



Short communication

Photobleaching of lignin derived compounds from pulp mill effluents upon irradiation: The key role of receiving waters

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ABSTRACT

Lignin derived macromolecular compounds are the main constituents responsible for the hazardous effects of discharged effluents from the pulp and paper industry in receiving waters. It was shown by ultraviolet–visible (UV–vis) and fluorescence spectroscopies that a selective photodegradation of these structures occurred upon irradiation of fulvic acids (FA) from a kraft pulp mill effluent. Though photodegradation was not remarkably affected by the presence of the natural photosensitizer nitrate, it was inhibited under the presence of chloride. These results indicate that the fate of macromolecular organic matter from kraft pulp mill effluents may be different depending on the type of receiving waters, having a higher persistence when effluents are discharged in estuarine or marine waters than when they are discharged in fresh water.

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1. Introduction

Effluents from the pulping, bleaching and paper making processes are very rich in macromolecular dissolved organic matter, mainly lignin derived compounds, which are the main contributors to the colour and toxicity of this sort of effluents (Chandra et al., 2007).

Research about natural dissolved organic matter (DOM) has shown that irradiation affects its properties, decreasing its absorption and fluorescence intensity (Zhang et al., 2009) and leading to its degradation (Moran and Zepp, 1997; Del Vecchio and Blough, 2002; Brinkmann et al., 2003). Minor et al. (2006) observed a decrease of natural DOM photodegradation with an increase of salinity while Grebel et al. (2009) found an enhanced photodegradation of natural DOM in the presence of chloride.

Taking into account these results, this work aimed to determine: (1) the evolution of spectroscopic properties of DOM from kraft pulp mill effluents throughout irradiation; and (2) the effect of the presence of chloride and of the natural photosensitizer nitrate. The main goal was to consider, for the very first time, if the fate of

macromolecular organic matter from kraft pulp mill effluents could be different depending on the type of receiving waters.

2. Experimental

2.1. Working solutions

The final effluent (after biological activated sludge treatment) from a kraft pulp mill, which uses *Eucalyptus globulus* wood as raw material, was employed in this work. In the past, this effluent was discharged in a river but, nowadays, it is being discharged at the sea through a submarine outfall.

Fulvic acids (FA) were extracted from the final effluent, desalted and preserved by the procedures described by Santos and Duarte (1998). The characterization of these FA may be found elsewhere (Santos et al., 2000a). Three types of solutions were prepared in deionised water: (a) Solutions of FA (10 mg L⁻¹); (b) Solutions of FA (10 mg L⁻¹) and NaCl (30 g L⁻¹), in order to simulate the marine/estuarine concentration of chloride; (c) Solutions of FA (10 mg L⁻¹) and NaNO₃ (13.2 mg L⁻¹), in order to simulate the concentration of nitrate in aquatic environments (Espinoza et al., 2007).

2.2. Irradiation conditions

Immediately after preparation, in each case, 35 mL of solution were put in a quartz tube (50 mL) covered by punctured plastic. Tubes were placed in a solar simulator Solarbox 1500 (Co.fo.me.gra., Italy), equipped with a 1500 W arc Xenon lamp and special outdoor UV filters that restrict the transmission of light with wavelengths below 290 nm. The uniformity of the irradiation was provided by a parabolic reflection chamber and the irradiance was kept constant at 55 W m⁻² in the 295 < λ < 400 nm range (corresponding to 550 W m⁻² in the range 295–800 nm, according to the manufacturer specifications).

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Three not simultaneous replicates of each solution were irradiated during increasing times and in parallel with the respective dark controls (aluminium foil wrapped tubes containing the same solutions).

2.3. UV–vis and molecular fluorescence spectroscopies

UV–vis spectra were registered in the range of 200–600 nm on a spectrophotometer (UV 2101 PC from Shimadzu, Dusseldorf, Kent, Germany) in 5 cm path length quartz cells. Synchronous fluorescence spectra ($\Delta\lambda = 60$ nm) were obtained in a spectrofluorometer (FluoroMax-3 from HORIBA Jobin Yvon, Edison, NJ, USA). Spectra were acquired using λ_{exc} from 220 to 500 nm (1 nm increments; 0.1 s integration time) and using excitation and emission slit bandwidths of 5 nm. Triplicate UV–Vis and synchronous spectra were obtained for each solution and absorbance and fluorescence intensity values were normalized by the initial concentration of FA.

3. Results and discussion

3.1. Spectroscopic changes in FA from a kraft pulp mill effluent upon irradiation

The UV–Vis spectra corresponding to the FA solutions upon irradiation time, which are represented in Fig. 1a, show an absorbance that decays with increasing λ . Furthermore, a decrease of the absorbance of the FA solutions occurs throughout irradiation time while the spectra corresponding to control samples remained the same. This absorbance decrease has been observed to be caused by the photodegradation of DOM (Moran and Zepp, 1997; Kieber et al., 1990; Bertilsson and Tranvik, 2010), having been related to the partial mineralization of organic matter and/or the formation of less absorbing organic compounds.

Fig. 1b shows the molecular fluorescence synchronous spectra ($\Delta\lambda = 60$ nm) corresponding to the fulvic acid solutions at different

irradiation times. Spectra corresponding to control samples remained the same as the original while the irradiated solutions of FA experienced a decrease in fluorescence intensity over the course of time, which is coincident with results published on the effect of irradiation on DOM in natural waters (Patel-Sorrentino et al., 2004).

