Applications of nanotechnology in agriculture

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Classification of nanomaterials

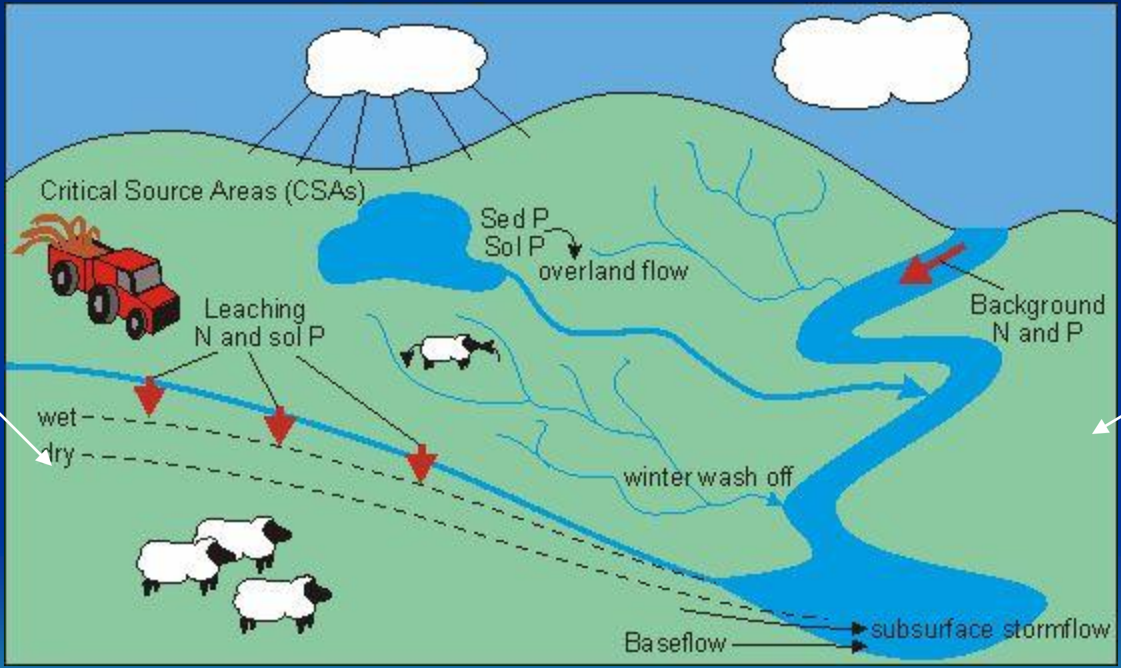
- Natural nanoparticles: particles with one or more dimensions at the nanoscale originating from natural processes, e.g. soil colloids, volcanic ash, mineral composites…
- Incidental nanoparticles: nanoparticles formed as a by-product of man-made or natural processes, e.g. welding, milling, grinding or combustion
- Engineered nanoparticles: nanoparticles manufactured to have specific properties of a specific composition, e.g. nanotubes, quantum dots, graphenes…

Key characteristics of nanomaterials for agricultural applications

- High surface area
- High surface reactivity
- Catalytic surface
- Adsorption properties

Agroecosystem example from database

- Using Nanotechnology to identify and characterize hydrological flowpaths in agricultural landscapes (Walter, et al. Cornell University)



. Photo from Quinn et al. http://www.ncl.ac.uk/wrgi/TOPCAT/TCTheory.html

Agrifood Nanotechnology Applications

- Nanodelivery systems for pesticides and fertilizers
- Nanotechnologies for soil and water decontamination
- Nanosensors

Nanotechnology and the Agriculture

The bad…

- Nature of nanoparticles themselves.
- Characteristics of the products made.
- <u>Manufacturing processes involved.</u>
  - As nano-xyz is manufactured, what materials are used?
- What waste is produced?
- Are toxic substances used in the manufacturing of nano-xyz?
- What happens when nano-xyz gets into the air, soil, water, or biota?

"The emerging fields of nanoscience and nanoengineering are leading to unprecedented understanding and control over the fundamental building blocks of all physical things. This is likely to change the way almost everything - from vaccines to computers to automobile tires to objects not yet imagined - is designed and made."

- Interagency Working Group on Nanoscience, Engineering, and Technology Report (1999)

"As EPA looks to the future, it will need to employ innovative approaches and sound science to investigate complex, interdisciplinary problems in environmental protection."

- EPA FY 2001 Annual Report

Nanotechnology and the Agriculture

The good…

Nanotechnology has the potential to substantially benefit environmental quality and sustainability through

- **Pollution prevention**
- **Treatment**
- **Remediation**
- **Information**

Topics

- ***Biosensors*—use of nanotechnology for sensors based upon biological processes or biological molecules, or for detection of biological molecules, processes, or organisms.**

- ***Sustainable agriculture*—use of nanotechnology for reducing agricultural inputs or outputs that can harm the environment or human health (e.g. pesticides) or are in short supply (e.g. water); or for making products from agriculture in a sustainable way.**

- ***Smart Treatment Delivery Systems***—delivery of molecules in agricultural production or processing in time-controlled, spatially targeted, regulated, responsive, or other precise ways. Also, systems could have the ability to monitor effects of delivery.

