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Man's activity and mismanagement of resources conducted to dangerous levels of pollution in water, air and earth and to incalculable deficiencies, harmful to the physical and social health of mankind. Industrial activities, heating systems and road traffic are the main responsible for the emission of pollutant gases such as nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds (VOCs). As so, its harmful impacts are observed far beyond large cities and jam-packed streets. It is important to refer that the health costs related only with road traffic air pollution represents 0.9%-2.7% of the gross domestic product (GDP) in France, for example. Under this context, the combination of nanostructured titanium dioxide (TiO<sub>2</sub>) and bituminous formulations represents a tool, with considerable degree of innovation, towards the reduction of environmental impacts.

In this work, conventional hot mix asphalt (HMA) was produced with standard materials to play the role of a control sample. Afterwards, an aqueous solution of TiO<sub>2</sub> nanoparticles was sprayed over sample's surface. By another hand, a HMA samples was also modified through the volume incorporation of small quantities of TiO<sub>2</sub> nanoparticles and recycled glass cullets. It is expected that the inclusion of glass in the asphalt formulations should promote an in-depth conduction and entrapment of light, thus enhancing the photocatalytic performance of this samples. Scanning Electron Microscopy (SEM) analysis were conducted in order to infer about the morphology of the modified HMA samples and the surface as well as the in-depth dispersion of TiO<sub>2</sub> nanoparticles and recycled glass cullets.

The produced samples were also subjected to wearing tests using the tire-road contact method. Before and after the wearing process, the photocatalytic efficiency was evaluated via the decomposition rate of an aqueous solution of Methylene Blue (MB) under UV light irradiation.

## Experimental Details

Table 1 - Samples identification.

Sample	Prod. Method	Dep. Temp. (°C)	TiO <sub>2</sub> wt%	[TiO <sub>2</sub> ] (g/L)	Glass cullets wt%
1	Volume	160	0.2	-	9.5
2	Volume	160	0.4	-	9.5
3	Spray	50	-	4	9.5
4	Spray	50	-	10	9.5



In this work, two methods were used to promote the photocatalytic capacity on asphalt formulations. The first strategy consisted on spraying an aqueous solution of TiO<sub>2</sub> nanoparticles onto the surface of the HMA samples. The other one was the volumetric incorporation of TiO<sub>2</sub> nanoparticles in the bulk HMA samples.

