



Photoinduced transformation of waste-derived soluble bio-based substances



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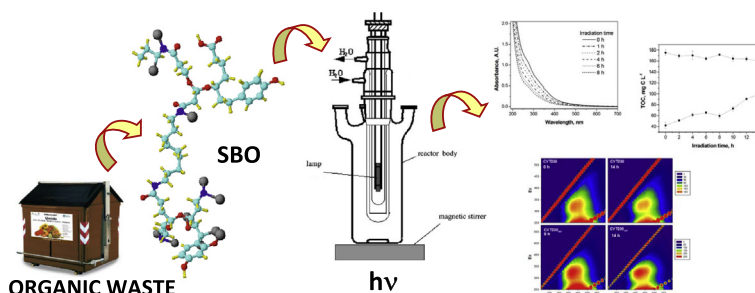
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HIGHLIGHTS

- Photoageing of waste-derived soluble bio-based substances (SBO) has been studied.
- The whole SBO material and its acid-soluble fraction were characterized.
- SBO structure, surfactant properties, dimensions and mineralization were considered.
- Irradiation induced SBO photobleaching and a progressive photochemical solubilization.

GRAPHICAL ABSTRACT



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ABSTRACT

Waste-derived, soluble bio-based substances (SBO), are effective low-cost photosensitizers that could find application in pollutant photodegradation. For this reason, it is important to understand if and to what extent irradiation could modify their properties. The exposure of SBO to simulated sunlight induced important spectral and structural modifications. Both the whole material and its acid-soluble fraction were characterized, highlighting several properties in common with humic and fulvic substances, including absorption spectra, specific absorbance and fluorescence behavior. The latter was described with a three-component model using PARAFAC analysis. Irradiation induced SBO photobleaching, but the absorbance of the acid-soluble fraction increased with irradiation. This finding suggests a progressive photochemical solubilization of SBO, which is confirmed by the increase of the carboxylic groups. In addition to absorbance, the fluorescence of whole SBO was also decreased by irradiation, thereby suggesting that both chromophores and fluorophores were photodegraded. The increasingly hydrophilic character given to SBO by irradiation also accounted for the photoinduced decrease of the surfactant properties of the material.

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1. Introduction

Among the general concern about waste collection, recycling, treatment and/or disposal, the development of processes to valorize the organic fraction of waste, either urban or from agriculture, is a challenge that is increasingly attracting research groups

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from all over the world. Up to a few years ago, the main goal has been to obtain energy out of organic wastes, by direct combustion or through their anaerobic fermentation for biogas production. However, none of these two approaches is self-sustainable in terms of either costs or energy balance. An alternative direction that is gaining increasing interest is the development of the so-called biorefinery. Here the integration of different approaches and processes for organic waste treatment should optimize their exploitation, in terms of both energy recovery and bio-fuel production. Moreover, it includes the separation of value-added chemicals to be released on the market for specific applications. For instance, from the soluble fraction of organic urban waste it has been possible to separate substances showing surfactant behavior and having promising performances in agriculture, animal husbandry, textile dyeing, material synthesis, and pollutant photodegradation [1,2].

Organic pollutant photodegradation has been studied because of the observed similarity, in terms of both structure and physical–chemical properties, between the waste-derived soluble bio-based substances (SBO) and the natural organic matter present in soils or as Dissolved or Particulate Organic Matter (DOM or POM) in natural waters, specifically the humic acid fraction. Therefore, SBO have also been presented as “humic acid-like” substances [3]. Many contributions can be found in the literature about DOM photoactivity in natural waters and on its important role in the photoassisted transformation of xenobiotics [4–6]. Based on these premises, SBO have been studied for their capability to promote the photodegradation of various pollutants, with several encouraging results [3,7–8]. In these studies it has also been evidenced a slow but progressive transformation of SBO upon irradiation under simulated sunlight [9].

SBO can be isolated from waste either in their acidic form, or as potassium/sodium salts. In the former case, the “humic-like” SBO can be separated from the “fulvic-like” fraction on the basis of their different solubility at $\text{pH} < 2$. In the latter case, isolation of the SBO “humic-like” fraction is attained through an ultrafiltration step, exploiting the different size of the “humic-like” and “fulvic-like” components of SBO [1,10]. At least theoretically, the substances obtained in the two cases should only differ in their acidic properties. However, a peculiar behavior has been observed with ultrafiltration-derived SBO, because they do not undergo complete precipitation when the solution pH is lowered to about 1.5. The brownish color of the aqueous phase suggests that some dissolved organic compounds were still present in solution. This fraction of SBO (hereinafter SBO_{sol}), which is soluble at $\text{pH} < 1.5$, deserves attention because of its stronger photosensitizing effect compared to SBO itself, shown in preliminary results.