- ***Smart System Integration for Agriculture and Food Processing***—integration of a working system with sensing, reporting, localization, and control. System could be used anywhere along farm to table continuum, or at multiple points.

Other Research Areas

- ***Pathogen and Contaminant Detection***—pathogen or contaminant detection in agriculture, food, or the environment.
- ***Identity Preservation and Tracking***—systems that provide producers, processors, and customers with information about the practices and activities used to produce a particular crop or agricultural product. Also, provide information on the origin and movement of crops, animals, or products.
- ***Nanodevices for Molecular and Cell Biology***—devices based on or applied to molecular and cellular biology that separate, identify, study, modify, or sense.
- ***Pathogen detection—use of nanotechnology to detect pathogens in surroundings, organisms or food.***
- ***Veterinary medicine[1]—use of nanotechnology to improve animal health and/or the safety of animal derived foods.***
- ***Bioprocessing for food—use of nanotechnology for better food processing or quality.***
- ***[1] Not in USDA Nanoscale Science and Engineering 2003 Report.***

Examples of Agricultural Applications

Sector	Application	Method or Material	Details
Agriculture	Basic Research on Energy Production	Nanodetection	Single molecule detection to determine enzyme/substrate interactions (e.g. cellulases in production of ethanol).
	Agrochemical Delivery	Nanoparticles, nano-capsules	Delivery of pesticides, fertilizers, and other agrichemicals more efficiently (e.g. only when needed or for better absorption).
	Animal Production	Nanoparticles Nanomaterials in chips (nanochips)	Delivery of growth hormone in a controlled fashion. Identity preservation and tracking.
	Animal or Plant Health	Nanosensors	Detect animal pathogens, such as foot and mouth disease virus. Detect plant pathogens early.
	Animal Medicine	Nanoparticles, nanodevices	Deliver animal vaccines.
	Plant Production	Nanoparticles	Delivery of DNA to plants towards certain tissues (i.e. targeted genetic engineering).

J. Kuzma, Nanotechnology in agriculture and food product, 2007

Nano agrochemicals under development

Type of product	Product name & manufacturer	Nano content	Purpose
Super combined fertilizer and pesticide	Pakistan-US Science	Nano-clay capsules contain growths stimulants	It can be designed for slow release of active ingredients
Herbicides	Tamil Nadu Agricultural University (India)	Nano-formulated	Designed to attack the seed coating weeds and destroy soil seed banks
Pesticides including herbicides	Australian Commonwealth Scientific and Industrial Research Organization	Nano-encapsulated active ingredients	Very small size of nanocapsules increase their potency and enable targeted release

Source: http://www.foeeurope.org/activities/nanotechnology

Examples of the current use of nanomaterials in agriculture

Type of product	Product name&manufacturer	Nano content	Purpose
Nutritional supplement	Nanoceuticals RBC Lifesciences	Molecular cages 1-5 nm diameter made from silicamineral hydride complex	Nano-sized mycrohydrin has increased bioavailability. Exposure to moisture releases H- ions acting as powerful antioxidants
Plant growth treatment	PrimoMaxx Syngenta	100 nm particle size emulsion	Nano-sized particles increase the potency of active ingredients potentially reducing the quantity to be applied

Source: http://www.foeeurope.org/activities/nanotechnology

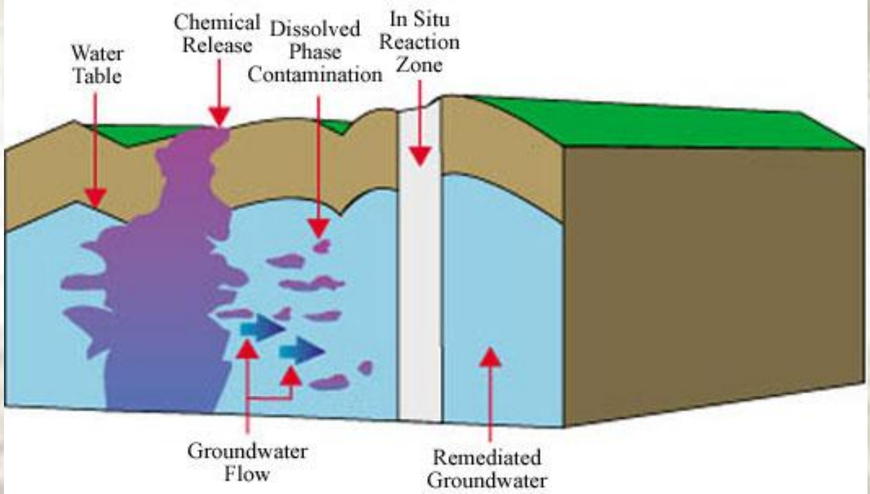
Nanotechnology for pollution prevention

- Synthetic or manufacturing processes which can occur at ambient temperature and pressure.
- Use of non-toxic catalysts with minimal production of resultant pollutants.
- Use of aqueous-based reactions.
- Build molecules as needed --“just in time.”
- Nanoscale information technologies for product identification and tracking to manage recycling, remanufacture, and end of life disposal of solvents.