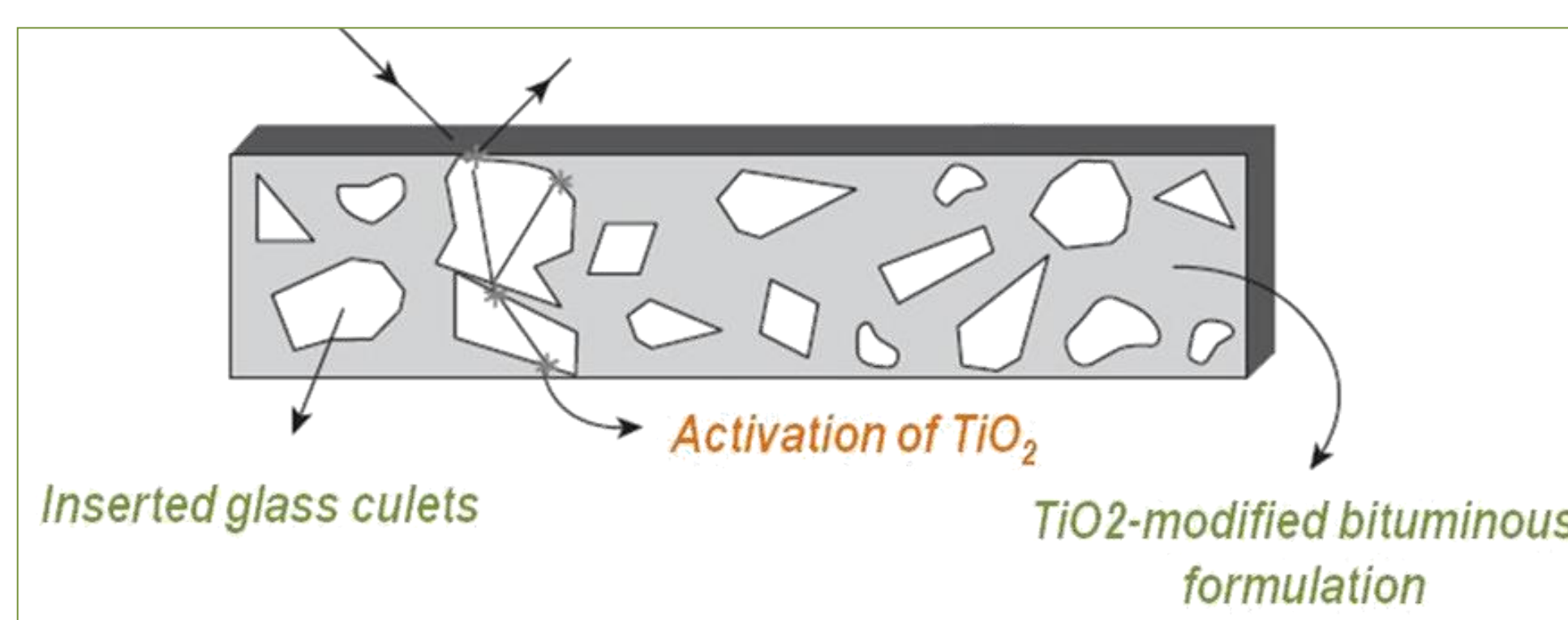


Fig. 2 - Pathways of light and activation of TiO<sub>2</sub> in road pavement materials using glass as aggregates. (Adapted from Chen, and Poon, 2009).

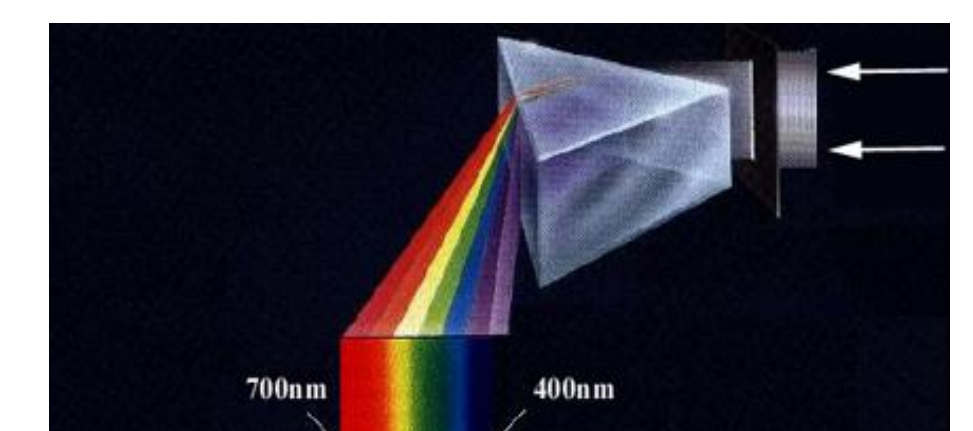


Fig. 3: Schematic representation of light in a prism showing the inherent refraction in glass materials.

Since photocatalytic activity depends on the available electron/hole photo-induced pairs on surface of TiO<sub>2</sub> nanoparticles, the option of adding recycled glass cullets onto road pavement formulations should promote an in-depth conduction and entrapment of light, increasing the photodegradation efficiency. In theory, solar light would be carried to a greater depth, activating the TiO<sub>2</sub> within the inner part of the surface layers as well as on the surface.

## Evaluation of Photocatalytic Properties

### Before Wearing test



Fig. 4 - Images showing the samples immersed in the MB aqueous solution and sample's final aesthetics.