Spectra in Fig. 1b displays an intense peak at $\lambda_{ex} \sim 280$ nm and a less intense region of fluorescence, centred at $\lambda_{ex} \sim 340$ nm. This last region is initially divided into two bands, one at $\lambda_{ex} \sim 320$ nm and another at $\lambda_{ex} \sim 360$ nm. However, after irradiation during 2 h or longer, only one band centred at $\lambda_{ex} \sim 340$ nm is evident. Thus, as seen in previous studies (Carvalho et al., 2008a,b), for all the irradiation times, there are two types of fluorophoric groups in solution, those responsible for fluorescence at $\lambda_{ex} \sim 280$ nm and those responsible for “humic-like” fluorescence. The emission of fluorescence by DOM of natural waters in the short wavelength range ($\lambda_{ex} < 300$ nm and $\lambda_{em} < 350$ nm) has been related to amino acid and protein chromophores (Coble, 1996; Matthews et al., 1996). In the case of the fulvic acids under study, the peak at $\lambda_{ex} \sim 280$ nm was attributed to lignin derived structures by Santos et al. (2000b) and by Duarte et al. (2003). This attribution is in agreement with the structural characterization of these fulvic acids using other techniques such as solid state ^{13}C NMR (Santos et al., 2000a; Duarte et al., 2003). The second type of fluorophores comprises those substances having fluorescence properties similar to those of humic substances and is characterized by $230 \text{ nm} < \lambda_{ex} < 240 \text{ nm}$ and $310 \text{ nm} < \lambda_{em} < 350 \text{ nm}$ (Mopper et al., 1996).

Trends observed in this work regarding absorbance and molecular fluorescence of solutions of fulvic acids from the kraft pulp industry under irradiation with simulated solar light are in agreement with results obtained under natural solar irradiation (Carvalho et al., 2008a). Furthermore, the decrease of the specific absorbance and fluorescence intensities was confirmed to occur also for fulvic acids extracted from solutions after irradiation with natural sunlight (Carvalho et al., 2008b), confirming that structural modifications of dissolved organic matter occur due to irradiation.

3.2. Effect of the presence of nitrate and chloride

In UV–Vis spectra, the ratio between the absorbance at 250 and 365 nm (E_2/E_3) has been related to structural differences in humic substances and high relative E_2/E_3 values have been linked to low relative aromaticity (Peuravuori and Pihlaja, 1997; Hautala et al., 2000; Osburn et al., 2001; Duarte et al., 2003). Furthermore, it is known that E_2/E_3 increases with the decrease of molecular weight (Peuravuori and Pihlaja, 1997) so this ratio has been used to follow the structural changes during natural DOM photodegradation in surface waters (Osburn et al., 2001; Brinkmann et al., 2003). Thus, in the present work, and in order to compare irradiation consequences on solutions of the same FA alone and in the presence of chloride or nitrate, the E_2/E_3 ratios from the corresponding UV–vis spectra as a function of irradiation time are represented in Fig. 2a. In all cases, an increase of the E_2/E_3 ratio with increasing irradiation time was observed, irradiation time significantly affecting this ratio (ANOVA, $p < 0.05$). This displacement of the spectral distribution of absorbance towards lower wavelengths points to a decrease of aromaticity and of molecular weight of these FA throughout irradiation time, as it was already pointed out by Carvalho et al. (2008a). The presence of chloride did not affect the increase of the E_2/E_3 ratio (ANOVA, $p > 0.05$). However, under the presence of nitrate, E_2/E_3 ratios were observed to be slightly higher than for FA alone, differences being significant ($p < 0.05$). This effect may be related to the fact that nitrate is a naturally occurring photosensitizer capable of increasing the phototransformation rate, which can be ascribed to the formation of OH radicals due to photolysis of nitrate (Zepp et al., 1987).

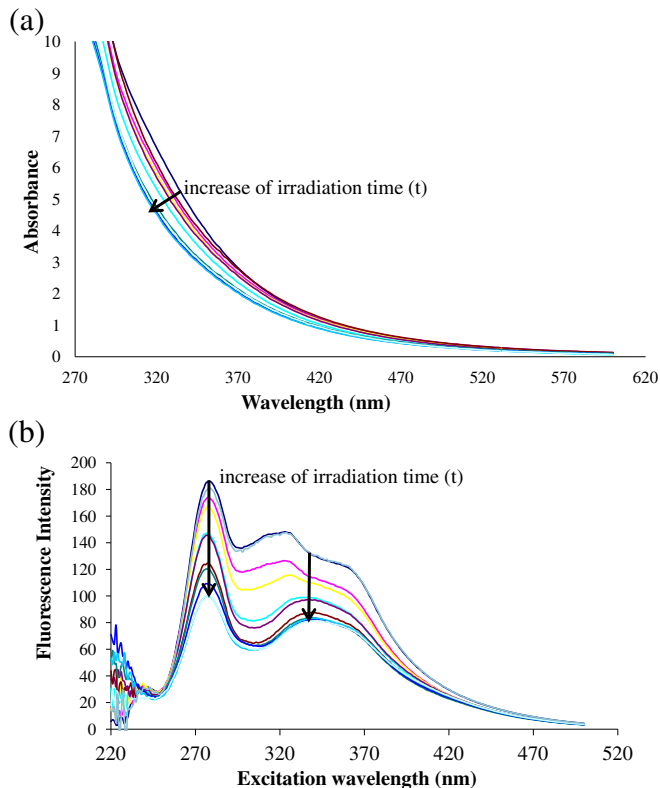


Fig. 1. (a) UV–Vis spectra corresponding to the solutions of fulvic acids from kraft pulp effluent before and after increasing irradiation time (indicated by the arrow). (b) Synchronous ($\lambda = 60$ nm) molecular fluorescence spectra corresponding to the solutions of fulvic acids from kraft pulp effluent before and after increasing irradiation time (indicated by de arrows).

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