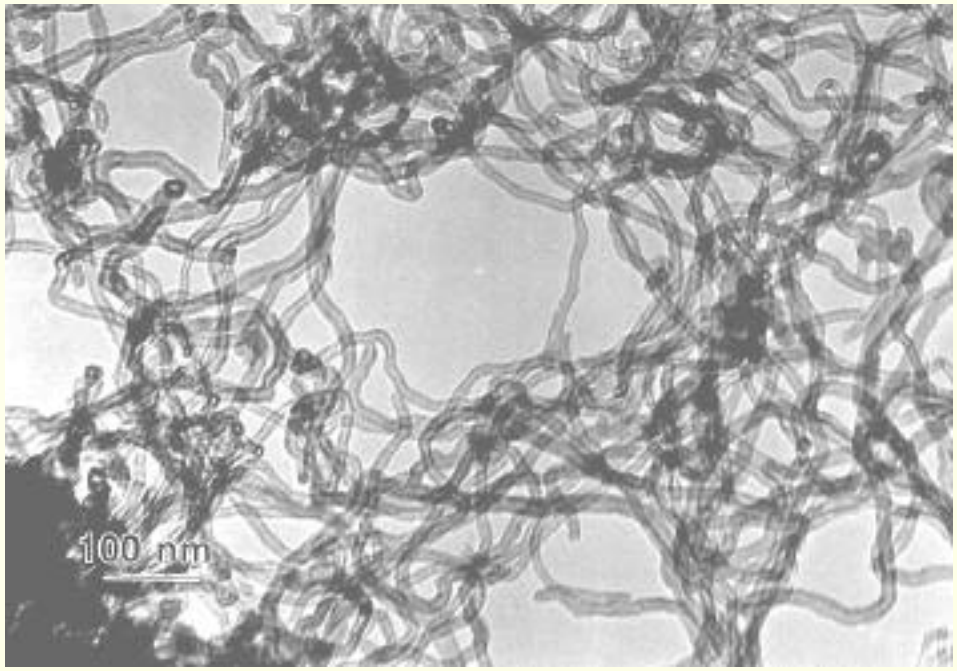
- Conventional and high resolution TEM are routinely used to establish the structure and crystallinity of CNF.
- Electron diffraction is also used to accurately measure d-spacing and determine crystal structure of metal catalyst particles.

Unsupported CNF



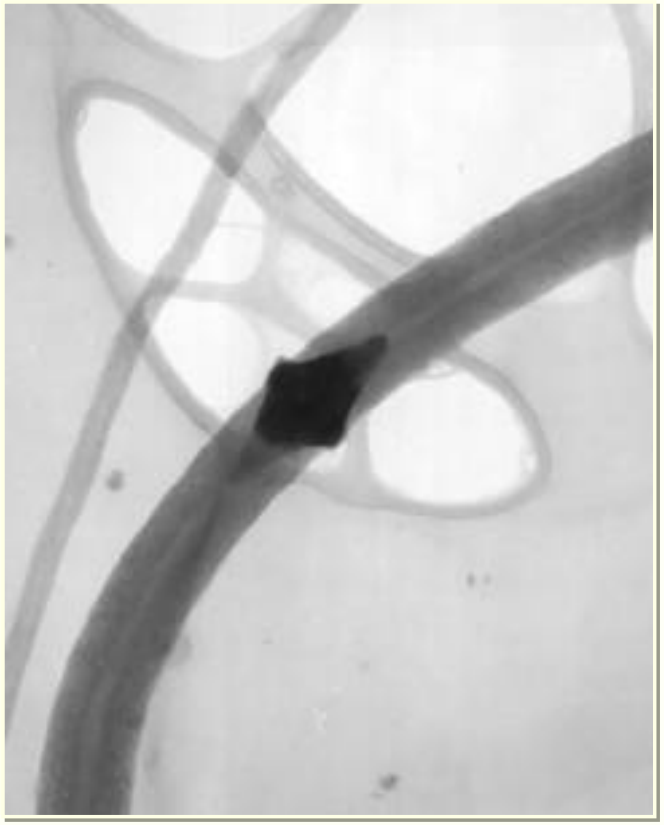
CNF produced from the interaction of Fe powder with CO/H_2 at 600°C.