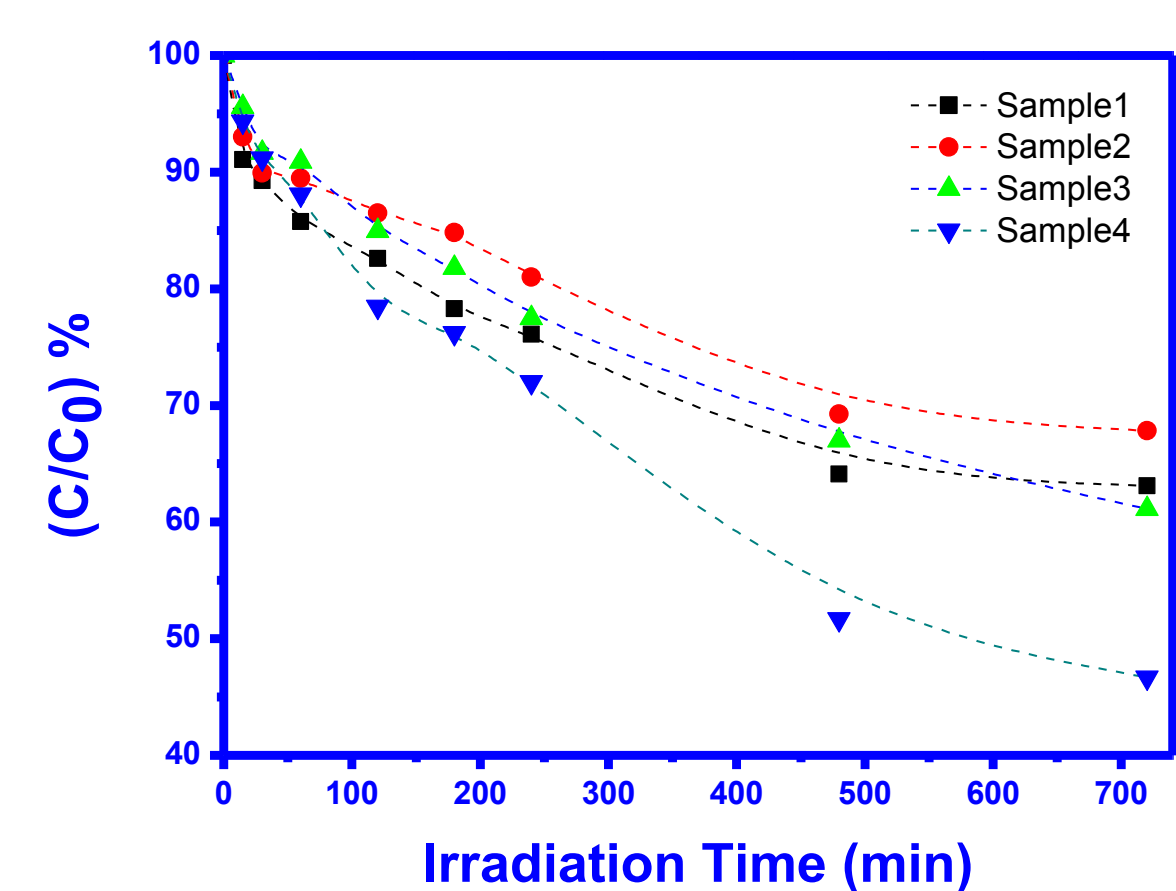


Fig. 5 - Photodegradation of the MB aqueous solution under the irradiation of UV light before wearing.

Table 2 - Photocatalytic Efficiency of the HMA samples before the wearing test.

Sample	Photodegradation rate, <i>k</i> (min <sup>-1</sup> )
1	2.97x10 <sup>-5</sup>
2	2.90x10 <sup>-5</sup>
3	4.43x10 <sup>-5</sup>
4	5.56x10 <sup>-5</sup>

Table 3 - Photocatalytic Efficiency of the HMA samples before the wearing test.

Sample	Efficiency (%)
1	29,63
2	25,6
3	32,26
4	45,22

### After Wearing test



Fig. 6 - Images showing the samples immersed in the MB aqueous solution and sample's final aesthetics.