- Involved in making a manufacturing process environmentally benign.
- An environmentally benign material or manufactured product that replaces toxic substances or minimizes raw materials.

Treatment & Remediation

End-of-pipe management and cleanup of pollution



Iron Treatment Walls…

- Used in groundwater treatment for many years.
- Iron chemically reduces organic and inorganic environmental contaminants.
- Currently involves granular or "microscale" iron (≥ 50 µm or 50,000 nm).

and Nanotechnology

- Nanosized iron enhances the reaction. Enhanced further by coupling with other metals (Fe/Pd)* on the nanoscale.
- Nano Fe^0 is more reactive and effective than the microscale.
- Smaller size makes it more flexible -- penetrates difficult to access areas.

* Elliot and Zhang *ES&T* **2001**, *35*, 4922-4926

Lead adsorption onto exfoliated graphitic nanoplatelets in aqueous solutions

- Preliminary results regarding the sorption behaviour of Pb(II) onto exfoliated graphite nanoplatelets (xGnPs) are presented in this study.
- xGnPs present good sorption capability of Pb(II) from aqueous solution after an oxidation treatment with HNO3, the sorption properties depending on the pH value of the solutions and on the presence of active sites and the size of the surfaces

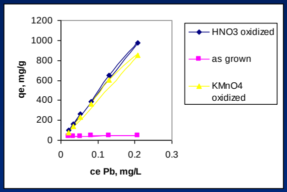


Fig. 3 – Effect of pre-treatment of xGnPs on
the % removal of Pb(II) from aqueous solutions

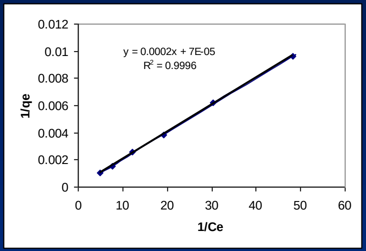


Fig. 7 – Langmuir-2 plot for the adsorption
of Pb(II) by xGnPs

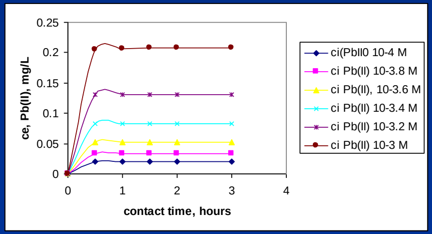


Fig. 4 – Effect of the contact time on Pb(II) adsorption rate for different concentration

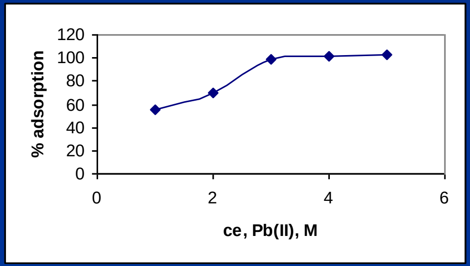


Fig.5 – Effect of the adsorbent concentration on
the adsorption of Pb(II)

Langmuir-2 constants		Freundlich constants	
q_m (mg/g)	333.3	K_F	13.592
K_a (L/mg)	0.003	n	1.142
R^2	0.9998	R^2	0.9999

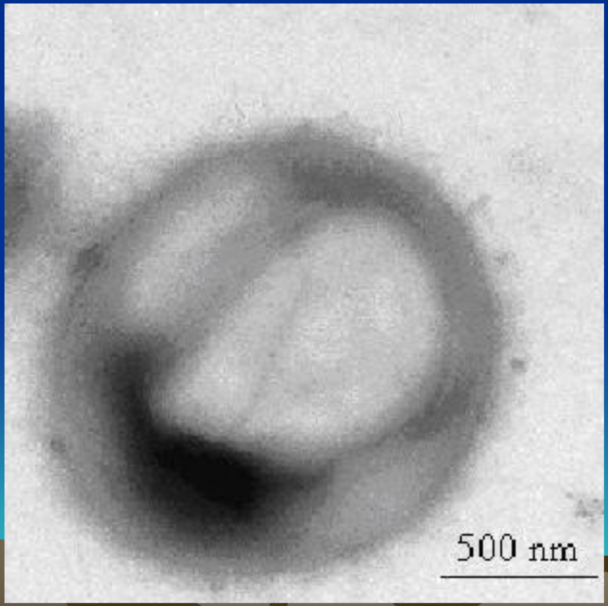
Tabel 1 – Parameters of Freundlich and Langmuir-2 adsorption isotherm models for Pb(II) on xGnPs

A. C. Ion, I. Ion, A. Culetu, Mater. Sci. Eng. B (2010), doi: 10.1016/j.mseb.2010.07.021

Multi-sector example

- Nano-and Micro-encapsulation of Agrochemicals
- SBIR Phase 1, LNK Chemsolutions

