Institut Mines-Télécom

HORIZON 2020

MATERIAUX COMPOSITES ENERGETIQUEMENT AUTONOMES POUR L'ASSAINISSEMENT DE L'AIR INTERIEUR

12e Colloque IMT : Matériaux pour la transition environnementale

8 octobre 2020
(visio-conférence)

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(IMT Mines Alès)

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CORRESPONDING EUROPEAN PROJECT (HORIZON 2020)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement 690968

NANOGUARD2AR

H2020-MSCA-RISE-2015

Nanomaterials-based innovative engineering solutions to ensure sustainable safeguard to indoor air

NANOGUARD2AR (NG2AR)

01/01/2016 – 31/12/2019

- **12** international partners
- Total funding: **1 386 000 €**
- Funds allocated to IMT Mines Alès: **139 000 €**
- Major research objective: *conceptualize, develop and test at pilot scale new solid active materials able to be applied in energetically autonomous mode (without any complementary energetic excitation) for the indoor air antimicrobial conditioning*

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LNEC LABORATÓRIO NACIONAL DE ENGENHARIA CIVIL

NANOGUARD2AR

ENERGETICALLY-INDEPNDENT COMPOSITE MATERILAS FOR THE INDOOR AIR ANTIMICROBIAL CONDITIONING

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Dutheil de la Rochère A., Bayle S., Lopez-Cuesta J.-M., Sabourin L., Ravel R.,
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LNEC, Portugal

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INNOVATIVE NANO- AND MICROCOMPOSITE MATERIALS FOR THE INDOOR AIR GERMICIDAL CONDITIONING CONCEPTUALIZED AND IMPLEMENTED BY IMT MINES ALÈS

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INNOVATIVE NANO- AND MICROCOMPOSITE MATERIALS FOR THE INDOOR AIR CONDITIONING

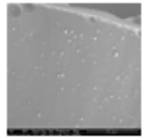
Innovative nano- and microcomposite materials for the indoor air germicidal conditioning

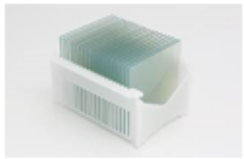
- **1** Energetically-Dependent Germicidal Nano- and Microcomposites (ED-GNM)
  - **1.1** Light-Excited Materials (ED-GNM-LE)
    - **1.1.1** FCCG-Sh* over porous granular supports (examples: [1], Fig. 4, 5, 10)
    - **1.1.2** FCCG-Sh* over non-porous planar supports (more info: [25])
  - **1.2** Electrically-Powered Dark Operating Materials (ED-GNM-EP-DOM)
    - **1.2.1** FCCG-Sh* over non-porous planar supports (more info: [26, 27])
    - **1.2.2** FCCG-Sh* over foam / honeycombed supports
    - **1.2.3** Conductor oxides deposited on foam (honeycombed, filamentous) supports
- **2** Energetically-Independent Germicidal Nano- and Microcomposites (EI-GNM)
  - **2.1** Dark Operating Highly Interactive Selective Hole Generators (EI-GNM-HI-FCCG-Sh*-DOM) (examples: [23], chapters 3, 4)
  - **2.2** Dark Operating Redox Materials (EI-GNM-Redox-DOM) (examples: read please the description below)
  - **2.3** Dark Operating Mechanically Obstructive Materials (EI-GNM-MO-DOM) (examples: [28])
  - **2.4** Dark Operating Multifunctional Materials (EI-GNM-MF-DOM) combining various features (examples: read please the description below)

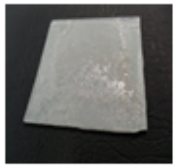
Porous granular supports, foam / honeycombed supports

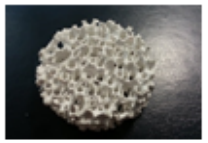
Act mainly as reactive oxygen species (ROS) generators; the target ROS – hydroxyl radicals HO•

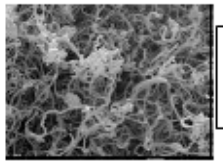
Act mainly as electrical shockers; ROS can be also generated (singlet oxygen atoms O• are generated dominantly)



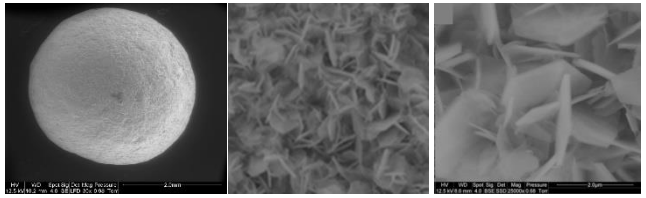








Supported carbon tubular nanostructures (2.3) [28]



Supported "knife-and-needle" oxide microstructures

IMT Mines Alès - C2MA product series presented for the first time during the REA Monitoring Meeting on the advancement of the project H2020 MSCA-RISE-2015 NANOGUARD2AR held in Lisbon, Portugal, on May 19th, 2017

CHAPITRE 2

DARK-OPERATING HIGHLY INTERACTIVE SELECTIVE HOLE GENERATORS AND DARK-OPERATING MECHANICALLY OBSTRUCTIVE MATERIALS: PROPERTIES AND MAIN RESULTS OF LABORATORY TESTS

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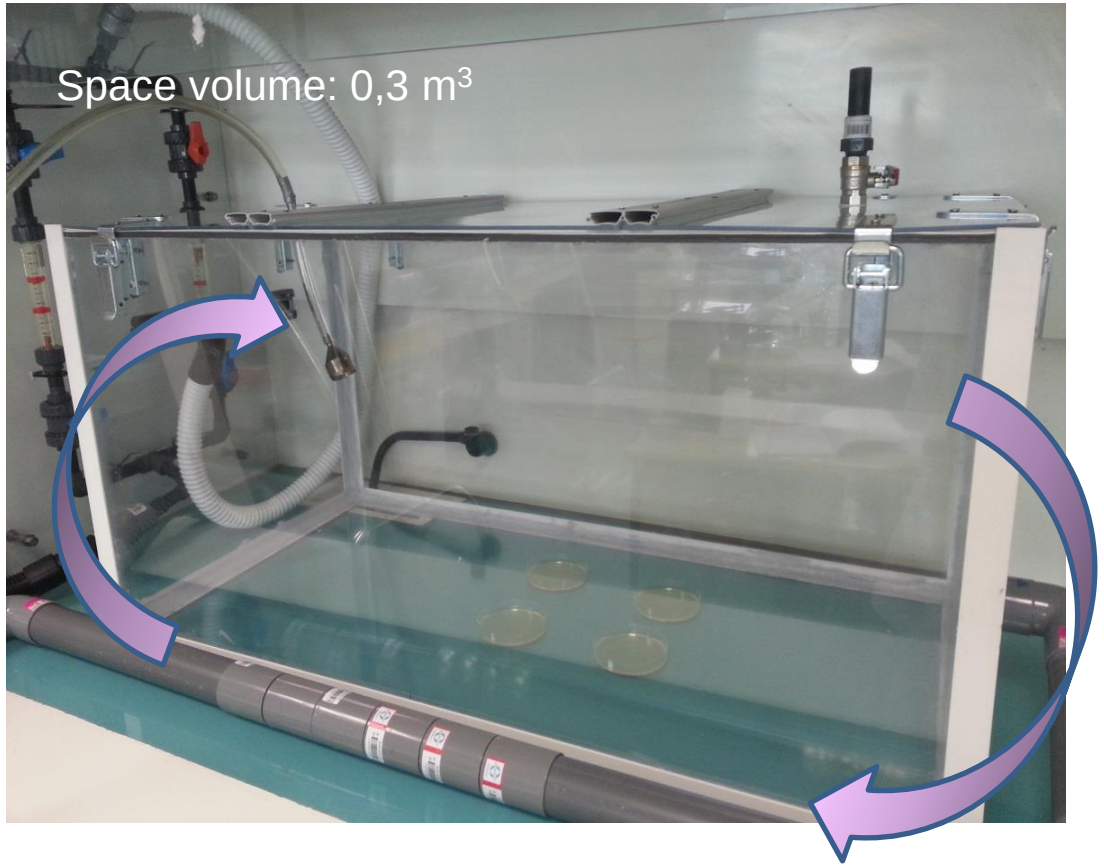
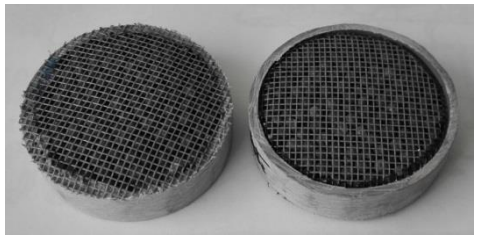
LABORATORY DYNAMIC TESTS OF DARK-OPERATING GERMICIDAL COMPOSITE MATERIALS: APPLIED EQUIPMENT