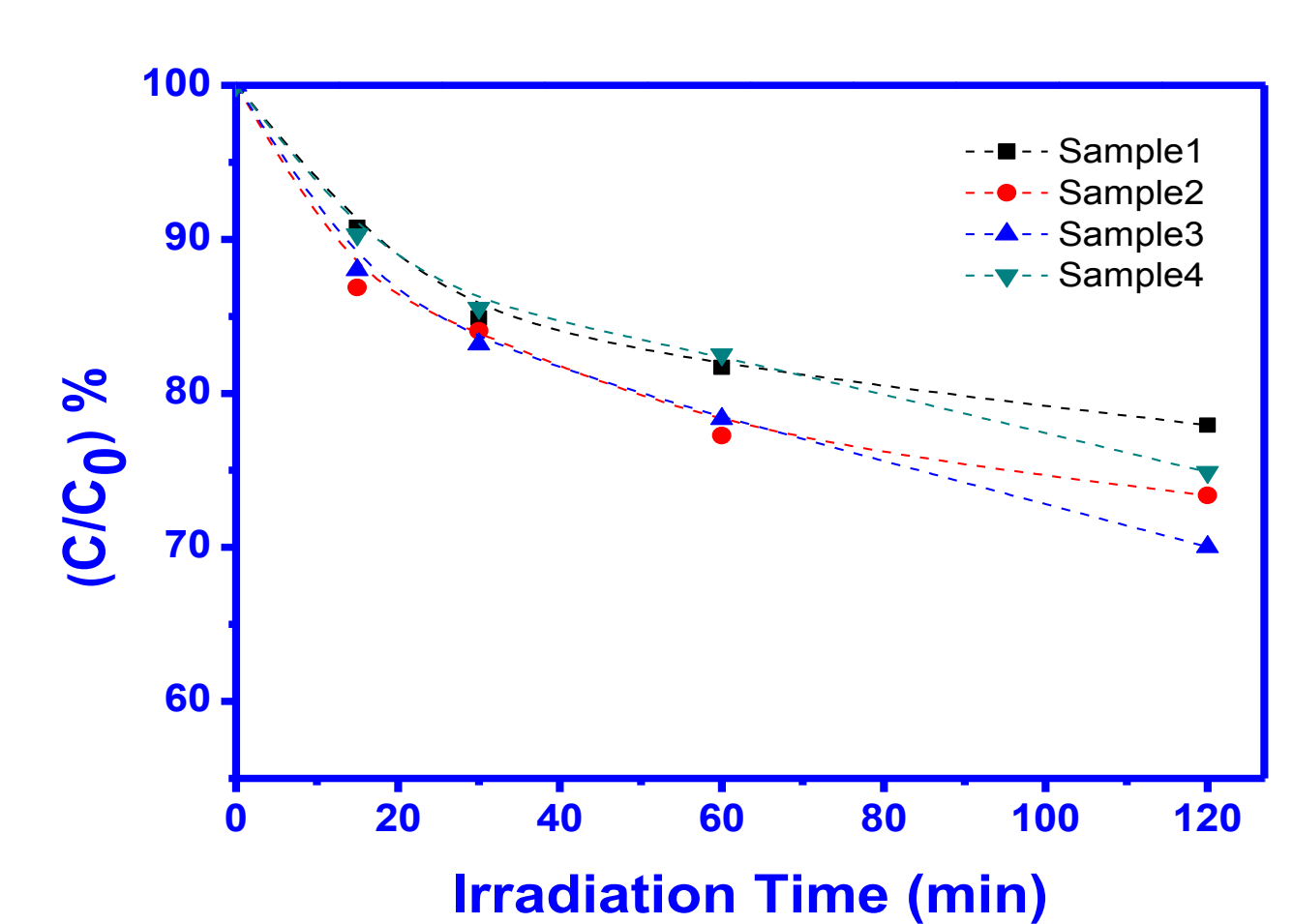


Fig. 7 - Photodegradation of the MB aqueous solution under the irradiation of UV light after wearing.

Table 4 - Photocatalytic Efficiency of the HMA samples before the wearing test.

Sample	Photodegradation rate, <i>k</i> (min <sup>-1</sup> )
1	5,45x10 <sup>-4</sup>
2	6,43x10 <sup>-4</sup>
3	5,24x10 <sup>-4</sup>
4	4,36x10 <sup>-4</sup>

Table 5 - Photocatalytic Efficiency of the HMA samples before the wearing test.

