O Papel da Nanotecnologia na Monitorização de Poluentes Emergentes em Águas

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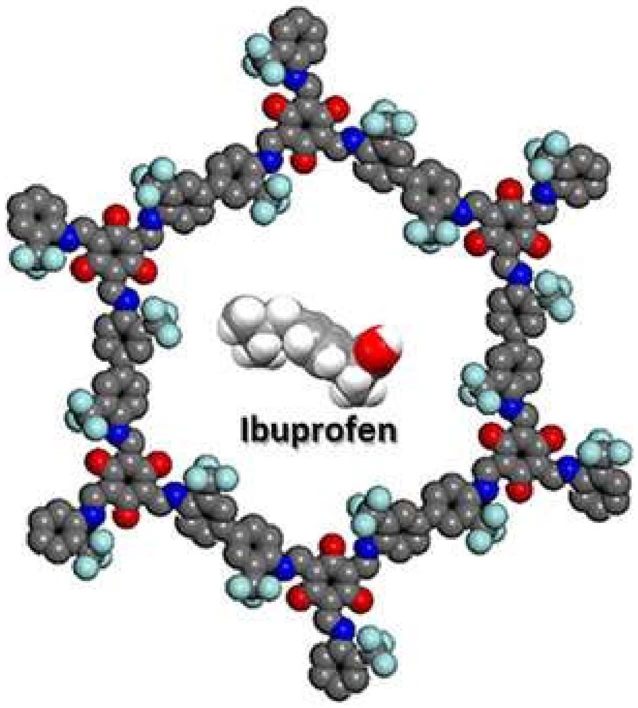
Water Quality group

Contents



$TpBD\text{-}(CF_3)_2$

Types of Nanomaterials

NANOMATERIALS

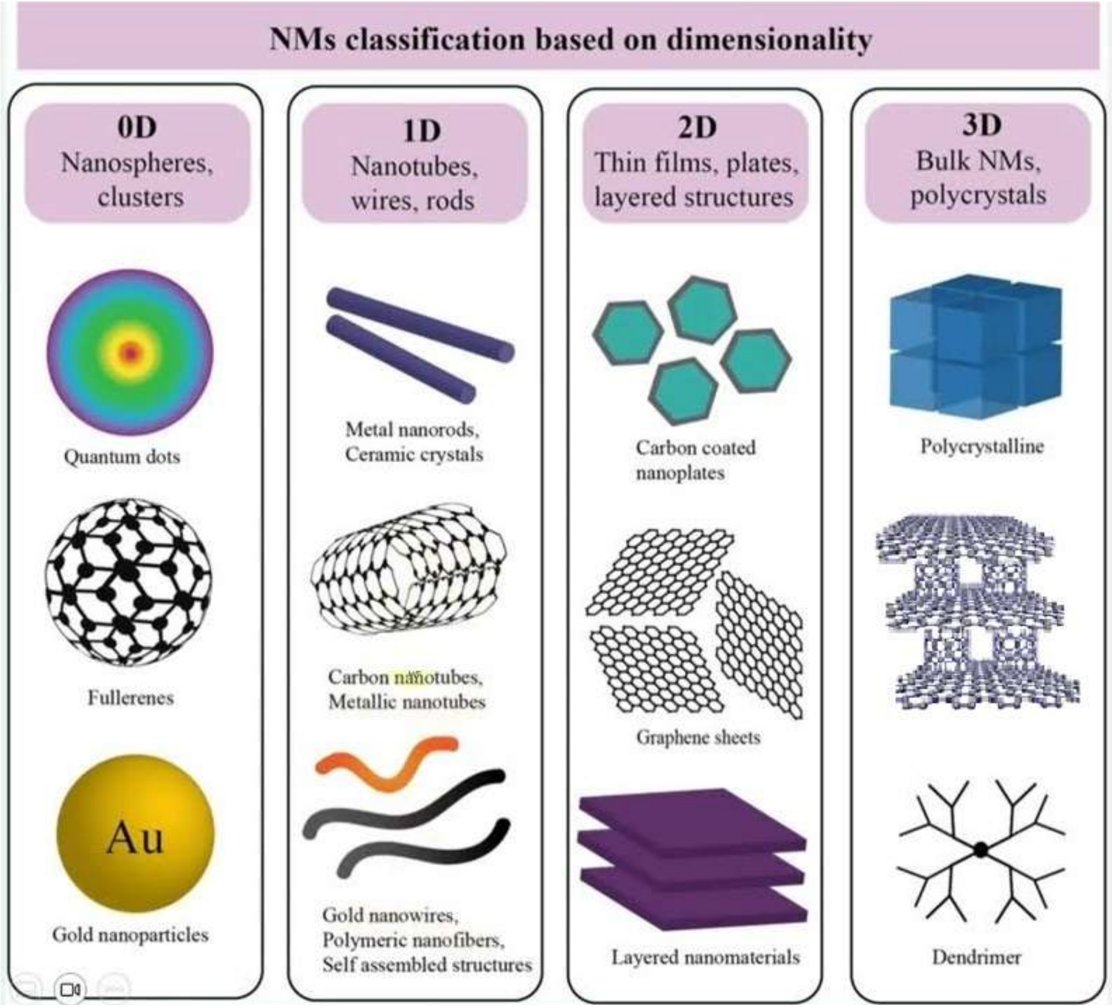
Materials with at least one dimension <100 nm

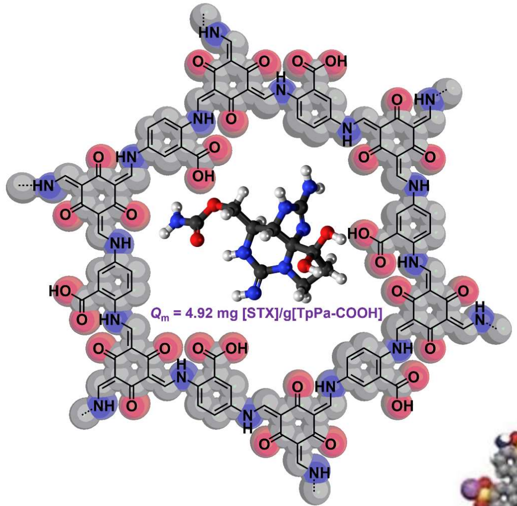
Have distinct physical, chemical and biological properties

Types of nanomaterials

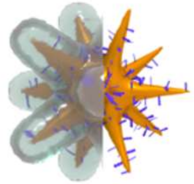
- **Organic**
  - Carbon
    - Fullerenes
    - CNT
    - Graphene
    - Buckyball
  - Others
    - Liposomes
    - Dendrimers
    - Micelles
    - Cellulose
    - COFs
- **Inorganic**
  - Metals
    - Au
    - Ag
    - Al
    - Zn
    - Cu
  - Metal Oxides
    - CuO
    - Fe_2O_3
    - Al_2O_3
    - TiO_2
    - SiO_2
  - Quantum dots
    - CdSe
    - ZnS
- **Hybrid**
  - Organic-inorganic
  - Organic-organic
  - Inorganic-inorganic

