Nanoparticles as sorbents in analytical processes

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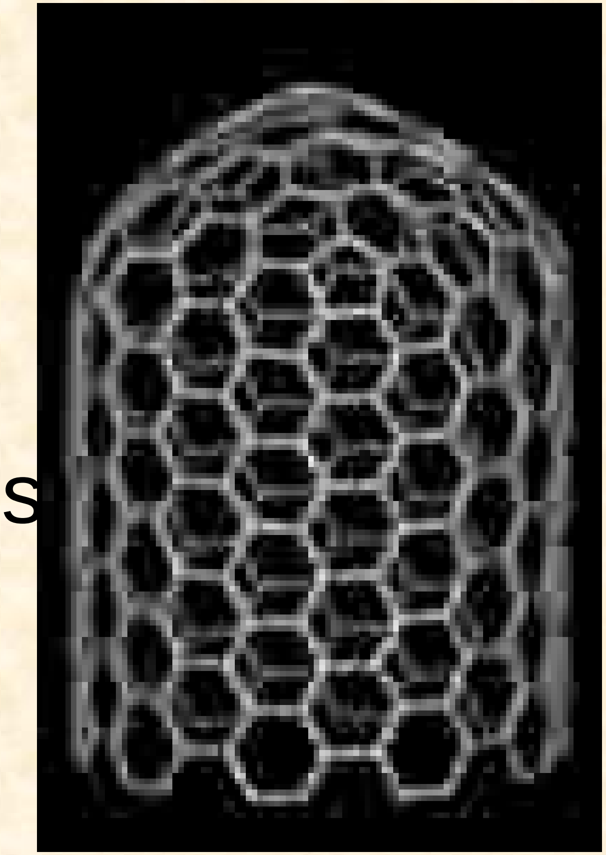
Presentation Overview

- Definition
- History
- Properties
- Current Applications
- Manufacturing Techniques
- Future Applications
- References



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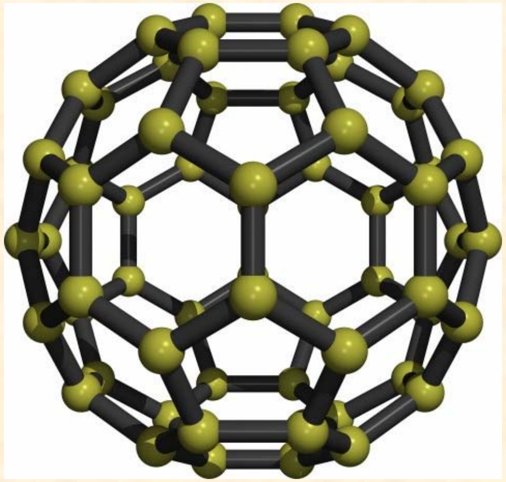
Important History

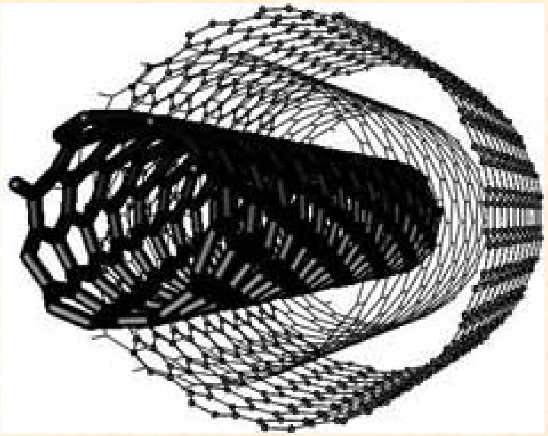
- 1991 Discovery of multi-wall carbon nanotubes by S. Iijima
- 1992 Conductivity of carbon nanotubes
  J. W. Mintmire, B. I. Dunlap and C. T. White
- 1993 Structural rigidity of carbon nanotubes
  G. Overney, W. Zhong, and D. Tománek
- 1993 Synthesis of single-wall nanotubes by S Iijima and T Ichihashi
- 1995 Nanotubes as field emitters
  By A.G. Rinzler, J.H. Hafner, P. Nikolaev, L. Lou, S.G. Kim, D. Tománek, P. Nordlander, D.T. Colbert, and R.E. Smalley
- 1997 Hydrogen storage in nanotubes
  A C Dillon, K M Jones, T A Bekkendahl, C H Kiang, D S Bethune and M J Heben
- 1998 Synthesis of nanotube peapods B.W. Smith, M. Monthioux, and D.E. Luzzi
- 2000 Thermal conductivity of nanotubes
  Savas Berber, Young-Kyun Kwon, and David Tománek