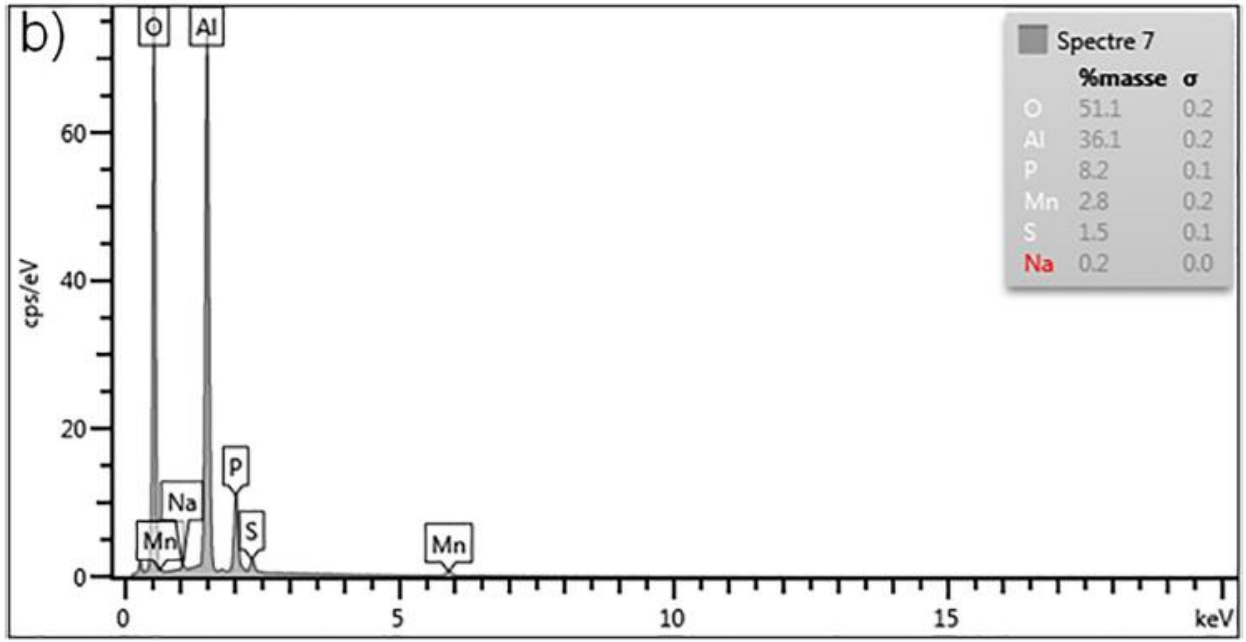
Automatic cell counter BioTrak

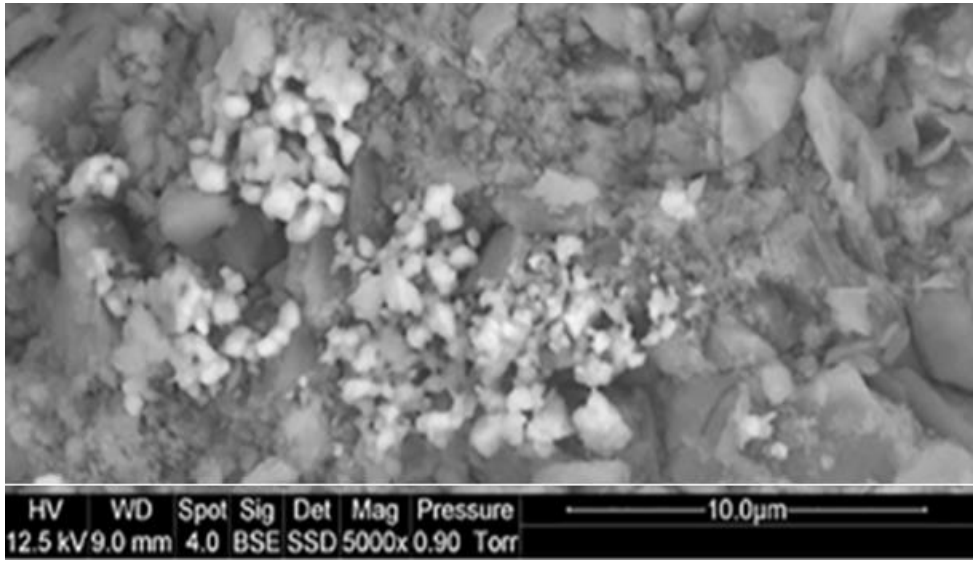


Front view of sample holders

DARK-OPERATING HIGHLY INTERACTIVE SELECTIVE HOLE GENERATORS (EI-GNM-HI-FCCG-SH$^+$-DOM): PRINCIPAL PROPERTIES _ 1

Chemical composition: **MnO_2/$AlPO_4$/γ-Al_2O_3 (support)**
(example: 4.5 % ms./32.3 % ms./63.2 % ms. (support))

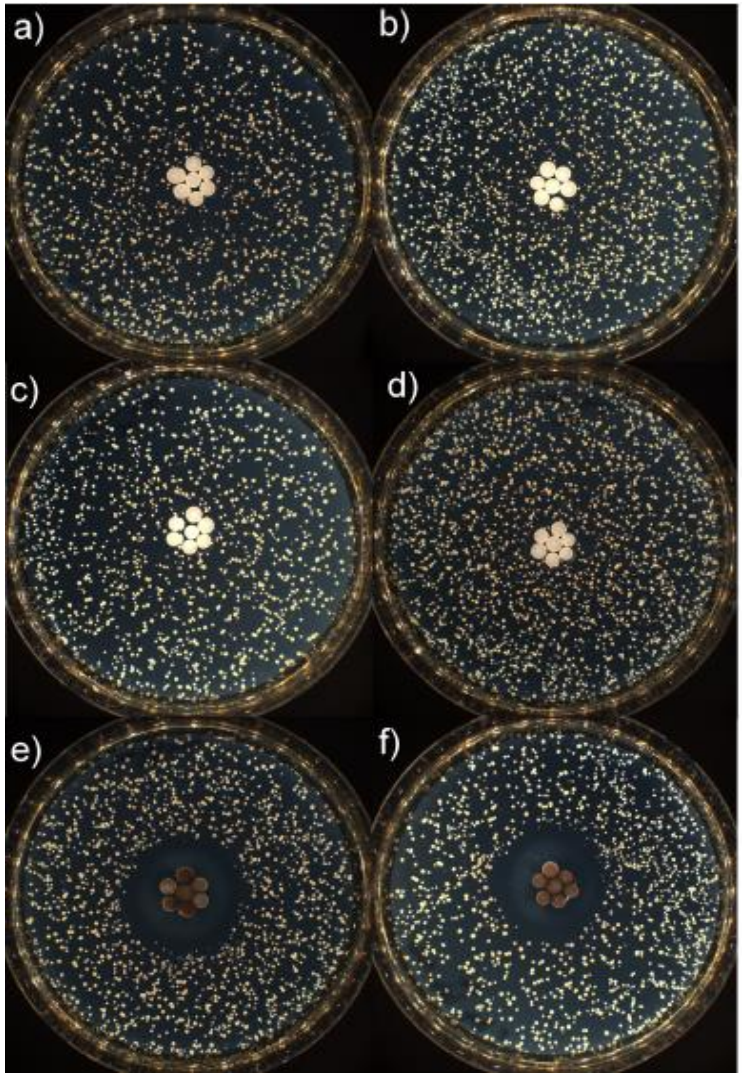




Results of the EDX (at the left) and SEM (at the right) analyses

Morphology: spherical alumina beads ∅ 2.5 – 3.0 mm covered with $AlPO_4$ (1st massive layer) and with MnO_2 (2nd island-type layer) using the wet impregnation method

