Nanomaterials: Origins of the Perturbations of biological activity in the environment

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Nanomaterials are present in our life:

Targeted National Sewage sludge Survey Statistical Analysis Report (Released in Jan 2009)

- 74 plants across the States
- Total metal contents
- Pharmaceuticals, steroids, and hormones

Sludge ID 68349 (from Midwest region)

Elemental Analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>(mg kg$^{-1}$)</th>
<th>Mg</th>
<th>13500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>856</td>
<td>Mn</td>
<td>1070</td>
</tr>
<tr>
<td>Al</td>
<td>57300</td>
<td>Na</td>
<td>6080</td>
</tr>
<tr>
<td>Ca</td>
<td>98900</td>
<td>P</td>
<td>57200</td>
</tr>
<tr>
<td>Cu</td>
<td>1720</td>
<td>Ti</td>
<td>4510</td>
</tr>
<tr>
<td>Fe</td>
<td>51000</td>
<td>Zn</td>
<td>1530</td>
</tr>
</tbody>
</table>

What are the Specificities of the NM

1st s: inorganic NM are in majority crystallized

2nd: The physical properties are present in majority for size < ~30 nm

Numerous « Nano Effects »
For size < 30 nm

M.Auffan et al., NATURE nano, 09-2009
Specific properties

3rd: the surface atom number increases as size decreases

4th: redox properties are size dependent (ex TiO_2, Ag°, MoS_2)

Ex: Anatase

Almquist C.B. and Biswas P., "Role of Synthesis Method and Particle Size of Nanostructured TiO_2 on Its Photoactivity", Journal of Catalysis 212(2) 145
Case of CeO$_2$

10-nm

Specific properties

5th: The surface excess energy depends on the size and morphology of the NM nanomaterials are metastable.

In the case of AlOOH, the face (010) is important but « not very active » the faces (101) and (100) will be very active.

Specific properties

6th: The large surface excess energy of some faces could have as origin the existence of vacant sites as the size decreases.


Increasing of Tetrahedrallacuna

New ad(ab)-sorption sites

M. Auffan et al., NATURE nano, 09-2009 (and following presentation)

Strong increase of the retention of As(III, V) and Co(II) onto Fe oxides vs size except for amorphous materials as HFO.

Bottero et al, CRAS 2010
7th: The hydration of fullerenes C60 transform them from ROS quencher to ROS producer under UV light.

Labille et al, Env Pollution 2010
Auffane et al; ES and T 2010
The production of singlet oxygen depends on the fractal structure of the Aggregates and Yield Quantum
Schematic mechanism of ROS production and toxicity vs aggregation state of C$_{60}$

Fullerene suspension after sonication

OH groups on the aggregate’s surface

ROS production and cytotoxicity

Size

OH number increases

So-Ryong Chae et al... ACS Nano 2010. CEINT
8th: Dissolution
Ag⁺, ZnO, CdSe, CeO₂...Fe(II) vs Fe(II)

\[
\ln K_b = \ln K_{sp} + \frac{2W/\rho}{3RT} (\gamma/\lambda)
\]

This equation is correct for micrometric crystal. For nanometric crystal, defects, strains, vacancies, non homogeneous \(\gamma\) values this equation is no longer valid.

Transfer and Transformation before reaching Living Media:

Transformation from products: speciation, surface properties and stability

bioavailability

transfer diffusion

III. Biodegradation

Toxicity

adsorption

coagulation

aggregation

Interaction with colloids

Porous media:

Biofilms; Sediments

Transfer
Transfer and aggregation in porous media (sand)

Aggregation of TiO2 within the porous media

Case of TiO2

Breakthrough curves of TiO2 nanoparticles for different ionic concentrations during transfer in sand column.

It depends on the aggregation

The affinity of TiO2 - TiO2 >> TiO2 - Sand

(pH 8, I=4 x 10^{-2} M)

pH = 6, I = 10^{-3} M

N. Solovitch et al, ES and T 2010
Transfer and diffusion in porous media

Case of Nano Ag°

Breakthrough curves GB

Sand and FeOOH

The affinity of Ag° for porous media Increases as FeOOH concentration increases

Shihong Lin et al 2010, Duke; CEINT
nOH-C60 mobility according to interactions with molecules and salts

Aggregation kinetic vs adsorption onto biological surface: CeO2 + salt + cells

Initial conditions:
3 mg/l NPs
10^8 cells/ml

In water: stable NPs only adsorption

In medium: unstable NPs adsorption + aggregation

Zeyons et al, ES and T 2009
Conclusion and future

- The complexity of the studies come from the complexity of the NM or NP in term of the chemistry, stability and reactivity at atomic level.

M Auffan et al, Env Pollution 2009
There is a necessity of a ‘Bio-physico-chemical approach’ to well characterize the mechanisms of cytotoxicity and genotoxicity.

**Membrane Integrity**
- Test Rouge neutre
- Mitochondrial activity
- WST1 test
- ROS detection

**ROS production**
- $O_2$, $O_2^*$, $OH^*$

**Cristalline Defects**
- TEM, Diffraction

**Surface Speciation and reactivity**
- EXAFS, XANES, RMN, FTIR
- Synchrotron

**NP Reactivity**
- Dissolution/aggregation

**Dissolution/aggregation**

**Internalisation**
- TEM: Micro-fluorescence

**ROS**
- Antioxidants, mutant strains

**Cytotoxicity**
- ADN comets tests
- Micronuclei tests

**Genotoxicity**

**Mitochondrial activity**
- WST1 test

**Oxidant stress**
- Anti-oxidants, mutant strains

**Synchrotron**

If the mechanisms of the toxicity must bestudied on « laboratory » NM, the researches must focus also on engineeredproductscontaining NP knowingthat the formulations are complexe.

Researches must prioritize a systemicapproachallowing to assess the toxicity in foodwebs and Prioritize in vivo testing at increasingtrophiclevels for « environmental concentrations of NM »

Try to be predictivefrom the:
- knowledge and Modelling of the interaction mechanisms of « nano » with water, components, biota

-Modelling of the kinetic interactions of NP in the aqueous media (water molecules, solutes, aggregation ......
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Thanks to CNRS and CEA
A very good BOOK not very expensive

- **NANOSCIENCES**
- **TOME 4 : NANOTOXICOLOGIE, NANOETHIQUE**
- Marcel Lahmani, Francelyne Marano, and Philippe Houdy
- Belin (october 2010) and Elsevier (2011)
Settling velocity of fractal aggregates $D_f < 2.3$ versus Stokes law and various size.