Ecotoxicity effects of multi walled carbon nanotubes (MWCNTs)

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EU project, FP7-KBBE: Byefouling - Low-toxic cost-efficient environment-friendly antifouling materials
Coordinator: SINTEF

אוניברסיטת תל-אביב
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National Technical University of Athens

EU FP7 project

http://www.sintef.no/Projectweb/BYEFOULING/

BYEFOULING-Low-toxic cost efficient environment friendly antifouling materials

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- Interuniversity Institute for Marine Sciences in Eilat
- TAU students and staff members
- Israel Nature and National Parks Protection Authority - permits.

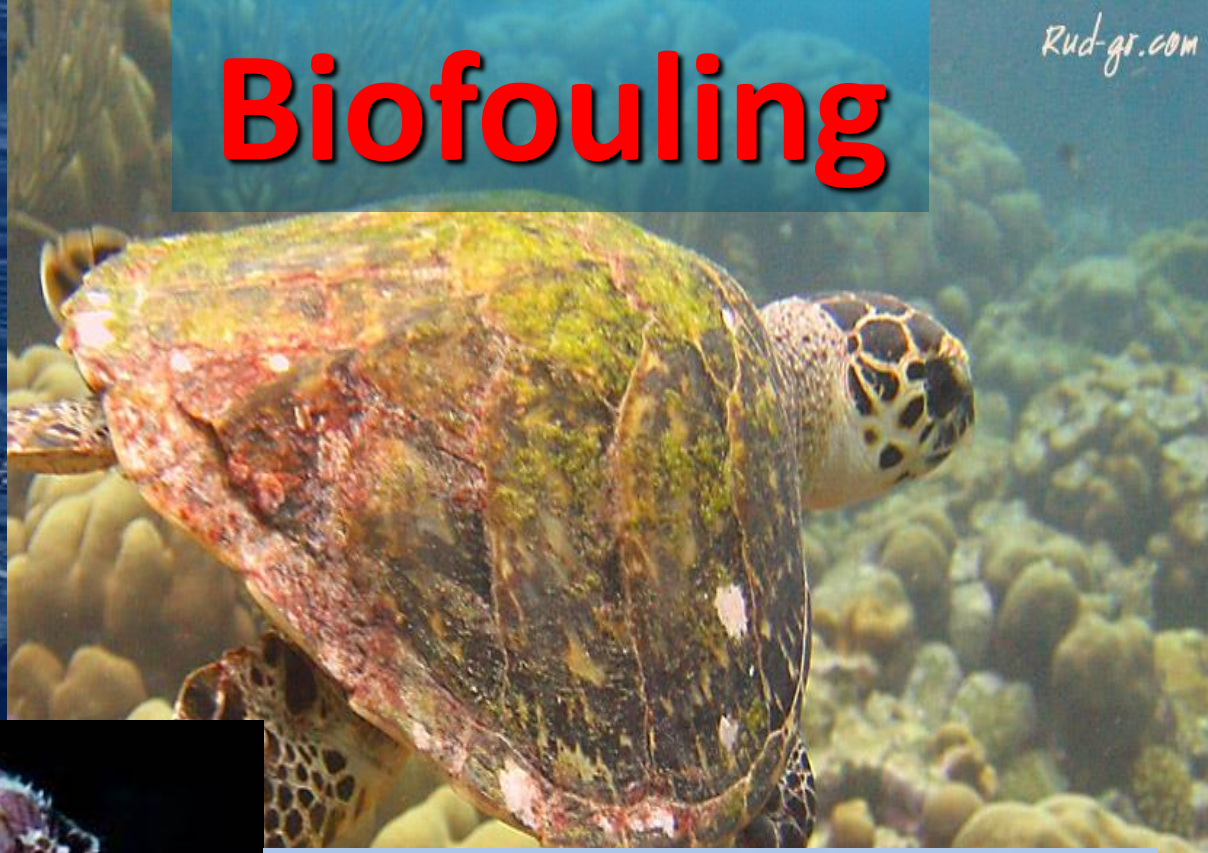
Byefouling

Biofouling: undesirable accumulation of marine microorganisms, plants, animals on submerged structures, especially ships' hulls

Ships hulls may gather 150 kg of fouling per square m in < 6 months. On oil tanker with 40,000 square m underwater area, this would add ~6,000 tons of fouling.

Anti-fouling: process of removing the accumulation, or preventing it

Biofouling



Marine structures are under constant attack from the environment being biofouled

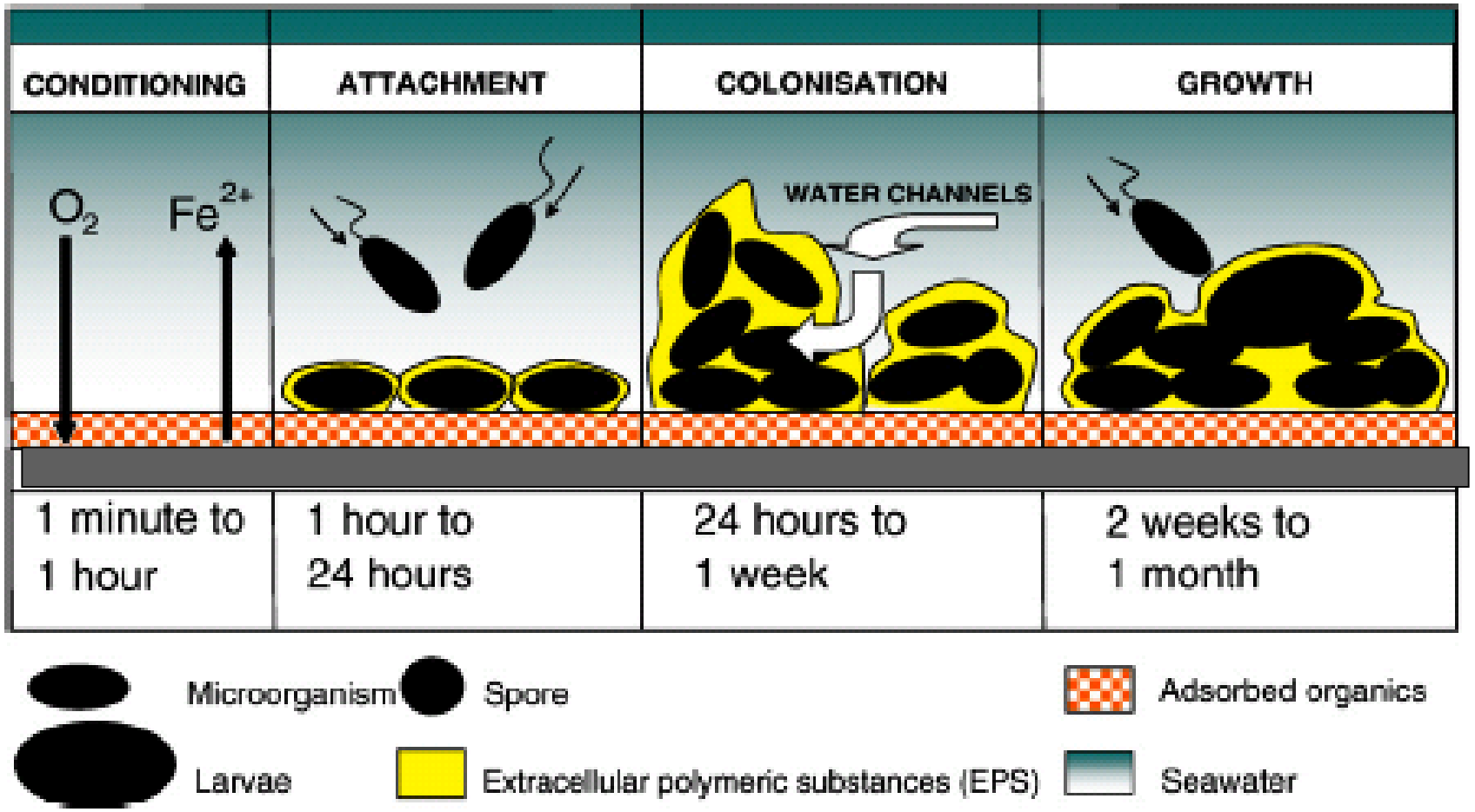
- Ship hulls
- Marine platforms
- Docks
- Offshore rigs
- Fish cage nets
- Floating buoys