DARK-OPERATING HIGHLY INTERACTIVE SELECTIVE HOLE GENERATORS (EI-GNM-HI-FCCG-SH$^+$-DOM): PRINCIPAL PROPERTIES _ 2



Agar diffusion inhibitory tests results (static operation conditions):
incubated Petri dishes containing *B. atrophaeus* being in contact with a, b) γ-Al_2O_3 beads; c, d) ZnO/γ-Al_2O_3 beads and e, f) MnO_2/$AlPO_4$/γ-Al_2O_3 beads

Inhibition radii obtained by agar diffusion inhibitory tests:

	γ-Al_2O_3 beads	ZnO/γ-Al_2O_3 beads	MnO_2/$AlPO_4$/γ-Al_2O_3 beads
Inhibition radius of the first plate	0 mm	0 mm	9 mm
Inhibition radius of the second plate	0 mm	0 mm	9 mm
Mean inhibition radius	0 mm	0 mm	9 mm

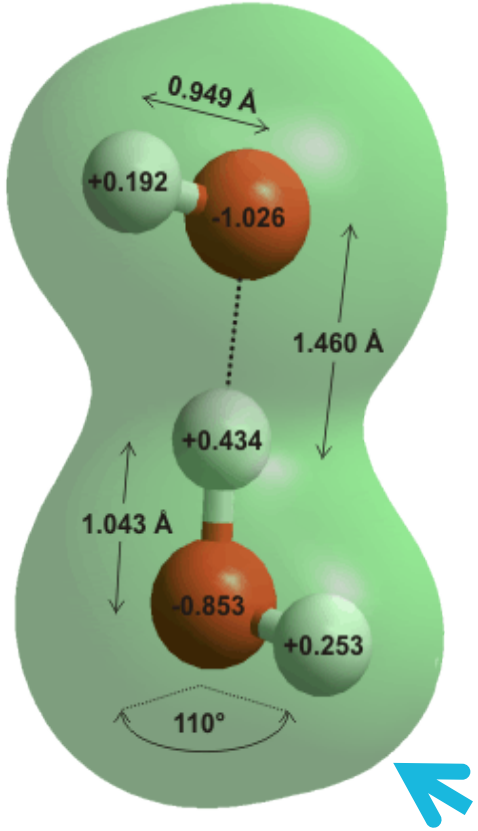
DARK-OPERATING HIGHLY INTERACTIVE SELECTIVE HOLE GENERATORS (EI-GNM-HI-FCCG-SH$^+$-DOM): PRINCIPAL PROPERTIES _ 3

It was supposed that in order to be able to manifest the germicidal ability after the results exposed at the previous slide the tested material has to proceed the following surface reactions:

$$\equiv M^{n+} - O^{2-}_{surf} \rightarrow \equiv M^{n+} - O^{-}_{surf\ h+(VB)} + 1\ e^{-}_{(CB)}, \quad (1)$$

$$\equiv M^{n+} - O^{-}_{surf\ h+(VB)} + HO^{-} \rightarrow \equiv M^{n+} - O^{-}_{surf\ h+(VB)} - HO^{-}_{ads}, \quad (2)$$

$$\equiv M^{n+} - O^{-}_{surf\ h+(VB)} - HO^{-}_{ads} \rightarrow \equiv M^{n+} - O^{2-}_{surf} - HO^{\bullet}_{ads}, \quad (3)$$



However, the applied active component, β-MnO_2, in its free state can not favor the reaction (3) because of a relatively great stability of the solvated forms of hydroxyl anions unable to stay single (non-hydrated) in humid media. For instance, the most probable monohydrated complex [$HO^{-}\cdot H_2O$] in order to be transferred in its active radical form requires the energy near to 3.0 eV [D.W. Arnold, C. Xu, D.M. Neumark, *J. Chem. Phys*., 102 (15), p. 6089, 1995].

The hydrated hydroxide ion $H_3O_2^{-}$

DARK-OPERATING HIGHLY INTERACTIVE SELECTIVE HOLE GENERATORS (EI-GNM-HI-FCCG-SH$^+$-DOM): PRINCIPAL PROPERTIES _ 4

In fact, the transparency for an electron of a 2D (flat) rectangular potential barrier–in particular, of a bandgap–in the simplest case can be evaluated as follows:

$$D = D_0 * e^{\frac{-2d}{\hbar}\sqrt{2m_e(U_0-E)}},$$

where D–coefficient of transparency to be determined ($0 < D \leq 1$); D_0 –coefficient of transparency without any energetic barrier to overcome ($D_0 = 1$); m_e–masse of electron ($9.11 \cdot 10^{-31}$ kg); $\hbar$–reduced Planck constant ($\hbar = h / 2\pi = 1.05 \cdot 10^{-34}$ $J \cdot s$); (U_0 –E)–difference between the barrier's height and the electron's energy, eV; d–thickness of the barrier, nm.

The following variables can be used as basic data:

- (U_0 –E) = 0.25 eV, where U_0 = 0.25 eV (the bandgap energetic barrier),
- E = 0 eV (the worst virtual case when the electron's own energy is not taken into consideration),
- d = 2.21 Å or 0.221 nm (the length of Mn_{CB}–O_{VB} bond in MnO_2 [30], where the indications "CB", "VB" signify the ion's position in the conduction band and in the valence band, respectively.

The calculation results show that D value reaches for β-MnO_2 0.32 or 32% (!)
(explain what does it mean)

DARK-OPERATING HIGHLY INTERACTIVE SELECTIVE HOLE GENERATORS (EI-GNM-HI-FCCG-SH$^+$-DOM): PRINCIPAL PROPERTIES _ 5

Pure β-MnO_2 is thus unable to proceed the reactions (1 – 3) cited on the slide n°11 because of the hydrated complex [$HO^{\bullet-}\cdot H_2O$] energetic stability is greater than the maximal excitation energy (0.25 – 0.28 eV) which can be fulfilled to an adsorbed species (hydrated hydroxide ion) by the surface of manganese dioxide.

However, for a donor-acceptor composite material $MnO_2/AlPO_4/\gamma$-Al_2O_3 the situation can be radically changed:

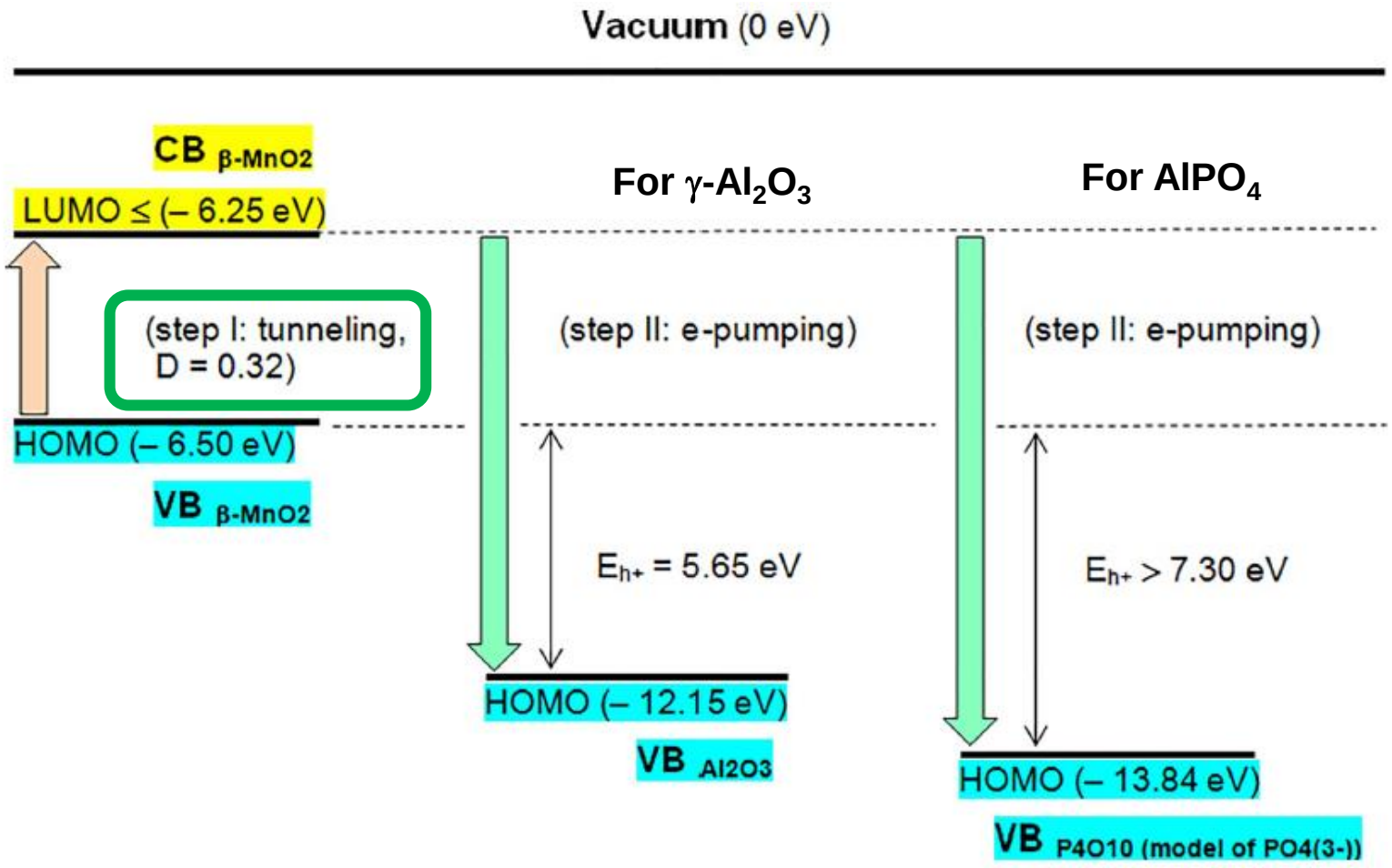
Donor oxide component (D) and its acceptor support (A)	β-MnO_2 (D)	Al_2O_3 (A)	P_4O_{10} (A) (model of PO_4^{3-})
Absolute HOMO position corresponding to the oxide's work function, eV	(– 6.50) [29]	(– 12.15) [41]	(– 13.84) [41]
Relative HOMO position $\Delta E_{HOMO} = HOMO_{MnO2} - HOMO_A$, eV	–	5.65	> 7.30
Estimative energy of electron holes h^+ occurring in the donor's valence band VB_{MnO2} for pure β-MnO_2 and for its donor-acceptor composites (separately for MnO_2/Al_2O_3 and for $MnO_2/AlPO_4$), eV	0.25–0.28 $E_{h+\ MnO2} = LUMO_{MnO2} - HOMO_{MnO2}$ [25, 29, 30, 31]	5.65 $E_{h+\ MnO2/Al2O3} = HOMO_{MnO2} - HOMO_{Al2O3}$	> 7.30 $E_{h+\ MnO2/AlPO4} = HOMO_{MnO2} - HOMO_{P2O10}$ (model)