- Timed release of drugs, agrochemicals, nutraceuticals, and probiotics
- Bioerodible capsules-
  - 1-Naphthalene Acetic acid (NAA, the target agrochemical) in chitosan
  - Gum arabic/maltodextrin formulation for the shell of citral capsules



Marie, et al. Biomolecules, 2002, Chitosan nanocapsule

Adsorption of naphthalene onto carbonaceous nanomaterials graphitic nanoplatelets in aqueous solutions

In this paper, we report the adsorption of naphthalene on exfoliated graphite nanoplatelets (xGnP) in aqueous systems, in the presence of small concentrations of NOM. The effect of the process variables: contact time and initial concentration of the adsorbate over the naphthalene adsorption is reported All adsorption isotherms were fitted well by Freundlich model and using the Freundlich isotherm, the adsorption capacity of naphthalene on xGnP was calculated to be 1.1652.

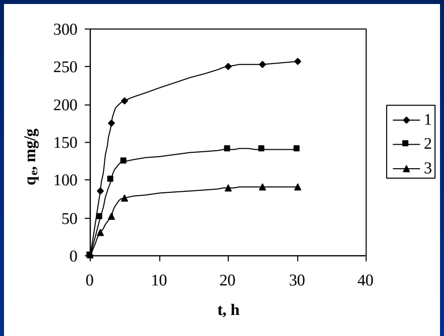


Fig. 3. The effect of the initial naphthalene concentration on the equilibration time. The concentration of naphthalene: (1) 10-4 M; (2) 5x10-4 M; (3) 3x10-4 M.

ISOTHERM PARAMETERS OBTAINED BY USING LINEAR METHOD

Isotherm type	Parameter	Value
Freundlich	K_F, (mg/g)(L/g) nF 1/n, R^2	1.1652 0.316 0.9895
Langmuir	q_m, mg g^{-1} K_a R^2	0.00162 18.43 0.8683

FREUNDLICH ISOTHERM PARAMETERS FOR OTHER CARBON MATERIALS USED AS SORBENTS FOR NAPHTALENE, AS REPORTED BY OTHER INVESTIGATORS, LISTED TOGETHER WITH THE xGnP RESULTS FROM THIS STUDY

Sorbent	K_F, (mg/g)(L/mg) nF	n	Reference
Activated carbon	200.2	0.35	This work
xGnP as received	1.1652	0.56	This work
Nano-C60	50	0.1	[28]
Charcoal	1.7	0.32	[18]

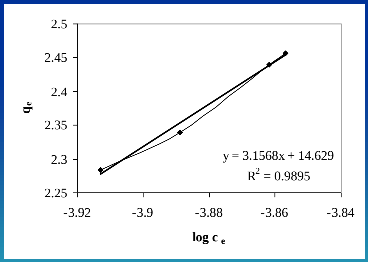


Fig. 5. Freundlich isotherm for the adsorption of naphthalene on xGnP.

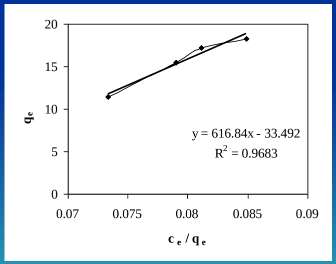
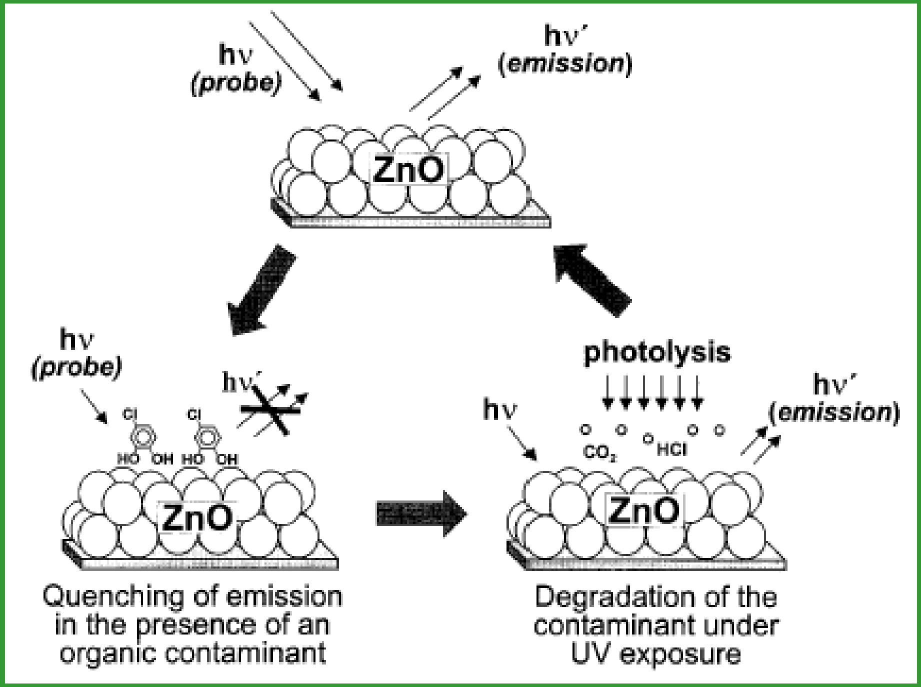


Fig. 6 Langmuir isotherm for the adsorption of naphthalene on xGnP.