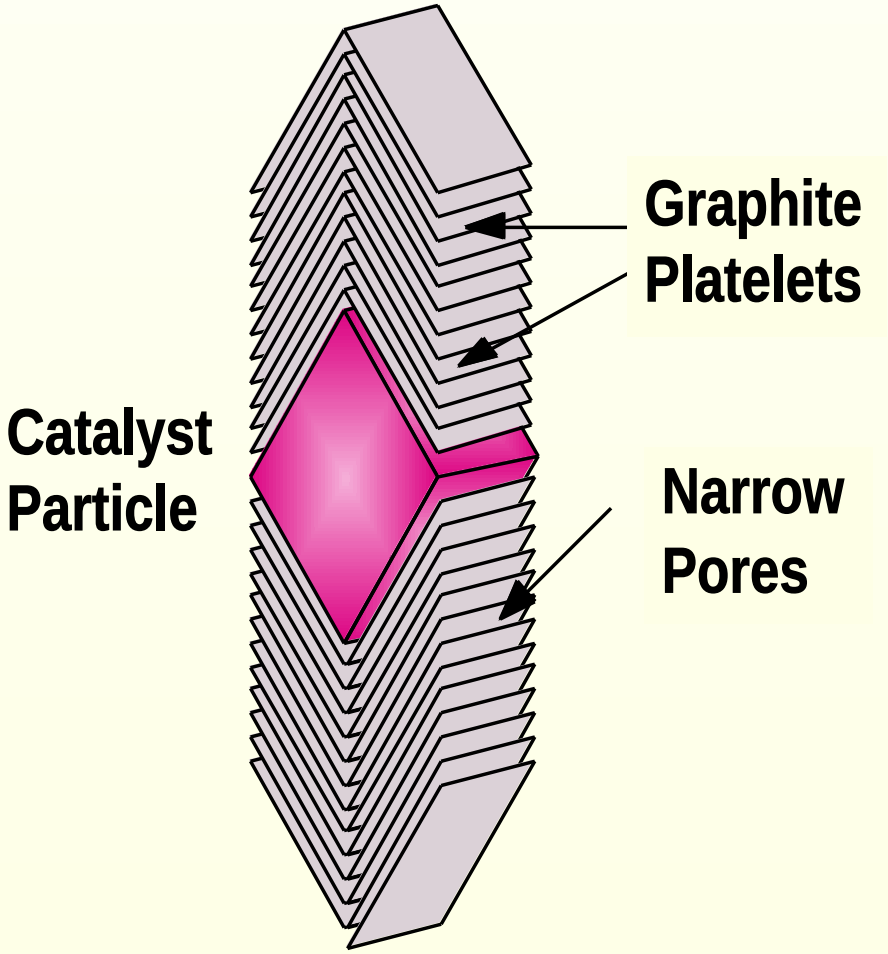
Supported CNF



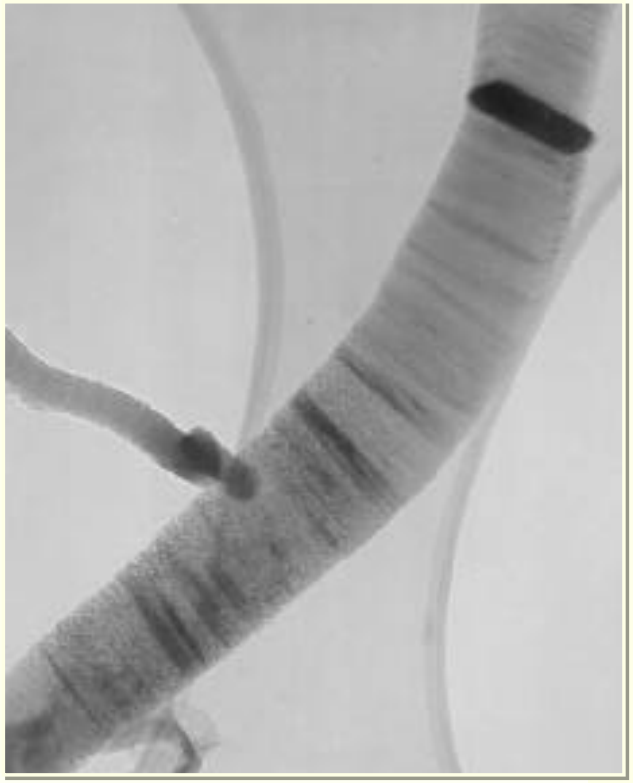
CNF produced from the interaction of silica supported Fe-Ni particles with CO/H_2 at 600°C.