LUMO—Lowest Unoccupied Molecular Orbitals.

[Dutheil de la Rochère A., Evstratov A., Bayle S., *et al., PLoS ONE*, 2019, **14**, n°10, 21 p.; doi.org/10.1371/journal.pone.0224114]

DARK-OPERATING HIGHLY INTERACTIVE SELECTIVE HOLE GENERATORS (EI-GNM-HI-FCCG-SH$^+$-DOM): PRINCIPAL PROPERTIES _ 6

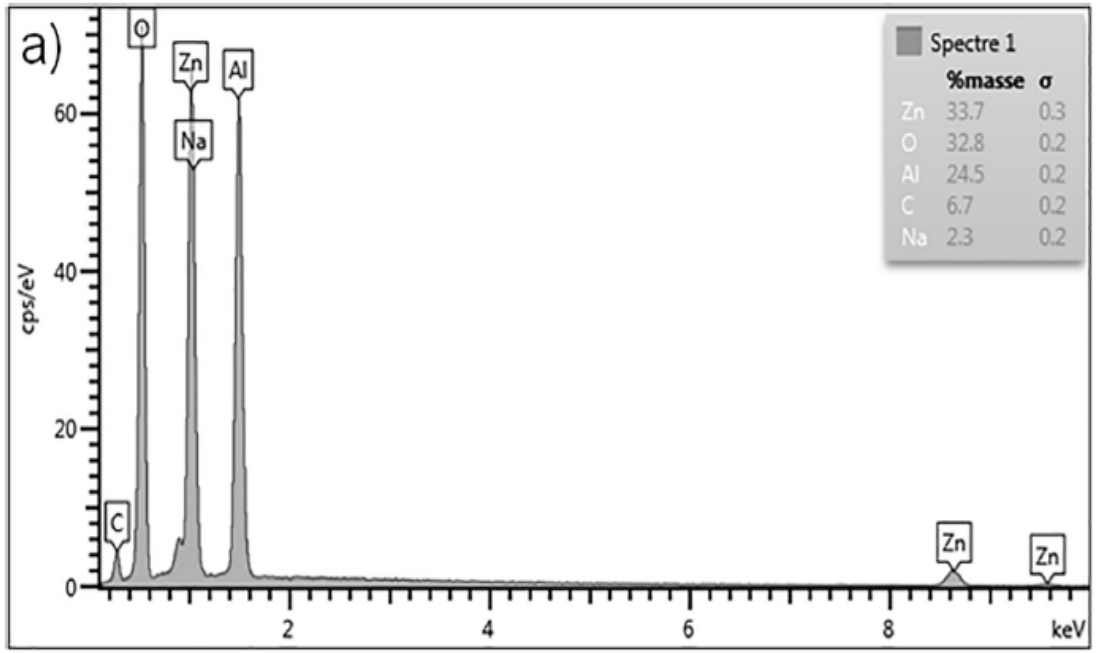
Free (!) electrons in CB of β-MnO_2



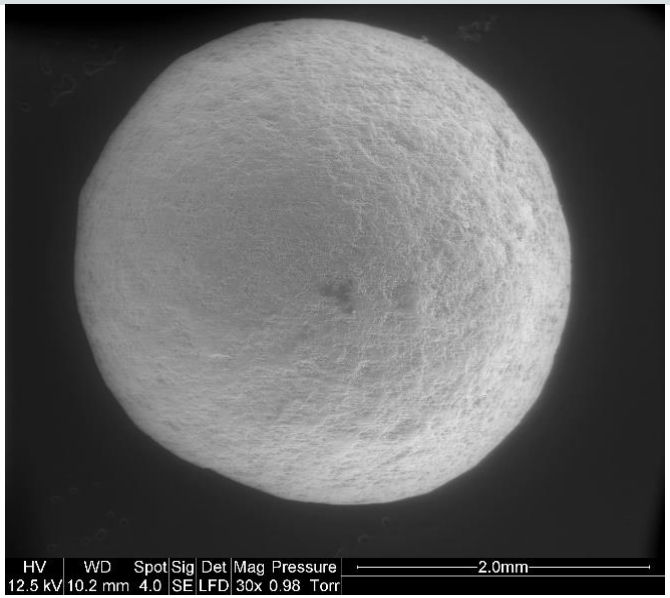
Donor-acceptor composites MnO_2/γ-Al_2O_3 and $MnO_2/AlPO_4/\gamma$-Al_2O_3 are extremely efficient in creation of high energy holes h^+_{VB} at their surfaces under dark-operating conditions, without any complementary energetic assistance (excitation).

