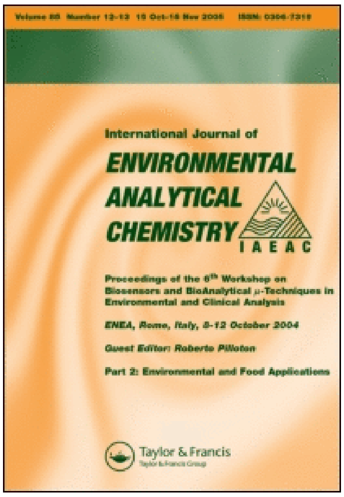

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STRUCTURAL CHARACTERISATION OF THE COLOURED ORGANIC MATTER FROM AN EUCALYPTUS BLEACHED KRAFT PULP MILL EFFLUENT

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XAD-8 and XAD-4 resins in tandem were used to isolate and fractionate the coloured organic matter from an eucalyptus bleached Kraft pulp mill effluent which is discharged into river Vouga (Portugal) near the lagoon that exists in its terminal part. The composition of the isolated organic matter was investigated by FTIR and CPMAS-^{13}C-NMR and compared to that of humic matter isolated before from the same river at a non-polluted site and a site very contaminated with the effluent of a sulphite pulp mill. The results put into evidence that the organic matter from both kinds of effluent is more aromatic and contains more lignin derived structural units than the humic matter from the unpolluted site. However, the organic matter from the sulphite pulp mill effluent is more soluble due to its content of sulphonic functional groups.

Keywords: Humic substances; eucalyptus bleached Kraft pulp mill effluent; natural waters; ir-spectroscopy; CPMAS-^{13}C-NMR

INTRODUCTION

Macromolecular organic compounds, essentially lignin derived, are the main waste products in pulp mill effluents[1]. They are responsible for the notorious colour of those effluents, which is one of the environmental problems associated to this type of industry. These compounds do have some similarity with natural humic substances [2] which are produced in soil, sediment and water from degradation of biomass and to whose formation lignin from vascular plants is an important precursor [3]. The knowledge of the composition of those humic-like

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compounds in pulp mill effluents is important to predict changes of the bulk properties of the dissolved organic matter in receiving waters and it can also be useful for choice of effluent treatment procedures.

In this paper FTIR (Fourier Transform Infra-Red) and CPMAS-^{13}C-NMR (Cross Polarization and Magic Angle Spinning-^{13}C-Nuclear Magnetic Resonance) spectroscopies were applied to the structural characterisation of the humic-like substances isolated from the treated effluent of an eucalyptus bleached kraft pulp mill which is discharged into river Vouga (Portugal) near the lagoon that exists in its terminal part. The results were compared with the spectra of humic substances isolated from the same river some years ago [4–6] at a non-polluted site and a site contaminated with a sulphite pulp mill effluent. That factory is no longer working and only the bleached Kraft pulp mill discharges its effluent in the river. The characterisation of the humic-like materials from this effluent is important to evaluate differences between different types of pulp mill effluents in what concerns their effects on the composition of the dissolved organic matter in receiving surface waters.

MATERIALS AND METHODS

Humic matter isolation

The Kraft pulp mill effluent was filtered through 0.45 μm membrane filters, acidified to pH 2.0 and then pumped through columns of XAD-8 and XAD-4 resins connected in series. Due to the high concentration of coloured organic matter in the effluent and in order to guarantee its complete recover, the sample volume processed in each run was much lower than the sample volume for isolation of humic matter from natural waters [7] and it was determined as the volume for which the absorbance at 250 nm at the outlet of the XAD-4 column was not higher than 1% of the original sample absorbance. The adsorbed organic acids were back eluted from each column with NaOH 0.1 M and the eluates were immediately acidified to pH 3.0–4.0. The humic acids were precipitated by acidifying the XAD-8 eluate to pH 1.0 and were then separated by centrifugation at more than 6000 rpm. Humic acids were dissolved in NaOH 0.1 M, under nitrogen, and were then immediately acidified to pH 3–4. The humic and fulvic acids were desalted according to a procedure described in detail elsewhere [6]. The XAD-4 fraction was desalted by an identical procedure [5]. The solutions were then freeze-dried and the three fractions of organic matter were kept in a desiccator over silica gel.