A.C. Ion, A. Alpatova, I. Ion, research report 2010

"Sense and Shoot" Approach to Pollution Treatment

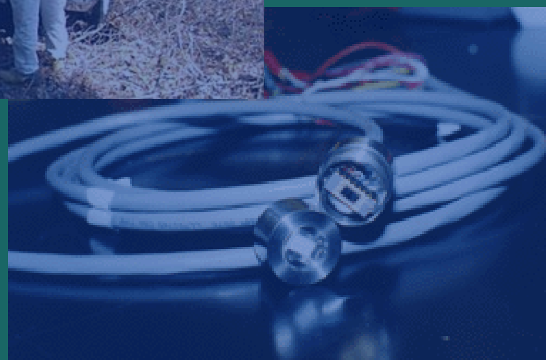
Dual role of ZnO semiconductor film as a sensor and photocatalyst



Kamat, P.V, et al. *J.Phys.Chem. B* **2002**, *106*,788-794.

- Nanosized zinc oxide (ZnO) "senses" organic pollutants indicated by change in visible emission signal.
- The ZnO "shoots" the pollutants via photocatalytic oxidation to form more environmentally benign compounds.
- Sensing capability means that the energy-consuming oxidation stage only occurs when the pollutants is present.
- Multifunctionality and "smartness" is highly desirable for environmental applications.

Sensors



Used for

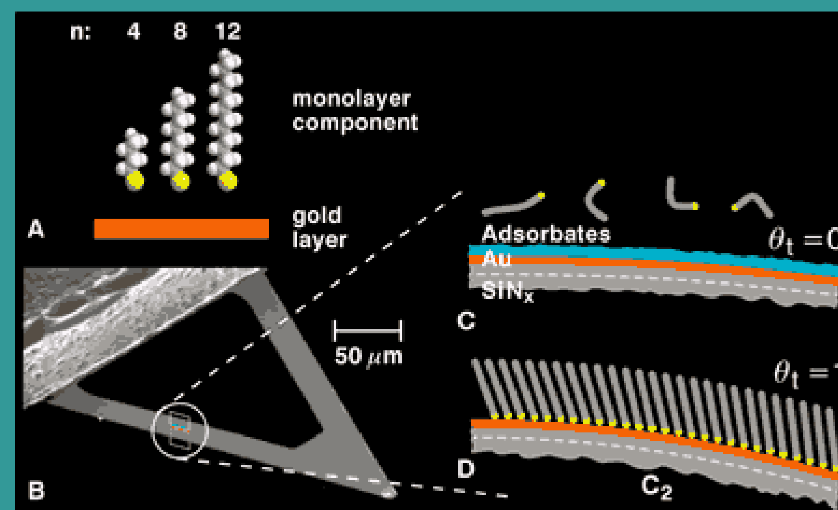
- Process control, compliance and ecosystem monitoring, and data/information interfaces.

Need to be

- Low cost, rapid, precise, and ultra sensitive.
- Operated remotely and continuously, *in situ*, and in real time.

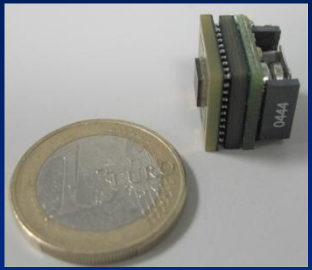
Single Molecule Detection

- Molecules adsorb on surface of micro cantilever, causes a change in surface stress, cantilever bends.
- Used to detect chemicals using either a specific reaction between analyte and sensor layer or chem/physisorption processes.
- Applications to bio-toxins as well.