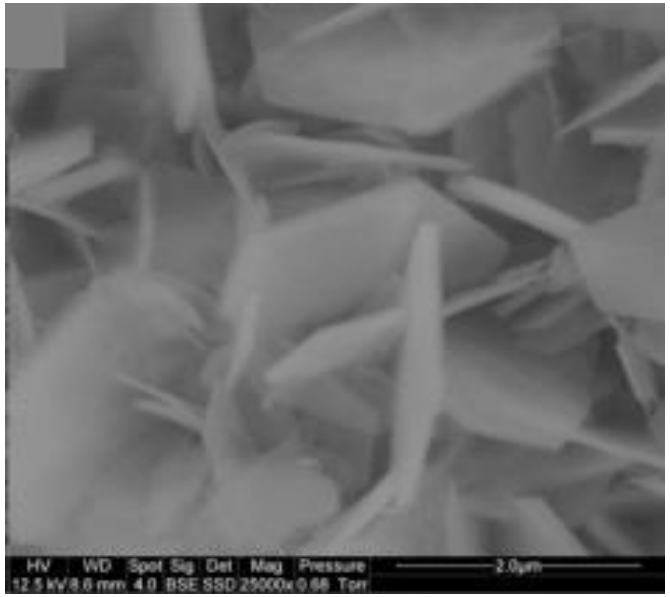
DARK-OPERATING MECHANICALLY OBSTRUCTIVE MATERIALS: PRINCIPAL PROPERTIES

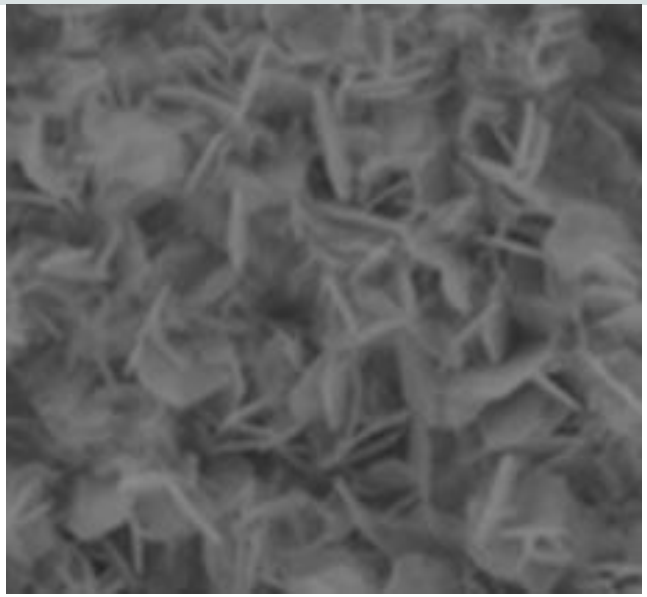
Chemical composition: **ZnO/γ-Al_2O_3 (support)** (example: 41.9 % ms. active component / 58.1 % ms. (support))



Results of the EDX (at the left) and SEM (at the right) analyses





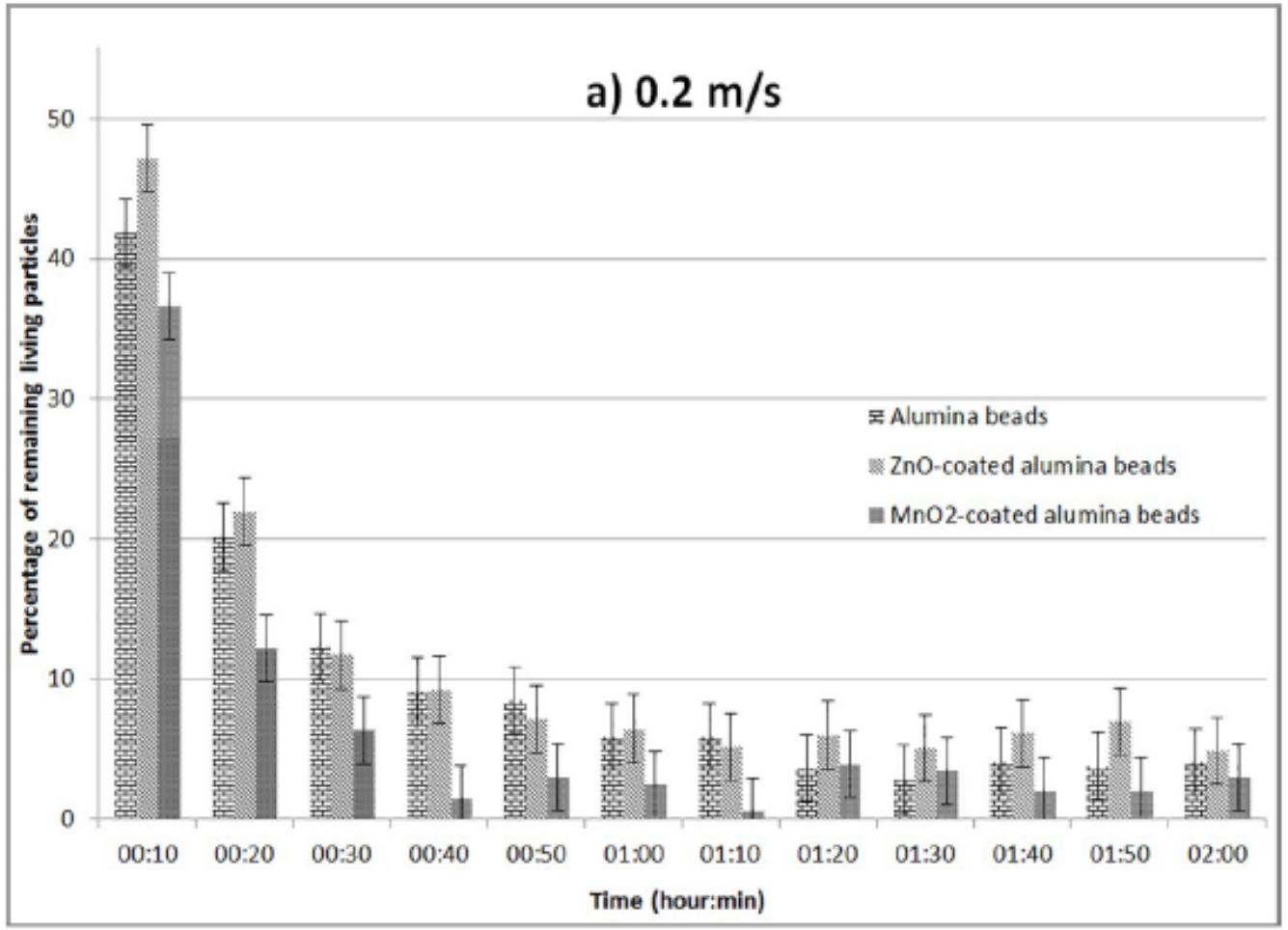


"Knife-and-needle" surface microstructures

Morphology: spherical alumina beads ∅ 2.5 – 3.0 mm covered with ZnO using the method of thermal synthesis in aqueous solution