Elemental and thermogravimetric analysis

Elemental analysis (C, H, N, S) was performed with a LECO CHNS-932 analyser. The results were corrected for the moisture and ash content of the samples, which were determined by thermogravimetric analysis. The thermogravimetric analysis was performed using a Shimadzu TGA-50 thermobalance connected to a computer through a Shimadzu TA-50WS1 interface. Samples of about 5 mg were placed in platinum crucibles and heated until 750°C under air (20 mL/min flow). The temperature program used includes three steps of heating at 10°C/min, with a hold time at the final temperature of each step: 60 min at 60°C, 60 min at 100°C and 30 min at 750°C. The moisture content was considered as the weight lost after 1 hour at 60°C and the ash content as the final weight at 750°C. Blank analysis were performed, using empty crucibles, and the average weights of those blanks at the end of each step were introduced as corrections on the calculations of moisture and ash contents of samples.

Fourier Transform Infrared Spectroscopy

Infrared spectra were recorded on a Magna 550 Fourier Transform spectrometer using KBr-pellet technique (0.8 mg sample to 50 mg KBr). The sample compartment was purged with nitrogen for 15 minutes before recording each spectrum. The spectra resolution was 4 cm^{-1} and 100 scans were averaged.

^{13}C Solid State NMR Spectroscopy

^{1}H-^{13}C CPMAS spectra were recorded at 100.61 MHz on a Bruker MSL-400 NMR spectrometer using a standard 4 mm double-bearing probehead. Transients were recorded with a contact time of 1 ms and a spinning rate of 12 kHz. The recycle delay was 3 s and the length of the proton 90° pulse was 4.5 μs. Chemical shifts are quoted in ppm from external tetramethylsilane (TMS).

RESULTS AND DISCUSSION

Elemental analysis

The elemental composition of the organic fractions isolated from the Kraft pulp mill effluent are shown in Table I. The results for humic and fulvic acids isolated from river Vouga [6] from a non-polluted site (Carvoeiro) and a site very contaminated with a sulphite pulp mill effluent (Sernada) are also shown. The most important differences concern the sulphur content which is significatively higher in the samples from the Kraft pulp mill effluent and from Sernada than in the samples from Carvoeiro. The sulphur content of the humic substances from the two pulp mill effluents is also higher than the sulphur contents reported for the IHSS (International Humic Substances Society) reference humic substances [8]. The incorporation of sulphur in the structural units of lignin and also in carbohydrate fragments occurs during the pulping processes (kraft and sulphite) [9]. The samples from pulp mill effluents do also exhibit lower nitrogen contents than the samples from the non-polluted river water.

TABLE I Elemental composition of samples

	C (%)	*N (%)*	*H (%)*	*S (%)*
Kraft pulp mill effluent:				
Humic acids	60.3	0.32	4.8	4.0
Fulvic acids	54.4	0.15	4.5	3.4
XAD-4 fraction	47.5	0.53	3.6	3.8
River Vouga (Sernada)[6]:				
Fulvic acids	52.9	0.9	4.4	3.5
River Vouga (Carvoeiro)[6]:				
Humic acids	55.4	2.4	3.9	0.71
Fulvic acids	53.4	1.5	4.5	0.58

Fourier Transform Infrared spectra

The infrared spectra of fulvic acids, humic acids and XAD-4 fraction isolated from the effluent are shown in Figure 1. As the spectra of natural humic substances [10], also the spectra of the organic fractions isolated from the Kraft pulp mill effluent present a broad and strong band centred at about 3415 cm^{-1}, due to H-bonded OH stretching of phenol, hydroxyl and carboxyl groups [6,10], and, superimposed to it, a few bands in the 3000–2840 cm^{-1} region which can be attributed to CH stretching of methyl and methylene groups [6,10]. The band at 1720 cm^{-1} is due to C=O stretching, mainly of carboxyl groups [6]. The relative intensity of that band is lower in the humic acid fraction than in the other two fractions isolated from the effluent.

The three fractions of dissolved organic matter isolated from the Kraft pulp mill effluent exhibit bands typical of lignin structural moieties in the region 1900–900 cm^{-1}, which is expanded in Figure 2a. Bands at ~1600 cm^{-1} and

