Nanomaterials in the Environment
An application and comment on implications

Nanotechnology and the Environment
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Center for Biological and Environmental Nanotechnology

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U.S. Activities in Nano-Envi

- EPA – basic research and regulatory policy
  - $7M/year in academic research
  - Last three calls <u>exclusively</u> implications research
- Department of Energy very active in area (remediation, clean-up)
- NSF does fund some interdisciplinary work in fundamental nano-envi
  - CBEN is a NSF funded research center

Today's Talk

The Public

Benefits *Risks*

1. Exploiting size in environmental remediation
   - *Nanosized magnetite for arsenic removal*

2. Is size dangerous? Implications of nanotechnology

Water Treatment Technologies: A Real Need

From 1900 to 2000:
- life expectancy at birth increased from 47 to 76 years
- infant mortality decreased from 165 to 7 (per 1000 births)

- Waterborne illnesses major cause of death
- Increasing contamination in water
- Population growth increasing demand

Arsenic in Drinking Water

- Arsenic in water linked to cancer
- EPA standards: 50 ug/L to 10 ug/L
- Natural and anthropogenic sources
- Enormous interest in removal
  - Plants (phytofiltration)
  - Muds and sediments
  - Zero valent iron – in-situ
  - Mine tailings (e.g. iron oxides)

Ayotte et al, Envi. Sci. Tech. 2003 37, p.2075

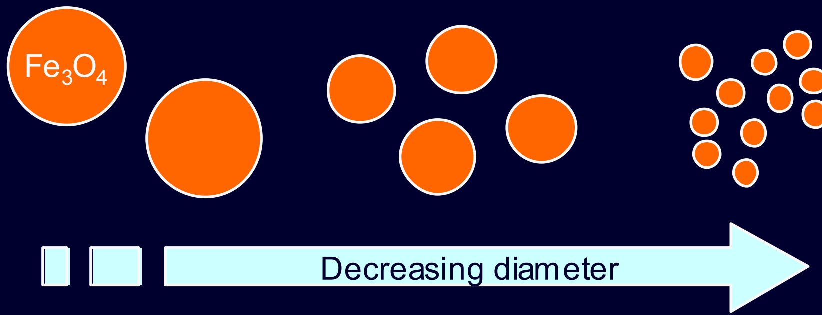
Existing Sorbents for Arsenic Removal

" Our two year study showed that none of the (18) Arsenic Removal Plants could maintain arsenic in … water … below the WHO guidelines …."
- Hossain *et al* in ES&T 2005, p. 4300

Material	Sorbent (kg) / month	1 gram treats ____ L water	Waste to dispose of kg (1 yr)	Backwash frequency (day)
Alumina + Metal Oxide	0.24	3.8	2.88	14
Red Mud [As(III)]	360.7	0.002	4328.1	Periodic
Ion Exchange	No Removal of Toxic As(III)			~ 3

For a family of four, using 900 L water/month, at 500 ppb As levels (7.9 pH)

Nanomagnets: Two Advantages

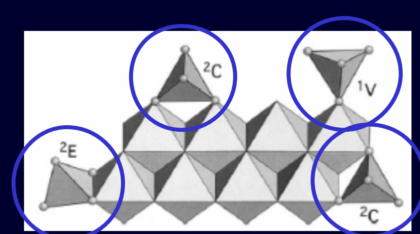


1. Increased surface area for arsenic sorption

2. Enhanced magnetic susceptibilities improve separations

Arsenic sorption onto iron oxides

- *Strong and specific sorption*
- *Chemical transformation*
- *Subjected to interferences*
  - *Silicate and phosphates*
  - *Humic acids*



Models for surface interactions*

Are Nanoscale iron oxides are good candidates for sorbents?

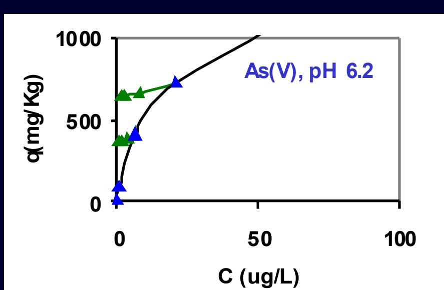
MASON TOMSON, AMY KAN, SUJIN YEAN

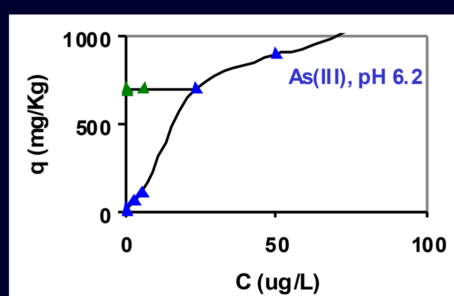
* D. M. Sherman, S. R. Randall Geochimica et Cosmochimica v. 67 no. 22 p. 4223