MAIN RESULTS OF LABORATORY DYNAMIC TESTS _ 1

Airborne bacteria

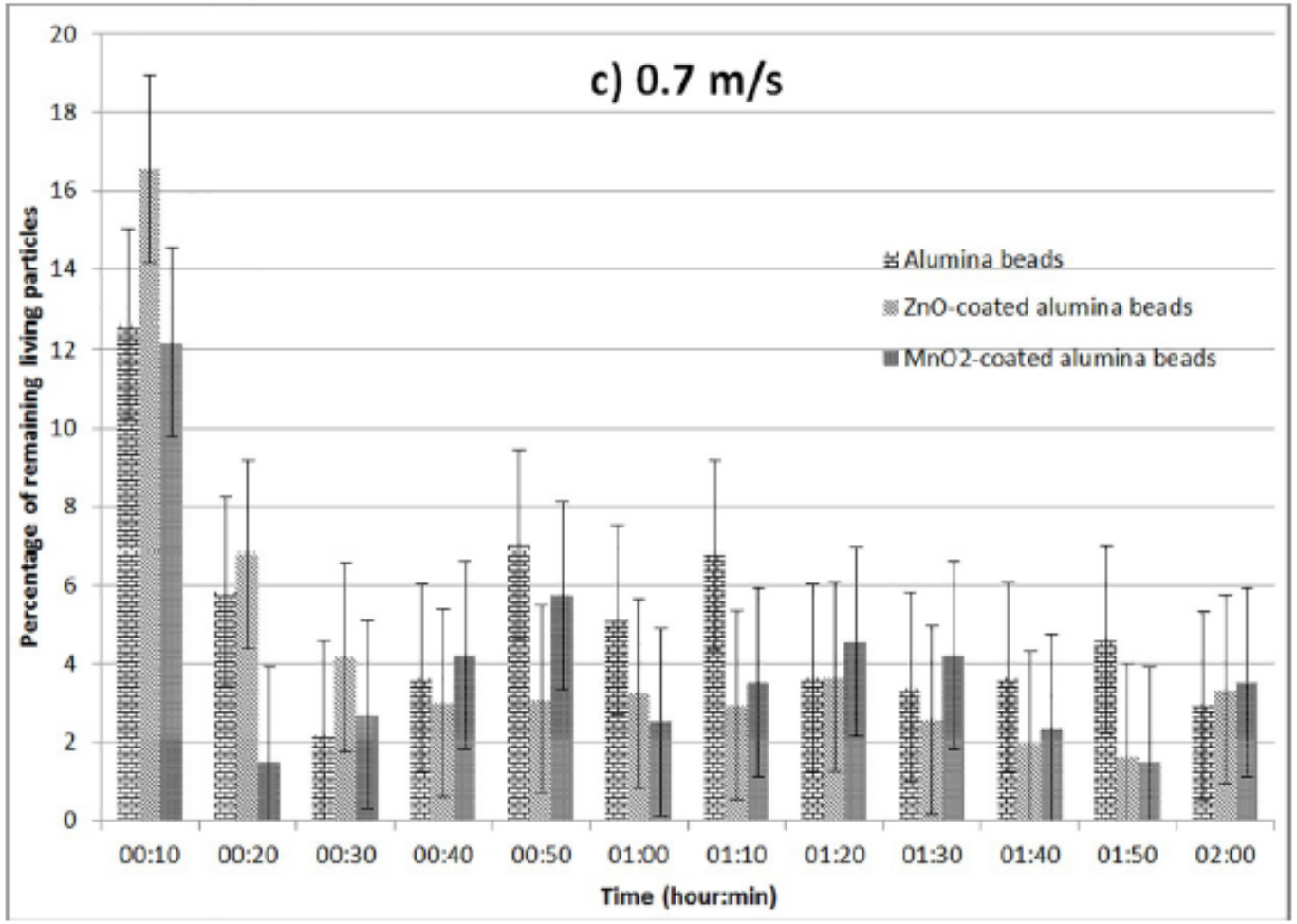


Test of the germicidal efficiency of materials in dynamic operating conditions (air linear velocity: 0.2 m/s)

$MnO_2/AlPO_4/\gamma\text{-}Al_2O_3$ manifests the best germicidal performance

MAIN RESULTS OF LABORATORY DYNAMIC TESTS _ 2

Airborne bacteria

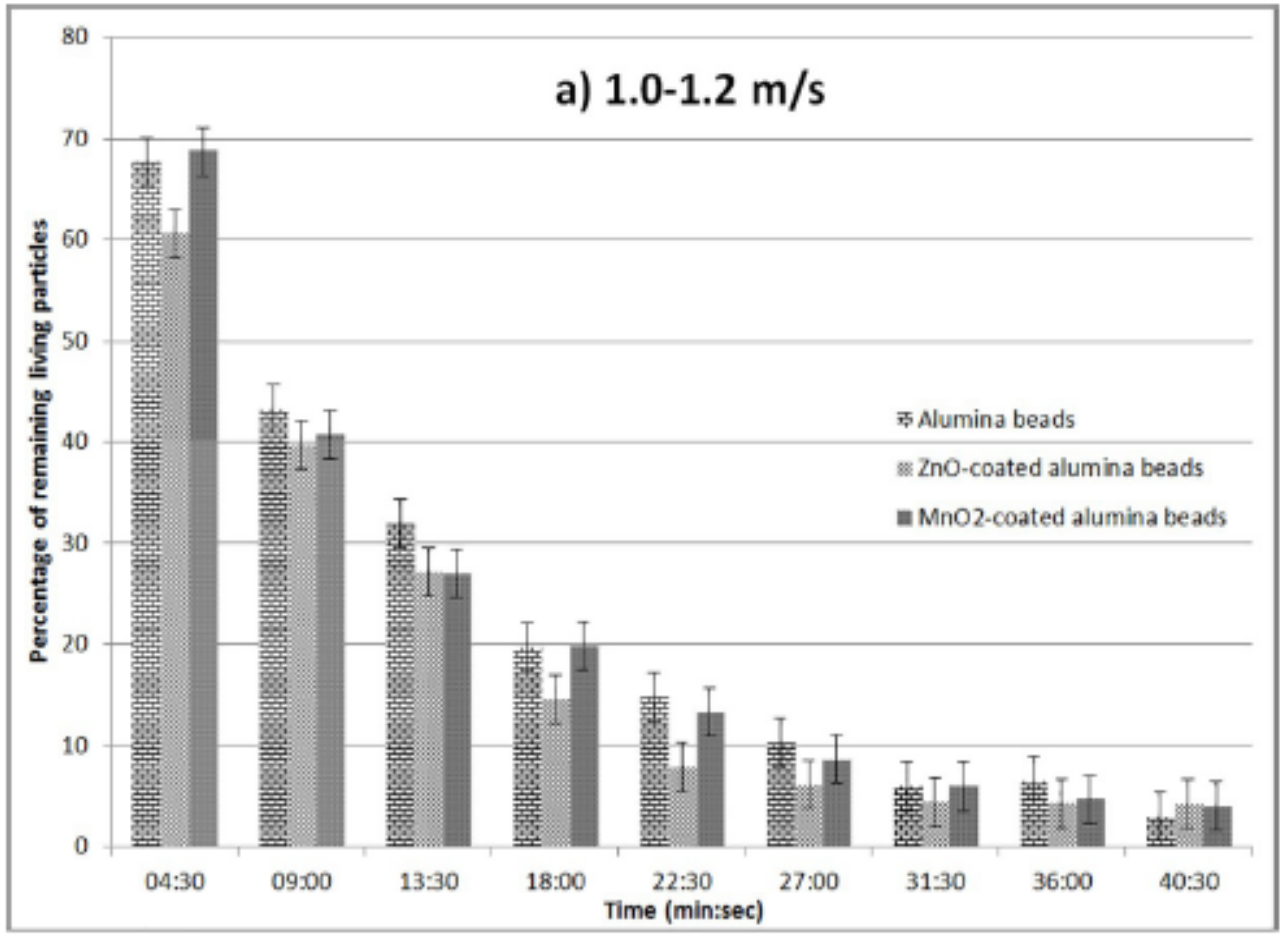


Test of the germicidal efficiency of materials in dynamic operating conditions (air linear velocity: 0.7 m/s)

$MnO_2/AlPO_4/\gamma\text{-}Al_2O_3$ and $ZnO/\gamma\text{-}Al_2O_3$ germicidal performances are quite similar