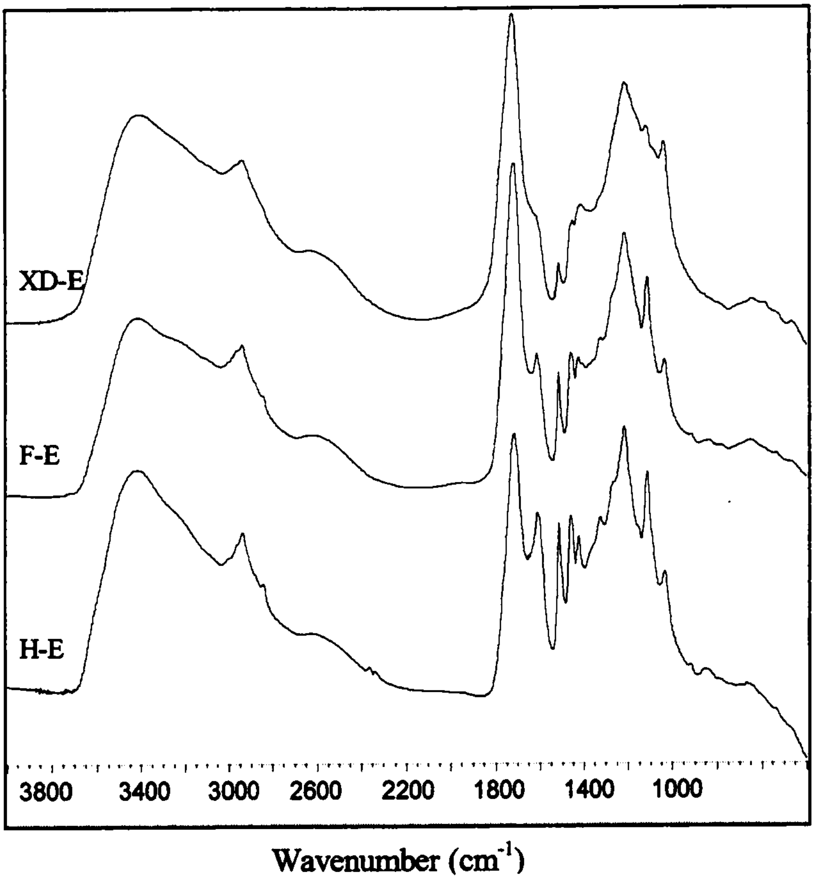
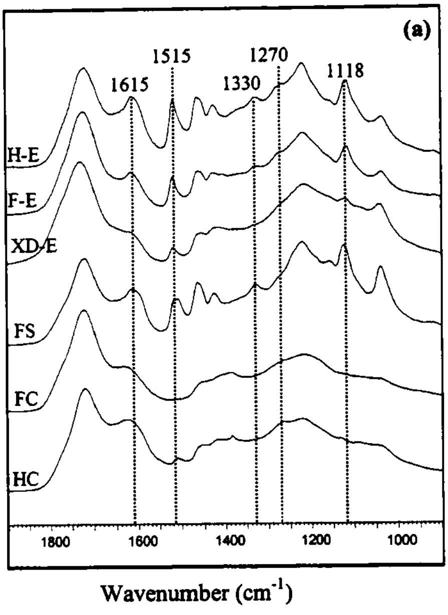


FIGURE 1 FTIR spectra of the organic fractions isolated from the Kraft pulp mill effluent (H-E for humic acids, F-E for fulvic acids and XD-E for XAD-4 fraction)

~1510 cm^{-1} are quite strong in the spectra of lignins and they are due to C-C stretching vibrations of aromatic rings of siringyl and guaiacyl units [9,11]. These structural units also give rise to bands at ~1330 cm^{-1} (siringyl ring breathing vibrations or guaiacyl ring substituted in position 5) and ~1270 cm^{-1} (guaiacyl ring breathing vibrations) [9,11]. The strong band at 1118–1130 cm^{-1} (ring breathing + C-O stretching) is quite typical in the spectra of lignins [11–13]. These five bands are more intense in the humic acid fraction and they present their lower intensity in the spectrum of the XAD-4 fraction.

The comparison of the spectra of humic substances from the effluent of the Kraft pulp mill with those of the humic substances isolated from a non-polluted



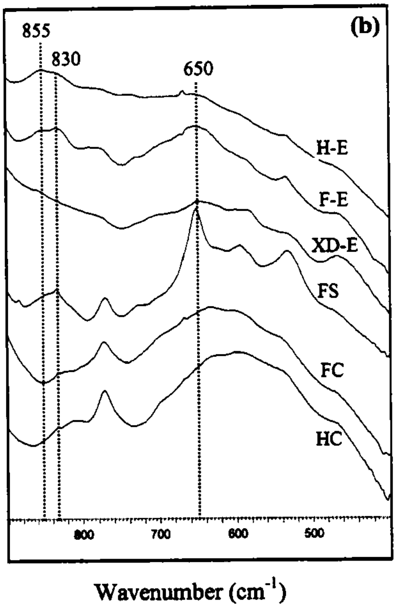


FIGURE 2 FTIR expanded scale spectra in the zones 1900–900 cm^{-1} (a) and 900–400 cm^{-1} (b): humic substances from the Kraft pulp mill effluent (H-E for humic acids, F-E for fulvic acids and XD-E for XAD-4 fraction) and humic substances from river Vouga[6] (HC and FC are the humic and fulvic acids from Carvoeiro, respectively and FS are the fulvic acids from Semada)