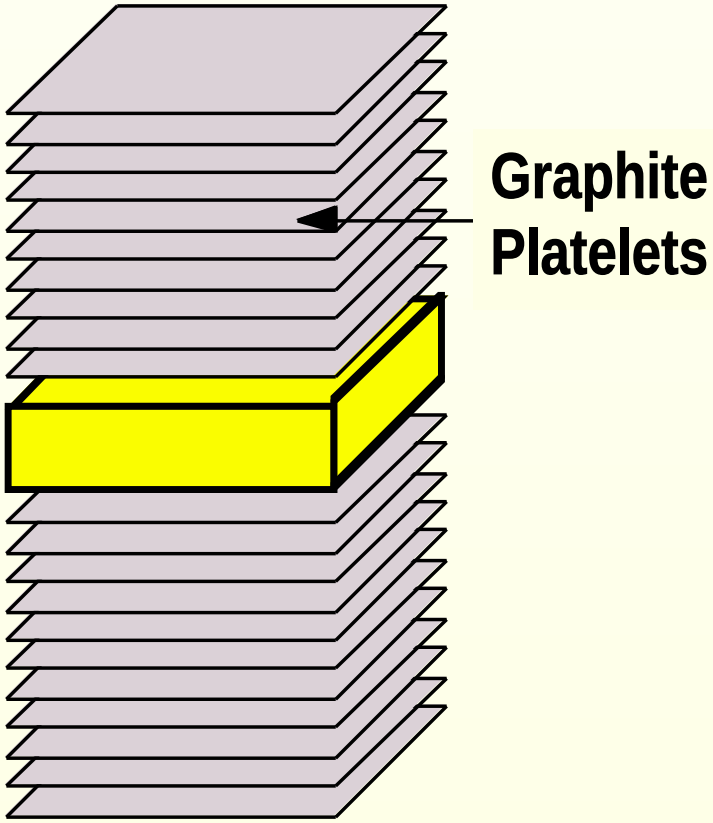
Herring-bone CNF





Platelet CNF





Materials

“Platelet” CNF

- **Graphene layers are perpendicular to the nanofiber axis.**
- **These nanofibers possess a high degree of crystalline perfection.**

“Herring-bone” CNF

- **Graphene layers are arranged at an angle with respect to the nanofiber axis.**
- **These materials exhibit a lower degree of crystalline perfection.**

Characterization of CNF

Temperature Programmed Oxidation

- **This technique is based on the principle that in the presence of CO_2, the onset of gasification (oxidation) of disordered carbons occurs at ~ 550°C.**

$$C + CO_2 \longrightarrow 2CO$$

- **On the other hand, highly crystalline carbons start to oxidize at ~ 850°C in a similar atmosphere.**

Surface Areas of CNF Materials

Material	Surface Area BET/N_2 (m^2/g)
Norit Carbon	646.1
P-CNF (pristine)	122.8
P-CNF (HCl treated)	111.2
P-CNF (HNO_3 treated)	65.2
P-CNF (H_2SO_4 treated)	70.5
H-CNF (pristine)	161.3
H-CNF (HCl treated)	257.3
H-CNF (HNO_3 treated)	161.7
H-CNF (H_2SO_4 treated)	187.7