http://www.ausmepa.org.au/pests/default.asp?pageid=40&nav=20

Need to be protected from biological attack

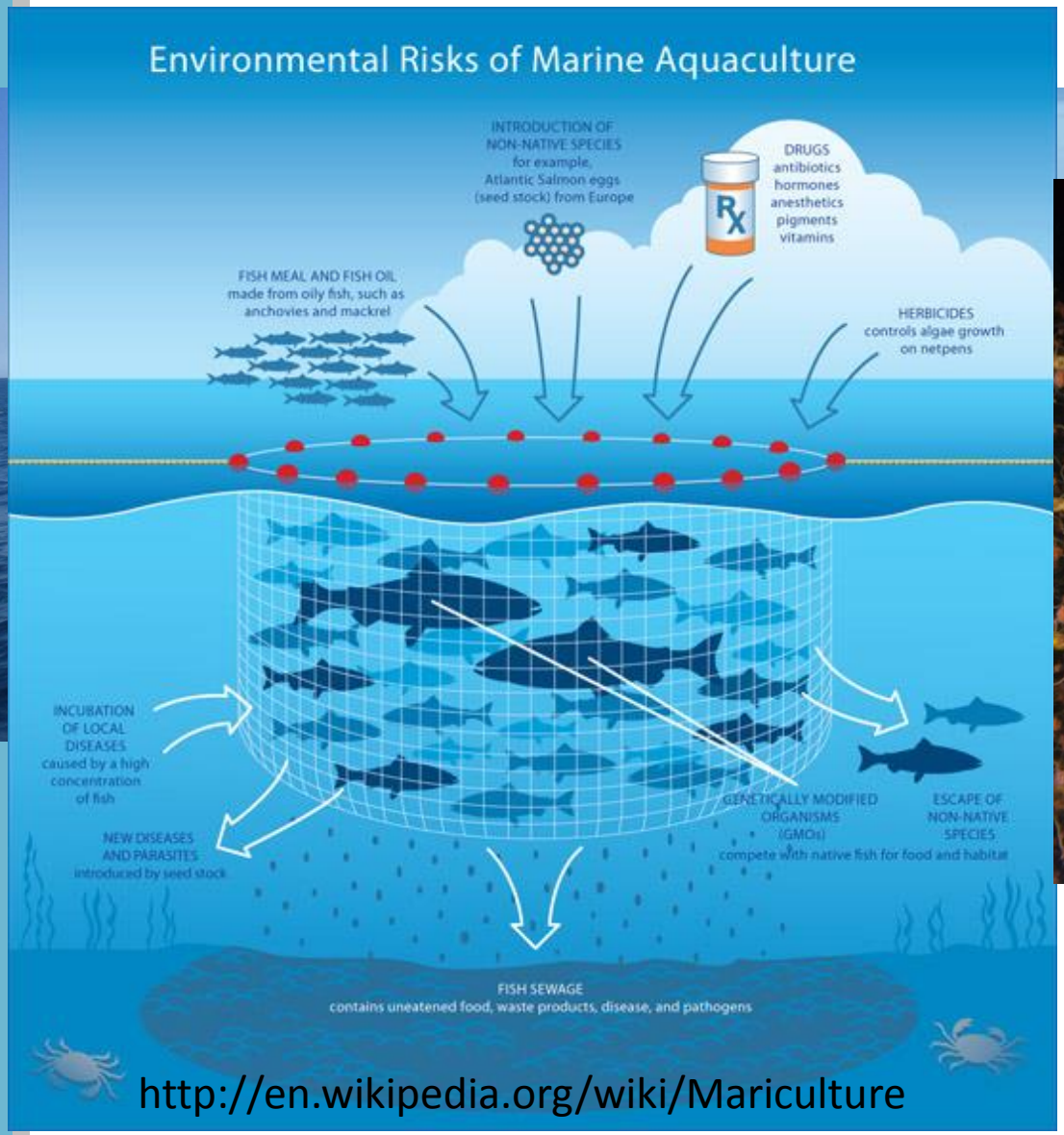
Process of biofouling: succession and growth stages

L.D. Chambers et al. / Surface & Coatings Technology 201 (2006) 3642–3652



Sequence of events – the first event: biofilm formation

Mariculture/ aquaculture – fish net cages



http://en.wikipedia.org/wiki/Mariculture

http://www.sciencedaily.com/rele

Oceanographic measuring and navigation buoys

http://www.fouling-atlas.org/images/images_ug/oceanography_geology_pic.jpg

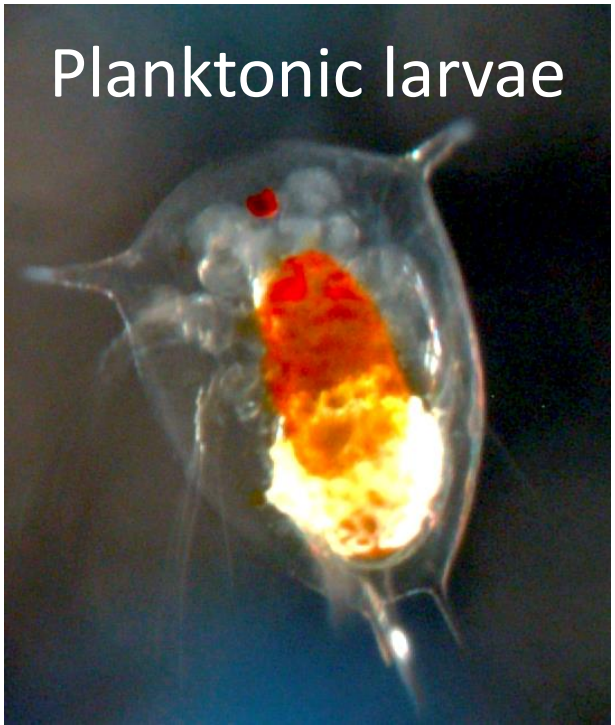
https://www.whoi.edu/page.do?pid=10095&tid=3622&cid=155889

Accumulation of both indigenous and invasive fouling organisms: barnacles, mussels, sponges, algae, etc.

