Environmental applications of graphene-based materials

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Nanoparticles and the Environment

- Nature of nanoparticles themselves.
- Characteristics of the products made.
- Manufacturing processes involved.
- 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)

Nanotechnology -

Possibility for Environmental Benefit

- Improved monitoring & detection capabilities
- Ultra-Green manufacturing and chemical processing – eliminate toxic constituents
- Waste-minimization via designed-in pollution prevention at the source - less material to dispose of, atom-by-atom construction
- Reduced energy usage
- Commercially-viable alternative clean energy sources (fuel cells, solar, wind)
- Inexpensive, rapid remediation, treatment and sensing technologies
- Sustainability

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

5µm

- EPA FY 2001 Annual Report

Nanotechnology and the Environment

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

- Pollution prevention
- Treatment
- Remediation
- Information

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



Applications of graphene-based materials

- Removal of heavy metals such as: Cu(II), Pb(II), Cd(II), CO(II);
- Organic pollutants (benzene containing) with π - π interactions between graphene and the adsorbate;
- Magnetic particles are introduced to form magnetic graphene composites;
- Graphene-based photodegradants for removing organic pollutants;

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

<complex-block>

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

Nanomaterials in analytical chemistry

- partitioning mechanism of the extraction, which is characterized by significantly higher linearity range when compared to commercial fibre
- enabling highly polar sorbents to be used without the risk of dissolving in polar sample matrix
- povides opportunity of application of quite new kinds of materials, which due to low melting temperatures or solubility in water have not been taken into consideration so far in this kind of applications
- high extraction efficiency of phenols and VOCs obtainable with M-SPME fibres, comparable and better than the extraction efficiency using commercially available fibres
- applicable on the sample preparation step prior to the final quantitative determination of analytes on the ppb level

MILESTONES IN ANALYTICAL CHEMISTRY

- 1974 Development of flow injection analysis FIA
- 1974 Development of purge-and-trap technique PT
- 1976 Development of solid phase extraction SPE
- 1978 Development of cloud point extraction CPE
- 1985 Development of microwave-assisted extraction MAE Development of supercritical fluid extraction - SFE
- 1987The concept of ecological chemistry (H. Malissa)The concept of sustainable development
- 1990 Development of **solid-phase microextraction** SPME Development of micro total analysis system - μTAS





1993 Development of molecularly imprinted solid-phase extraction - MIMSPE

- 1995 The concept of environmentally friendly analytical chemistry (M. de la Guardia, J. Ruzicka)
- 1996 Development of presurized solvent extraction PSE Development of liquid phase micro extraction - LPME Development of **single drop microextration** -SDME

1999 The concept of green chemistry (P.T. Anastas) The concept of clean analytical method (M. de la Guardia) The concept of green analytical chemistry (J. Namieśnik) Development of stir bar sorptive extraction- SBSE



SOLID PHASE MICROEXTRACTION chem 03



(SPME)

- simplicity of operation
- short extraction and desorption time
- solvent-free operation
- small size (convenient for designing portable devices)

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- possibility of full automation
- direct linkup with a GC
- possibility to in-situ and in-vivo sampling
 - Plunger
 - Barrel 2.
 - Injection needle 3.
 - Inner needle 4
 - Coated fused silica fiber 5.

C. L. Arthur, J. Pawliszyn, Anal. Chem., 62 (1990) 2145

PRINCIPLES OF SPME



- 1. direct-immersion SPME
- 2. headspace-SPME

Operation steps:

- 1. Immersion of the needle in the sample
- 2. Exposition of the fiber
- 3. Extraction of an analytes
- 4. Retraction of the fiber
- 5. Introduction of the fiber to injection port
- 6. Desorption of analytes

COMMERCIAL SPME FIBERS

- limited choice
- high cost
- poor selectivity for polar analytes
- some fiber coating have active adsorption centerspossibility of competing of the matrix compounds with the analytes for available adsorbent sites
- need to high temperatures to be used to desorb the less volatile compounds- can lead to degradation of the analytes, adsorbent materials and promote catalytic breakdown of the trapped analytes



APPLICATION OF NANOPARTICLES IN NANOEXTRACTION TECHNIQUES



Solid-phase nanoextraction(SPNE)



Schematic illustration of silanization of graphene



Silanized chemically reduced graphene oxide with improved dispersability

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Representative examples of the use of carbon nanostructures as stationary (GC, LC) and CEC phases

