



Photoproducts of carminic acid formed by a composite from *Manihot dulcis* waste



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ARTICLE INFO

Article history:

Received 29 July 2014

Received in revised form 6 October 2014

Accepted 16 October 2014

Available online 22 October 2014

Keywords:

Natural red 4

Carminic acid

Photolysis

Photocatalysis

Product identification

Manihot waste

TiO₂/carbon composite

ABSTRACT

Carbon–TiO₂ composites were obtained from carbonised *Manihot dulcis* waste and TiO₂ using glycerol as an additive and thermally treating the composites at 800 °C. Furthermore, carbon was obtained from *manihot* to study the adsorption, desorption and photocatalysis of carminic acid on these materials. Carminic acid, a natural dye extracted from cochineal insects, is a pollutant produced by the food industry and handicrafts. Its photocatalysis was observed under different atmospheres, and kinetic curves were measured by both UV–Vis and HPLC for comparison, yielding interesting differences. The composite was capable of decomposing approximately 50% of the carminic acid under various conditions. The reaction was monitored by UV–Vis spectroscopy and LC–ESI–(Qq)–TOF–MS–DAD, enabling the identification of some intermediate species. The deleterious compound anthracene-9,10-dione was detected both in N₂ and air atmospheres.

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1. Introduction

Carminic acid (CA) is a natural dye extracted from cochineal insects that can yield shades of red. The Food Standards Agency in Europe and the United States Food and Drug Administration (FDA) have not banned its use in food. CA is also used in histology, as well as the coloring of pharmaceuticals, cosmetics, plastics and fabrics. Particularly in Oaxaca (Mexico), CA is also the most important insect-derived dye used in the production of rugs and handicrafts. During the fabrication of both food and hand-woven carpets, significant amounts of CA are released in the food industry and artisanal carpeting effluents. Fortunately, CA showed negative genotoxicity in a somatic mutation and recombination test of *Drosophila melanogaster* (Sarikaya, Selvi, & Erkoç, 2012).

If we consider the problem of removing CA by the most common technique used for dyes, adsorption (Rangabhashiyam, Anu, & Selvaraju, 2013), the only reports of such removal are early ones using activated carbon. In recent years, the application of adsorbents in this respect have focused on the recovery and purification of CA (Bibi, Galvis, Grasselli, & Fernández-Lahore, 2012; Cabrera &

Fernández-Lahore, 2007). In contrast to adsorption, heterogeneous photocatalysis can be regarded as a water purification process that can achieve mineralisation by producing, at times, toxic intermediates during degradation. Incidentally, authors reported observing a higher toxicity after the biodegradation of CA than before the microbiological treatment of effluent (Arroyo-Figueroa et al., 2011). The fact that hydroxylated anthraquinones have presented significant toxicity is important because these compounds can be photoproducts of CA (Brack et al., 2003). This fact makes the identification of the compounds produced during the degradation of CA necessary.

In the food industry, CA is considered not only a colorant that resists degradation over time but also one of the most light-stable, heat-stable and oxidation-resistant dyes among all natural dye-stuffs. However, Jørgensen and Skibsted (1991) found that the photolability of CA increased with deprotonation and was enhanced with irradiation at 254 nm. Recently, Gosetti, Chiuminatto, Mazzucco, Mastroianni, and Marego (2015) studied the effect of sun irradiation on CA in aqueous solution and in sixteen different beverages to mimic the action of sunlight during transport. In the presence of TiO₂, authors degraded CA using UVA (366 nm) irradiation and demonstrated the adsorption of the dye onto the photocatalyst (Baran, Makowski, & Wardas, 2008). Furthermore, with the addition of H₂O₂, UV irradiation

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