Anti-fouling systems

Barnacles are quite unlike other crustacean, because they permanently attach to the substrate by means of an adhesive cement, and secrete calcareous shell

Anti-fouling paints using metallic compounds slowly "**leach**" into the sea water, killing marine life that have attached to substrate



Fouling effects

- Hydrodynamics - negatively affected
- Increase hull roughness
- Increased fuel consumption
- Degradation of ship performance
- Frequent docking
- Spread of invasive species

Byefouling

Revolutionary self polishing copolymer technique employing TBT (tributyltin) to deter fouling

Considered as the most toxic substance ever deliberately introduced into aquatic environment

Imposex – endocrine disruption causing development of male organs in female snails – bio-indicator of TBT

- 2003: ban on TBT based paints application
- 2008: ban on TBT based paints

Modern antifouling alternatives

- Ban on TBT created a gap in the market.
- Research began into environmentally acceptable replacements

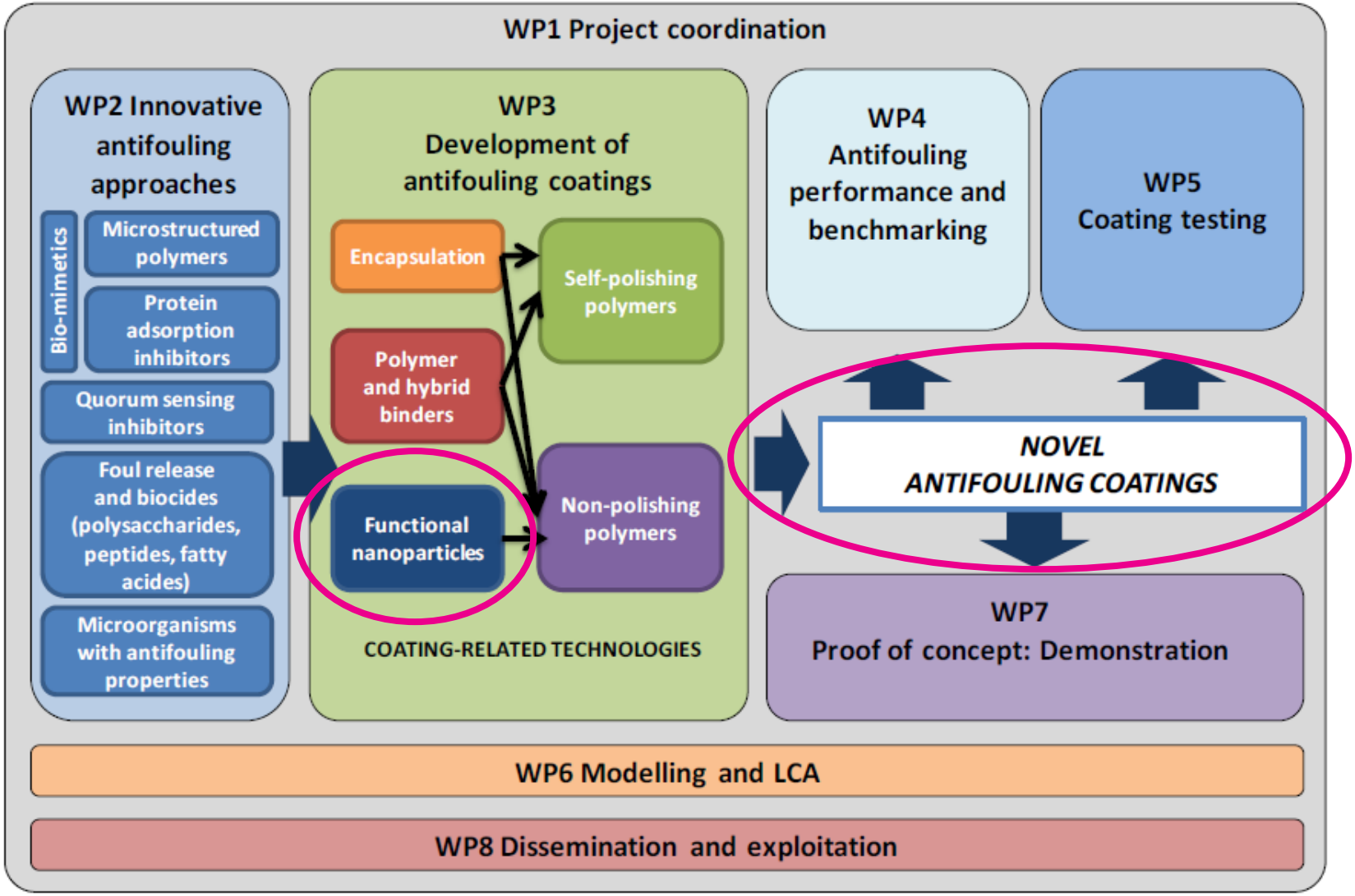
Interim solutions:

- Copper & zinc self-polishing copolymers
- Booster biocide approach (phenols, phosphorous, sulfurous, aldehydes etc.)

Species specific, influencing non-target organism, short life time, slow drying time, expensive, leaching rate not constant

BYEFOULING

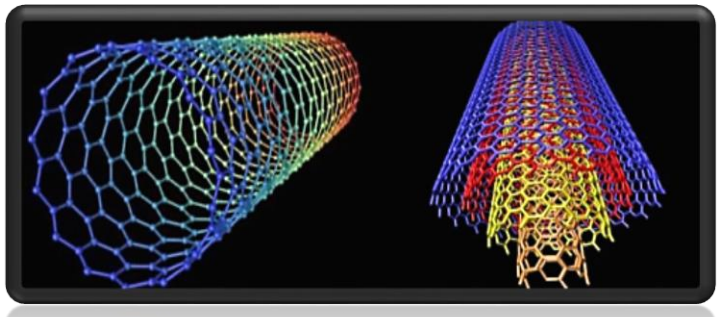
Low-toxic cost-efficient environment-friendly antifouling materials



Carbon Nanotubes (CNTs)

Due to their properties are leading materials in technology :

- composites as reinforcements
- coatings
- energy storage
- electronics and sensors.