The present research aims at giving more insight into SBO photodegradation processes. To better understand SBO photoaging, different analytical approaches have been chosen to assess the photoinduced SBO transformation in terms of structure, surfactant properties, aggregate dimensions and degree of mineralization. Attention was also devoted to the acidic functions present in the SBO structure, which could form bonds with metal ions, e.g. iron. Indeed, SBO are promising compounds to perform photo-Fenton processes under mild conditions, because they can maintain Fe(III) in solution at pH values above 4.5–5 [11]. In contrast, the classical photo-Fenton reaction requires acidic conditions where Fe(III) does not precipitate as hydroxide and the $\cdot\text{OH}$ radical production via the Fenton process reaches its maximum efficiency.

2. Experimental

2.1. Reagents

NaOH, KOH, HCl, HClO_4 , H_2O_2 and tetraethylammonium chloride were purchased from Aldrich and used as received. All

aqueous solutions were prepared with ultra-pure water, obtained from a Millipore Milli-Q™ system.

Among different available SBO, the so-called CVT230 was chosen as a model because most of the published papers about the photosensitized degradation of pollutants with SBO dealt with this material. CVT230 has been isolated from urban bio-wastes (UBW) sampled from the process lines of ACEA Pinerolese waste treatment plant in Pinerolo, Italy. The UBW was obtained in the compost production section, from urban public park trimming and home gardening residues aged for 230 days. It was further processed in a pilot plant located in Rivarolo Canavese, Italy [2], by means of an electrically heated and mechanically stirred 500 L reactor, a 102 cm long \times 10.1 cm diameter polysulfone ultrafiltration (UF) membrane with 5 kD molecular weight cut-off (supplied by Idea Engineering s.r.l.), and a forced ventilation drying oven. According to the operating experimental conditions, UBW were digested for 4 h at 60 °C, pH 13 and 4/1 V/w water/solid UBW ratio. The resulting heterogeneous mixture was allowed to settle, with the upper liquid phase containing the hydrolyzed soluble UBW. The liquid phase was recovered and circulated at 40 L h^{-1} flow rate through the UF membrane, operating with tangential flow at 7 bar inlet and 4.5 bar outlet pressure. This step yielded a retentate with 5–10% dry matter content, which was finally dried at 60 °C. The solid CVT230 was obtained in 15–30% w/w yield with respect to the starting UBW dry matter, and it was characterized according to a previously reported procedure [10]. Before use, CVT230 was taken up with Milli-Q™ water under sonication, centrifuged and filtered through a cellulose acetate filter with 0.45 μm pore diameter (Millipore), to remove any residual insoluble matter.

To obtain the $\text{CVT230}_{\text{sol}}$ fraction, CVT230 aqueous solutions were acidified under stirring with HClO_4 and centrifuged (3500 rpm for 30 min). The supernatant solutions were then filtered through a cellulose acetate filter (0.45 μm pore diameter, Millipore). When needed, the solution pH was adjusted to 8.0 by dropwise addition of NaOH.

2.2. Irradiation tests

Photolysis of CVT230 (total volume 0.500 L, 500 mg L^{-1}) and (when relevant) of $\text{CVT230}_{\text{sol}}$ was carried out at the naturally occurring CVT230 solution pH (equal to 9.6), in a cylindrical photochemical reactor (Helios-Italquartz, Milan), equipped with a 125 W medium pressure Hg lamp (the reactor schematic representation and the lamp emission spectrum are reported in the Supporting information, Fig. 1S). The system was kept under continuous stirring; cold water circulating in the quartz jacket surrounding the lamp kept the temperature within the reactor at 25 °C. The reaction was monitored at different irradiation times by measuring the following parameters on both CVT230 and $\text{CVT230}_{\text{sol}}$ (this latter irradiated as such from the beginning or, more often, extracted from CVT230 after irradiation): absorbance spectra, Excitation-Emission fluorescence Matrix (EEM), Total Organic Carbon (TOC), Dynamic Light Scattering (DLS), and surface tension. Potentiometric titrations were also performed on $\text{CVT230}_{\text{sol}}$ before and after irradiation.

Details regarding the instrumentation and analytical procedures are provided in the Analytical Procedures section of the Supporting information.

3. Results and discussion

3.1. UV–Vis spectral analysis

Fig. 1 reports the UV–Vis spectra recorded for CVT230 (500 mg L^{-1}) and the corresponding $\text{CVT230}_{\text{sol}}$ fraction, isolated

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