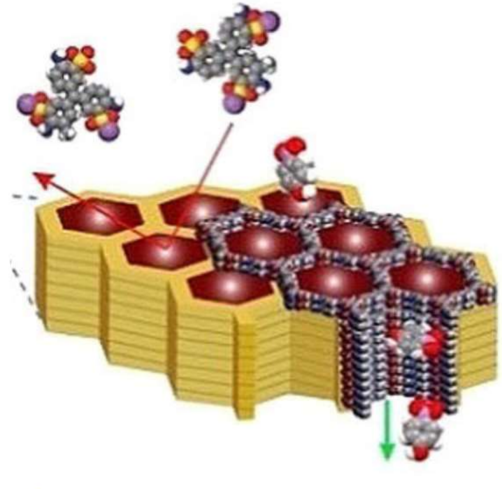
Classification of the Nanomaterials



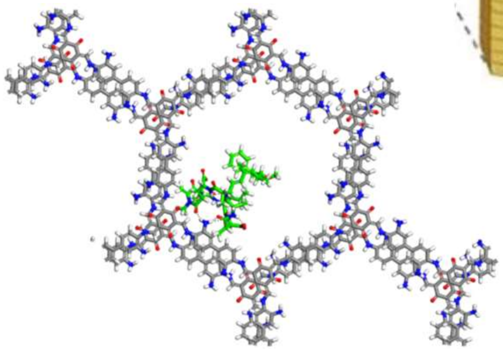


GNS





COFs



Tuang Yeow Poh, Nur A'tikah Binte Mohamed Ali, Micheál Mac Aogáin, Mustafa Hussain Kathawal,Magdiel Inggrid Setyawati, Kee Woei Ng and Sanjay Haresh Chotirmall. Inhaled nanomaterials and the respiratorymicrobiome: clinical, immunological andtoxicological perspectives. Particle and Fibre Toxicology (2018) 15:46

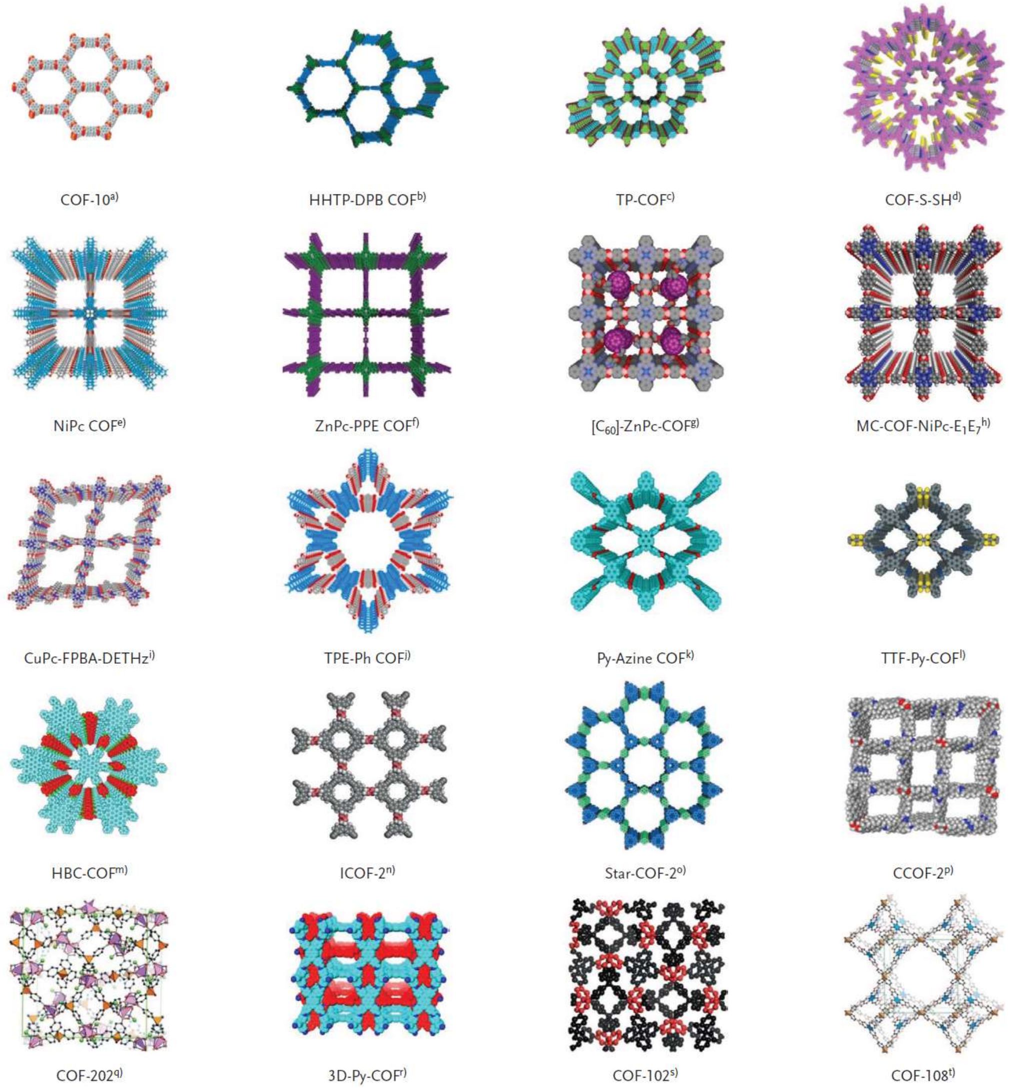
Fernandes et al. Chem. Eur. J. 2019, 25, 6461 – 6473

COFs (Adrien Côté et al. 2005)

- Crystalline materials composed of light elements (H, B, C, N, and O) linked by strong covalent bonds in a two- or three-dimensional periodic structure

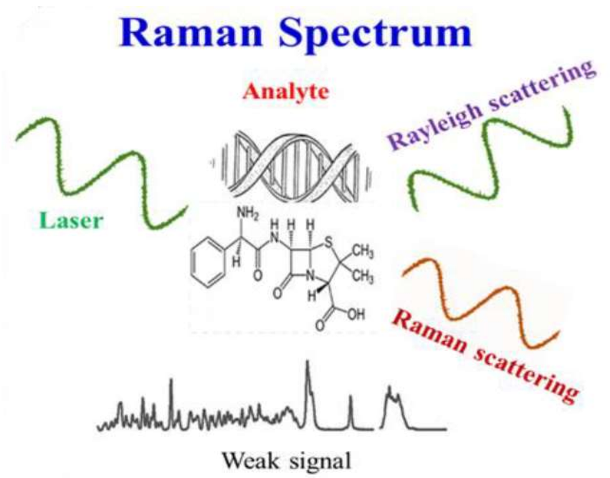
- Possess high surface area (e.g. TH-COF 1254 m^2/g), tuneable pore sizes and functional groups, low density, chemical stability → selectivity & high adsorption capacity (e.g. 12% m/m).

- Appplied in gas storage and separation, **adsorption,** catalysis, **sensing,** optoelectronics and drug delivery.