IBM--Berger et al., Science 1997 June 27; 276: 2021-2024

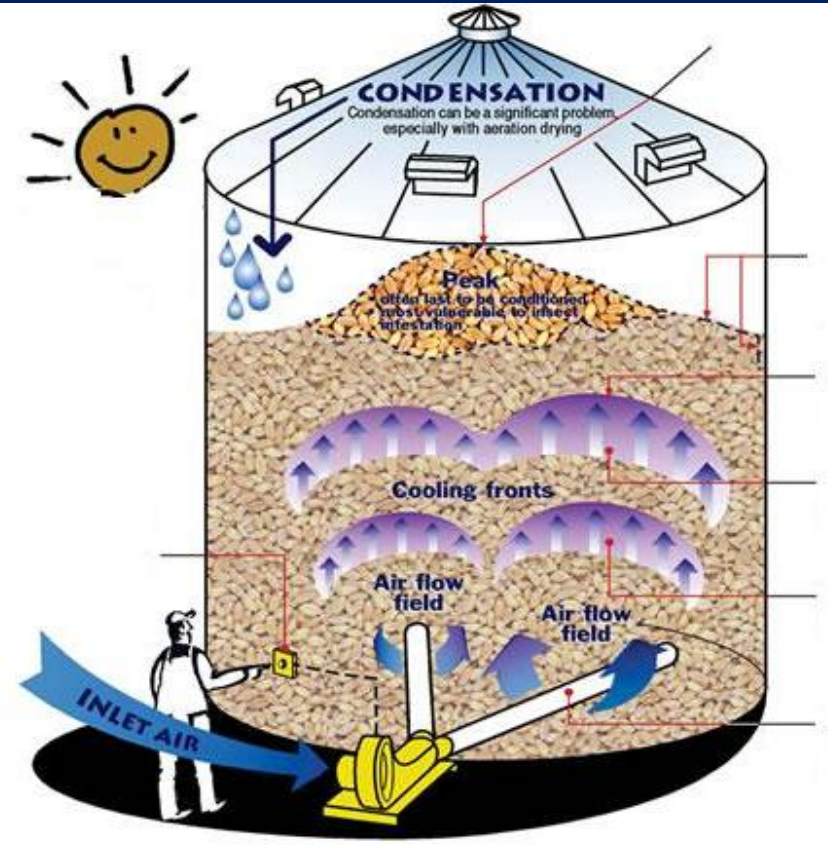
Nano Sensors for Grain Storage



Carbon dioxide Sensor

Acoustic Sensors

Odour Sensor



Grain Bin

Pressure Sensor

Temperature Sensor

Humidity and Dust Sensor

Applications of Nanobiosensors

Biological Applications

- DNA Sensors; Genetic monitoring, disease
- Immunosensors; HIV, Hepatitis,other viral diseas, drug testing, environmental monitoring…
- Point-of-care sensors; blood, urine, electrolytes, gases, steroids, drugs, hormones, proteins, other…
- Bacteria Sensors; (E-coli, streptococcus, other): food industry, medicine, environmental, other.
- Enzyme sensors; diabetics, drug testing, other.

Environmental Applications

- Detection of environmental pollution and toxicity
- Agricultural monitoring
- Ground water screening
- Ocean monitoring

Biosensors based on carbon-nanostructures for environmental contaminants

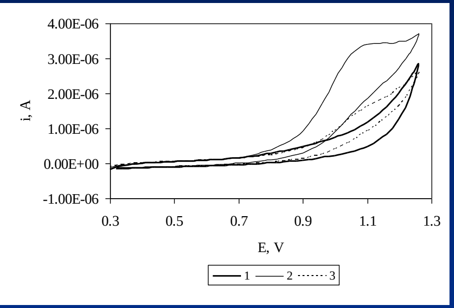


Fig. 1 Cyclic voltammograms: AChE – chitosan modified-GCE in pH 7.4 phosphate buffer; scan rate 100 mVs-1 (1) chitosan-GCE in 0.01 M phosphate buffer pH 7.4;(2) AChE-xGnP-chitosan modified-GCE+ 0.250 mM ATCl; (3) AChE-chitosan modified-GCE without xGNP + 0.250 mM ATCl

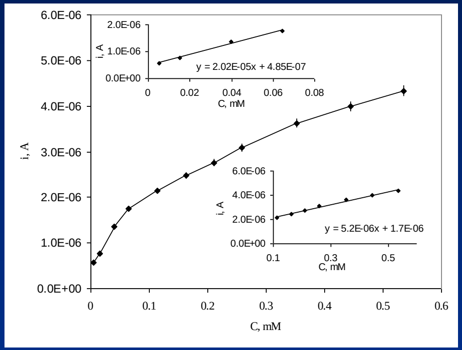


Fig. 4 – Calibration plot of the voltammetric response of AChE-chitosam modified GCE electrode towards ATCl.

A sensitive biosensor for chloropyrifos (CPF), an organophosphorus pesticide, was developed by immobilizing acetylcholinesterase (AChE) through covalent bonding to an oxidized exfoliated graphite nanoplatelets (xGnPs) – chitosan cross-linked composite.. The response of the sensor was a linear function of ATCl concentration in two segments, one from 0.005 - 0.039 mM and the second from 0.064 mM to 0.258 mM. The corresponding equation for the first range was ip(A) = 2.26x10-5 c + 4.39x10-7 (R2 = 0.992) and the equation for the second was ip(A) = 6.80x10-6 c + 1.30x10-6 (R2 = 1.000), with a detection limit of 1.58x10-10 M. The fabrication of the sensor was simple, the response was fast and the stability acceptable. This sensor has many potential applications, the foremost being in organophosphorus pesticides.