- 2001 Integration of carbon nanotubes for logic circuits
  P.C. Collins, M.S. Arnold, and P. Avouris
- 2001 Intrinsic superconductivity of carbon nanotubes
  M. Kociak, A. Yu. Kasumov, S. Guéron, B. Reulet, I. I. Khodos

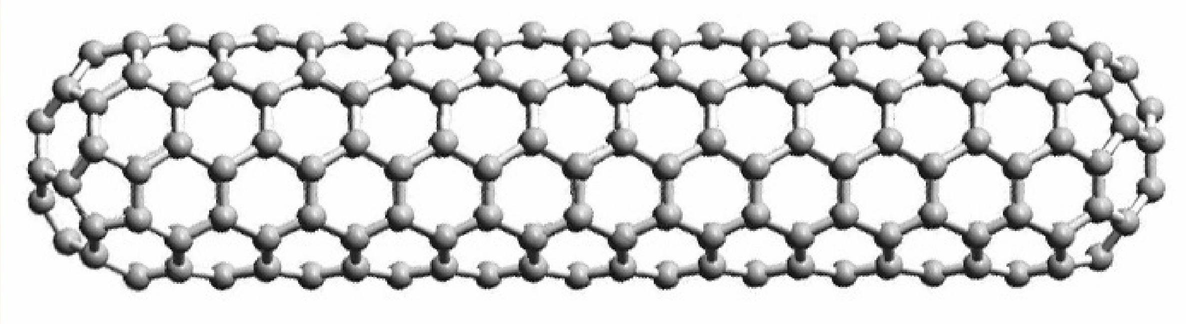
Carbon nanostructures



C_{60}



MWCNT



SWCNT

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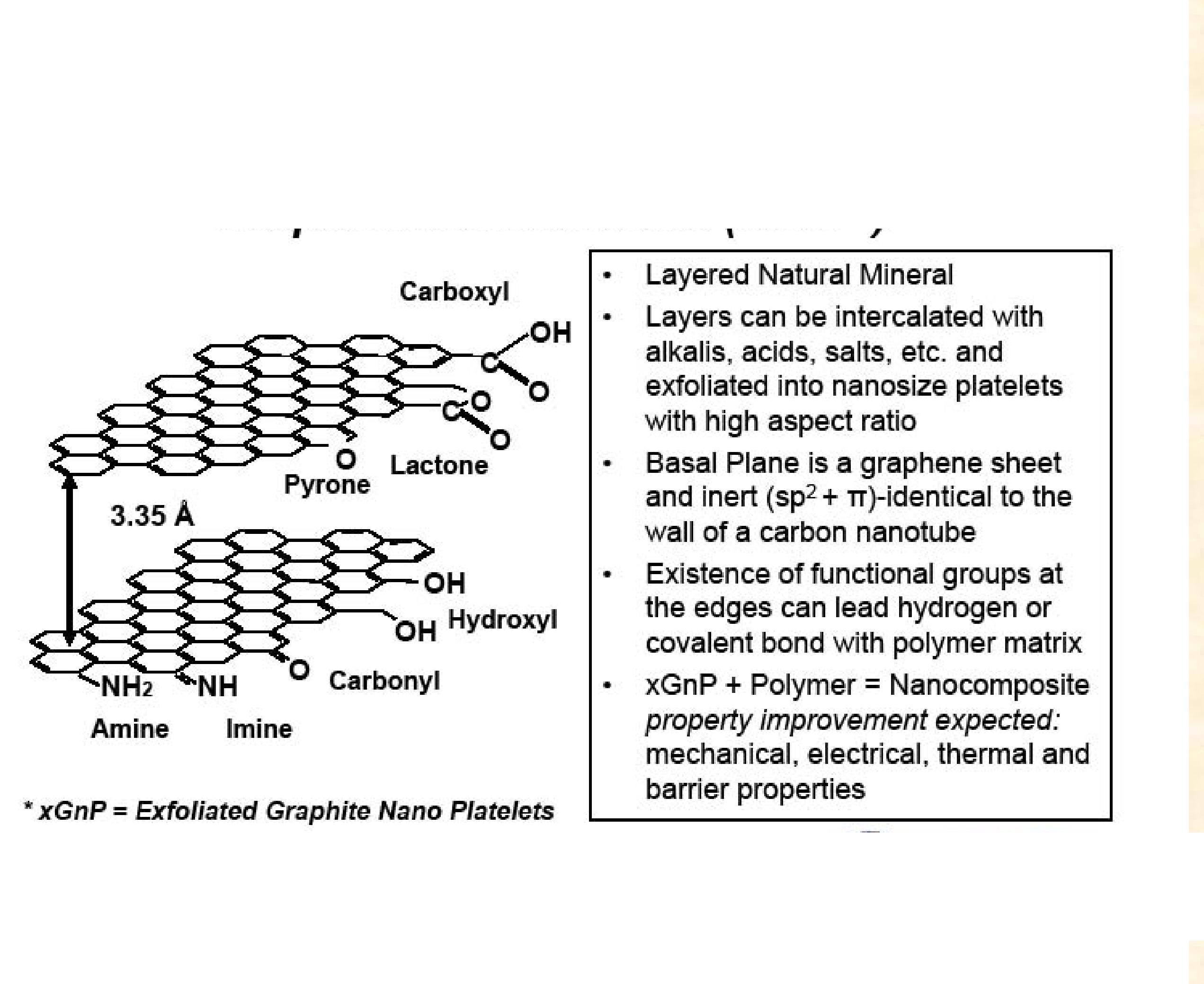
Graphite Nanoplatelets (xGnP*)



