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National Institute for Research and Development of Isotopic and Molecular Technologies

INCDTIM

TiO_2 nanotubes/graphene-based nanomaterials to address the emerging contaminants pollution

Crina Socaci, 08.10.2020

General information

- **NO Grants - Collaborative Research Projects 2019 Call**
- **Duration time**: 01/09/2020 to 31/08/2023
- **Total budget from the program**: 1.164.000 Euro
- **Partners**:
  - INCDTIM Cluj-Napoca – PP (Project promoter)
  - University of South-Eastern Norway (P1)
  - IFIN – HH (P2)

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General information

- **Main thematic area**: Environment;
- **Main key topic**: Management of emerging pollutants in aquatic systems (impact, remediation and recycling techniques) to improve ecosystem services of water resources and wetlands;
  - Starting point of the proposal: Project number PN-III-P1-1.2-PCCDI-2017 0743/44PCCDI/2018, within PNCD III, Development of eco-nano-technologies for surface functionalization of textile and leather materials by plasma treatment at atmospheric pressure - Grant responsible Marcela Rosu
  - Further help received from Dr. Mary Anderson-Glenna, senior EU project advisor at External Funding Team Coordinator, Research and Innovation Unit, USN Norway

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General information

- **Contaminants of Emerging Concern**: a group of chemicals (e.g. drugs, personal care products, detergents, pesticides, food additives), typically detected in aquatic ecosystems and wastewater are not yet monitored and well regulated by authorities
- They are mainly discharged into WWTPs and only incompletely removed during conventional treatment;
- Concentration levels range from few ng/L up to several µg/L;
- No trends towards decreasing concentrations can be seen over the last decades;
- Knowledge on eco-toxicological effects is limited.

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e 1. Average Concentration of EOCs in Influent and Effl

family	compounds	WWTPs influent (ng L^{-1})	WWTPs effluent (ng L^{-1})	removal rate (%)
iotics	clarithromycin	344	150	56.40
	ciprofloxacin	620	234	62.25
	doxycyclin	650	420	35.38
	erythromycin	580	297	48.79
	methronidazole	90	55	38.89
	norfloxacin (NFX)	115	53	45.74
	ofloxacin (OFX)	482	171	64.52
	roxithromycin	780	472	39.49
	sulfamethoxazole (SMZ)	320	264	17.50
	sulfapyridin	492	81	83.54
	tetracyclin (TC)	48000	2375	95.05
	trimethoprim	430	424	1.40
analgesics and anti-inflammatories	codeine	2860.5	1930	32.53
	diclofenac (DCF)	1550	900	41.94
	ibuprofen (IBU)	13482	3480	74.19
	ketoprofen (KTP)	2650	800	69.81
	ketorolac	407	228	43.98
	naproxen (NPX)	7800	2200	71.79
lipid regulators	bezafibrate	1948	763	60.83
	clofibric acid (CFA)	215	131	39.07
	gemfibrozil	2100	1300	38.10
beta-blockers	acebutolol	335	140	58.21
	atenolol (ATL)	1250	800	36.00
	celiprolol	440	280	36.36
	metoprolol	1535	679	55.77
	propanolol	198	102	48.48
	sotalol	1667	790	52.61
diuretics	amidotrizoic acid	2500	2494	2.40

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Table 4
Advantages, drawbacks and recommendations for each advanced treatment.

Advanced Treatment	Advantages	Drawbacks	Recommendations
UV/H_2O_2	• Moderate-good CEC removal at lab/pilot scale • Effective as disinfection process too	• Formation of oxidation transformation products • No full-scale evidences on CEC removal • Higher energy consumption compared to ozonation, specifically when high organic matter concentration acts as inner filter for UV radiation.	Toxicity tests recommended
Photo-Fenton	• High CEC removal • Use of solar irradiation • Effective as disinfection process too	• Formation of oxidation transformation products • No full-scale evidences on CEC removal • At neutral pH 7 addition of chelating agents necessary. • Large space requirements for solar collectors	Toxicity tests recommended
UV/TiO_2	• High CEC removal • Use of solar irradiation • Effective as disinfection process too	• Low kinetics • Formation of oxidation transformation products • Catalyst removal • Large space requirements for solar collectors	Not possible to apply until more efficient photocatalysts (at least one order of magnitude) will be developed
Ozonation	• High CEC removal • Full scale evidence on practicability • Partial disinfection • Lower energy demand compared to UV/H2O2 and membranes	• Formation of by-products (NDMA, bromate) and other unknown oxidation transformation products • Need for a subsequent biological treatment (e.g., slow sand filtration) to remove organic by-products	• Toxicity tests recommended • NDMA and bromate should be monitored
Powdered activated carbon (PAC)	• High CEC removal • Full scale evidence on practicability • Additional DOC removal • No formation of by-products • Partial disinfection possible by the combination with membrane filtration (UF)	• PAC must be disposed • Post-treatment required (membrane, textile or sand filter) to prevent discharge of PAC • Production of PAC needs high energy • Adsorption capacity may fluctuate with each batch	Test with different products/process configurations recommended

