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

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12e Colloque IMT : Matériaux pour la transition environnementale

8 octobre 2020 (visio-conférence)
Corresponding European Project (Horizon 2020)

H2020-MSCA-RISE-2015

Nano-materials-based innovative engineering solutions to ensure sustainable safeguard to indoor air

**NANO GUARD2AR (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
ENERGETICALLY-INDEPENDENT COMPOSITE MATERIALS FOR THE INDOOR AIR ANTIMICROBIAL CONDITIONING

Acknowledgements:

Dutheil de la Rochère A., Bayle S., Lopez-Cuesta J.-M., Sabourin L., Ravel R.,
IMT Mines Alès, France

Viegas J.-C., Pinto I.,
LNEC, Portugal
1. INNOVATIVE NANO- AND MICROCOMPOSITE MATERIALS FOR THE INDOOR AIR GERMICIDAL CONDITIONING CONCEPTUALIZED AND IMPLEMENTED BY IMT MINES ALÈS

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

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

4. CONCLUSIONS AND DISSEMINATION OF THE RESULTS (SHORTENED LIST)
CHAPITRE 1

INNOVATIVE NANO- AND MICROCOMPOSITE MATERIALS FOR THE INDOOR AIR GERMICIDAL CONDITIONING CONCEPTUALIZED AND IMPLEMENTED BY IMT MINES ALÈS
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
LABORATORY DYNAMIC TESTS OF DARK-OPERATING GERMICIDAL COMPOSITE MATERIALS: APPLIED EQUIPMENT

Space volume: 0.3 m³

Automatic cell counter BioTrak

Front view of sample holders
**Chemical composition**: MnO₂/AlPO₄/γ-Al₂O₃ (support)
(example: 4.5 % ms./32.3 % ms./63.2 % ms. (support))

**Morphology**: spherical alumina beads Ø 2.5 – 3.0 mm covered with AlPO₄ (1ˢᵗ massive layer) and with MnO₂ (2ⁿᵈ island-type layer) using the wet impregnation method
Agar diffusion inhibitory tests results (static operation conditions):
incubated Petri dishes containing *B. atrophaeus* being in contact with
a, b) $\gamma$-Al$_2$O$_3$ beads; c, d) ZnO/$\gamma$-Al$_2$O$_3$ beads and
e, f) MnO$_2$/AlPO$_4$/γ-Al$_2$O$_3$ beads

**Inhibition radii** obtained by agar diffusion inhibitory tests:

<table>
<thead>
<tr>
<th></th>
<th>$\gamma$-Al$_2$O$_3$ beads</th>
<th>ZnO/$\gamma$-Al$_2$O$_3$ beads</th>
<th>MnO$_2$/AlPO$_4$/γ-Al$_2$O$_3$ beads</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhibition radius of the first plate</td>
<td>0 mm</td>
<td>0 mm</td>
<td>9 mm</td>
</tr>
<tr>
<td>Inhibition radius of the second plate</td>
<td>0 mm</td>
<td>0 mm</td>
<td>9 mm</td>
</tr>
<tr>
<td>Mean inhibition radius</td>
<td>0 mm</td>
<td>0 mm</td>
<td>9 mm</td>
</tr>
</tbody>
</table>
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:

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

\[
\equiv M^{n+} - O^{-}_{\text{surf} \text{ h+(VB)}} + HO^{-} \rightarrow \equiv M^{n+} - O^{-}_{\text{surf} \text{ h+(VB)}} - HO^{-}_{\text{ads}},
\]

\[
\equiv M^{n+} - O^{-}_{\text{surf} \text{ h+(VB)}} - HO^{-}_{\text{ads}} \rightarrow \equiv M^{n+} - O^{2-}_{\text{surf} \text{ h+(VB)}} - HO^{-}_{\text{ads}}.
\]