P-CNF: Platelet CNF

H-CNF: Herringbone CNF

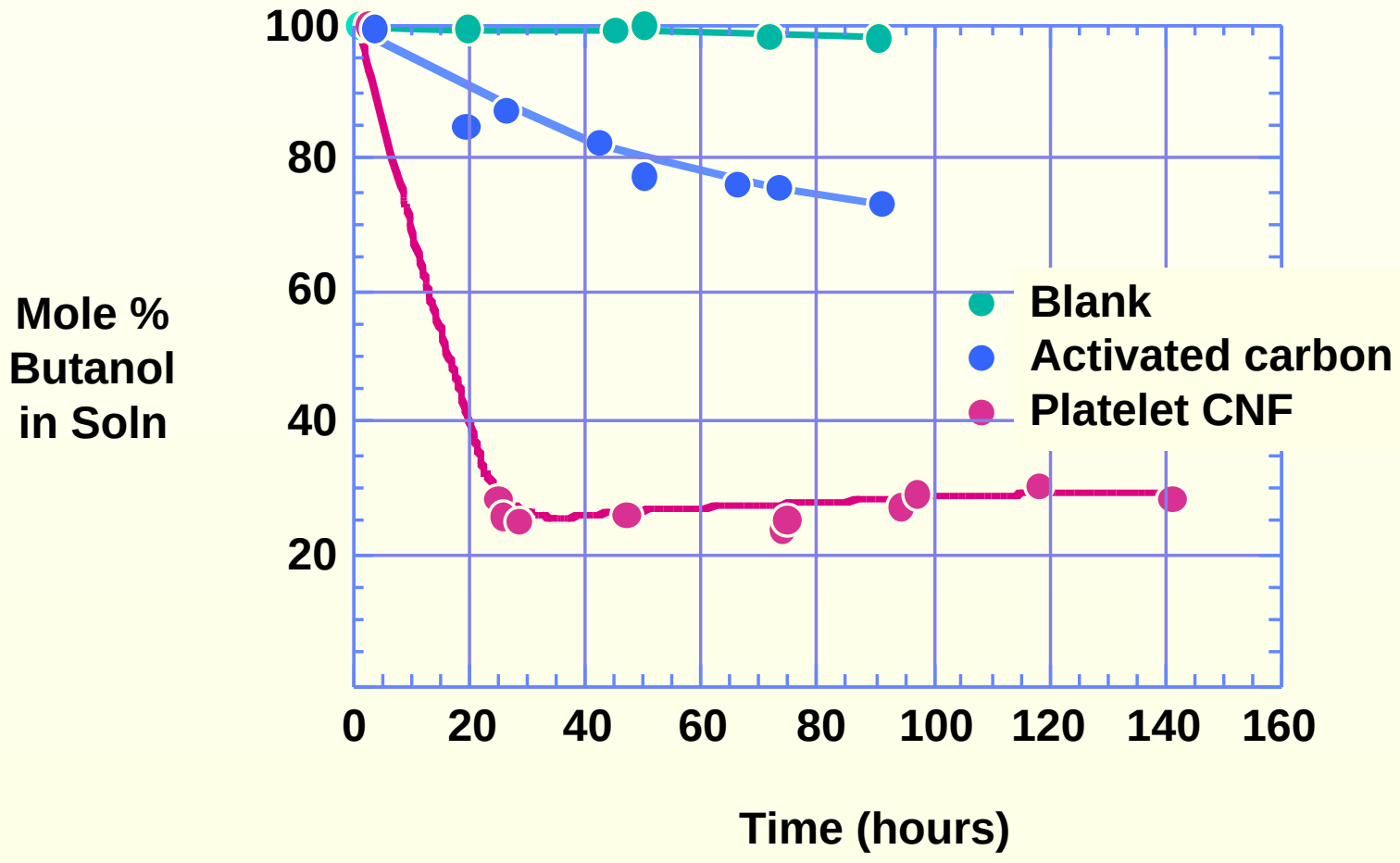
X-Ray Diffraction Analysis

Material	Mean d-spacing (nm)
P-CNF (pristine)	0.335
P-CNF (HNO_3 treated)	0.336
P-CNF (HCl treated)	0.338
P-CNF (H_2SO_4 treated)	0.340
P-CNF (HCl/Ethanol Adsorption)	0.338
P-CNF (HCl/Butanol Adsorption)	0.344
H-CNF (pristine)	0.347
H-CNF (HNO_3 treated)	0.346
H-CNF (HCl treated)	0.347
H-CNF (H_2SO_4 treated)	0.349