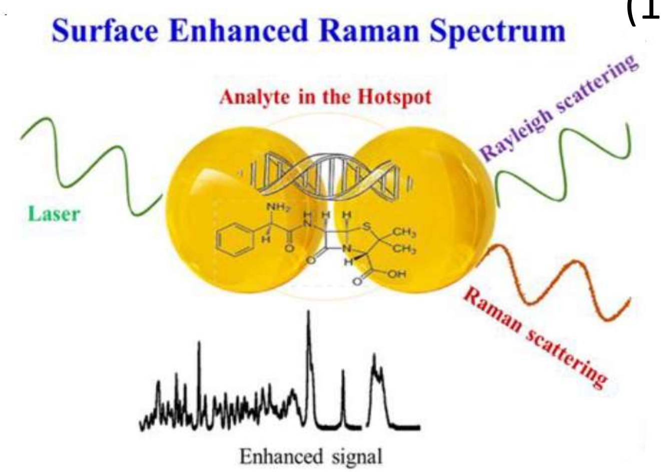


Adv. Funct. Mater. 2018, 28, 1705553

RAMAN spectroscopy

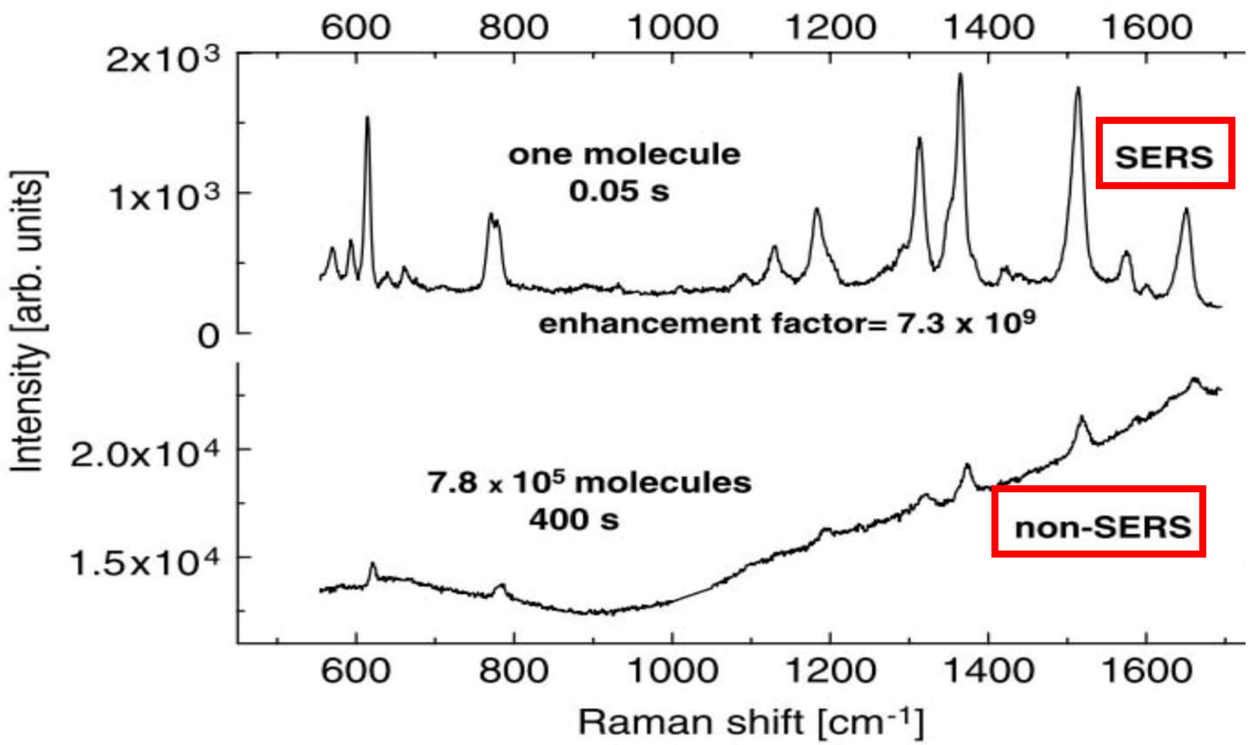


(1928)



(1973)

Bulk Raman VS SERS

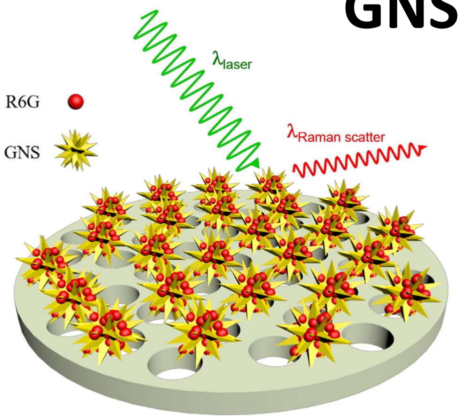


Raman (non-SERS) and SERS spectra at 633 nm laser excitation (3 mW) for rhodamine 6G molecules.

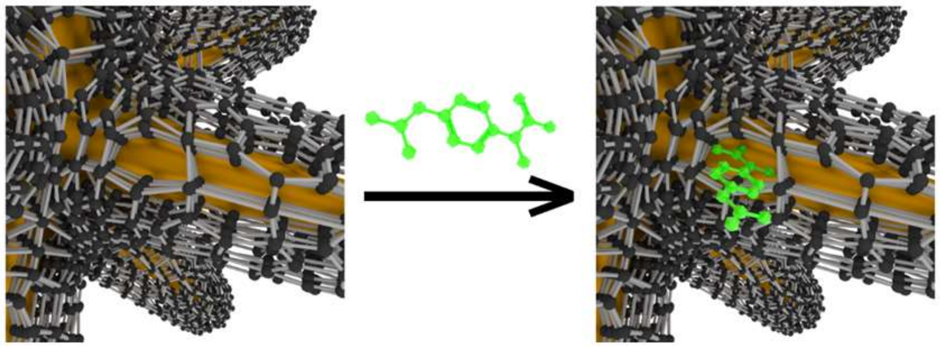
PPT: Plasmon mediated Surface Enhanced Raman Spectroscopy by R.Gandhimathi

PPT: Surface Enhanced RAMAN Spectroscopy (SERS) by Rahutosh Ranjan

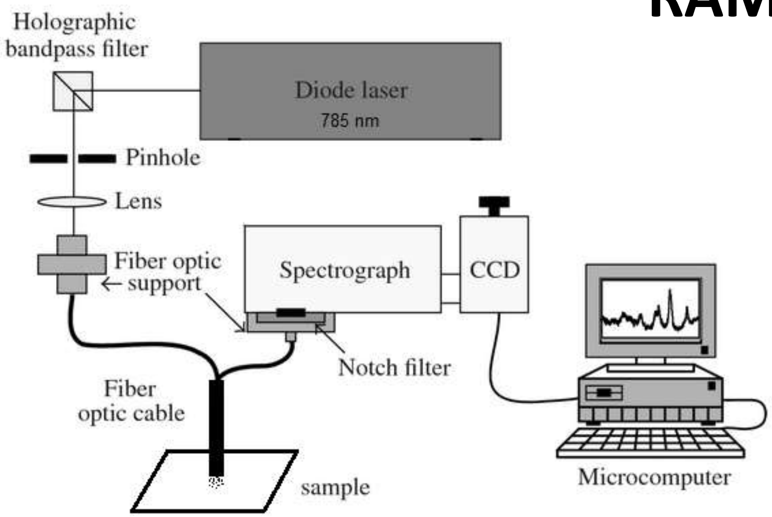
GNS <<< SERS substrates >>> GNS@COF



https://doi.org/10.1016/j.saa.2022.120955



RAMAN spectrometer



1. Enhanced Sensitivity and Selectivity:

- Large surface area-to-volume ratio / adjustable pore size / specific functional groups → provides high capacity and selectivity towards particular pollutants.