site of river Vouga (Carvoeiro) (Figure 2a) [5,6] show that the former are more aromatic and contain much more lignin structural moieties. The comparison with the fulvic acid isolated from the site of river Vouga highly contaminated with the sulphite pulp mill effluent (Figure 2a) [6] puts into evidence a great similarity of the spectrum of that sample with the spectrum of the humic acids from the Kraft pulp mill. It is interesting to refer that during the isolation of humic substances from the site contaminated with the sulphite pulp mill effluent, no humic acids were obtained, since no precipitation was observed even when the DOC of the eluate of the XAD-8 resin was higher than 2000 mg L^{-1}. As previously referred [6], the high hydrophilicity of these humic substances is due to the high content of sulphonic groups. These functional groups give rise to a FTIR band at 650 cm^{-1} (S-O stretching) [6]. As can be seen in Figure 2b, that band is considerably more intense in the spectrum of the fulvic acid from Sernada than in the other samples. That band is also well defined in the spectrum of the XAD-4 fraction from Sernada, as observed by Esteves [5]. The inclusion of sulphonic groups in the lignin structural moieties occurs during the sulphite pulping process [9].

In the 900–400 cm^{-1} zone, Figure 2b, the spectra of humic and fulvic acids from the Kraft pulp mill effluent exhibit bands at 855 cm^{-1} and 830 cm^{-1}, which, according to Faix [11], may be assigned to C-H out-of-plane deformation in position 2, 5 and 6 of guaiacyl units, and to C-H out-of-plane deformations in position 2 and 6 of syringyl units, respectively. These bands are more intense in the humic and fulvic acids from the Kraft pulp mill effluent and in the fulvic acids from Sernada.

^{13}C Solid State NMR Spectra

The ^{13}C NMR spectra of the humic substances isolated from the Kraft pulp mill effluent are shown in Figure 3. The spectra of the humic and fulvic acids are dominated by signals at 55 and ~147 ppm, which are typical of lignin structural units [2,3,14–16]. Those signals are also present, but considerably less intense, in the spectrum of the XAD-4 fraction. The narrow and intense peak at 55 ppm is due to methoxyl groups like those of syringyl and guaiacyl units and the signals between ~160 ppm and ~140 ppm are due to oxygen-substituted aromatic ring carbons (e.g., carbons 3 and 4 in syringyl and guaiacyl units and carbon 5 in syringyl units) [14–16].

The comparison of the relative intensities of zones 108–160 ppm (aromatic carbons) [17,18] and 0–90 ppm (aliphatic carbons) [16–18] of the spectra of humic substances isolated from Kraft pulp mill effluent, puts into evidence that, as happens with natural aquatic organic matter [5], the XAD-4 fraction is the most aliphatic while the humic acid is the most aromatic. However, the comparison