Sample	Efficiency (%)
1	22,08
2	26,64
3	29,97
4	25,13

## Morphological Characterization before wearing

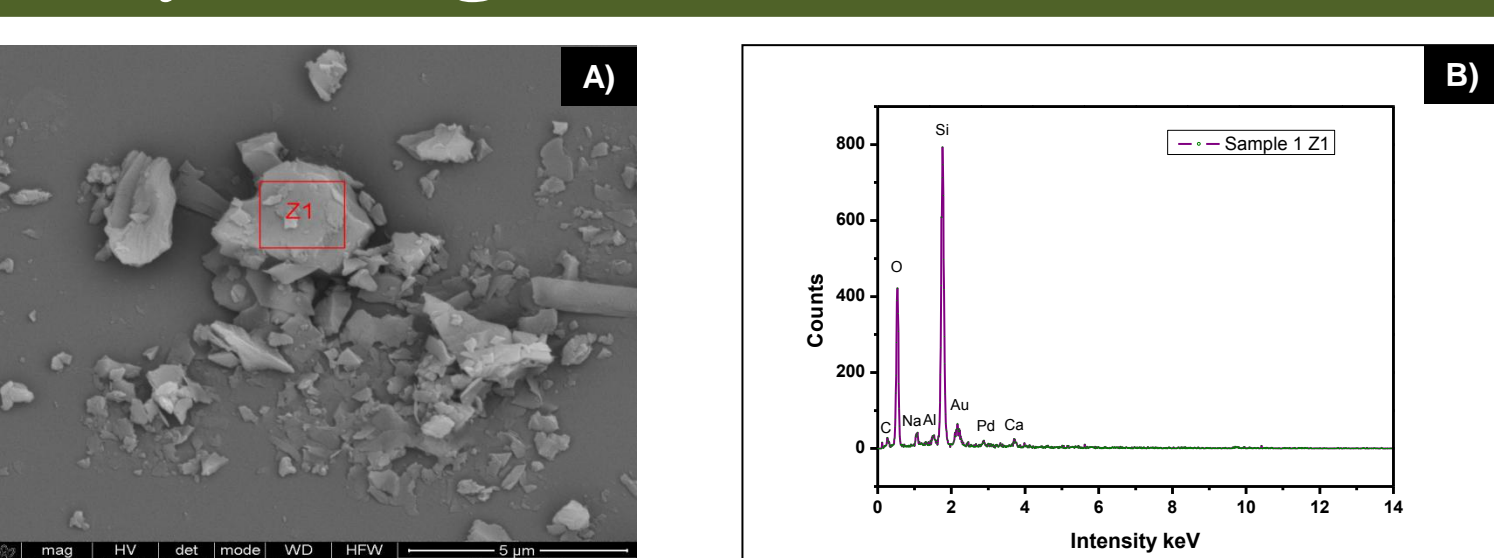


Fig. 8 - A) Top-view SEM Micrograph of Sample 1 to verify the presence of glass at the sample's surface; B) EDS spectra of region Z1 identified in the SEM image.

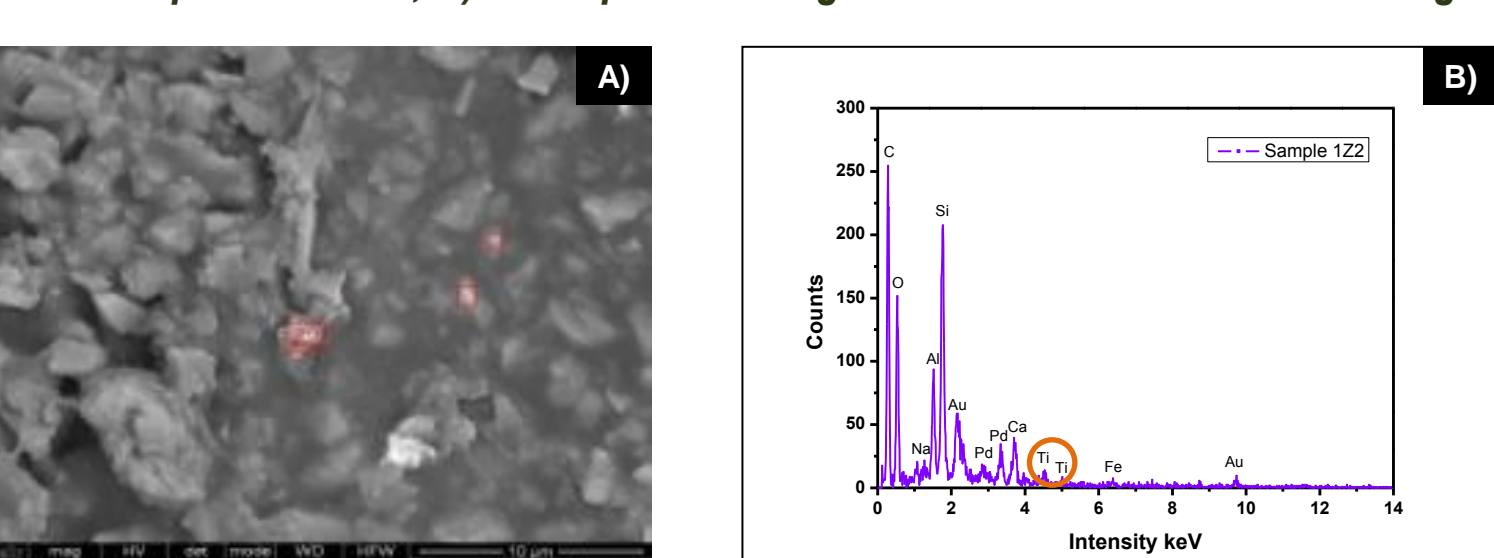


Fig. 9 - A) Top-view SEM Micrograph of Sample 1 to verify the presence of glass and TiO<sub>2</sub> nanoparticles at the sample's surface; B) EDS spectra of region Z2 identified in the SEM image.