2. Rapid and Real-Time Detection:

- Early warning signs of contamination and helping to prevent potential health risks (e.g. projects AtlantiClam, Pacto da Bioeconomia Azul and D4Runoff).

. Electrochemical Sensors – e.g., based on the use of graphene or molecularly imprinted polymers

. Optical Sensors – e.g. those based on surface plasmon resonance and fluorescence, offer fast detection and quantification of pollutants with high precision.

. SERS sensors – fast detection and identification of pollutants. Acquire molecular features (fingerprint)

3. Miniaturization and Portability:

- Compact, portable devices for on-site and continuous water quality monitoring, e.g. with microfluidics
- Integrated Systems for automated and remote monitoring, including sampling and continuous real-time data acquisition and processing (associated with AI/ML)

4. Multiplexing Capabilities:

- Sensors capable of detecting multiple pollutants simultaneously. This is achieved through the use of different multiplexed sensor arrays (e.g., microplastics, metals and organics) or coupled to advanced data processing algorithms to interpret complex signals (e.g. SERS sensors).

5. Improved Stability and Durability:

- excellent chemical and physical stability, making sensors more durable and reliable over extended periods and in harsh environmental conditions. Reduced need for frequent calibration or replacement

Surface Area and Capacity of COFs

COF	Surface Area (m^2/g)	Capacity (mg/g)	Analyte	Ref.
mTpBD-Me_2	538	270	Chlorpyrifos	1
		54	Atrazine	1
		low	Diquat	1
TpBD-Me_2	468 bulk	812*	Okadaic acid	2
		830	DTX-1	2
TpPa-COOH	177	4.9	STX	3
TpBD-CF_3	874	150 (pH 2)	Ibuprofen	4
TpBD-CF_3	860		19 drugs	5
TpBD-CF_3	1090	42 (L), 27 (R), 15 (E)	Ibuprofen	6
		19	Paracetamol	6
TpBD-CF_3	870	65	Sulfapyridine	GB
		132	Sulfamethoxazole	GB

1- https://doi.org/10.1016/j.micromeso.2020.110523
2- https://doi.org/10.1039/C9NR00388F
3- https://doi.org/10.1016/j.jhazmat.2023.131247
4- https://doi.org/10.1002/chem.201801649
5 - https://doi.org/10.1016/j.chemosphere.2021.130364
6 - https://www.mdpi.com/1420-3049/25/14/3132

Application of Nanotechnology in monitoring CECs

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Adsorption of marine phycotoxin okadaic acid on a covalent organic framework

Journal of Chromatography A, 1551 (2018) 1–9
Contents lists available at ScienceDirect
Journal of Chromatography A
journal homepage: www.elsevier.com/locate/chroma

Mechanochemical synthesis of covalent organic framework for the efficient extraction of benzoylurea insecticides

ChemPubSoc Europe
DOI: 10.10
CHEMISTRY A European Journal

Microporous Materials |Hot Paper|

Adsorption of Pharmaceutical
Covalent Organic Frameworks

Abdelkarim Mellah+,[a, b, c] Soraia P. S. Ferna
Jairo Paz,[d] Jacobo Cruces,[d] Dana D. Med
Laura M. Salonen*[a]

Microporous and Mesoporous Materials 307 (2020) 110523
Contents lists available at ScienceDirect
Microporous and Mesoporous Materials
journal homepage: http://www.elsevier.com/locate/micromeso

Efficient adsorption of endocrine-disrupting pesticides from water with a reusable magnetic covalent organic framework

Vanesa Romero[a,b], Soraia P.S. Fernandes[a,c], Petr Kovář[d], Milan Pšenička[d], Yury V. Kolen'ko[a], Laura M. Salonen[a,**], Begoña Espiña[a,*]

Journal of Chromatography A, 1572 (2018) 20–26
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journal homepage: www.elsevier.com/locate/chroma

of covalent organic framework as the adsorbent for extraction of trace levels of pesticide residues prior to mance liquid chromatography-ultraviolet detection

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Talanta
journal homepage: www.elsevier.com/locate/talanta

Fabrication of cross-linked hydrazone covalent organic frameworks by click chemistry and application to solid phase microextraction

Mingxue Wu[a], Gang Chen[a], Jiutong Ma[a], Ping Liu[b], Qiong Jia[a,*]
[a] College of Chemistry, Jilin University, Changchun, 130012 China
[b] Changchun GeneScience Pharmaceuticals Co., Ltd., Changchun, 130012 China

Journal of Chromatography A, 1595 (2019) 11–18
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journal homepage: www.elsevier.com/locate/chroma

Amino-modified covalent organic framework as solid phase extraction absorbent for determination of carboxylic acid pesticides in environmental water samples

Wen-Hua Ji[a], Yu-Shuang Guo[a], Xiao Wang[b,*], Xiao-Fan Lu[a], Dian-Shun Guo[a,*]

Soraia Fernandes *et al.* Molecules (2020) ´´Extraction of ibuprofen from natural waters using a covalent organic framework``, https://www.mdpi.com/1420-3049/25/14/3132

TpBD-(CF3)$_2$ showed a capacity of 119 mg/g for ibuprofen in ultrapure water but it reduced to 42, 27 and 14 mg/g in lake, river, and estuary water, respectively. This is due to dissolved organic matter or competing molecules. The highest adsorption efficiency (85%) was found in lake water (more acidic).

Soraia P.S. Fernandes et al. Chemosphere (2021) "Study on the efficiency of a covalent organic framework as adsorbent for the screening of pharmaceuticals in estuary waters"

https://doi.org/10.1016/j.chemosphere.2021.130364

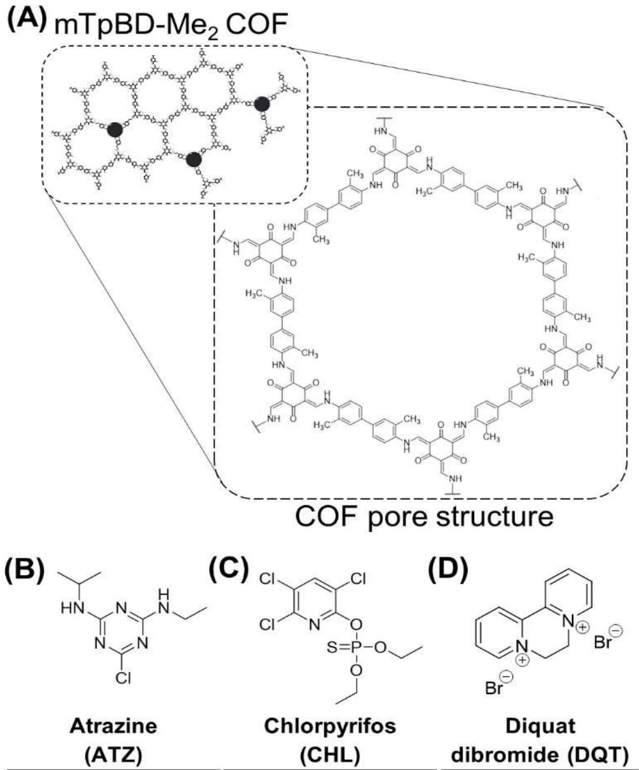
Extraction of 19/22 pharmaceuticals >96% and 17/22 pharmaceuticals > 80% efficiency. Families included: β-blocker, anti-hypertensive, lipid regulator, anti-convulsant, antibiotic, antidepressant and NSAID. Desorption is difficult for 13 analytes. Acetonitrile is more efficient than methanol for diclofenac.