SWCNTs MWCNTs

Structure

- **Single Walled Carbon Nanotubes (SWCNTs):** A rolled-up, single layer graphene sheet, diameter ~1 nm, length several µm.
- **Multiwalled Carbon Nanotubes (MWCNTs):** 2 or more layers

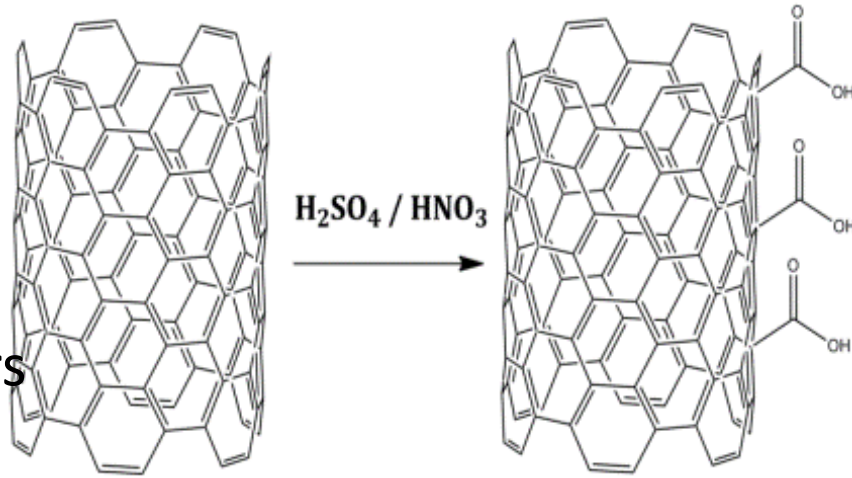
Antifouling activity of CNTs – fouling resistance in shape of nanocomposites with metal, gaseous compounds, metal oxide biomolecules, polymers etc.

Surface functionalization for lower toxicity

Production of CNTs

❑ Chemical Vapor Deposition (CVD) method

- Camphor as carbon source & ferrocene as catalyst compound (20:1 ratio)
- Growth temperature: 850^{o}C
- Silicon wafers substrate



❑ *Functionalization*

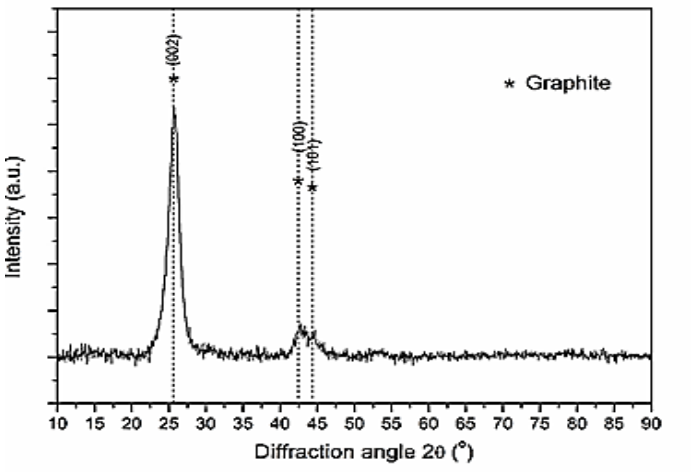
- Better compatibility with polymers matrices
- Better dispensability in polar solvents
- Lower toxicity

❑ Characterization techniques

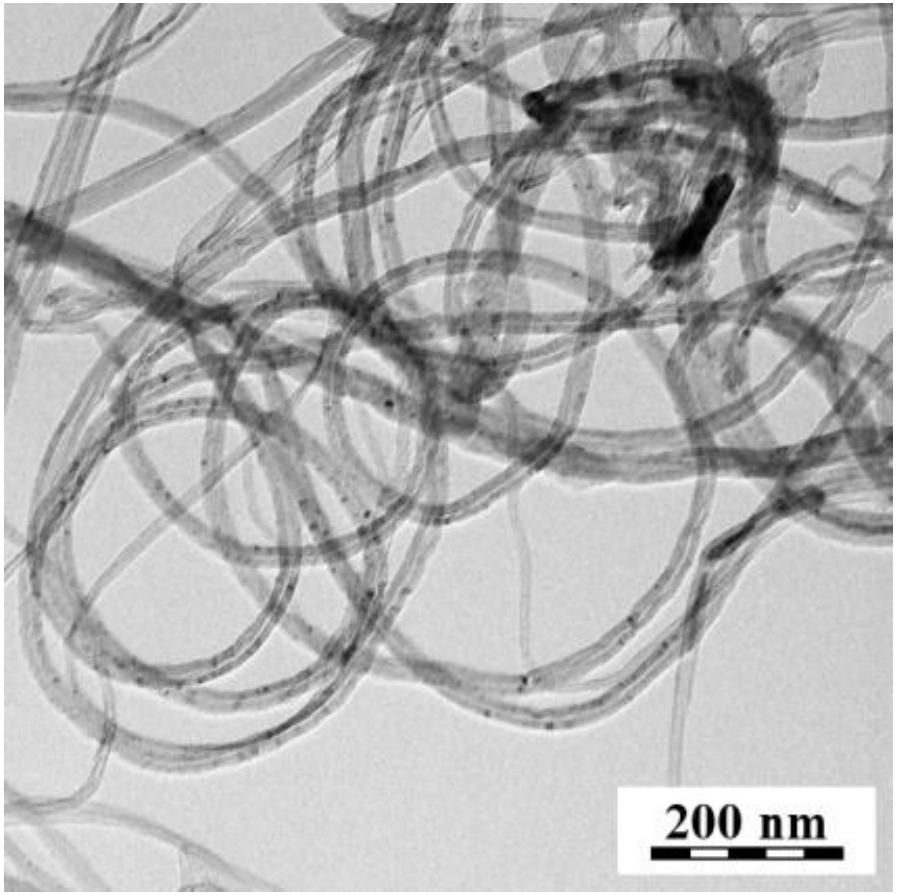
- SEM, TEM, X-Ray Diffraction XRD, Thermogravimetric Analysis (TGA), etc.