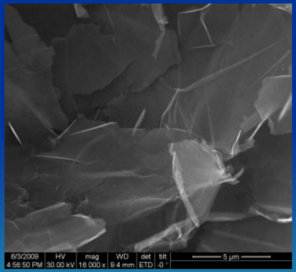


Fig. 2 – FEG SEM images of the dispersed oxidized xGnP in chitosan

Inhibition	Enzyme	Technique	Sample	LOD	Ref.
CPF	AChE	Voltammetric	Wine	< 300 ng mL^{-1}	[i]
CPF	BChE	Voltammetric	Grape juice	2x10^{-8} M	[ii]
CPF	AChE	Voltammetric	Aqueous samples	3x10^{-8} M	[iii]
CPF	AChE	Voltammetric	Aqueous samples	1.58x10^{-10} M	This work

[i] M. Del Carlo, M. Mascini, A. Pepe, D. Compagnone, J. Agric. Food Chem., 2002, 50, 7206-7210
[ii] A. Ivanov, G. Evtugyn, H. C. Budnikov, F. Ricci, D. Moscone, G. Palleschi, Anal. Bioanal. Chem., 2003, 377, 624-631
[iii] E. V. Suprun, H. C. Budnikov, G. A. Evtugyn, Kh. Z. Brainina, Bioelectrochemistry, 2004, 63(1-2), 281-284

A.C. Ion, I.Ion, A. Culetu, D. Gherase, C. Moldovan, A. Dinescu, Mater. Sci. Eng. C (2010), 30(6), 817-821

Type of Research and Time Categories

- ***Type of Research*:**
- *Development*—specific product cited, largely experiments or studies to optimize product
- *Applied*—specific application noted, but may also lead to better understanding
- *Basic*—fundamental understanding is goal, specific application not stated (although there could be one in the future)
- ***Time to Commercialization:***
- *0-5 years* –applied/development projects which directly address regulatory or product optimization issues. The applications of the work appear to be very near- term with minimal regulatory concerns, or they are already in the marketplace and properties are being studied or optimized.
- *5-10 years* –applied/development research that is based upon proven technology and for which there are not serious safety concerns
- *10-15 years—*applied research that is in the early stages of concept or development
- *15-20 years*—applied/basic research for which applications are not specified, but they can be envisioned.
- *20-50 years*—basic research for which few, if any, applications are envisioned, but for which fundamental knowledge will eventually lead to some.

Smart Nano Platforms for Farm Management

- Injectable Nano-chips for Animal Tracking
- Nanosensors and Drug Delivery Systems for Animals
- Nano-Bo-Peep for health monitoring of Crops and Animals
- Nanosystems for Identity Preservation and Tracking

Nanoparticles: Natural Agricultural Nanomaterials in Soil, Water, and Air

- Fundamental properties
- Nutrient and contaminant transport
- Biological interactions

Applying the Tools and Concepts of Nanoscale Science and Technology to Ag-related Problems

Nanoparticles in Water

- Aluminum and iron oxides and other colloidal particles
- Transport nutrients and pollutants, both organic and inorganic
- Markers of sources
- Modify (increase or decrease) concentrations and bioavailability calculated from simple equilibria of dissolved species

Nanoparticles in Soil

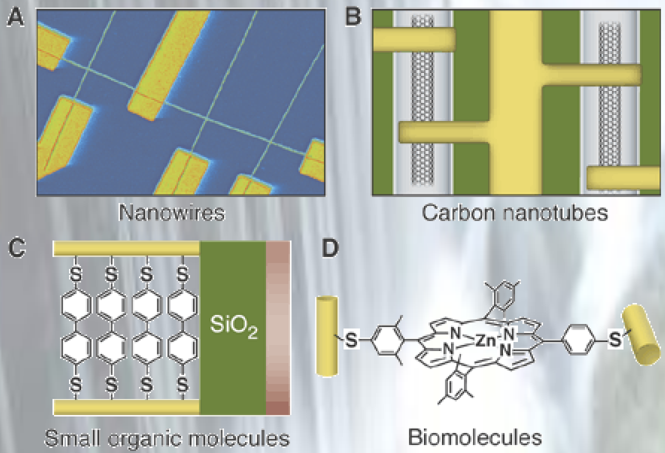
- Clays, zeolites, imogolite
- Iron and manganese oxides
- Organic particles
- Coated and core-shell particles
- Issues of nutrient and pollutant transport, water retention, texture, bioavailability.
- **Soil is a *nano- micro- macro-composite***

Understanding Nanoparticles and Nanoscale Phenomena

- can make agriculture more efficient and
- help mitigate environmental problems

Conclusions

Science and Engineering approaches are needed that offer new capabilities to prevent or treat highly toxic or persistent pollutants, and that result in the more effective monitoring of pollutants or their impact in ways not currently possible.



Nanoscience, engineering, and technology holds great potential for the continued improvement of technologies for environmental protection. The recent breakthroughs in creating nanocircuitry, give further evidence and support the predictions that nanoscale science and engineering "will most likely produce the breakthroughs of tomorrow."

BUT the environmental implications (nano in the environment) need to be considered as we consider nano for the environment.