MAIN RESULTS OF LABORATORY DYNAMIC TESTS _ 3

Airborne bacteria

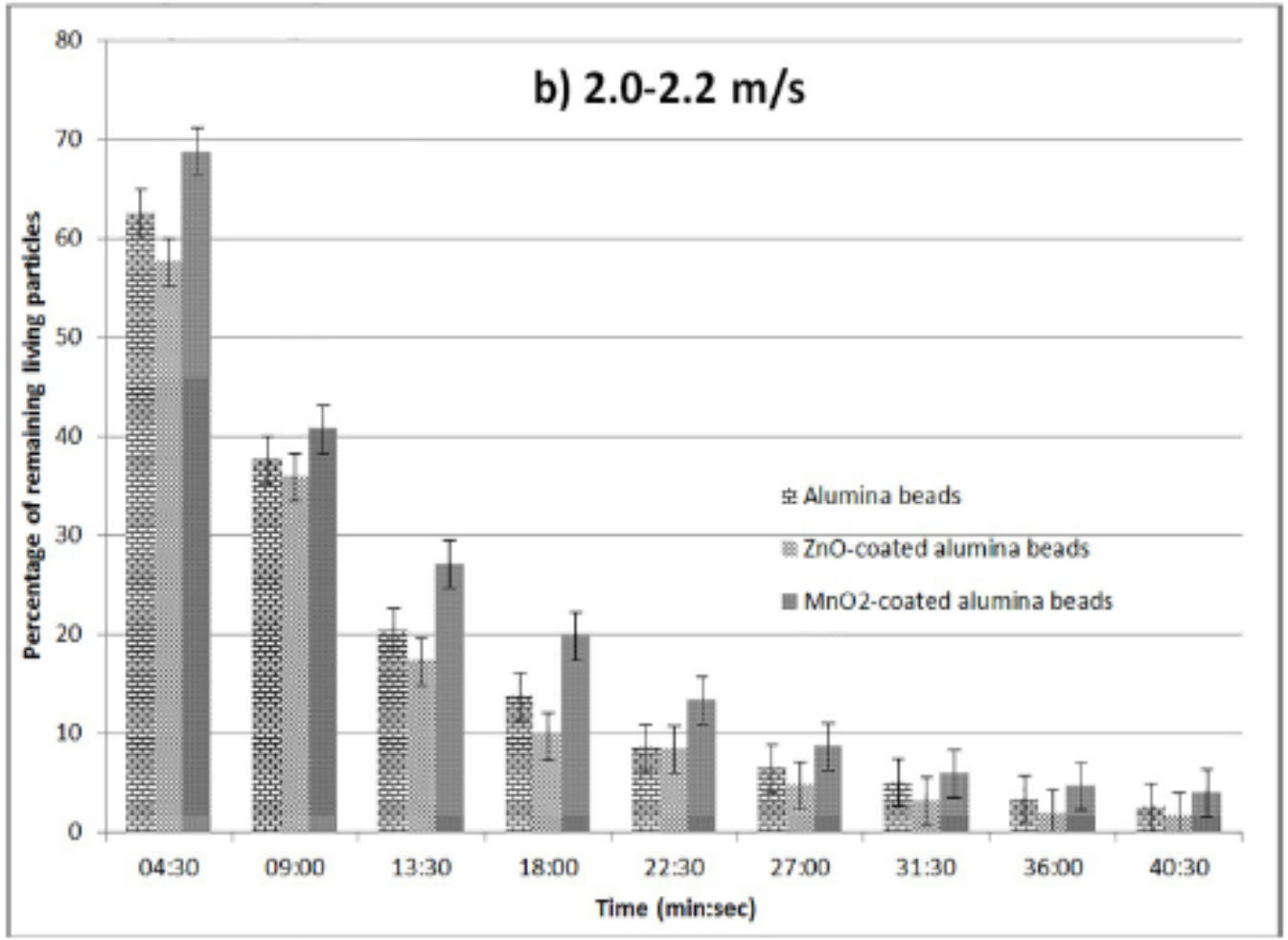


Test of the germicidal efficiency of materials in dynamic operating conditions (air linear velocity: 1.0 – 1.2 m/s)

The germicidal activity of $ZnO/\gamma\text{-}Al_2O_3$ begins to overcome the one of $MnO_2/AlPO_4/\gamma\text{-}Al_2O_3$

MAIN RESULTS OF LABORATORY DYNAMIC TESTS _ 4

Airborne bacteria



Test of the germicidal efficiency of materials in dynamic operating conditions (air linear velocity: 2.0 – 2.2 m/s)

$ZnO/\gamma\text{-}Al_2O_3$ manifests the best germicidal performance

CHAPITRE 3

DARK-OPERATING MECHANICALLY OBSTRUCTIVE MATERIALS: MAIN RESULTS OF PILOT TESTS CARRIED OUT AT LNEC, PORTUGAL (JUNE 2019)

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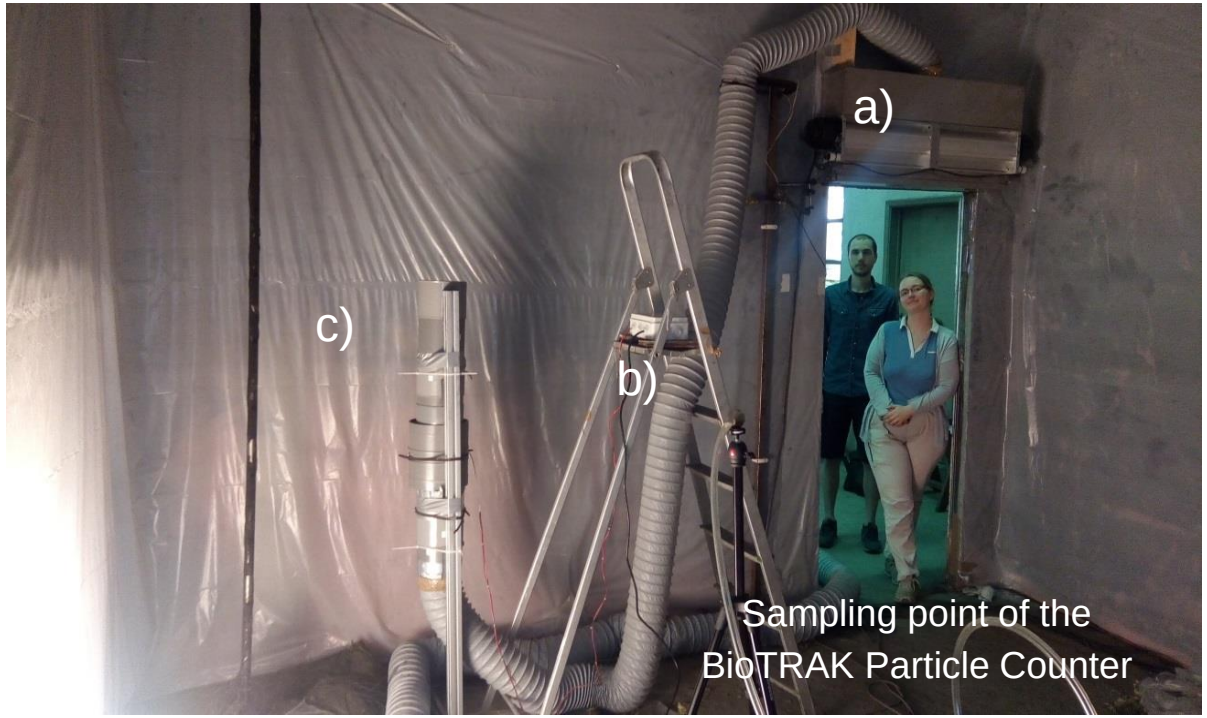
PILOT INSTALLATION (IMT MINES ALES)

EXPERIMENTAL PILOT WORKSHOP (LNEC, JUNE 2019)

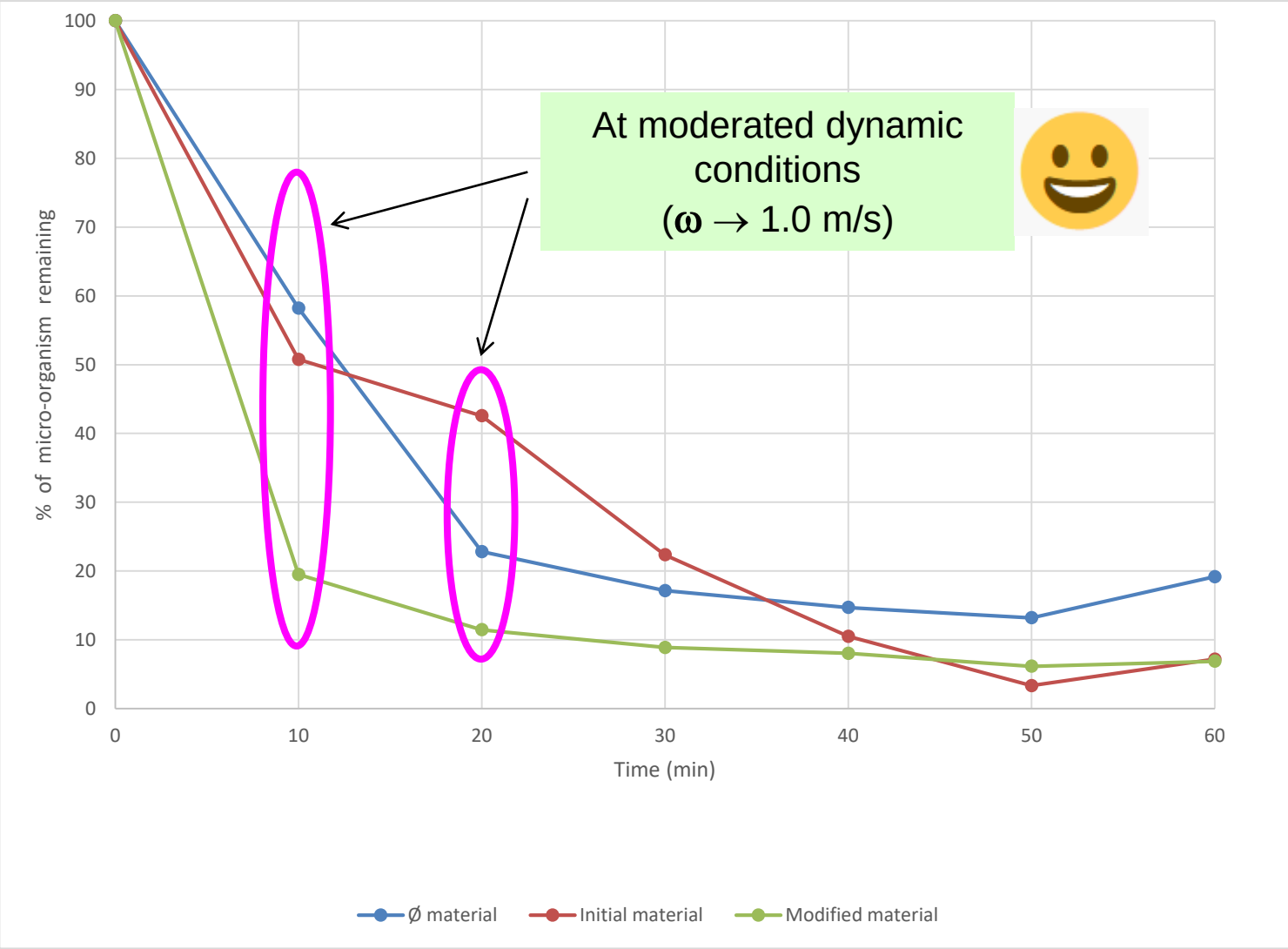


Test installation assembled and tested in the premises of LNEC (general view):
a – air curtain; b – coupling element (ventilation duct);
c – dark-operating test unit of IMT Mines Alès