- Layered Natural Mineral
- Layers can be intercalated with alkalis, acids, salts, etc. and exfoliated into nanosize platelets with high aspect ratio
- Basal Plane is a graphene sheet and inert ($sp^2 + \pi$)-identical to the wall of a carbon nanotube
- Existence of functional groups at the edges can lead hydrogen or covalent bond with polymer matrix
- xGnP + Polymer = Nanocomposite *property improvement expected:* mechanical, electrical, thermal and barrier properties

** xGnP = Exfoliated Graphite Nano Platelets*

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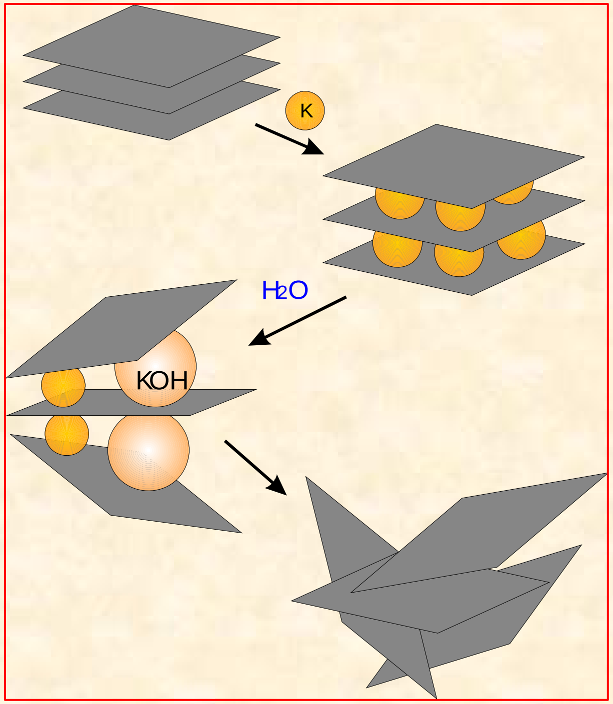
Graphite Nanoplatelets