Vanesa Romero *et al.* Microporous and Mesoporous Materials (2020) ´´Efficient adsorption of endocrine-disrupting pesticides from water with a reusable magnetic covalent organic framework``.

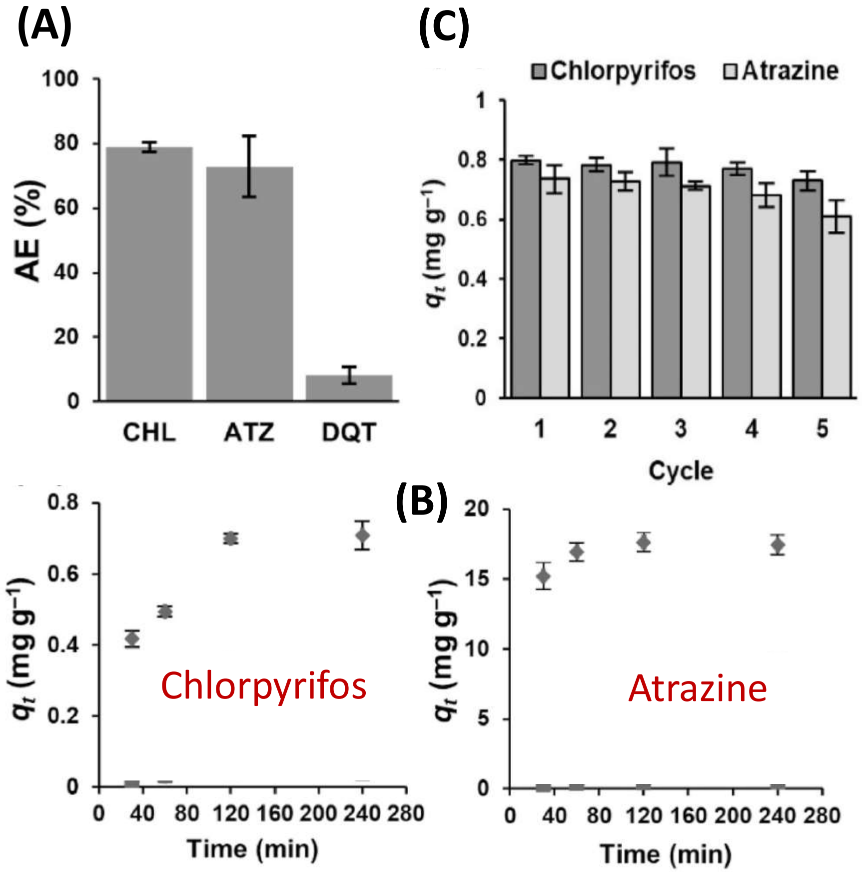
https://doi.org/10.1016/j.micromeso.2020.110523

Extraction of atrazine, chlorpyrifos and diquat *using Fe_3O_4@DOPA-TpBD-Me$_2$ (mTpBD-Me$_2$) from water – dispersive solid-phase extraction. Efficiencies of 80% for chlorpyrifos and 73% for atrazine. Separation by a magnetic field.*

Extraction of pesticides using mTpBD-Me2 COF



Atrazine (ATZ)		Chlorpyrifos (CHL)		Diquat dibromide (DQT)	
log*P*	2.7	log*P*	4.7	log*P*	– 4.6
Water sol. (g L^{-1})	0.035	Water sol. (g L^{-1})	0.0011	Water sol. (g L^{-1})	720



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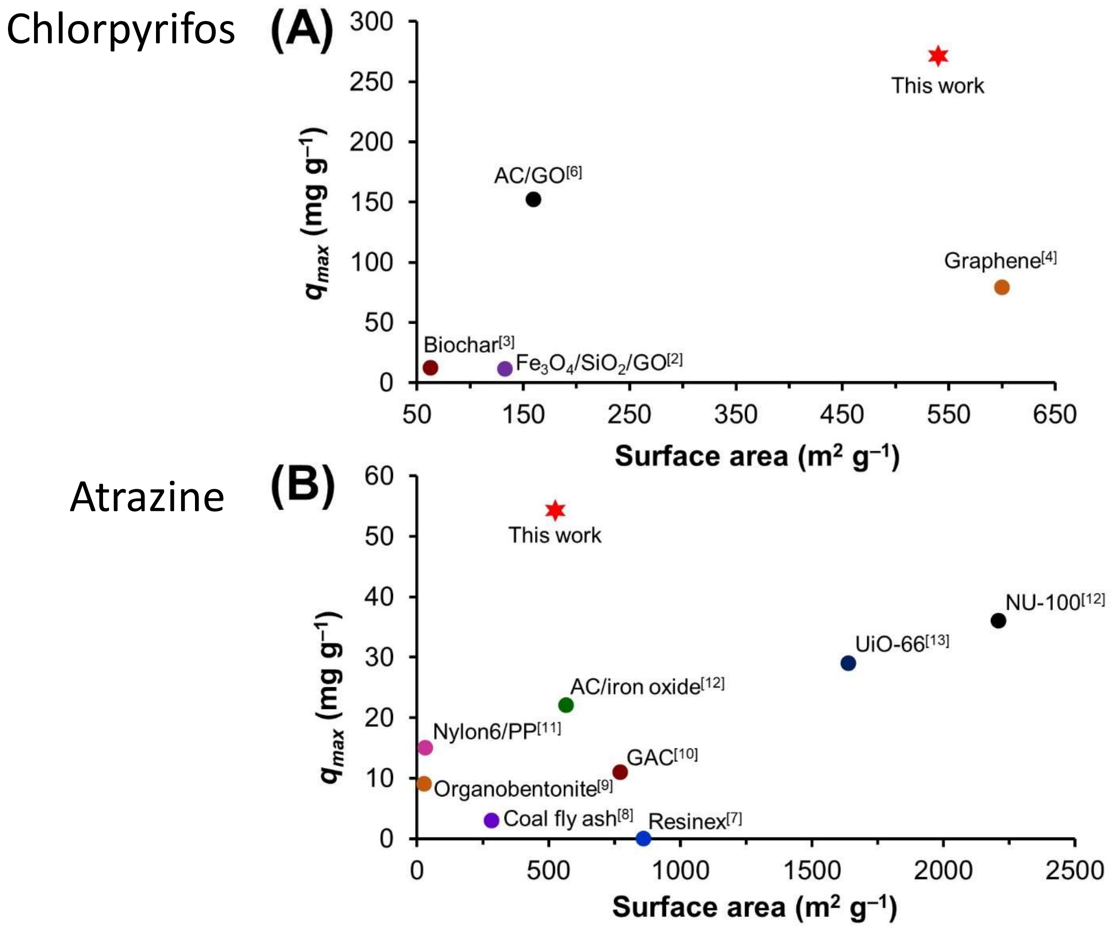

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Microporous and Mesoporous Materials 307 (2020) 110523, https://doi.org/10.1016/j.micromeso.2020.110523 .