Carbon	Separation	Column	Analytes	Ref
nanostructure	technique	caracteristics		
MWCNTs	GC	30 cm lenghtx0.30 cm i.d.Packed	Aromatic hidrocarbons, halogenated hydrocarbons,	56
		glass column	alcohols, ketones, ester	
MWCNTs	GC	Stainless steel tub(MWCNTs radically aligned inside)	Alkane and alkene	57
Self assembled SWCNTs	GC	Stainless steel tube	Alkanes and PAHs	58
SWCNTs	Ultrafast GC	100 μm x100 μm square 50 cm long microfabricated channels	Alkanes and functional group mixtures	60
SWCNTs	μ - HPLC	40 cm fused silica capillary monolithic stationary phase	Uracil, phenol,N,N'-diethyl-m-toluamide, toluene	63
Si-SWCNTs and Si- MWCNTs	LC	Narrow-bore stainless steel column	Aromatic compounds	64
SWCNTs-BSA conjugates	Microchip- CE	Protein stationary phase immobilized in a microfluidic chip	Tryptophan enantiomers	65
SWCNTs	CEC	-	Chlorophenols, antiinflammatory drugs and penicillins	66
MWCNTs	CEC	-	Chiral separation of ephedrines	67
β – CD modified MWCNTs	CEC	-	Chiral separation of clenbuterol	68
Fullerene C60	CEC	-	PAHs	69
c- SWCNTs	CEC	-	Caffeine and threobromine	71
SWCNTs	CEZ	-	Purine and pyrimidine bases	72

Determination of phenols using SPME and GC

Compound	Linearity	D ²	LOD (µg/L)	
Compound	range (µg/L)	K-	M-SPME	PA
4-Chloro-3-methylphenol	15-1500	0.9953	7	50
2-Chlorophenol	3-300	0.9936	43	530
2,4-Dichlorophenol	3-300	0.9987	15	120
2,4-Dimethylphenol	3-300	0.9921	9	110
2,4-Dinitrophenol	10-1000	0.9963	110	950
2-Methyl-4,6-dinitrophenol	15-1500	0.9898	81	680
2-Nitrophenol	3-300	0.9945	9	60
4-Nitrophenol	15-1500	0.9937	150	1800
Pentachlorophenol	15-1500	0.9914	83	740
2,4,6-Trichlorophenol	10-1000	0.9932	61	440

A. Kloskowski, M. Pilarczyk, J. Namieśnik, Anal. Chem., 81 (2009) 7363

Adsorption of Organic Contaminants from Solution to xGNPs

Batch Adsorption/Desorption Study:







xGNPs large aggregates

xGNPs small aggregates

xGNPs colloidal particles

Adsorption of naphthalene onto carbonaceous nanomaterials graphite 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.

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]

ISOTHERM PARAMETERS OBTAINED BY USING LINEAR METHOD

Isotherm type	Parameter	Value
Freundlich	$K_{F^{2}}$ (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





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

Top view and side view of naphthalene and 1-naphthol on the hexagonal carbon network



Naphtalene molecules adsorbed parallel to the sulfonated graphene surface in two orientations and 1-naphtol in one orientation

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Study on phenol adsorption from aqueous solutions on exfoliated graphitic nanoplatelets



Effect of contact time on phenol adsorption to 400 mg/L xGnPs at 125 mg/L initial phenol concentration for as-grown and oxidized xGnP



Phenol removal as function of asgrown xGnPs loading. Initial phenol concentration is 100 mg/L.



70

Effect of the initial phenol concentration on the adsorption of phenol on as-grown xGnPs at a loading of 125 mg/L.

A.C. Ion, A. Alpatova, I. Ion, A. Culetu, Mater. Sci. Eng. B 176 (2011) 588-595

Study on phenol adsorption from aqueous solutions on exfoliated graphitic nanoplatelets



pH effect on the phenol adsorption by asgrown xGnPs. Initial conditions: xGnP loading is 400 mg/L; initial phenol concentration is 125 mg/L.



Adsorption isotherms of phenol on as-grown and oxidized xGnP. Initial conditions: xGnPs loading 400 mg/L; initial phenol

A.C. Ion, A. Alpatova, I. Ion, A. Culetu, Mater. Sci. Eng. B 176 (2011) 588-595

Study on phenol adsorption from aqueous solutions on exfoliated graphitic nanoplatelets

The sorption capacity of various sorbents for phenol at optimum pH values

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

Lead adsorption onto exfoliated graphite 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



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





Effect of the contact time on Pb(II) adsorption rate for different concentration



Effect of the adsorbent concentration on the adsorption of Pb(II)

Langmuir-2 plot for the adsorption of Pb(II) by xGnPs

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

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

A schematic diagram of the formation of the surface complexes of Pb(II) ions on the surfaces of GO



Formation of surface complexes of metal ions with oxygen functional groups on graphene oxide (GO)

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Study on lead adsorption from aqueous solutions on oxidized exfoliated graphite nanoplatelets