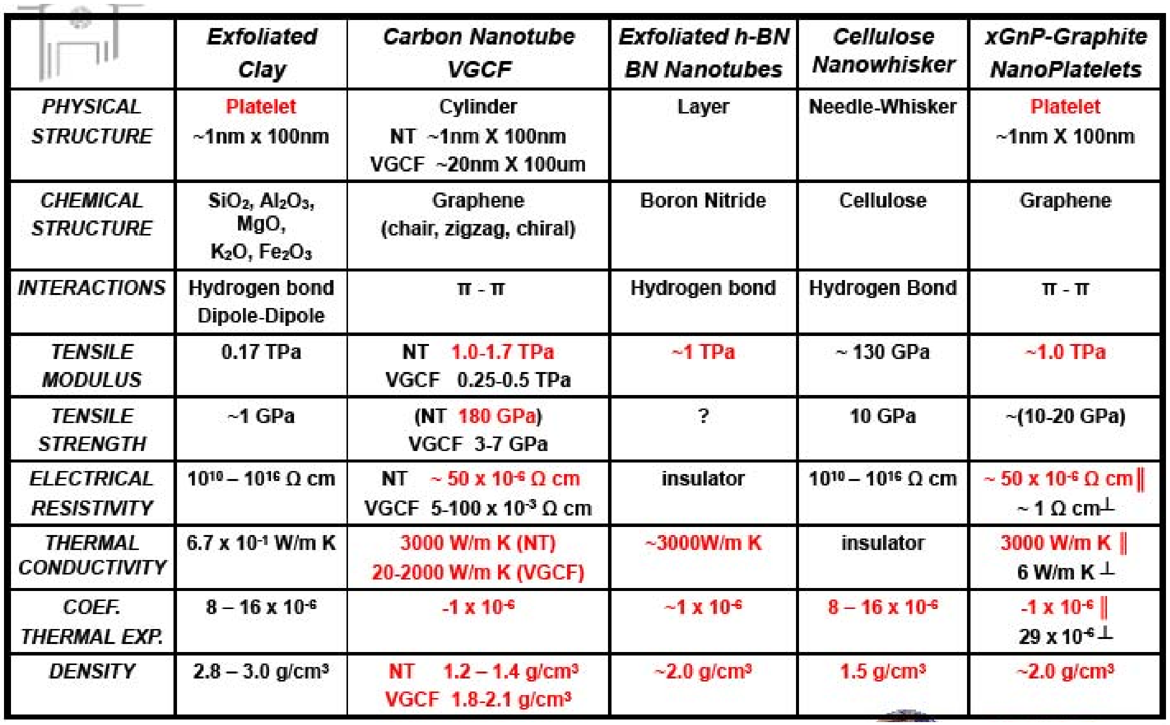
Schematics of Graphite Nanoplatelet

- Exfoliation tremendously increases total surface area of graphite
- Exfoliated nanoplatelets have aspect ratio of 100 ~1000 and are ideal for increasing mechanical properties
- Nanoplatelets increase conductivities

Processing

- Uniform dispersion of nanoplatelets
  - Ex-situ exfoliation: magnetic stirring and sonication
  - In-situ exfoliation: surfactants
- Degassing at an elevated temperature to remove air
- Curing followed by post curing

Comparison of nanoreinforcement properties



	Exfoliated Clay	*Carbon Nanotube VGCF*	*Exfoliated h-BN BN Nanotubes*	*Cellulose Nanowhisker*	*xGnP-Graphite NanoPlatelets*
PHYSICAL STRUCTURE	Platelet ~1nm x 100nm	Cylinder NT ~1nm X 100nm VGCF ~20nm X 100um	Layer	Needle-Whisker	Platelet ~1nm X 100nm
CHEMICAL STRUCTURE	SiO_2, Al_2O_3, MgO, K_2O, Fe_2O_3	Graphene (chair, zigzag, chiral)	Boron Nitride	Cellulose	Graphene
INTERACTIONS	Hydrogen bond Dipole-Dipole	π - π	Hydrogen bond	Hydrogen Bond	π - π
TENSILE MODULUS	0.17 TPa	NT 1.0-1.7 TPa VGCF 0.25-0.5 TPa	~1 TPa	~ 130 GPa	~1.0 TPa
TENSILE STRENGTH	~1 GPa	(NT 180 GPa) VGCF 3-7 GPa	?	10 GPa	~(10-20 GPa)
ELECTRICAL RESISTIVITY	$10^{10} – 10^{16}$ Ω cm	NT ~ 50×10^{-6} Ω cm VGCF 5-100 x 10^{-3} Ω cm	insulator	$10^{10} – 10^{16}$ Ω cm	~ 50×10^{-6} Ω cm ‖ ~ 1 Ω cm ⊥
THERMAL CONDUCTIVITY	6.7 x 10^{-1} W/m K	3000 W/m K (NT) 20-2000 W/m K (VGCF)	~3000W/m K	insulator	3000 W/m K ‖ 6 W/m K ⊥
COEF. THERMAL EXP.	8 – 16 x 10^{-6}	-1 x 10^{-6}	~1 x 10^{-6}	8 – 16 x 10^{-6}	-1 x 10^{-6} ‖ 29 x 10^{-6} ⊥
DENSITY	2.8 – 3.0 g/cm^3	NT 1.2 – 1.4 g/cm^3 VGCF 1.8-2.1 g/cm^3	~2.0 g/cm^3	1.5 g/cm^3	~2.0 g/cm^3