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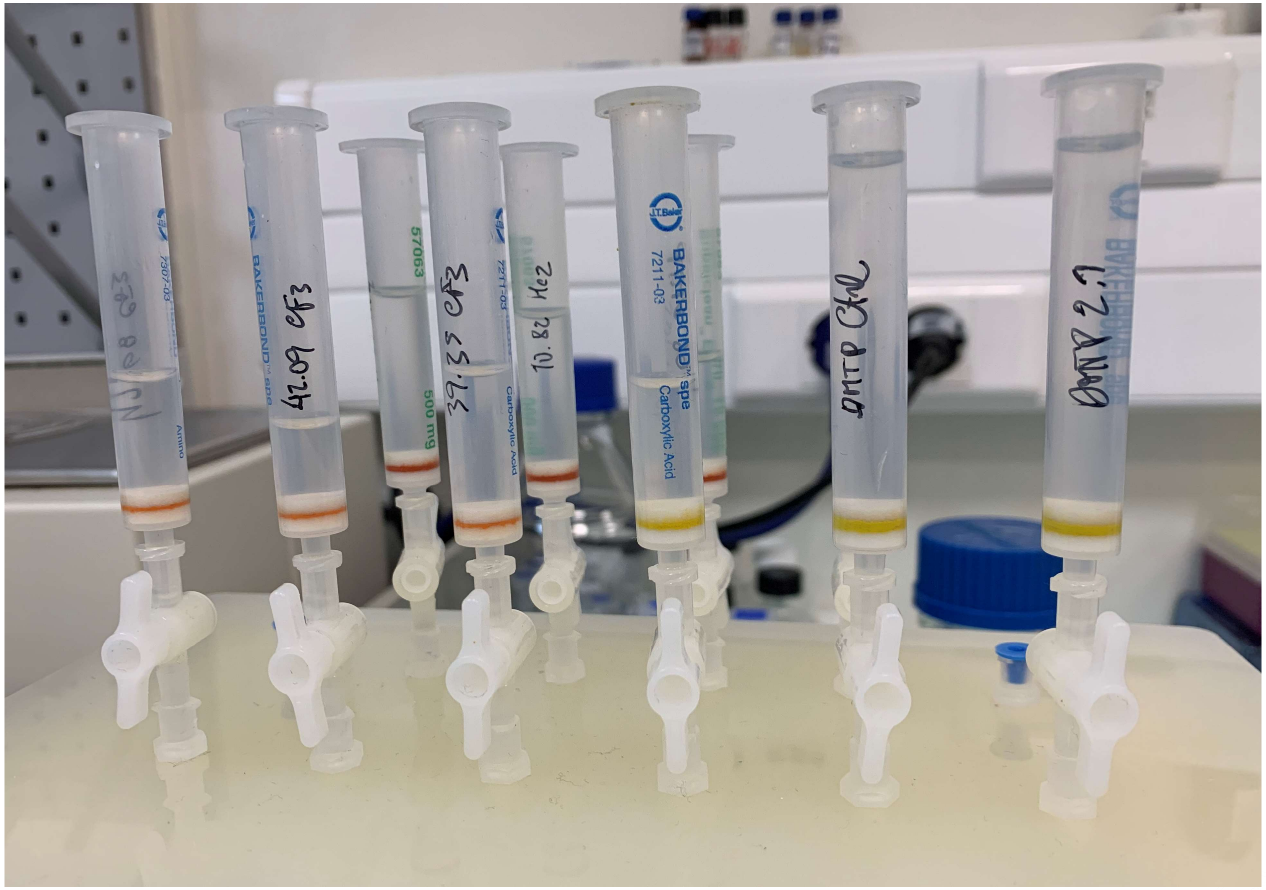
TpBD-$(CF3)_2$ – Orange COF

TpBD-$(CH3)_2$ – Red COF

TAPB-DMTP – Yellow COF



Extraction of Triazines and 6PPD-Q using COFs - SPE

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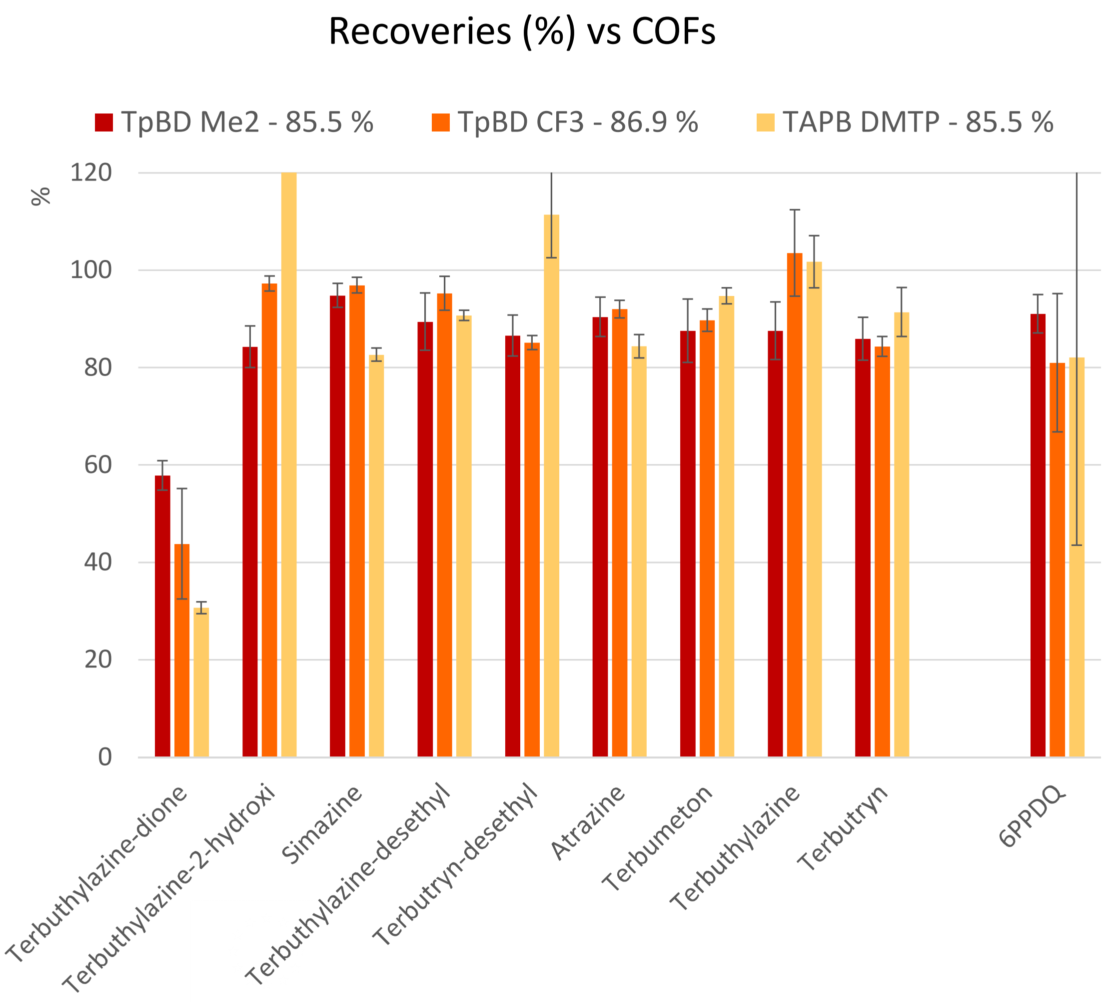