Commercial nanoscale iron oxides

As particle size gets smaller sorptive area increases with R^2

Sorption of Arsenic Onto Magnetite





- 20 nm Magnetite can sorb both As(V) and As(III)
- Sorption capacities (▲) of .1 % (w/w)
- Arsenic is irreversibly sorbed (▲) stable in storage

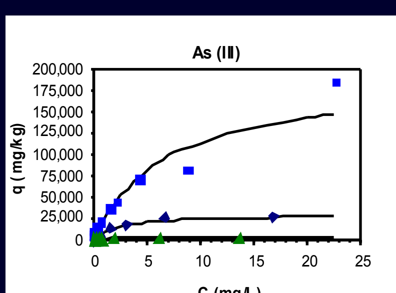
Synthesis of monodisperse nano-Fe_3O_4

Commercial nano-oxides have problems

- Agglomerated → poor magnetic separation
- Larger nanoparticles → lower sorption
- Bad size distribution → no optimization

Nanomagnets: Large Sorption Capacity

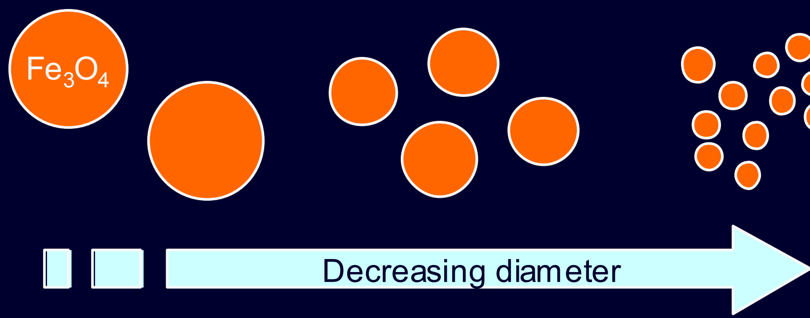
Volume of water treatable by 1 Kg magnetite



Particle Size (nm)		Volume of Water (L)
12	As(III)	2,283
20	As(III)	594
300	As(III)	21
12	As(V)	1,435
20	As(V)	1,145
300	As(V)	150

Remaining Challenge: Nanoparticles are difficult to remove

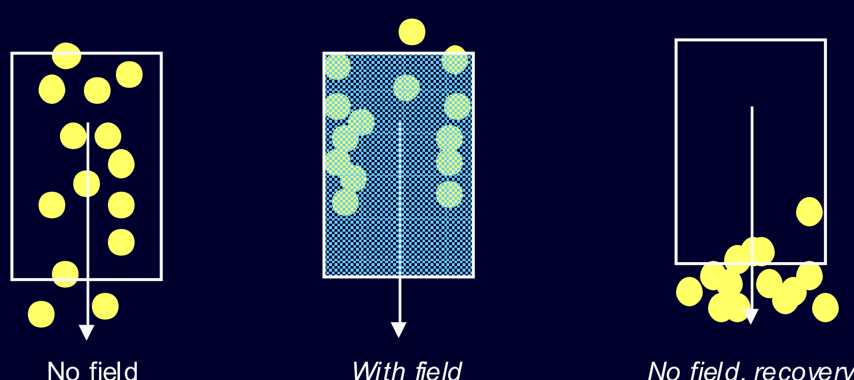
Nanomagnets: Two Advantages



1. Increased surface area for arsenic sorption

2. Enhanced magnetic susceptibilities improve separations

Magnetic Filtration for Nanosorbents



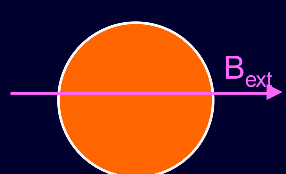
- Requires no pressure gradients
- No fouling of separation system

Magnetic Separations in Water Treatment

- Gravitational settling
- Filtration
- Induced coagulation
- Magnetic Separations

Kakihara, Y., T. Fukunishi, et al. (2004). "Superconducting high gradient magnetic separation for purification of wastewater from paper factory." Ieee Transactions on Applied Superconductivity **14**(2): 1565-1567.

