analysed using Microtox test with *Vibrio fischeri* bacteria and compared to a quantitative structure–activity relationship (QSAR) model.

Results and Discussion: The $BiVO_4$ modifications resulted in improved photocatalytic activity under visible light. The designed precursor changed light harvesting ability and dispersion stability remarkably, leading to high photocatalytic activity toward naproxen and ofloxacin degradation. In the case of facet-engineered $BiVO_4$, the highest activity was observed for octahedral $BiVO_4$ photocatalysts with exposed {0 2 1} and {1 2 0} facets. CuO_x nanoclusters deposition improved charge carriers separation, also increasing the observed rate constants of 1.18 and 3.29 times for naproxen and ofloxacin degradation. Finally, the addition of PMS at a low concentration of 0.1 mM accelerated the pharmaceuticals degradation. However, too high PMS concentration resulted in Bi leaching and increased bioluminescence inhibition of bacteria.

Conclusions: In summary, the present study introduces new insight into $BiVO_4$-based photocatalyst preparation for improving light harvesting ability and photocatalytic activity, which plays a crucial role in the degradation of emerging contaminants.

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Self-assembling reduced graphene oxide and TiO_2-based materials for solar photocatalytic wastewater treatment

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In this study, we employed a simple and eco-friendly method to prepare self-assembling self-standing membranes of: i) graphene oxide (GO), ii) reduced GO (rGO), iii) rGO and TiO_2 (rGO-TiO_2). We tested the three membranes for adsorption and solar photodegradation of Imidacloprid in water, obtaining evidence of a remarkable solar photocatalytic activity of rGO. To the best of our knowledge, no other photocatalytic rGO self-standing membranes have been reported yet.

Background: As declared in the United Nations SDG 6, wastewater treatment and reuse must be urgently improved. In this context, titanium dioxide (TiO_2) and reduced graphene oxide (rGO) have raised great interest. The former is one of the most studied photocatalytic materials. The latter combines a significant adsorption capability toward both inorganic and organic contaminants with a noticeable photocatalytic activity, strongly dependent on the reduction level [1]. Moreover, TiO_2/rGO nanocomposites show a reduced band gap compared to TiO_2, which makes them promising materials for visible and solar light-driven photocatalysis [2]. The wide study of this materials, however, is mainly limited to slurry or supported systems. To the best of our knowledge, the self-assembling rGO-TiO_2 membrane recently developed by our research group [3] is the only self-standing membrane of rGO and TiO_2 reported yet.

Methodology: Membranes were prepared following a procedure previously reported [3,4]. A 4 mg/mL graphene oxide commercial suspension from Graphenea was used as starting material. It was chemically reduced with L-Ascorbic Acid (L-AA) in 10:1=L-AA:GO mass ratio, by stirring for 24 h at ambient temperature. To produce rGO-TiO_2 membranes, TiO_2 nanopowder (Degussa P25) was added in 1:1=TiO_2:GO mass ratio in the last 30 min of stirring. Self-assembling GO, rGO and rGO-TiO_2

membranes were obtained by vacuum filtration of the suspensions on a PVDF filter. Upon drying at 40 °C for 20 min, membranes were detached from the PVDF filters.

For photocatalytic tests, each membrane was immersed in 30 mL of a 5 mg/L Imidacloprid aqueous solution, in static conditions. After 30 min in dark, it was irradiated for 5 h with simulated solar light. Experiments in dark were also carried out to assess the membranes adsorption capability. The variation in concentration of solutions over time was monitored by means of a UV-Vis spectrophotometer, measuring the absorbance at = 269 nm.

Results and Discussion : The methodology previously described allowed to obtain three self-standing membranes: GO (8 mg), rGO (8 mg) and rGO-TiO_2 (16 mg).

Results from Imidacloprid removal experiments in dark and simulated solar light conditions are reported in Figure 1. After 5 h in dark (Figure 1a), 16% adsorption of contaminant was registered for GO, while 25% was achieved with both rGO and rGO-TiO_2. Under simulated solar irradiation (Figure 1b), no photocatalytic activity was observed for GO, as the highest reduction of Imidacloprid concentration (15% after 3 h) can be entirely ascribed to adsorption and photolysis. Both rGO and rGO-TiO_2, instead, showed a significant photodegradation of Imidacloprid, reducing its concentration of an extra 25% with respect to adsorption after 5 h.

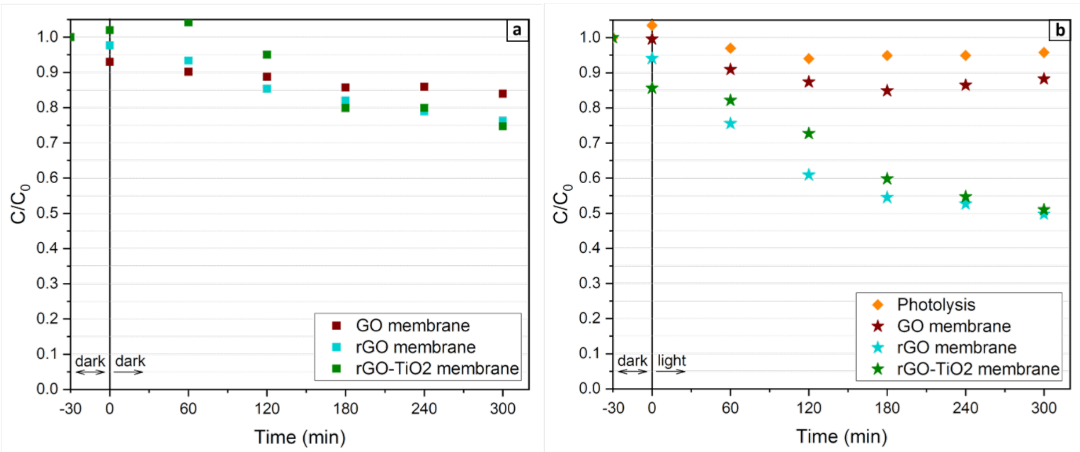

Figure 1. Imidacloprid a) adsorption and b) photodegradation experiments using GO, rGO and rGO-TiO_2 membranes.

Conclusions: This preliminary study highlights a remarkable solar photocatalytic activity of rGO membranes. The findings will be consolidated by performing photodegradation tests toward other organic contaminants and in dynamic conditions. To maximize the contact area between photocatalyst and water, open cell foams will also be used as supports for rGO-based self-assembling coatings.

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