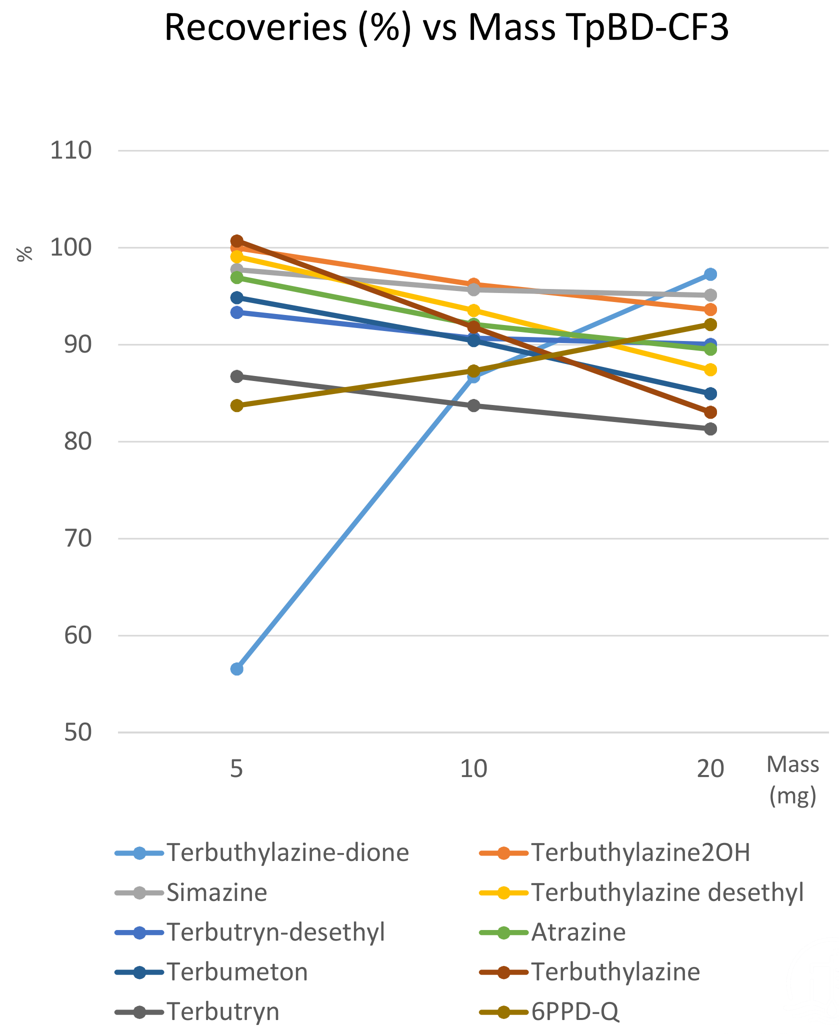

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REAL SAMPLES

Recoveries in River Water:
TpBD CF3 - 64 to 93% ⇔ JTBaker H2Ophilic

Parking lot:
Terbutryn ≈ 170 ng/L
6PPD-Q ≈ 20 ng/L

Rubber from football fields
6PPD-Q - 900 to 1700 ng/L

INL PROJECTS - SERS

ATLANTICLAM – WP *iii)* a portable biotoxins test to monitor harmful algae blooms

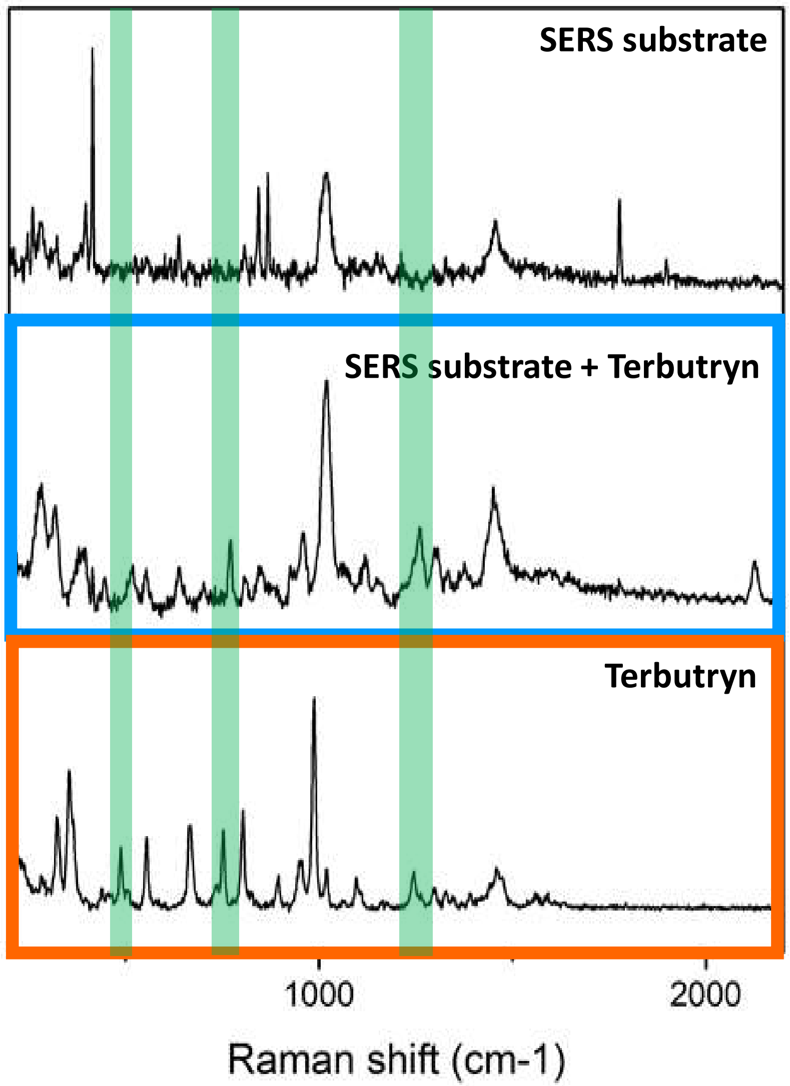
PACTO DA BIOECONOMIA AZUL – Vertical bivalves