However, the applied active component, $\beta$-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 $[\text{HO}^- \cdot \text{H}_2\text{O}]$ 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 $\text{H}_3\text{O}_2^{-}$
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:

\[ D = D_0 \times e^{-\frac{2d}{h} \sqrt{\frac{2m_e(U_0 - E)}}}, \]

where \( D \)—coefficient of transparency to be determined (0 < \( D \) ≤ 1); \( D_0 \)—coefficient of transparency without any energetic barrier to overcome (\( D_0 = 1 \)); \( m_e \)—mass of electron (9.11 \times 10^{-31} \text{ kg}) \); \( h \)—reduced Planck constant (\( h = \hbar / 2\pi = 1.05 \times 10^{-34} \text{ J·s} \)); \( (U_0 - E) \)—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:

- \( (U_0 - E) = 0.25 \text{ eV} \), where \( U_0 = 0.25 \text{ eV} \) (the bandgap energetic barrier),
- \( E = 0 \text{ eV} \) (the worst virtual case when the electron’s own energy is not taken into consideration),
- \( d = 2.21 \text{ Å} \) or 0.221 nm (the length of \( \text{Mn}_{\text{CB}} - \text{O}_{\text{VB}} \) bond in \( \text{MnO}_2 \) [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 \( \beta\text{-MnO}_2 0.32 \) or 32% (!) (explain what does it mean)
Pure $\beta$-MnO$_2$ is thus unable to proceed the reactions (1 – 3) cited on the slide n°11 because of the hydrated complex [HO$^-$•H$_2$O] 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$_4$/γ-Al$_2$O$_3$ the situation can be radically changed:

Donor-acceptor composites MnO$_2$/$\gamma$-Al$_2$O$_3$ and MnO$_2$/AlPO$_4$/$\gamma$-Al$_2$O$_3$ 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-Al₂O₃ (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 Ø 2.5 – 3.0 mm covered with ZnO using the method of thermal synthesis in aqueous solution
Test of the germicidal efficiency of materials in dynamic operating conditions (air linear velocity: 0.2 m/s)

MnO₂/AlPO₄/γ-Al₂O₃ manifests the best germicidal performance
MAIN RESULTS OF LABORATORY DYNAMIC TESTS _ 2

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

MnO₂/Al₂O₃/γ-Al₂O₃ and ZnO/γ-Al₂O₃ germicidal performances are quite similar
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/γ-Al₂O₃ begins to overcome the one of MnO₂/AlPO₄/γ-Al₂O₃
Test of the germicidal efficiency of materials in dynamic operating conditions (air linear velocity: 2.0 – 2.2 m/s)

ZnO/γ-Al₂O₃ manifests the best germicidal performance
DARK-OPERATING MECHANICALLY OBSTRUCTIVE MATERIALS: MAIN RESULTS OF PILOT TESTS CARRIED OUT AT LNEC, PORTUGAL (JUNE 2019)
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
At moderated dynamic conditions 
(\(\omega \rightarrow 1.0 \text{ m/s}\))

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 \(\omega\) 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 (\(\gamma\)-Al\(_2\)O\(_3\));
- green curve – mode 3 (ZnO/\(\gamma\)-Al\(_2\)O\(_3\))
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 $\omega$ approximately equal to 2.6 m/s (gas flow rate – 90 m$^3$/h):

- blue curve – mode 2 ($\gamma$-Al$_2$O$_3$);
- red curve – mode 3 (ZnO/$\gamma$-Al$_2$O$_3$)

The optimal air velocity is certainly overcome ($\omega > 2.5$ m/s)
CHAPITRE 4

CONCLUSIONS AND DISSEMINATION OF THE RESULTS (SHORTENED LIST)
CONCLUSIONS

The dark-operating selective hole / hydroxyl radical generators (example – MnO₂/AlPO₄/γ-Al₂O₃) and the dark-operating mechanically obstructive composite materials (example – ZnO/γ-Al₂O₃) 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.


Thank you for your attention