Magnetic Separation: possible for d < 40nm?



1. Magnetic Tractive Force

$$F_m = \boxed{\mu_0 \chi v_p} H \nabla H$$

2. Thermal diffusive Force

$$F_d = -\frac{kT^*}{n} \nabla n$$

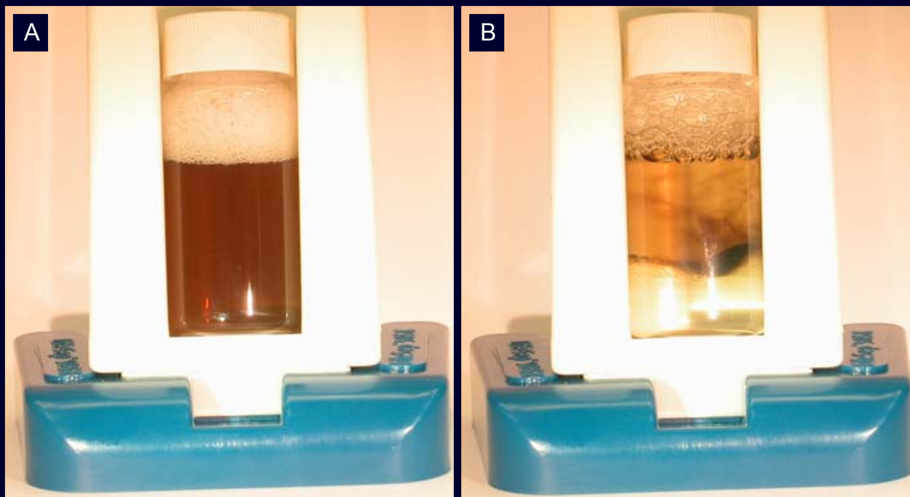
3. Viscous Drag

$$F_{0r} = -6\pi\eta b \frac{dr}{dt} \qquad F_{0\theta} = -6\pi\eta b r \frac{d\theta}{dt}.$$

Convention to expect no separation below 40 nm

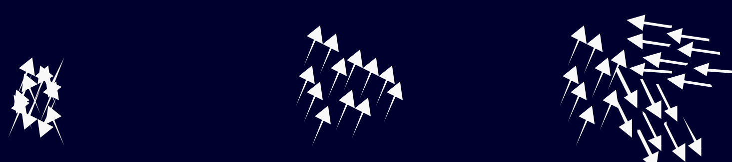
Cotton et.al.,Separ. Sci. Technol 37 (16): 3755-3779 2002; Fletcher.,IEEE T Magn 27 (4): 3655 – 3677 Jul 1991

Nanocrystals Do Separate in Low Fields



0.0 Tesla → 0.36 Tesla

“Nano” Improves Magnetic Behavior



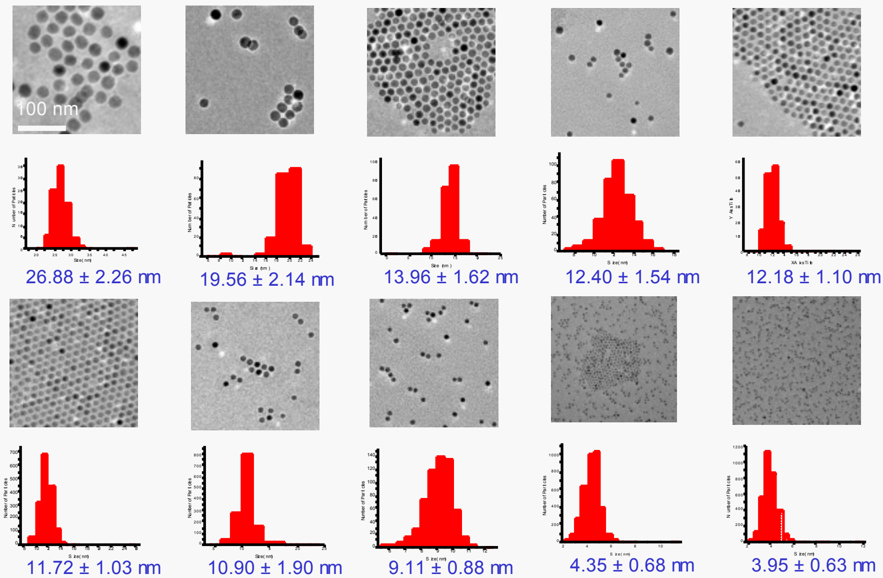
Small cluster: Supraparamagnetic
Easy to magnetize