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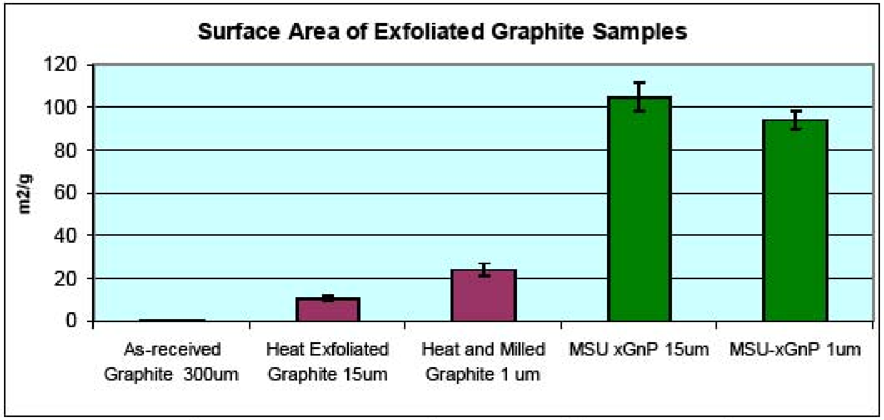
BET Surface Area and Thickness of xGNPs



	BET Surface Area (m2/g)	Diameter(um)	Thickness (nm)	Aspect Ratio (d/t)
As-received	0.2	300	5172.4	58.0
Heat Exfoliated Graphite	10.5	15	96.5	155.5
Heat Milled Graphite	24	1.1	45.1	24.4
MSU xGnP	105	15	9.5	1573.0
MSU xGnP	94	0.86	10.9	78.8

From ESEM

Theoretically calculated

Adsorption of Organic Contaminants from Solution to xGNPs

Batch Adsorption/Desorption Study:

xGNPs large aggregates

xGNPs small aggregates

xGNPs colloidal particles

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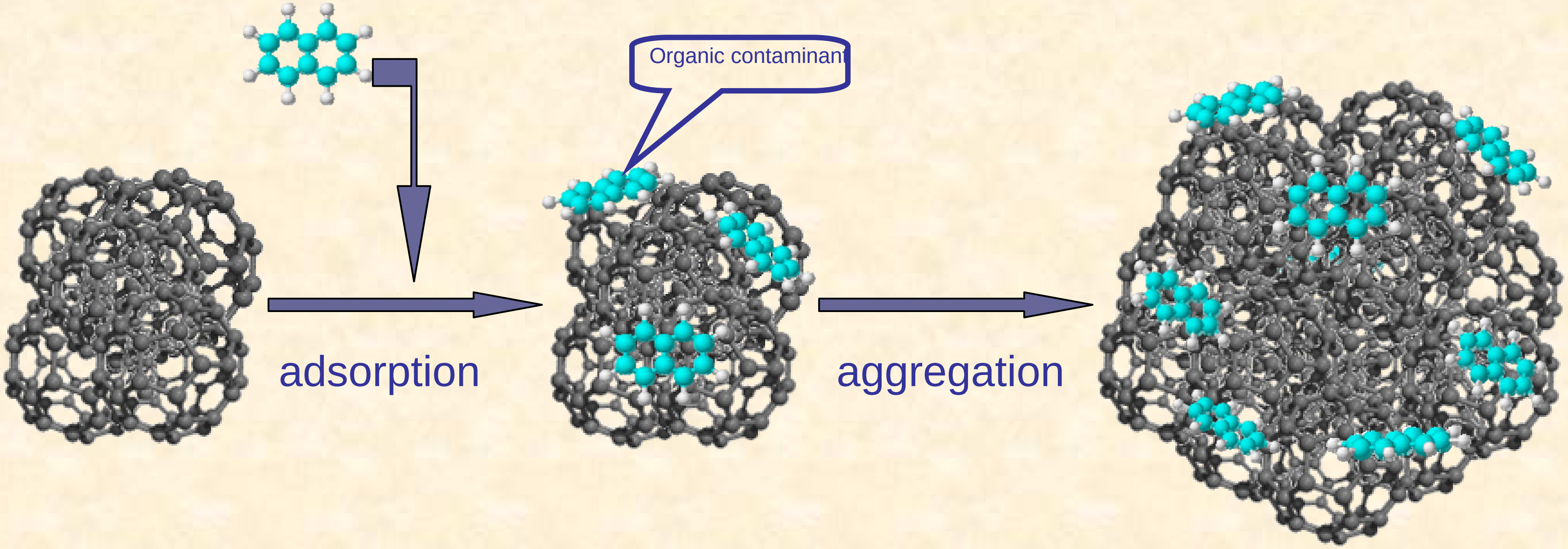
What Happened During Adsorption?