Air curtain turbine with damper setting facilities

MAIN RESULTS OF PILOT TESTS CARRIED OUT AT LNEC _ 1

Airborne bacteria



Evolution of the concentrations of airborne micro-organisms in time in the indoor air of the test chamber (53 m^3) at the gas linear velocity ω approximately equal to **1.0 *m/s***

(gas flow rate – 36 m^3/h):

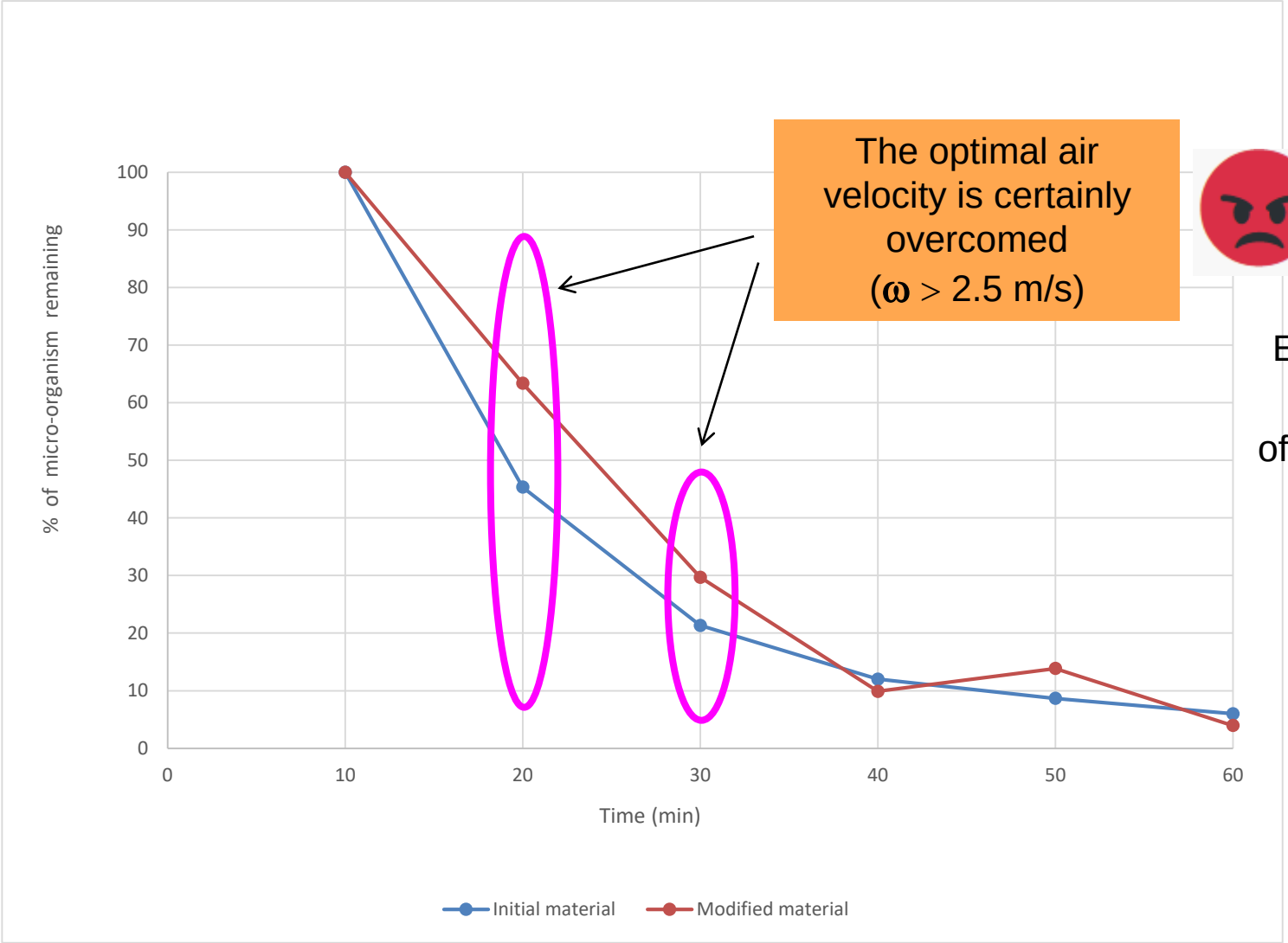
blue curve – mode 1 (no active material);

red curve – mode 2 (γ-Al_2O_3);

green curve – mode 3 (ZnO/γ-Al_2O_3)

MAIN RESULTS OF PILOT TESTS CARRIED OUT AT LNEC _ 2

Airborne bacteria



Evolution of the concentrations of airborne micro-organisms in time in the indoor air of the test chamber (53 m^3) at the gas linear velocity ω approximately equal to **2.6 *m/s***

(gas flow rate – 90 m^3/h):

blue curve – mode 2 (γ-Al_2O_3);

red curve – mode 3 (ZnO/γ-Al_2O_3)

CHAPITRE 4

CONCLUSIONS AND DISSEMINATION OF THE RESULTS (SHORTENED LIST)

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CONCLUSIONS

The dark-operating selective hole / hydroxyl radical generators (example – $MnO_2/AlPO_4/\gamma\text{-}Al_2O_3$) and the dark-operating mechanically obstructive composite materials (example – $ZnO/\gamma\text{-}Al_2O_3$) can be applied as germicidal agents for the indoor air antimicrobial conditioning in dynamic mode.

The application of the second group, namely of the dark-operating mechanically obstructive composite materials, seems preferable taking into account the fact that the first group of active materials can be successfully applied only at extremely moderated dynamic conditions or in static mode → much less interest for industrial use (**!**).

Both tested groups of active materials can be applied in cyclic operating mode thanks to the easiness of their thermal regeneration *in situ*.

DISSEMINATION OF THE RESULTS (SHORTENED LIST)

1. Chauvin A., Evstratov A., Bayle S., Sabourin L., Indoor Air Disinfection in Dynamic Dark Operating Conditions, *5th International Conference on Advances in Chemical Engineering and Technology* (October 04th – 05th, 2018, London, United Kingdom), Proceedings, p. 41;
   abstract according to https://chemicalengineering.insightconferences.com/abstract/2018/indoor-air-disinfection-in-dynamic-dark-operating-conditions); reference *J Adv Chem Eng*, 2018, **8**; doi: 10.4172/2090-4568-C3-011.

2. Dutheil de la Rochère A., Evstratov A., Sabourin L., Bayle S., Matériaux nanocompositesgermicides pour l'assainissement de l'air intérieur, *Grand congrès unitaire de la Fédération Française des Matériaux MATERIAUX-2018* (19 – 23 novembre 2018, Strasbourg, France), Programme, p. 57.

3. Dutheil de la Rochère A., Evstratov A., Bayle S., Sabourin L., Frering A., Lopez-Cuesta J.-M., Exploring the antimicrobial properties of dark-operating ceramic-based nanocomposite materials for the disinfection of indoor air, *PLoS ONE*, 2019, **14**, n°10, 21 p.; doi.org/10.1371/journal.pone.0224114.

4. Duteil de la Rochère A., *Matériaux nanocomposites sur supports céramiques pour l'assainissement de l'air intérieur (Nanocomposite materials developed using ceramics supports for the indoor air sanitation)*, *Doctoral thesis* (thesis director Evstratov A., thesis co-director Lopez-Cuesta J.-M.), Doctoral School Sciences Chimiques Balard (ED-459), 2019, IMT Mines Alès, 231 p., annexes;
   doi: 10.5281/zenodo.3686078; https://zenodo.org/record/3686078#.XlQIjvRCdhE.

Thank you
for your attention