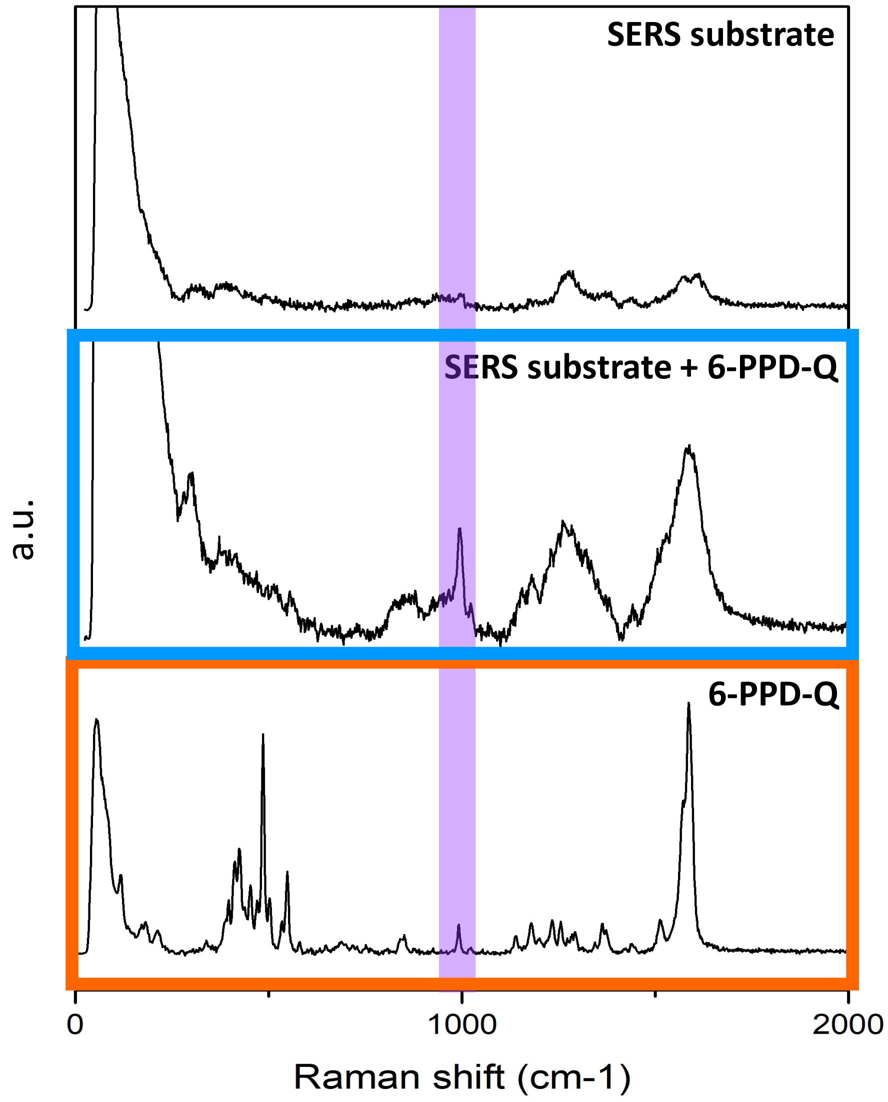
SMARTgNOSTICS – PPS3: Portable SERS platform for antibiotic residues detection

D4RUNOFF – WP2: Novel sensors for remote measurement of CECs and new pollutants

Funded by European Union's Horizon Europe, grant No 101060638.

Detection of triazines and 6PPD-Q using SERS





COF/SERS – based prototype

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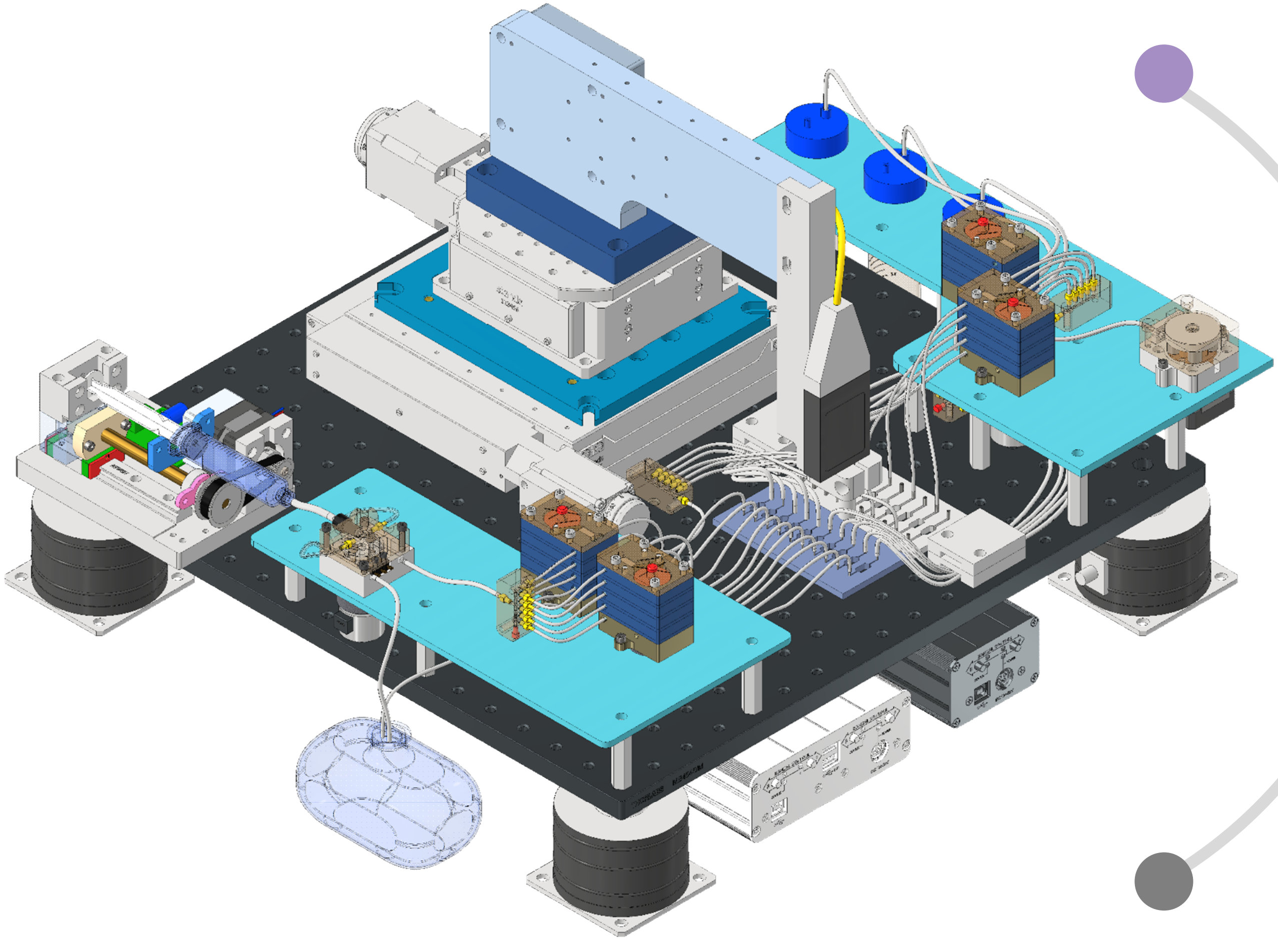

SERS substrate
Design and fabrication

Microfluidic chip
Design, fabrication and integration

Selection of the
Portable Raman system

Hardware and Software
Integration hardware- (mechanical and fluidics) and software (AI-data analysis and control)

Conclusions

Nanomaterials are promising in many fields
> high adsorption capacity but desorption needs to be improved by tailoring the solvent composition

COFs packed into SPE cartridges are very effective
> high extraction efficiency of pesticides, pharmaceuticals and tire wear compounds

SERS have the potential for fast, selective response and integration with microfluidics and AI
> works are ongoing to further improve sensitivity

Triazines, their degradation products and 6PPD-Q are found in the environment
> Terbutryn used in gardening and 6PPD-Q released from car tyre and recycled rubber

Many Thanks to the Team

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Begoña Espiña

WQ group leader, water contaminants, COFs as adsorbents and standard analytics

Laura Rodriguez-Lorenzo

SERS substrates and detection strategy

Mónica Quarato

Detection strategy

Marilia Santos

Sample preparation, cartridges design and fabrication

Carlos Gonçalves

Standard analytics

Technology Engineering Group

Electromechanical components, AI for data analysis, integration

Miguel Chaves

COF-GNS SERS substrates

Aitor Alvarez

COF-GNS SERS substrates

Laura M. Salonen

COFs design