Collaborations

- RWTH Aachen, Germany, bilateral project(2009-2010) "**Natural nanoparticles in soils as possible environmental vectors for contaminants**"
- Michigan State University, USA, bilateral project (2009-2010) "Graphitic nanoplatelets as sorbents for PAHs)
- 2 PN II projects 2008-2011

LABORATORY for quality control of products (LCCP)

List of the staff:

Prof. dr. Ion Ion
Prof. dr. eng. Alina C. Ion
PhD Luminita Barbu
PhD Anton Ficai
PhD Alina Culetu

Research directions:

- Preparation and characterization of electrodes with high electrocatalytic efficiency
- Characterization of different kinds of nanosized materials
- Preparation and characterization of ion-selective electrodes and biosensors
- Analytical applications of electrochemical sensing

Available facilities:

GC/MS and HPLC
Potentiometric interface for ion-selective electrodes
electrochemical cell, apparatus for polarization measurements, cyclic voltammetry, electrochemical impedance spectroscopy

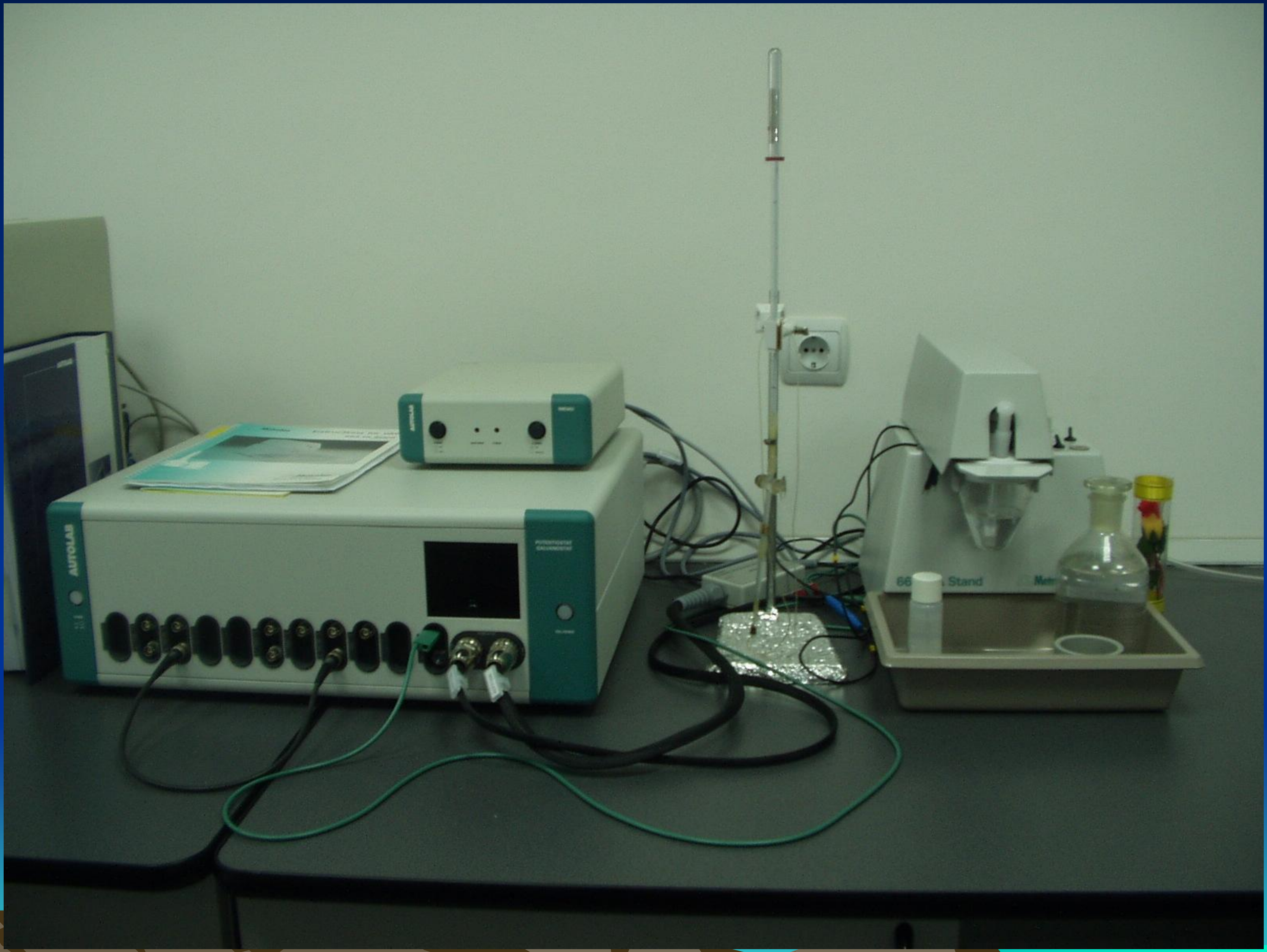
LCCP – accredited methods

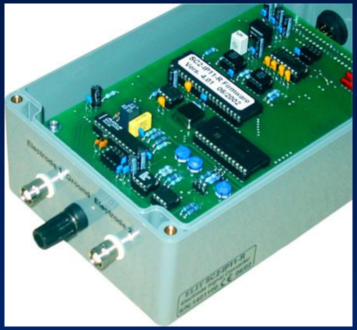
- Analysis: GC/MS
- Analysis: HPLC
- Analysis: AAS

GC/MS Varian 3900, Saturn 2200

HPLC Waters 600

Autolab PGSTAT 30





Ion-selective electrode interface