Effect of pre-treatment of xGnPs on the % removal of Pb(II) from aqueous solutions; (1) HNO3 oxidized, (2) as grown, (3) KMnO4 oxidized



Effect of the pH on the uptake of lead; conditions: contact time 120 minutes, xGnPs concentration 400 mg/L, pH between 1.5 and 7.5

A. C. Ion, I. Ion, A. Culetu, Mater. Sci. Eng. B 176 (6) (2011) 504-509

Study on lead adsorption from aqueous solutions on oxidized exfoliated graphite nanoplatelets





Effect of the contact time on Pb(II) adsorption rate for different concentrations (1) 10-4 M, (2) 10-3.8 M, (3) 10-3.6 M, (4) 10-3.4 M, (5) 10-3.2 M, (6) 10-3 M Pb(II)), pH=6, T=298 K, xGnPs oxidized with concentrated HNO3

Effect of the adsorbent concentration on the adsorption of Pb(II); (1) as grown, (2) KMnO4 oxidized, (3) HNO3 oxidized; pH = 6; adsorbent concentration 200 mg/L; contact time 60 minutes

Study on lead adsorption from aqueous solutions on oxidized exfoliated graphite nanoplatelets





Linearized Freundlich isotherms for Pb(II) adsorption by xGnPs at T=298 K

Langmuir plot for the adsorption of Pb(II) by xGnPs: pH = 6.0, adsorbent concentration 400 mg/L, contact time 30 minutes

Langmuir constants		Freundlich constants	
$q_{\rm m} ({\rm mg/g})$	333.3	K _F	13.592
K _a (L/mg)	0.003	n	1.142
r ²	0.9994	r ²	0.9996

Parameters of Freundlich and Langmuir adsorption isotherm models for Pb(II) on xGnPs

A. C. Ion, I. Ion, A. Culetu, Mater. Sci. Eng. B 176 (6) (2011) 504-509

Applications of different graphene-based materials in the removal of pollutants

Graphene-base materials	Morphology	Properties	Ref.
Layers of graphene sheets	Overlapped and mesoporous	Adsorption of fluoride	40
Graphene oxide	Few layers nanosheets	Adsorption of Pb(II) ions	42
Ionic liquid functionalized	Graphene thin films	Removal pf Pb(II) and	44
graphene		Cd(II) from wastewater	
Sulfonated graphene	Few layered nanosheets	Removal of naphthalene	45
		from waters	
ZnO/graphene composites	ZnO nanoparticles on reduced	Photocatalytic degradation	53
	graphene oxide sheets	organic dyes	
Magnetic graphene hybrids	Fe ₃ O ₄ nanoparticles on reduced	Arsenic removal	50
	graphene oxide sheets		
Graphene-based	Magnetic reduced graphene oxide	Escherichia Coli	51
photothermal agent for rapid	functionalized with glutaraldehyde		
killing of bacteria			

POTENTIOMETRICS



PVC electrodes

Metal-metal Oxide electrodes

Biosensors

Composites electrodes

- Amalgam electrodes

Bismuth film electrodes

Carbon nanotubes, graphene, carbon paste and carbon composite electrodes

Boron-doped diamond (BDD) electrode

Amorphous carbon nitride (a-CNx) electrode

Biosensors

Biosensors based on carbon-nanostructures for environmental contaminants



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) AChExGnP-chitosan modified-GCE+ 0.250 mM ATCI; (3) AChE-chitosan modified-GCE without xGNP + 0.250 mM ATCI

Inhibition	Enzyme	Technique	Sample	LOD	Ref.
CPF	AChE	Voltammetric	Wine	$< 300 \text{ ng mL}^{-1}$	1
CPF	BChE	Voltammetric	Grape juice	2x10 ⁻⁸ M	ü
CPF	AChE	Voltammetric	Aqueous	3x10 ⁻⁸ M	iii
			samples		
CPF	AChE	Voltammetric	Aqueous	1.58x10 ⁻¹⁰ M	This
			samples		work

ⁱ M. Del Carlo, M. Mascini, A. Pepe, D. Compagnone, J. Agric. Food Chem., 2002, 50, 7206-7210



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



FEG SEM images of the dispersed oxidized xGnP in chitosan

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 ATCI 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.