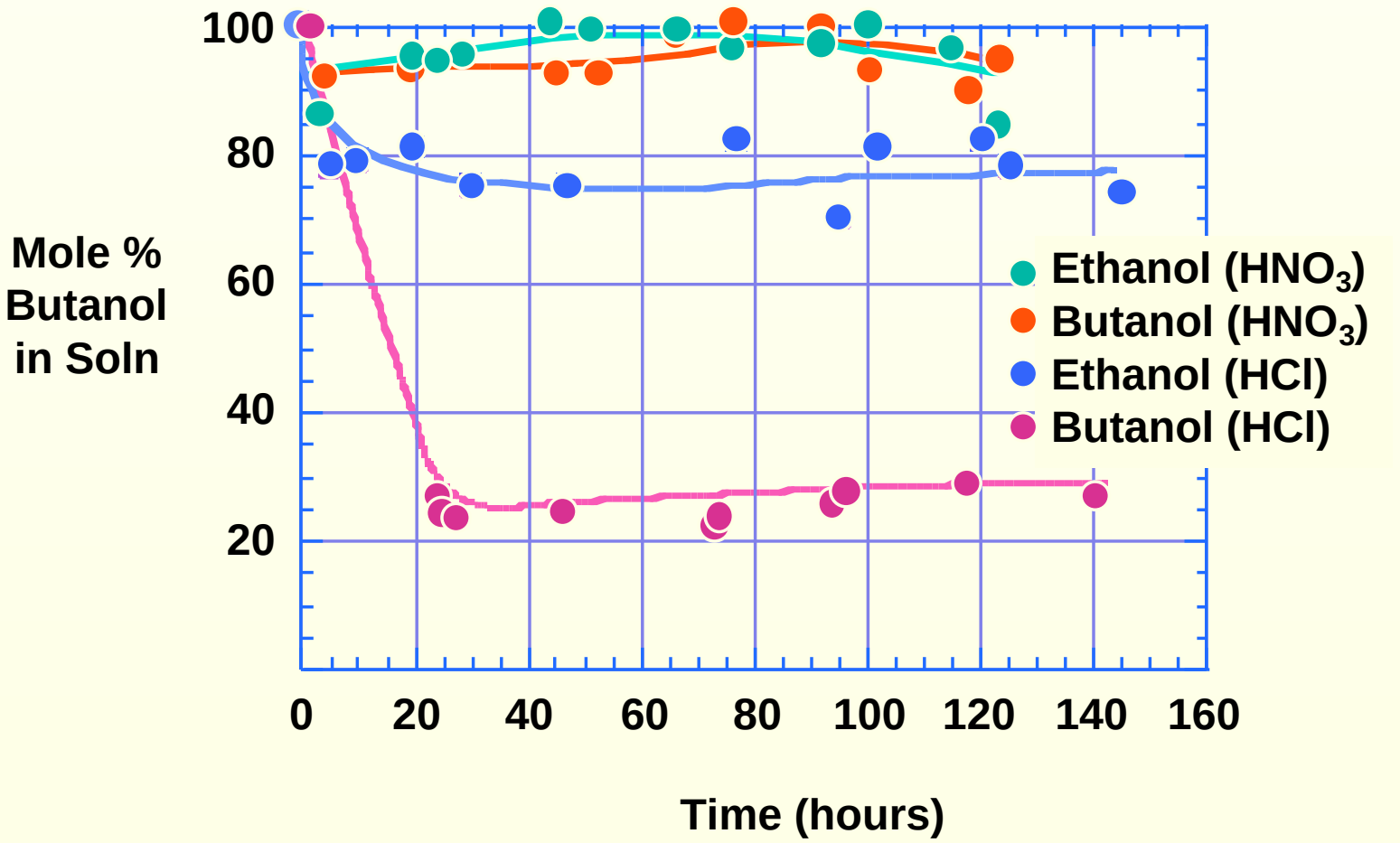
Prospects for CNF Technology

- 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
  - Catalyst support media
  - Lithium ion rechargeable batteries