Larger cluster: Single Domain
Magnetization can shift

Bulk solid: Permanent magnet
Small magnetization

Nanocrystals are better magnets than larger bulk materials

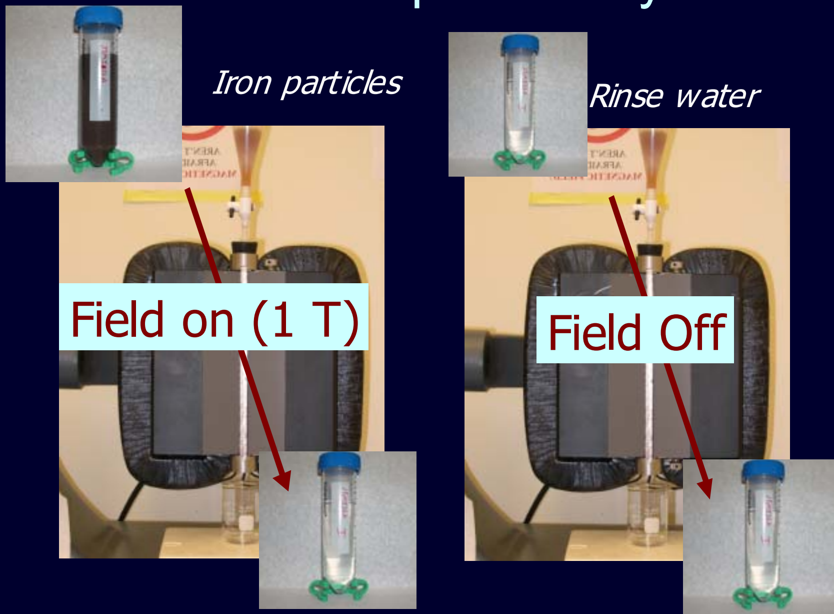
Library of nanoparticles for optimization