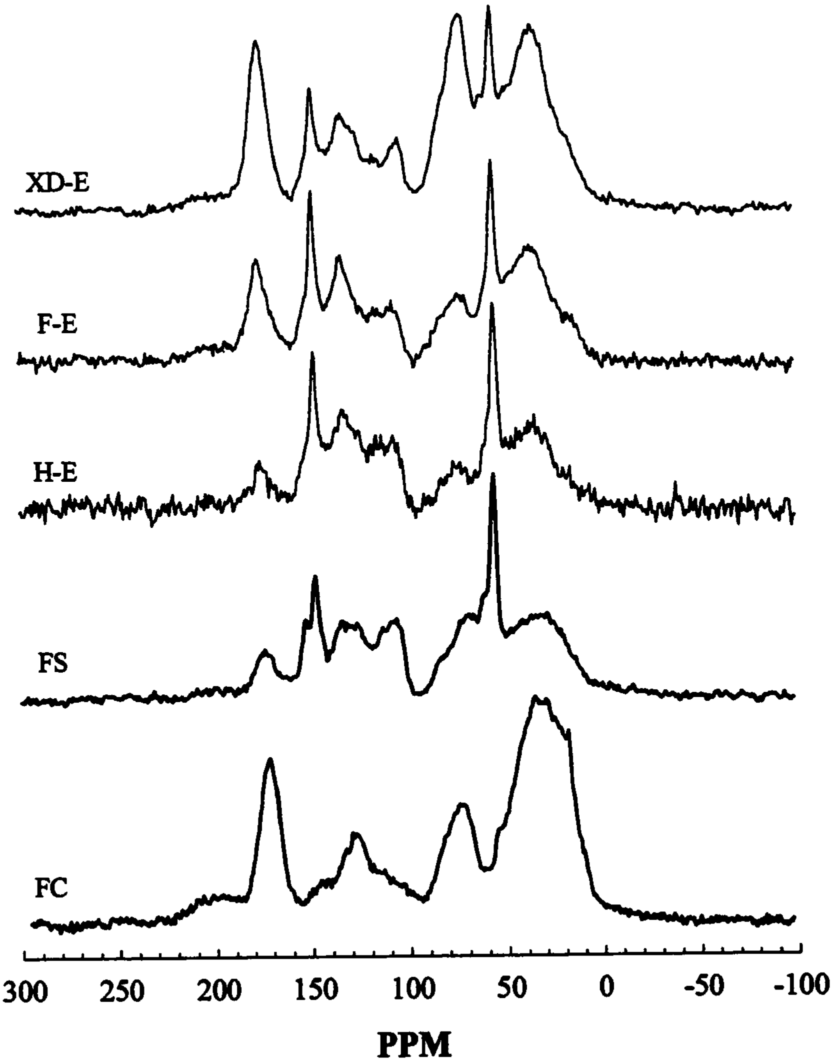


FIGURE 3 CPMAS- ^{13}C NMR spectra of samples (see Fig. 2 for the legend)

with the same fractions isolated from the non-polluted site of river Vouga [4–6] or from other natural waters [5,17–19] shows that the fractions isolated from the kraft pulp mill effluent are considerably more aromatic, and they exhibit much more intense lignin typical ^{13}C NMR signals. For example, the presence of a well resolved peak at 55 ppm and a so intense band at 140–160 ppm are not observed in the fulvic and XAD-4 fractions isolated from Carvoeiro, the non-polluted site of river [4–6] and they are usually not observed in fulvic and XAD-4 fractions of natural aquatic organic matter [5,17–19]. However, the fulvic and XAD-4 fractions isolated from the site of river Vouga highly polluted with a sulphite pulp mill effluent (Sernada) [4–6] also exhibit intense absorption at 55 and 140–160 ppm. The spectra of the fulvic acids from Carvoeiro and Sernada are also shown in Figure 3 for comparison. These results put into evidence that both Kraft and sulphite pulp mill effluents introduce humic-like materials into natural waters which are more aromatic and which contain more lignin structural moieties than the natural aquatic humic substances.

The signal at ~174 ppm is assigned to carbons of carboxyl groups and its functional derivatives [18]. Its intensity is considerably lower in the spectrum of the humic acids than in the other two fractions from the Kraft pulp mill, which is in agreement with the lower intensity of the band at 1720 cm^{-1} (COOH vibrations) in its infrared spectrum. The relative intensities of the 174 ppm signal show that the fulvic acids and the XAD-4 fraction from the kraft pulp mill effluent do have a higher carboxyl content than the corresponding fractions from Sernada [5,6], the site with high influence of a sulphite pulp mill effluent. So, the nature of the organic matter from the two types of pulp mill effluents is different.

CONCLUSIONS

XAD-8 and XAD-4 resins in tandem were used to isolate and fractionate the coloured organic matter from an eucalyptus bleached Kraft pulp mill effluent Three fractions of organic matter were obtained: humic acids, fulvic acids and XAD-4 fraction. The ^{13}C-NMR spectra of the three fractions do reveal the presence of a relatively high content of aromatic carbons and do exhibit intense signals due to carbons of phenol and methoxyl groups which are typical of lignin structural units. The FTIR spectra also exhibit bands which can be attributed to lignin moieties. All those structural features are more intense in the humic acids fraction.

The three fractions do exhibit a higher sulphur content, a higher aromaticity and a higher content of lignin derived structural moieties than the corresponding fractions from non-polluted waters. Similar structural properties were observed in the humic substances isolated some years ago [6] from a site of river Vouga contaminated with a sulphite pulp mill effluent, but the organic matter from the Kraft pulp mill effluent is less soluble. Due to the high concentration of coloured organic matter in these effluents their discharge changes the bulk properties of the dissolved organic matter in natural waters.

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