General information

- **The overall objective** of the present proposal is *the development of a method for the removal of emerging contaminants from aqueous solutions*. As such, **we propose an experimental laboratory set-up based on nanostructured ternary systems with improved visible-light-driven degradation capability**.

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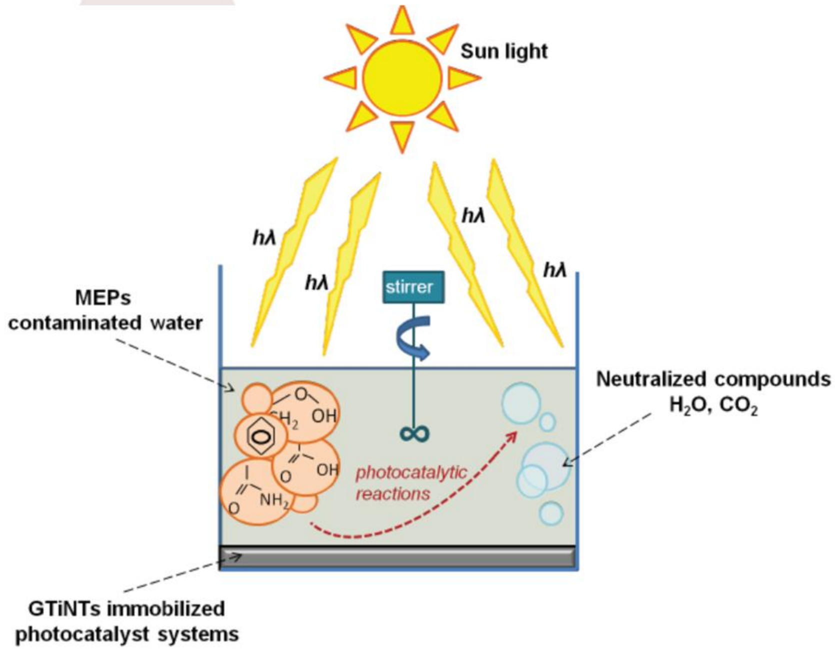

***Figure 5.** Schematic presentation of the experimental laboratory set-up.*

Development to TRL = 4. The TRL 4 means that the method is proved to function at laboratory scale and will contain: (i) Fundamental research - the optimum photocatalyst in terms of reactivity;

(ii) Engineering – optimization of reaction conditions – optimal deposited surface, irradiation wavelength, reaction time.

The specific objectives and estimated results

- (O1) Identification of hierarchical nanostructures with improved photocatalytic activity in the UV-visible spectrum (towards visible) that will be applicable for the model emerging contaminants degradation.
  - Variants of ternary nanohybrids based on TiO_2 nanotubes/graphene/metallic nanoparticles with tailored physicochemical characteristics and enhanced photocatalytic properties on the degradation of the model emerging pollutants.
- (O2) Evaluation of the photodegradation performance of the ternary nanohybrids based on TiO_2 nanotubes/graphene/metallic nanoparticles in the degradation processes of emerging pollutants.
  - To determine the photocatalytic reaction pathways of the model emerging pollutant degradation.

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The specific objectives and estimated results

- (O3) For practical advantages, **the determination of the most efficient method of ternary nanopowder deposition on a suitable support** that ensures the highest efficiency in the photocatalytic degradation of the various emerging pollutants from water.
  - Variants of ternary nanohybrids immobilized on a surface as photocatalytic systems.
  - Study regarding the photocatalytic properties of ternary nanohybrids immobilized systems

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The INCDTIM team

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