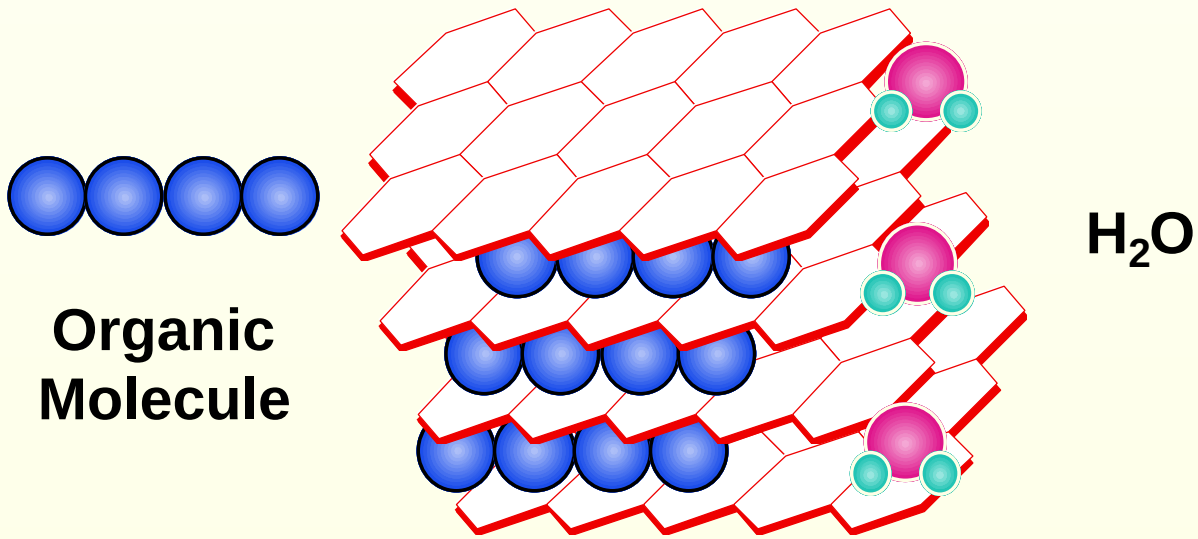
Adsorption of Butanol



Adsorption in acid-treated CNF



Adsorption Mechanism



Effect of Support on CNF Widths

Metal	SP1 Graphite	Silica	Platelet CNF	Unsupported
Ni	3-50	4-49	5-50	35-450
Co	4-49	2-18	4-28	25-250
Fe	4-35	3-20	20-150	-

Width in nm

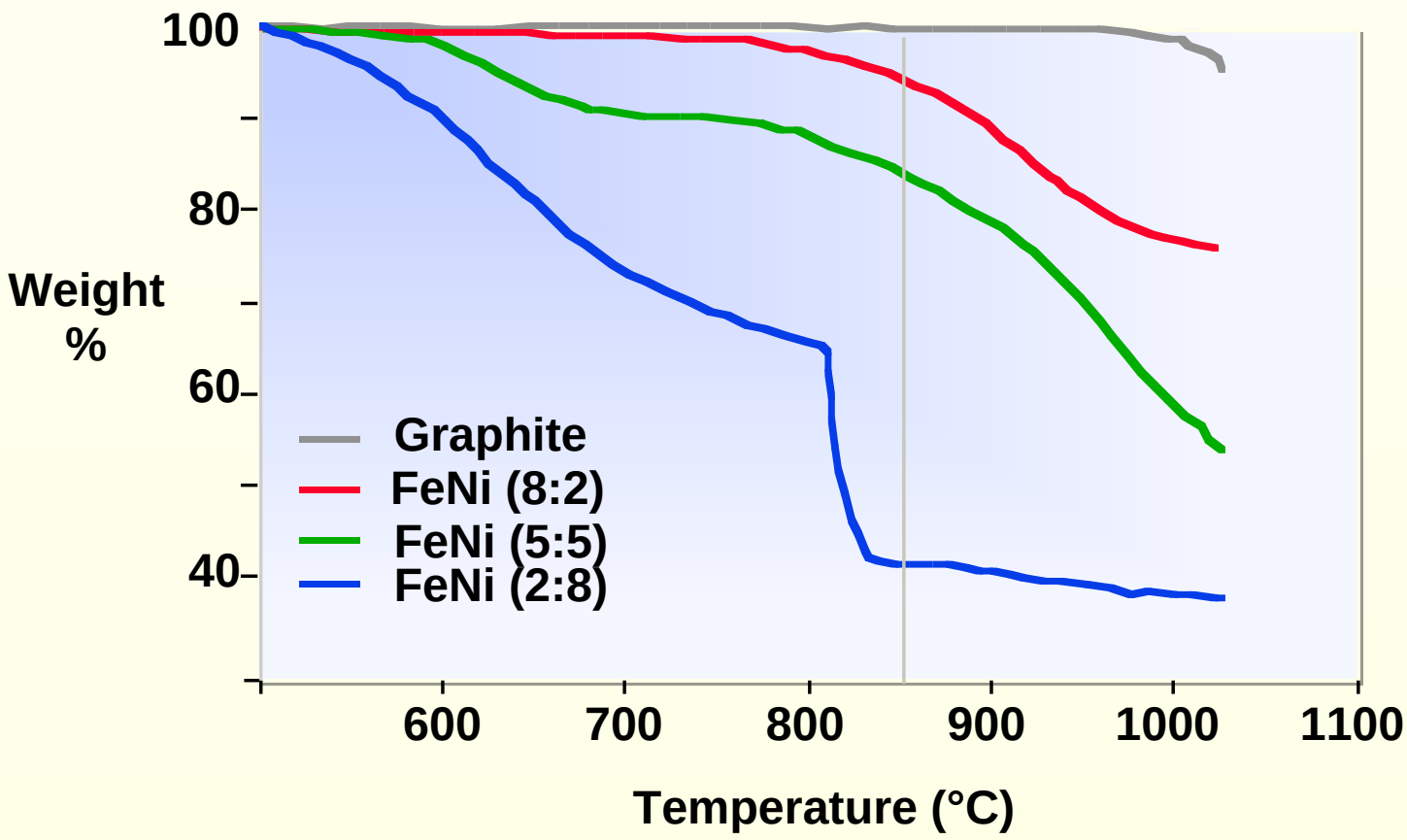
Project "Spin-Offs"