Characterization of MWCNTs

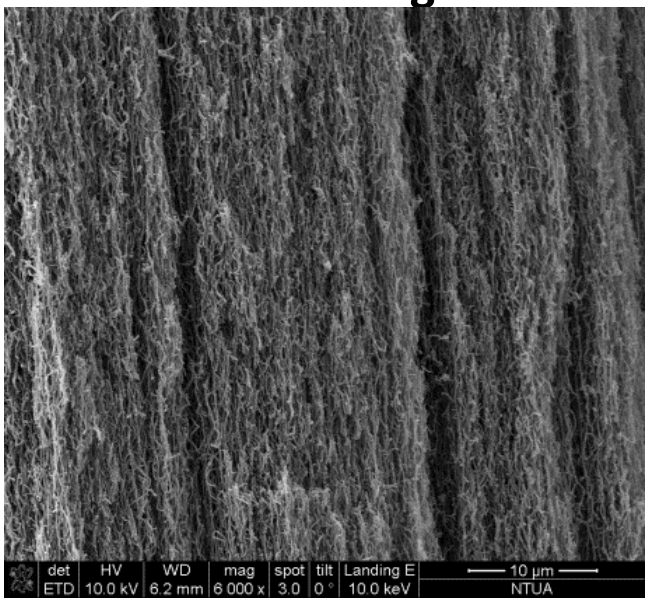
XRD pattern



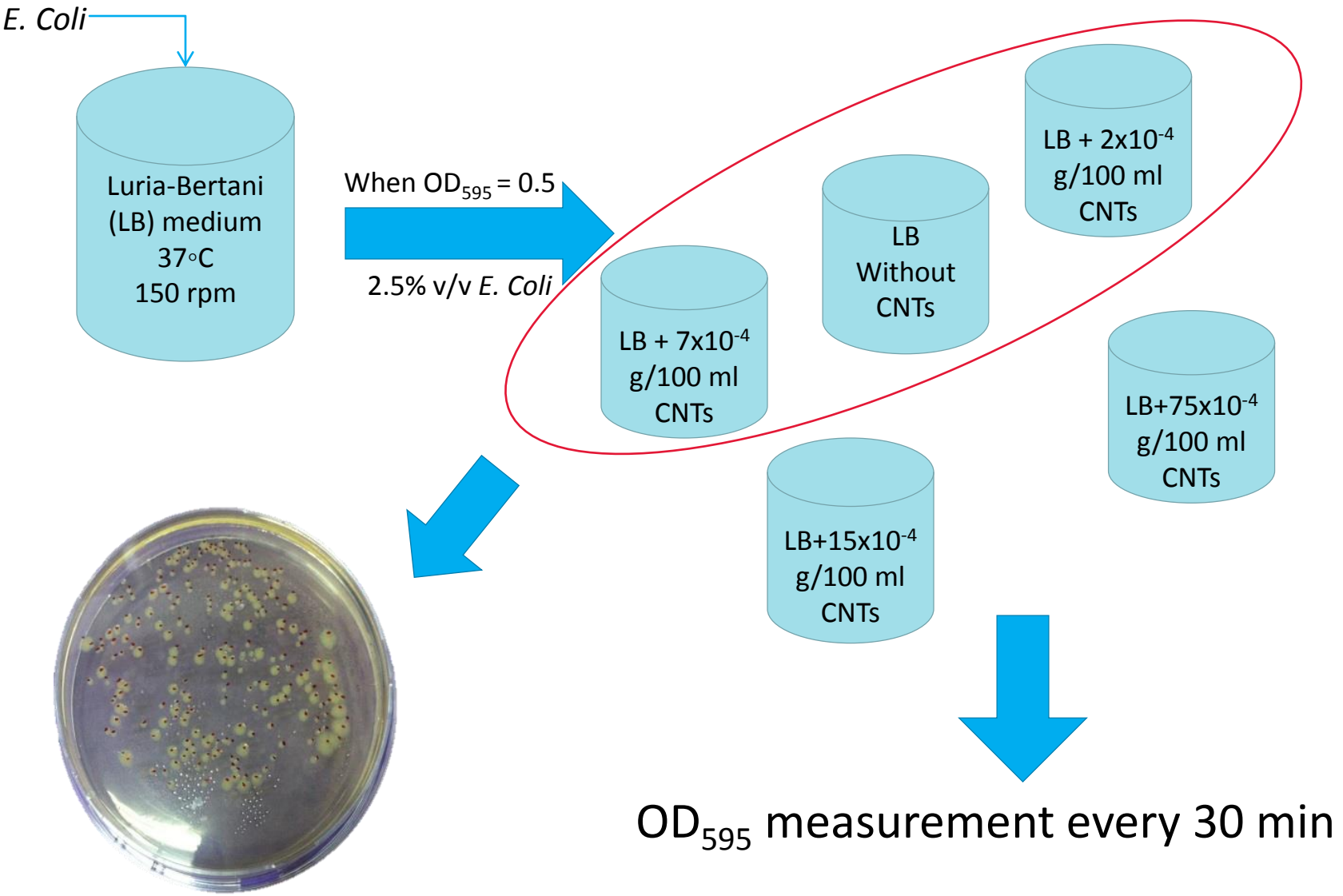
TEM image



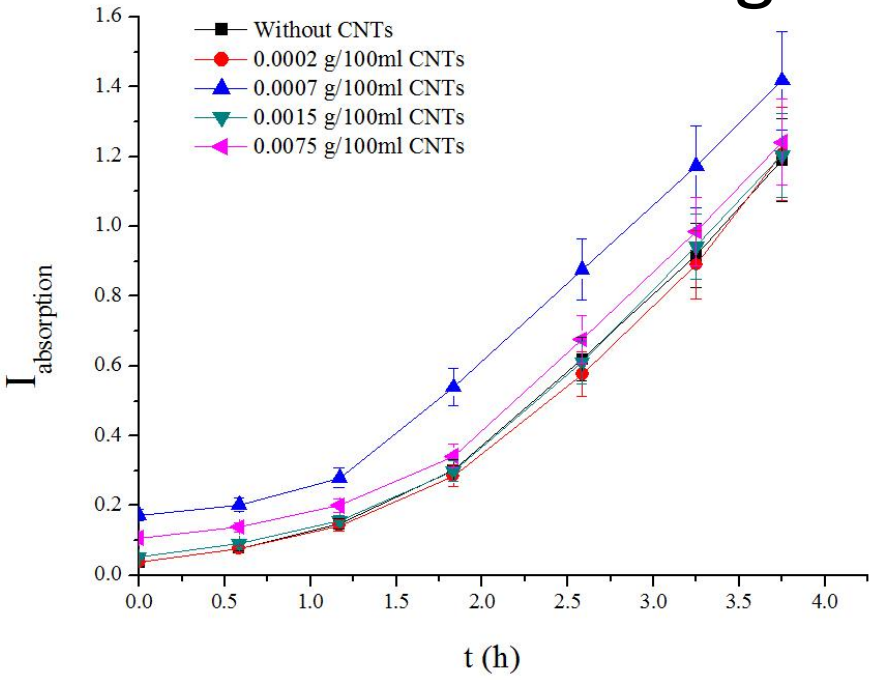
SEM image

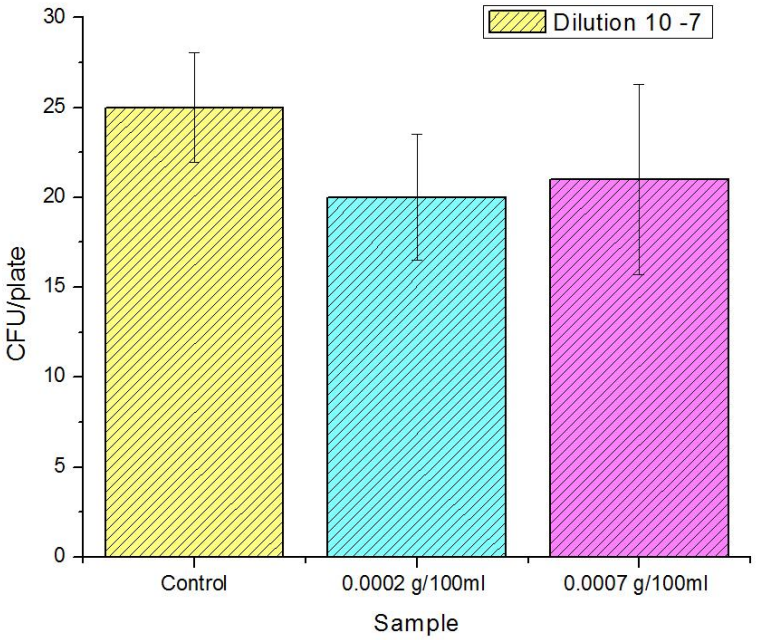


Antibacterial – *E. coli* - testing



Antibacterial Testing





Increase of CNTs concentration - lowered growth rate (μ_{max}) & cell growth (x_{max})

Without CNTs : $\mu_{max} = 1.0361\ h^{-1}$

0.0002g/100ml MWCNTs: $\mu_{max} = 1.0075\ h^{-1}$

0.0007g/100ml MWCNTs: $\mu_{max} = 0.9797\ h^{-1}$

0.0015g/100ml : $\mu_{max} = 0.9566\ h^{-1}$

0.0075g/100ml : $\mu_{max} = 0.7624\ h^{-1}$

Lower CNTs concentration reduced colony growth

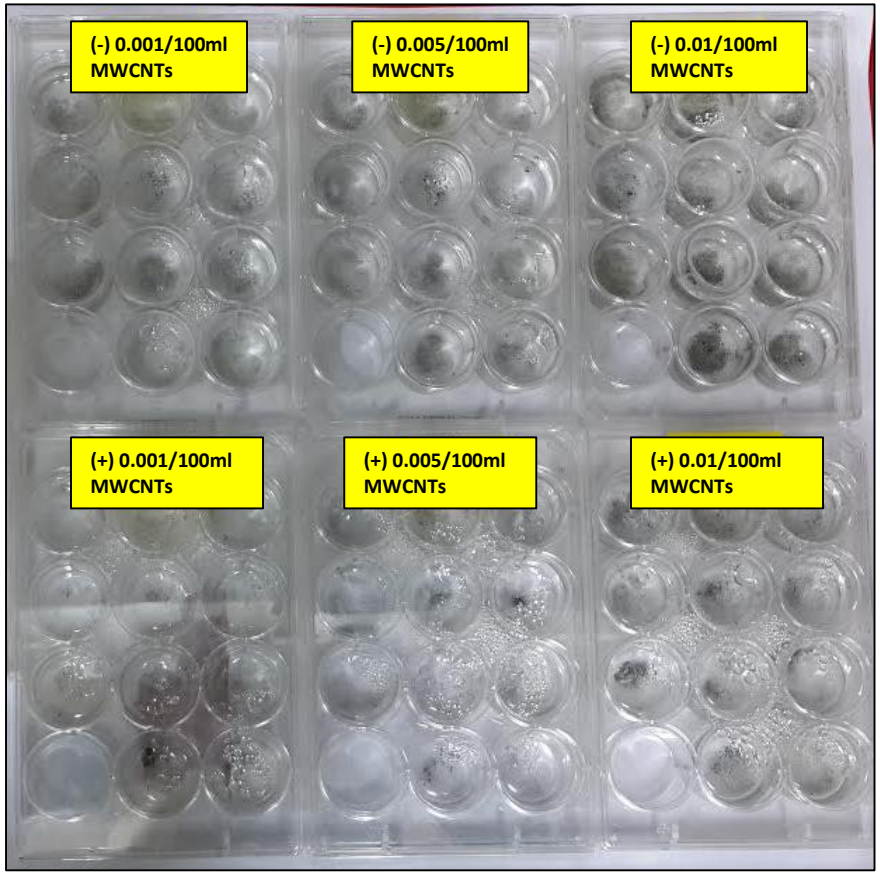
Fewer & smaller colonies

Daphnia similis assays

- Planktonic freshwater crustaceans
- “Water fleas”
- Filter feeders
- Short life cycle
- Model organism for ecotoxicity assays

MWCNTS ASSAY: LAYOUT AND CONDITIONS

Criteria	Conditions
Organisms	*Daphnia similis* 7 days post-hatch Same clade
Acclimation period	No acclimation
Temperature / Photoperiod (L:D)	Ambient / 12:12 (L:D)
Test chambers and support equipment	12-multiwell test plate
Medium	ADaM medium
Dilutions	3 concentrations x 2 different types of MWCNTs + 1 control (ADaM medium)
Replicates	12 for each concentration tested
Observation points	24, 48, 72, 96 and 144 h
Endpoints	% mortality
Feed	Yes- *Scenedesmus gracilis*
Duration of the experiment	144 h