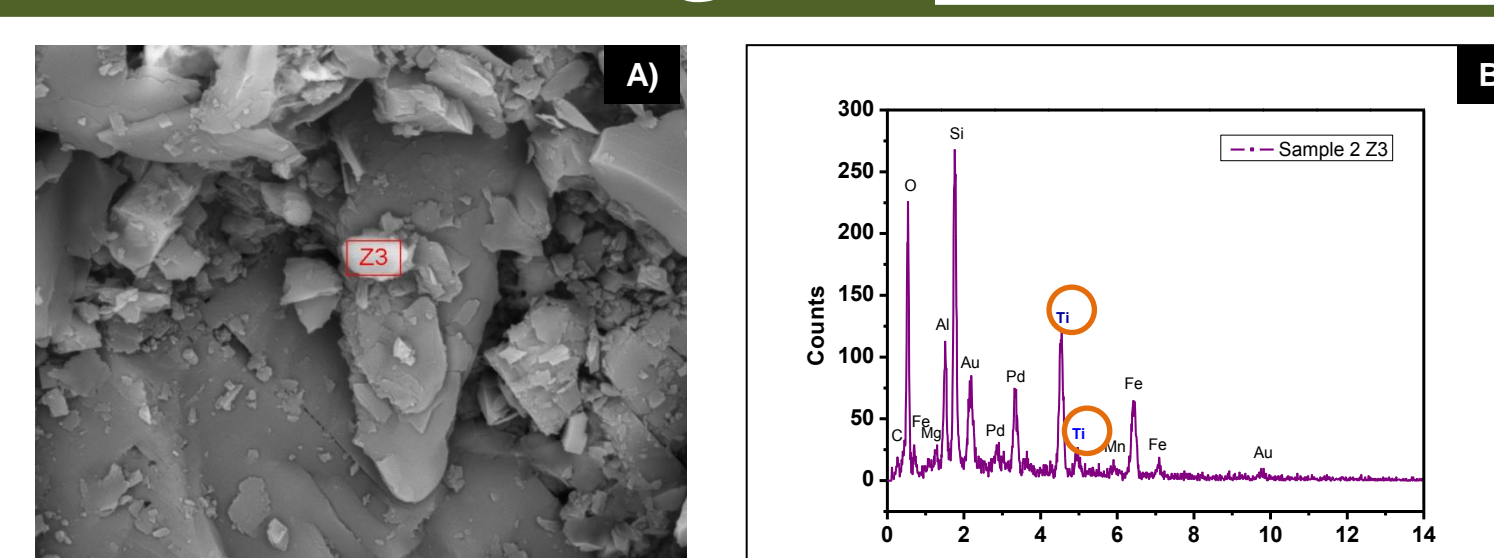


Fig. 10 - A) Top-view SEM Micrograph of Sample 2 to verify the presence of TiO<sub>2</sub> nanoparticles and glass cullets; B) EDS spectra of region Z3 identified in the SEM image.