- **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.**

Project "Spin-Offs"

- **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.**

Temperature Programmed Oxidation



Summary

- Highly crystalline CNF were found to exhibit excellent adsorption properties for the removal of small amounts of alcohols from aqueous solution.
- When experiments were carried out using CNF possessing a less ordered structure, their performance towards adsorption of alcohols was poor.
- In contrast, these latter materials can concentrate solutions due to their ability to adsorb large amounts of water.

Summary

- The adsorption properties of platelet-CNF were superior to those of activated carbon, even though the former possess only one fifth of the surface area.
- The current results indicate that CNF constitute a unique adsorption system, where non-polar molecules can be effectively removed from aqueous solution to be trapped within slit-shaped pores.

Summary

- X-ray diffraction measurements show that following adsorption of organic molecules, widening of the CNF pores occurs as demonstrated by the increase of the d_{0002} interplanar spacing.
- Although the physical properties of a material play a major role in its ability to adsorb molecules, the key factor that ultimately controls the selectivity is the chemical nature of the solid.

Future Studies

- Since diffusion is the rate limiting step in the selective adsorption process, we shall endeavor to improve the performance of the system by using smaller width CNF.
- We shall continue to explore the potential of the CNF to remove more complex organic molecules from water, including aromatics, chloro-olefins and MTBE.
- Attempts will be made to remove alkali metals, including Cs, from water by ion exchange methods.

Acknowledgments

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Publications from this Award

- P. E. Anderson and N. M. Rodriguez, Synthesis of Graphite Nanofibers from the Decomposition of CO/H_2 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, in press.
- C. Park, E. Engel, A. Crowe, T. R. Gilbert and N. M. Rodriguez, "Removal of Organic Molecules from Aqueous Solutions using Graphite Nanofibers", Langmuir, in press.

Publications from this Award

- 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, in press
- P. E. Anderson and N. M. Rodriguez, "Effect of the Support on the Synthesis of Carbon Nanofibers", Mat Res. Soc. Symp. Proc. (2000) submitted.
- 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.

Research Personnel

- Post-doctoral Fellows
  - Colin Park
  - Christopher Toles
- Graduate Students
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  - Elizabeth Engel
  - Rajesh Satyamurthi
- Undergraduate Students
  - Andrea Crowe
  - Dalia Hildebrand