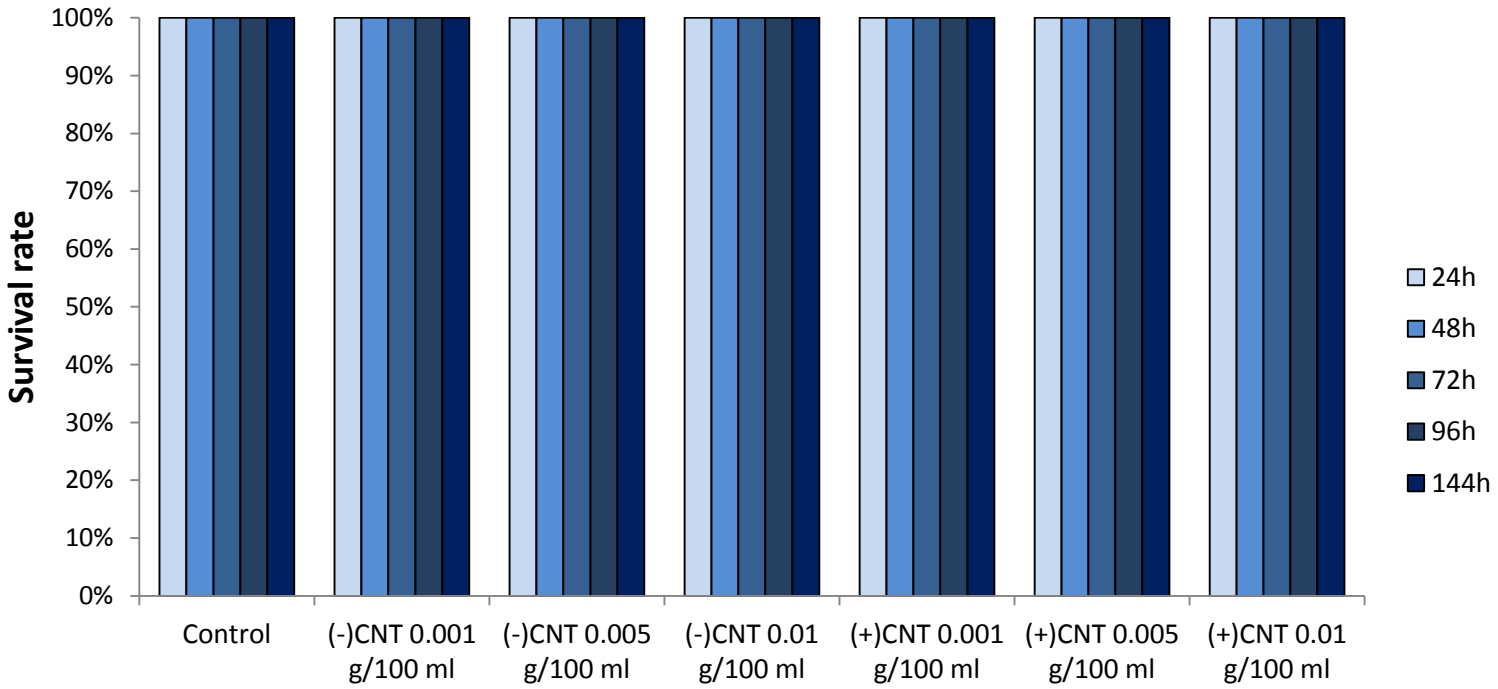


(+) – With active component

(-) – Without active component

* ADaM = Aachener Daphnien Medium

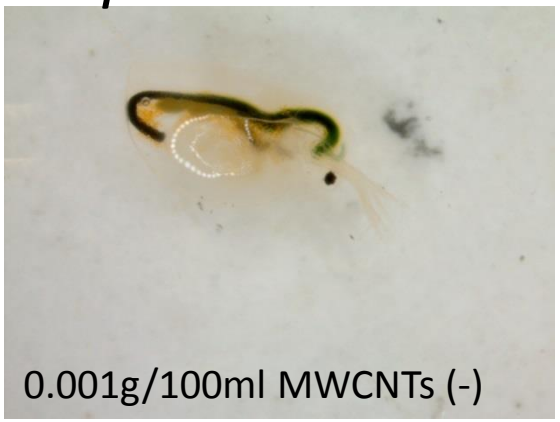
Survival rate of *Daphnia* in different concentrations of MWCNTs

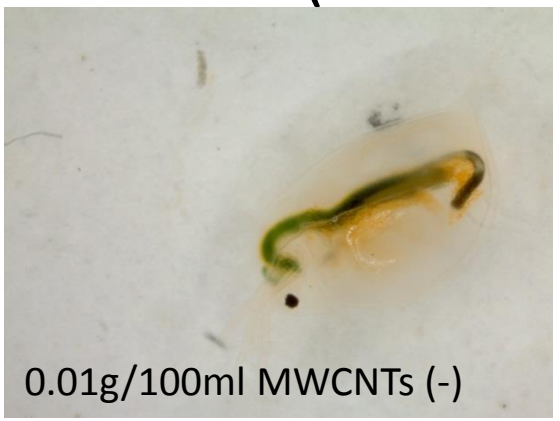


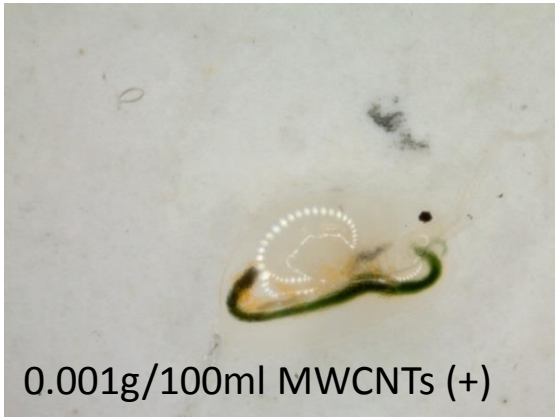
(+) – With active component
(-) – Without active component

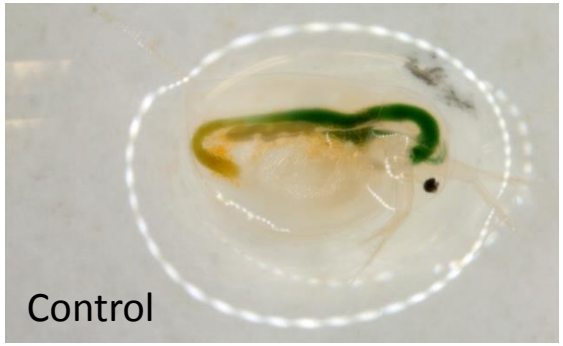
Conclusion: MWCNTs do not cause mortality of *Daphnia*

Daphnia similis after exposure to MWCNTs– 96 h (All alive)