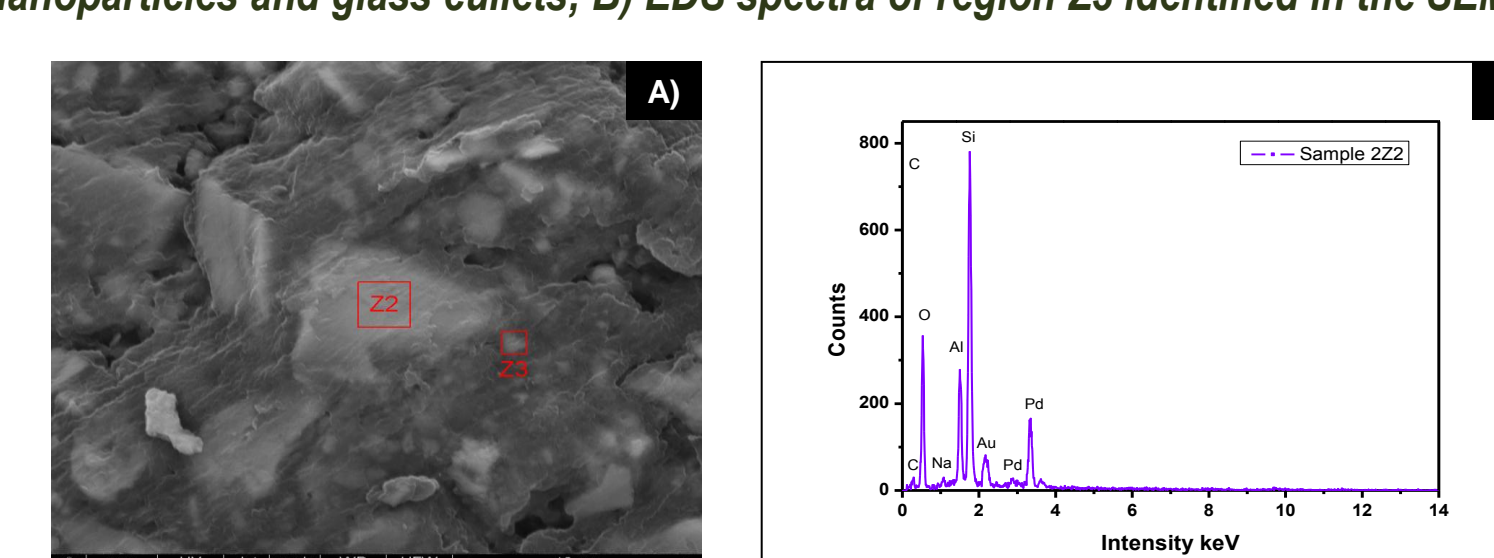


Fig. 11 - A) Cross-section SEM Micrograph of Sample 2 to verify the presence of glass; B) EDS spectra of region Z32 identified in the SEM image.

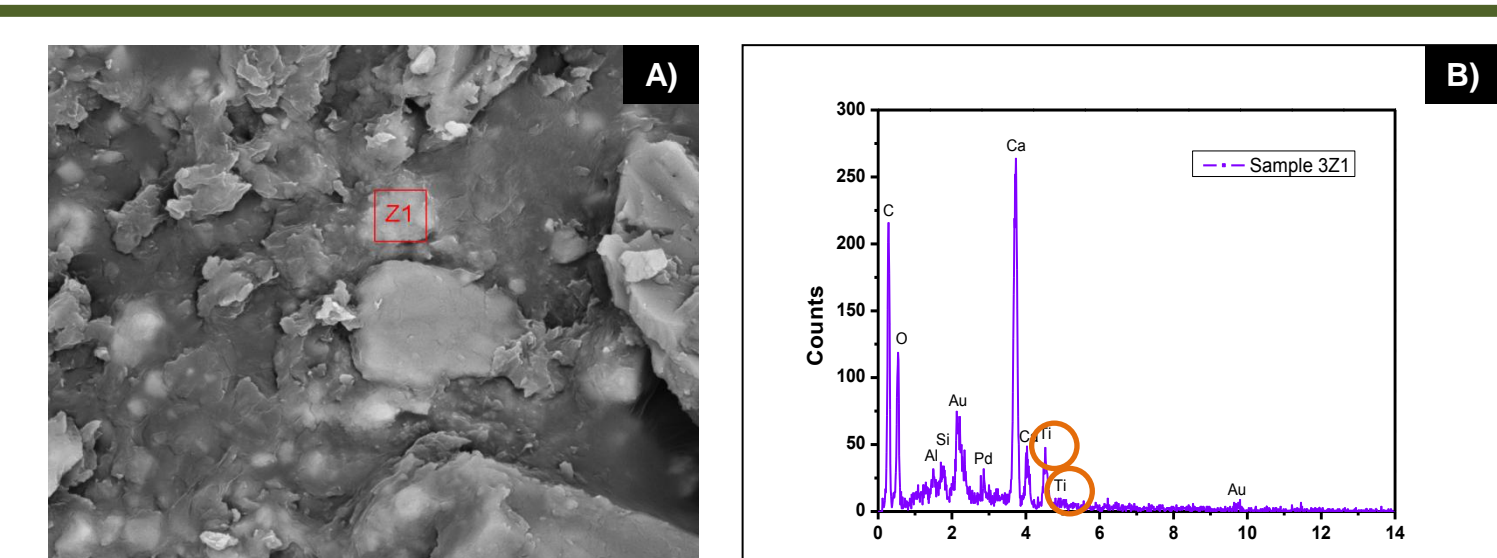


Fig. 12 - A) Top-view SEM Micrograph of Sample 3 to verify the presence of TiO<sub>2</sub> nanoparticles and glass cullets; B) EDS spectra of region Z3 identified in the SEM image.