Organic contaminant

adsorption

aggregation

Small
Aggregates

Organic contaminant
Adsorption

Clusters Aggregation
&
Contaminant Entrapment

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Fate of Contaminants Adsorbed to xGNPs (original results)

Will the sorption and desorption of organic compounds to xGNPs particles cause enhanced environmental contaminant transport?

Table 1. Concentration of xGNPs in NOM solutions and mass of NOM bound to unit mass of xGNPs

C xGNPs, mg/L	q_e SR-NOM	q_e humic acid	q_e fulvic acid
100	1.59	1.33	1.06
200	0.93	0.65	0.55
300	0.64	0.40	0.39
400	0.50	0.29	0.30

Fig. 4. Langmuir of adsorption of phenol and equilibrium adsorption uptake qe (mg/g) in the presence of NOM (50 mg/L) in aqueous solutions containing 400 mg/L xGNPs

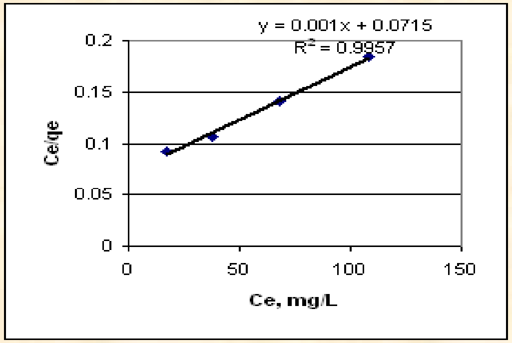

Table 2. . Effect of the concentration of the xGNPs in the solution on the percentage removal of phenol

C_{xGNPs}, mg/L	$C_{i,phenol}$, mg/L	$C_{r,phenol}$, mg/L	% removal
100	400	190.56	52.36
200	400	160.01	60.01
300	400	140.38	64.90
400	400	90.97	72.25

Table 4. Percentage removal (% removal) of phenol and equilibrium adsorption uptake q_e (mg/g) in a 10 mg/L concentration of NOM in aqueous solutions containing 400 mg/L xGNPs

$C_{i,phenol}$, mg/L	$C_{e,phenol}$, mg/L	% removal	q_e, mg/g
100	20.56	79.85	187.45
200	40.25	79.87	347.28
300	59.60	80.13	488.52
400	91.19	77.20	701.28

Sorption of organic contaminants to xGNPs particles is the same as to soil organic matter and to activated carbon. When xGNPs particles migrate, contaminant transport will be enhanced.

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The sorption capacity of various sorbents for phenol at optimum pH values (original results)

Sorbent	Phenol, q_e, mg/g
Activated carbon	720
Activated sludge	236.8
Fly ash	3.85
S. muticum	4.6
Rice husk	42.2
Bentonite	1.712
Present work	702

Properties Enhancements and Applications with xGNPs

- Mass reduction (low density, low concentration);
- Increased stiffness (high aspect ratio);
- Increased toughness (engineered interfacial adhesion);
- Electrical conductivity;
- Thermal conductivity;
- Improved appearance;
- Surface conductivity (controlled deposition and alignement);

Expected Risks

- Provides the information needed to assess whether this risk is substantial for nanoparticles disposed of in groundwaters.
- Yields the necessary parameters to understand the fate of engineered nanoparticles in the environment.
- Yields the necessary parameters for future development of risk assessment of the engineered nanoparticles.

References

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D. Lin, B. Xing, Environ. Sci. Technol., 42, 2008, 7254-7259

H. Hiung, J. D. Fortner, J.B. Hughes, J.H. Kim, Environ. Sci. Technol., 41, 2007, 179-184