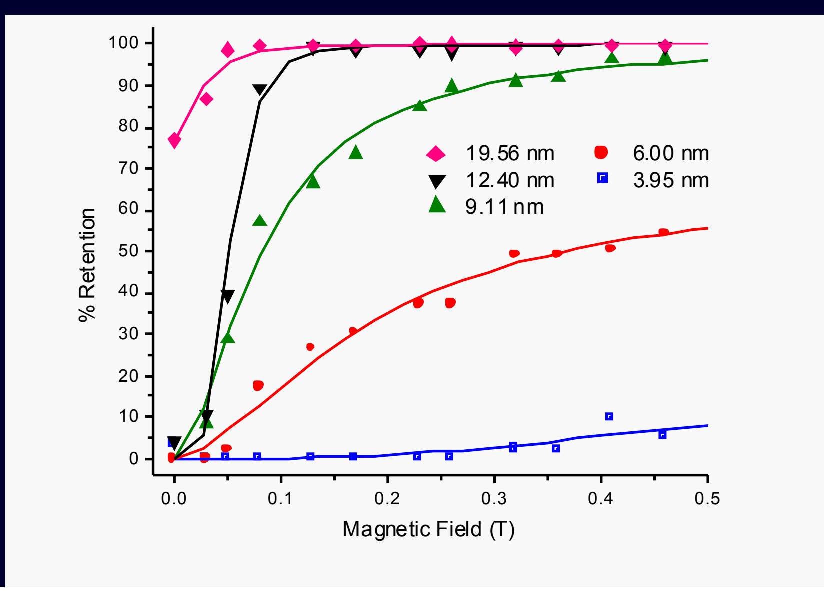
Lower fields = Simpler Systems

Best to use larger nanoparticles that reduce needed fields

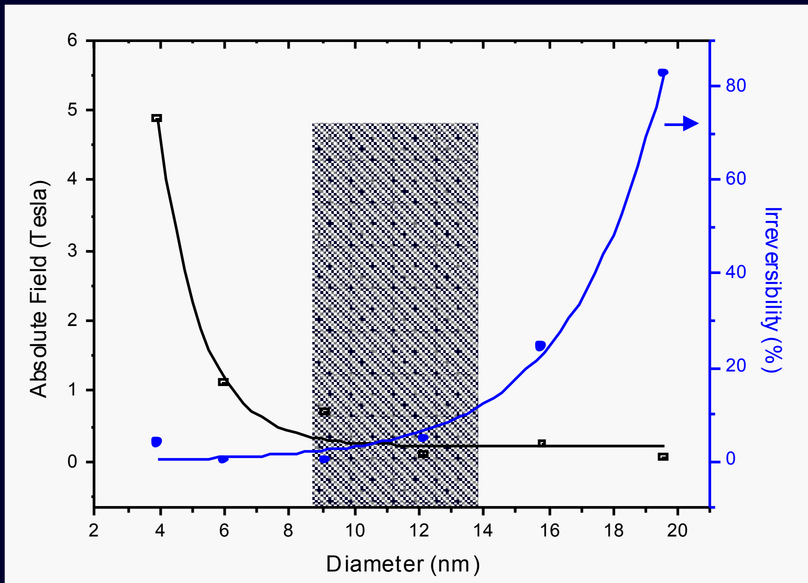
Irreversible Sorption: Stay SPM



Size dependent separation



Separations optimal ~12 nm



Arsenic Removal, with Magnetic Field

Particle Size (nm)	As(V) or As(III)	Initial As Concentration (mg/L)	Residual As Concentration (mg/L)	% Removal
12	As (III)	500	3.9	99.2
20	As (III)	500	45.3	90.9
300	As (III)	500	375.7	24.9
12	As (V)	500	7.8	98.4
20	As (V)	500	17.3	96.5
300	As (V)	500	354.1	29.2

Existing Sorbents for Arsenic Removal

Material	Sorbent (kg)/ month	1 gram treats ____ L water	Annual waste to dispose kg [3]	Backwash Frequency (day)	Efficiency[1]
Alumina + Metal Oxide	0.24	3.8	2.88[3]	14	0.003
Red Mud [As(III)]	360.7	0.002	4328.1[3]	Periodic	~0.003
Ion Exchange	No Removal of Toxic As(III)			~ 3	0.014
Nanoscale Iron Oxides	**0.09**	**10**	**1.1**	**0**	**~7.5 to 75 [2]**

1. "Efficiency" as defined by NAE in the "Granger Challenge, June, 2005" The object is to maximize the efficiency.
2. 12 nm magnetite cost estimated as a synthesized chemical at $2.00/lb and a multiplication factor of cost by 3x to 30x for estimated conditioning chemicals and packaging.
3. The amount (kg) + the backwash frequency

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1. Exploiting size in environmental remediation
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2. Is size dangerous? Implications of nanotechnology

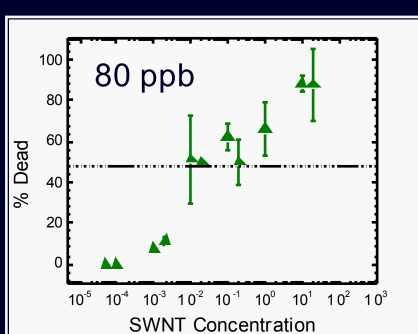
The WOW to YUCK trajectory

DDT cured malaria →	Endangered birds
Pesticides improved crop yields →	Toxic to animals
Refrigerants made houses cool →	Lead to ozone hole
Asbestos improved insulation →	Liability expenses

Early examination of nanomaterial's effects will create a responsible technology

NanoX: Not Toxicology As Usual

Are single-walled carbon nanotubes toxic?



- 20 major types of SWNT
- 4 manufacturing types (trace impurities)
- Lengths ranging from 5 – 300 nm
- 5 methods of purification
- 10 possible surface coatings

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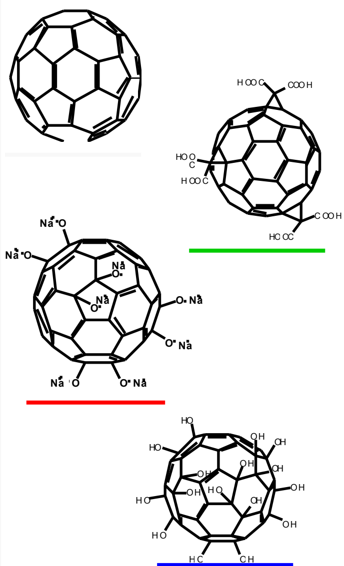
> 50,000 SWNT samples

Basic structure-function relationships for nanomaterials and biological impacts are necessary

