

TiO₂/Carbon Dots Nanocomposites: Photocatalysts For The Solar Driven Removal Of Antibiotics From Aquaculture Effluents

Valentina Silva^{1,2*}, Carla Patrícia Silva¹, Marta Otero², Diana Lima¹

¹Department of Chemistry, CESAM, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal; ²Department of Environment and Planning, CESAM, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal; *valentinagsilva@ua.pt

In order to satisfy the world's demand for fish and seafood, the industry of aquaculture has impressively developed¹. However, like in all zootechnics, aquacultures use antibiotics, such as oxolinic acid (OXA), for disease treatment and prevention². This constitutes a problem since a significant part of these antibiotics remains in the aquaculture recirculating systems, as well as in effluents, ending up in the surrounding water. Since the presence of antibiotics in the aquatic environment promotes the increase of antimicrobial resistance², the development of sustainable treatments for antibiotics' removal is essential to avoid their discharge. Among them, photodegradation under natural irradiation may be a promising alternative as long as a proper efficiency is achieved. Semiconductor photocatalysts, like titanium dioxide (TiO₂), and the versatile carbon quantum dots (CQDs) have risen great interest in the scientific community since they are solar driven photocatalysts, inexpensive to produce and easy to use. This work intended to study the photocatalytic capacity of nanocomposites of TiO₂/CQDs, optimizing the conditions used in their synthesis for efficient solar driven removal of OXA from water. Two types of CQDs were synthesized under hydrothermal treatment: (i) using citric acid and urea (CQDs-CAU); or (ii) using only citric acid (CQDs-CA). Through a facile hydrothermal-calcination method, various nanocomposites were produced by incorporating different percentage ((4%, 5%, 6% and 8%) (w/w)) of CQDs in commercial TiO₂ (P25). For comparative purposes, calcination was also applied to the single TiO₂ and CQDs. All the materials were tested for OXA photocatalysis. Solutions of OXA (10 mg/L) with pH adjusted to 8.6 were prepared either in 0.001 mol/L phosphate buffer (PB) or in 30 g/L of synthetic sea salts (SSS). Photodegradation studies under laboratory-controlled conditions were performed using a solar radiation simulator (Solarbox 1500; Co.fo.me.gra, Italy), equipped with an arc xenon lamp (1500 W) and outdoor UV filters that limited the transmission of light with wavelengths shorter than 290 nm. Among the produced CQDs and their nanocomposites with TiO₂, TiO₂/CQDs-CA 4% (w/w) was the most efficient for OXA photodegradation in both matrices, at concentrations of 500 mg/L in PB and 1000 mg/L in SSS. The study of photodegradation kinetics showed that the half-life time ($t_{1/2}$) of OXA decreased from 53.4 min to 4.97 min in PB and from 3.00 h to 38.2 min in SSS. As for the application in an aquaculture effluent 1000 mg/L of TiO₂/CQDs-CA 4% (w/w) allowed for a decrease of the OXA $t_{1/2}$ from 3.71 h to 33.8 min. The results herein reported indicate that the utilization of solar driven photocatalysis may be a green solution to remove OXA from aquaculture effluents.

References

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- [2] R. Lulijwa, E. J. Rupia, A. C. Alfaro, *Reviews in Aquaculture*, 2020, 12, 640-663.