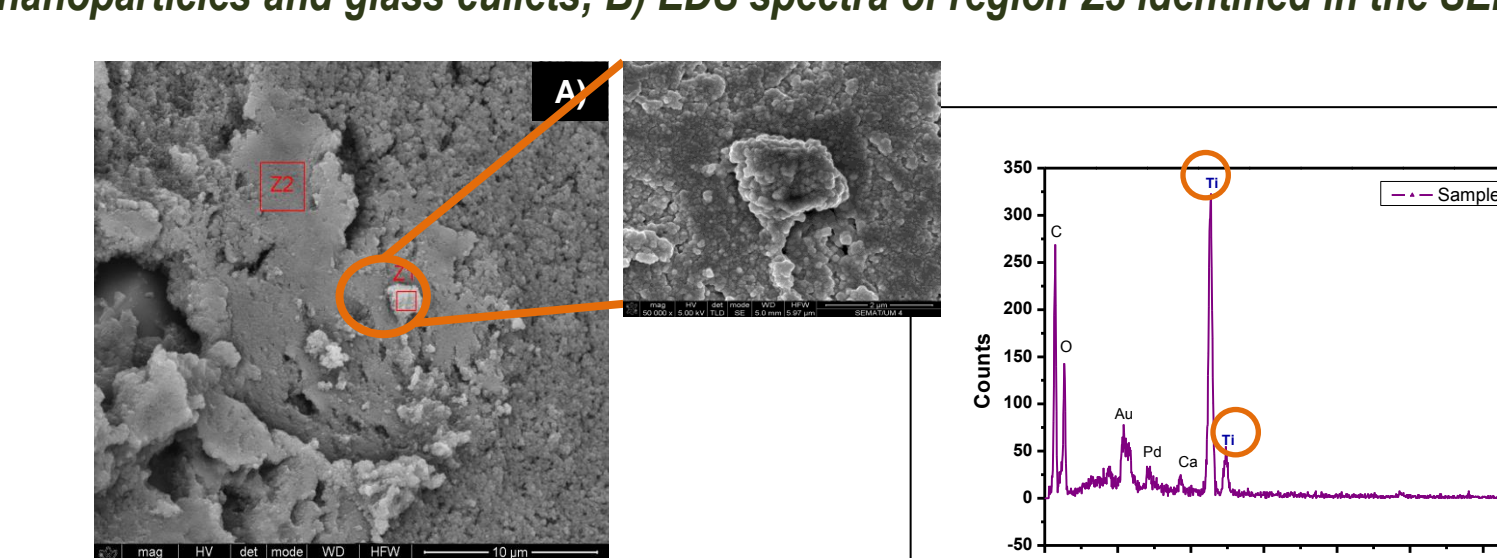


Fig. 13 - A) Top-view SEM Micrograph of Sample 4 to verify the presence of TiO<sub>2</sub> nanoparticles and glass cullets; B) EDS spectra of region Z3 identified in the SEM image.

## Conclusions

As a final remark, it can be stated that both production methods are viable strategies that can be used to produce asphalt formulations with photocatalytic ability. Indeed, this is extremely important for construction and building materials industry in the sense that it can represent a very important tool to achieve sustainable construction concepts that will contribute to the reduction of atmospheric pollution.

Moreover, from this preliminary experimental results it can be withdrawn that organic compounds (such as fuel, oil, among others) could be effectively photodegraded when using TiO<sub>2</sub> nanoparticles on road pavements, when exposed to real atmospheric conditions.

The results show that it was possible to obtain moderate photodegradation rate as well as efficiencies.

It can be concluded that the samples presenting the highest photocatalytic ability were the ones with more amount of TiO<sub>2</sub> nanoparticles, nevertheless the production method used.

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