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

Comparative analysis of organophosphate pesticides in broccoli and cabbage using the proposed biosensor and chromatographic methods

Probe de brocoli	Chlorpyriphos mg kg ⁻¹ (Cromatografic)	Clorpirifos mg kg ⁻¹ (Biosenzor cu AchE)
1	0.022	0.020
2	0.020	0.015
3	0.013	0.010
4	< LOQ	< LOQ
5	< LOQ	< LOQ

Probe de varza	Clorpirifos mg kg ⁻¹ (Cromatografic)	Clorpirifos mg kg ⁻¹ Biosenzor cu AChE
1	0.022	0.020
2	0.020	0.015
3	0.013	0.010

Differential pulse voltammetric analysis of lead in vegetables using a surface amino-functionalized exfoliated graphite nanoplatelet chemically modified electrode





Functionalization of the exfoliated graphite nanoplatelet (xGnP) with amide groups

FTIR spectra of oxidized (-) and of aminofunctionalized (-CO-NH2) (-)exfoliated graphite nanoplatelet (xGnP)



DPV for different concentrations of Pb(II) at the Bi film amino-functionalized (-CO-NH2) exfoliated graphite nanoplatelet (xGnP)/GCE modified electrode in 0.01 M phosphate buffer pH 4.5 in the range of Pb(II) concentrations between $0.005 - 0.045 \mu g L$ -1, y=3.75x + 0.73, R2 = 0.9933

Functionalization of the exfoliated graphite nanoplatelet (xGnP) with amide groups



SEM image of the as grown xGnP and of the amino-functionalized and $(-CONH_2)$ exfoliated graphite nanoplatelets (xGnPs)



FTIR spectra of oxidized (____) and of amino-functionalized (- CONH₂) and (____) exfoliated graphite nanoplatelet (xGnP).



Bismuth films on (1) GCE; (2) GCE modified with xGnP; (3) GCE modified with amino-functionalized (-CONH₂) exfoliated graphite nanoplatelet (xGnP) 30 μ g L⁻¹ Pb(II) in 0.1 M phosphate buffer (pH = 4.5), scan rate 100 mV s⁻¹.



DPV for different concentrations of Pb(II) at the Bi film aminofunctionalized (-CONH₂) exfoliated graphite nanoplatelet (xGnP)/GCE modified electrode in 0.01 M phosphate buffer pH 4.5 in the range of Pb(II) concentrations between 0.005 and 0.045 µg L⁻¹, y = 3.75x + 0.73, $R^2 = 0.9933$

DPV measurements in vegetables (cabbage juice) for Pb(II)

- using the Bi amino-functionalized (-CONH₂) exfoliated graphite nanoplatelet (xGnP)/GE electrode in acetate buffer solution (pH = 4.5) in the concentrations range 0.005– 0.035 µg L⁻¹, with the correspondent equations of regression: y = 13.06x + 0.46, $R^2 = 0.9970$.

Application of an exfoliated graphite nanoplatelet –modified electrode for the determination of quintozen

FEG-SEM (field emission gun scanning electron microscopy) images of xGnP in DMF and the dispersed xGnPs and chitosan in DMF solvent

Cyclic voltammograms of xGnP-chit/GCE modified electrode in 0.01 M phosphate buffer pH 4 for: the GC electrode in 0.01 M phosphate buffer pH 4 (1) xGnP-Chit/GC modified electrode in PBS pH 4 (2) and for xGnP-Chit/GC modified electrode in PBS pH 4 at a 10-5 M concentration of quintozen (3)

Effect of pre-concentration time on the differential pulse response of the adsorbed quintozen (the concentration of quintozen 10-5 M)

Effect of the pH of the adsorption medium

Cyclic voltammograms on xGnP-chit/GCE modified electrode in 0.01 M phosphate buffer pH 4 for increasing concentrations of quintozen from 10-12 - 10-5 M; (1) blank, (2) – 10-12 M, (3) – 10-11 M, ...(9) – 10-5 M, (12 μ L of xGnP –chit/DMF the solution added on the electrode surface)

Application of an exfoliated graphite nanoplatelet-modified electrode for the determination of QUINTOZEN

FEG-SEM (field emission gun scanning electron microscopy) images of xGnP in DMF and the dispersed xGnPs and chitosan in DMF solvent.

Fourier transform infrared (FTIR) spectra of as-prepared (_____) and oxidized xGnP (_____).

Cyclic voltammograms of xGnP–Chit/GCE modified electrode in 0.01 M phosphate buffer pH 4

(1) the GC electrode in 0.01 M phosphate buffer pH 4
(2) xGnP--Chit/GC modified electrode in PBS pH 4
(3) for xGnP--Chit/GC modified electrode in PBS pH 4 at a 10⁻⁵ M concentration of quintozen.

Influence of different parameters on the response of the sensor

Effect of the concentration of xGnP on a delimited electrode surface

Effect of the pH of the adsorption medium

Effect of pre-concentration time on the differential pulse response of the adsorbed quintozen (the concentration of quintozen 10⁻⁵ M)

Cyclic voltammograms on xGnP-chit/GCE modified electrode in 0.01 M phosphate buffer pH 4