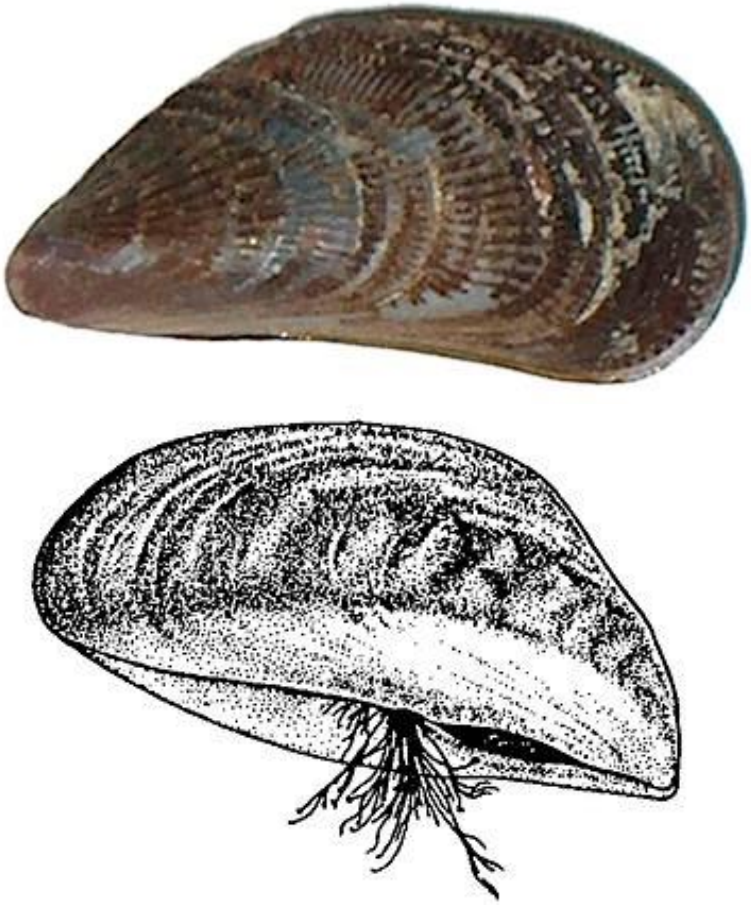






(**+**) – With active component
(**-**) – Without active component

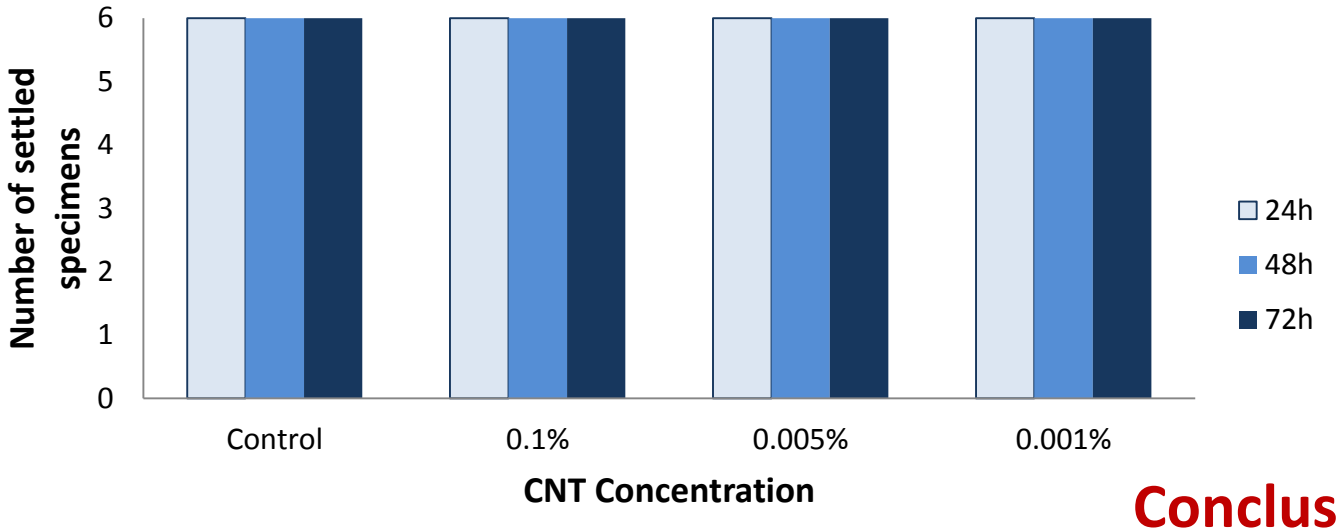
Mussel assay:
Brachidontes pharonis

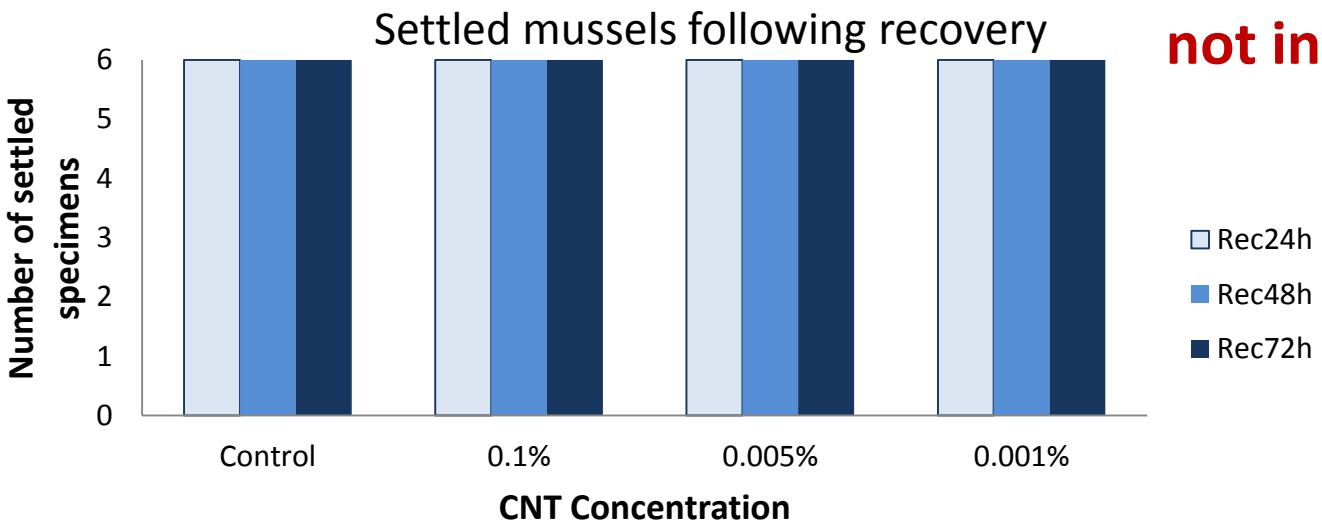


Settled *Brachidontes* mussels during CNTs assay

Replication #3
Jan. 2015
Temp. 23C

n=6 animals per treatment





<u>Conclusion</u>: MWCNTs do not inhibit settlement

Conclusions

- **Multi Walled Carbon Nanotubes** were synthesized via **Chemical Vapor Deposition Method** and **fully characterized** via SEM, TEM, XRD and Thermogravimetric analysis.
- MWCNTs with the **following characteristics** were produced:
  60 – 100 nm diameter, > 5μm length, 92 – 95 % purity
- MWCNTs were **further purified** and **functionalized with oxygen containing groups** in order to increase their **compatibility** with different solvents and matrices.
- **Carboxyl groups have introduced** onto MWCNTs sidewalls.
- Increased concentration of CNTs led to their **lower dispersion**.
- CNTs **lowered bacterial growth**.
- Quantitative plating results indicated that lower CNTs concentration appeared to prevent colonies' development.
- Higher the concentration of CNTs, the lower interactions with the organisms, probably due to the **creation of agglomerates**.
- **No effect on *Daphnia* or mussels**.


Thank you!

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