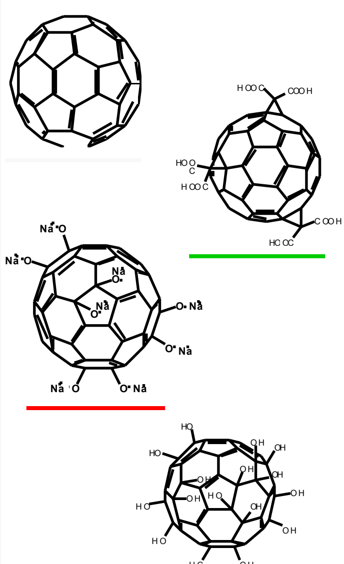
Systematic Variation of Surface Chemistry

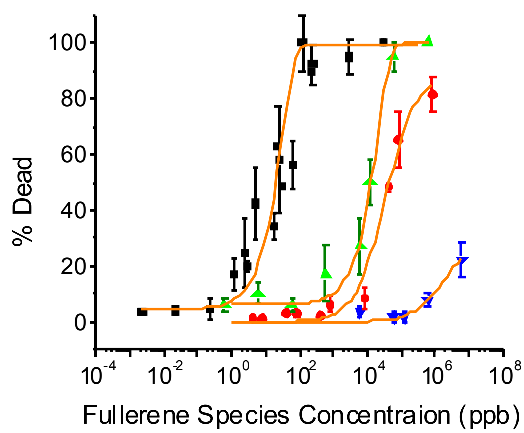


Increasing derivatization lowers photoinduced singlet oxygen generation

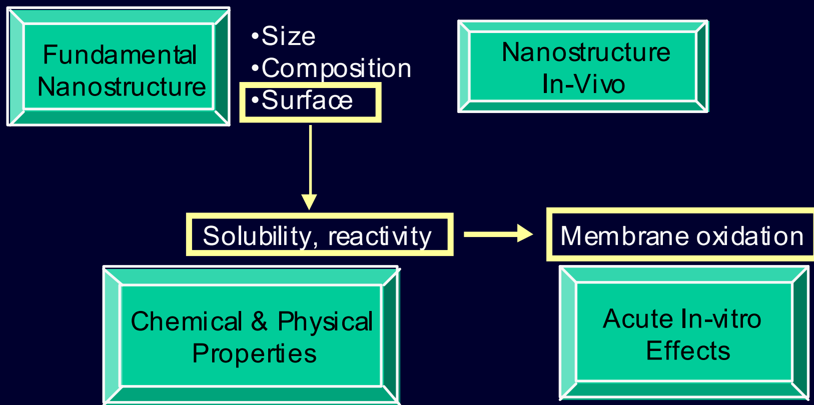
More polar functionality creates higher water solubility in materials

Structure/Activity Relationship Revealed





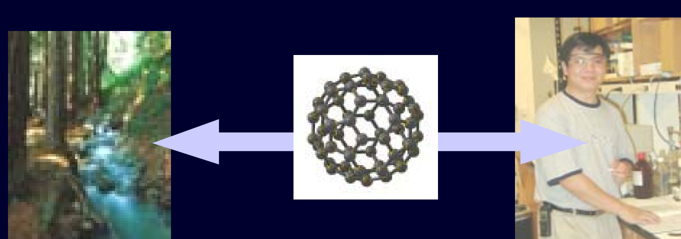
Structure-Function: Nanoscale Carbons



Case study #1: Carbon nanostructures – role of the surface

Case study #2: Titania nanostructures – composition

Information Supports Risk Management



- Development of pre-treatment schemes for waste
  - Mild oxidation for fullerenes
  - Thermal treatments for titania
- Simple ex-vivo screens for nanoparticle formulators
- Foundation for testing structure-function hypotheses

Early stage toxicology: Framing a new question

Are engineered nanoparticles dangerous?

↓

How can we engineer safe nanoparticles?

Challenges for nano-envi (US)

- Funding sources for research!
  - EPA only at $7M/year –
  - Ownership of area by one agency is not clear
- Business cases for environmental technology
  - People will not pay a premium for environmental tech.
  - Link environmental issues to public health
  - Developing nations are potentially huge markets
- Pilot testing is material intensive
  - Limits of material cost, material amount

Today's Talk

Benefits *Risks*

1. Nanocrystalline magnetite irreversibly sorbs Arsenic
2. "Nano" makes magnetic separations practical
   1. *Higher removal at lower fields*
   2. *Very high surface areas increase capacity*
3. Ongoing implications work improves technology

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Magnetic Separations Optimized

No recovery

1 Tesla Magnetic fields

.1 Tesla Magnetic fields